

Titre: Protective Coatings Against Surface Fouling and Sulfidation in
Title: Heavy Oil Environments

Auteur: Fellipy Samuel Rocha
Author:

Date: 2024

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Samuel Rocha, F. (2024). Protective Coatings Against Surface Fouling and
Citation: Sulfidation in Heavy Oil Environments [Thèse de doctorat, Polytechnique
Montréal]. PolyPublie. <https://publications.polymtl.ca/62506/>

 **Document en libre accès dans PolyPublie**
Open Access document in PolyPublie

URL de PolyPublie: <https://publications.polymtl.ca/62506/>
PolyPublie URL:

**Directeurs de
recherche:** Gregory Scott Patience, Ludvik Martinu, & Jolanta-Ewa Sapieha
Advisors:

Programme: Génie chimique
Program:

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

**Protective coatings against surface fouling and sulfidation in heavy oil
environments**

FELLIPY SAMUEL ROCHA

Département de génie chimique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

Génie chimique

Décembre 2024

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Cette thèse intitulée :

Protective coatings against surface fouling and sulfidation in heavy oil environments

présentée par **Fellipy SAMUEL ROCHA**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*

a été dûment acceptée par le jury d'examen constitué de :

Louis FRADETTE, président

Gregory PATIENCE, membre et directeur de recherche

Ludvik MARTINU, membre et codirecteur de recherche

Jolanta-Ewa SAPIEHA, membre et codirectrice de recherche

Jason Robert TAVARES, membre

François ROPITAL, membre externe

DEDICATION

To my family.

ACKNOWLEDGEMENTS

I am deeply grateful to my supervisors, Professors Gregory Patience, Jolanta-Ewa Klemberg-Sapieha, and Ludvik Martinu, for their trust, support, patience, and invaluable knowledge shared throughout this project. Thank you for giving me this opportunity; without your guidance, the completion of this work would not have been as fruitful.

My sincere thanks go to the members of the Functional Coating and Surface Engineering Laboratory (FCSEL), who were always willing to collaborate when needed. In particular, I am grateful to Bill Baloukas, Etienne Bousser, and Oleg Zabeida for their guidance and support; without them, this journey would have been much more challenging. I also extend my thanks to Francis Boutet and Francis Turcot, whose technical assistance was essential to the success of this project.

I would like to thank my colleagues from Professor Gregory's research group for the friendship and knowledge shared during this period.

I am also grateful to Velan Inc. for their support and confidence in this project, especially to Fadila Khelfaoui and Luc Vernhes, who closely followed the project from its inception.

I extend my thanks to the committee members, Professors François Ropital, Jason Tavares, and Louis Fradette, for accepting to be on my jury.

Finally, I give special thanks to my family—my parents, Mirlene and Gilberto—and my friends for their unwavering support, which has been a constant source of strength despite the physical distance. Without them, the completion of this work would have been far more difficult.

Yours sincerely,

Fellipy S. Rocha

École Polytechnique Montréal

RÉSUMÉ

L'encrassement reste un défi persistant dans l'industrie pétrochimique, en raison de la nature dynamique de la composition des matières premières et des conditions de fonctionnement difficiles. Lors du traitement des huiles lourdes, les températures élevées et la forte teneur en soufre accélèrent considérablement l'encrassement, principalement par sulfuration et dépôt de coke. L'imprévisibilité de la composition des matières premières complique également le développement de solutions universelles, car les couches d'encrassement formées sont en constante évolution. Maintenir l'intégrité des composants critiques tels que les vannes est essentiel pour assurer la sécurité du processus en prévenant les fuites et en gardant une étanchéité adéquate. Les matériaux utilisés dans les applications de vannes doivent donc présenter un équilibre entre résistance, ductilité, stabilité thermique et résistance à la fatigue. Bien que les alliages à base de nickel comme l'Inconel 718 offrent d'excellentes propriétés mécaniques, ils sont très sensibles à la sulfuration et présentent une résistance à l'usure insuffisante, nécessitant l'utilisation de revêtements protecteurs. Un modèle phénoménologique a donc été proposé pour décrire le mécanisme d'encrassement initial de l'Inconel 718 et du Wallex 50. Ce modèle a ensuite été complété en y intégrant le vieillissement des couches encrassantes basé sur une analyse de défaillance d'échantillons prélevés sur le terrain contenant du Ni. De plus, nous avons développé et mis en œuvre une méthode d'imagerie optique pour une évaluation semi-quantitative du degré d'encrassement.

Les revêtements HVOF (High Velocity Oxygen Fuel), généralement composés d'alliages à base de cobalt mélangés à des carbures, sont devenus la norme industrielle pour les vannes, renforçant leur résistance à l'usure et offrant une meilleure protection contre la sulfuration par rapport aux alliages de nickel non revêtus. Cependant, ces revêtements métalliques restent vulnérables à l'encrassement, ce qui peut provoquer le blocage des vannes et une défaillance opérationnelle due à l'application d'un couple accru. En réponse à ces défis, des revêtements HVOF de seconde génération ont été développés comme alternative aux normes actuelles. Plus précisément, les revêtements Co-2 et Co-3, après traitement thermique, ont montré une réduction significative de l'encrassement de surface, en faisant des candidats prometteurs pour une application industrielle.

Pour renforcer davantage la résistance à l'encrassement, des revêtements PVD de troisième génération ont été explorés, offrant des performances supérieures aux revêtements HVOF. Cependant, l'application industrielle des revêtements par pulvérisation cathodique pose des défis

pratiques, car il est difficile d'obtenir une épaisseur suffisante sur des géométries complexes pour assurer une bonne résistance à l'usure. Parmi ces revêtements avancés, le SiBCN s'est révélé prometteur grâce à sa structure amorphe, améliorant la résistance à la corrosion avec des performances mécaniques adéquates. Avec une dureté dépassant 15 GPa et une adhérence relativement adéquate, le SiBCN convient à certaines applications d'usure, bien qu'une optimisation supplémentaire soit nécessaire pour améliorer l'adhérence et la performance à long terme. Le TiAlN a, quant à lui, démontré une dureté et une adhérence bien supérieures, offrant une protection efficace contre la sulfuration, bien qu'il soit sensible à un dépôt accru de coke localisé. Le SiBCN et le TiAlN apparaissent ainsi comme des alternatives prometteuses pour une utilisation dans les composants de vannes, selon des exigences opérationnelles spécifiques.

L'alumine amorphe a montré des propriétés anti-encrassement exceptionnelles, mais ses performances mécaniques étaient insuffisantes. Un recuit du revêtement a permis d'augmenter sa dureté au-delà de 20 GPa et d'améliorer son adhérence, le rendant adapté aux zones exposées à une usure moindre. Cependant, il a été constaté, que le processus de recuit introduit des oxydes du substrat dans la matrice du revêtement, réduisant alors ses propriétés anti-encrassement. L'utilisation de CeO_2 s'est également révélée prometteuse, notamment pour la protection contre la sulfuration, bien que sa faible dureté et sa mauvaise adhérence limitent son application autonome.

Les présents résultats soulignent l'importance de solutions de revêtement adaptées pour relever les défis de l'encrassement et des performances mécaniques dans les environnements pétrochimiques. Des essais à long terme dans des conditions opérationnelles réelles, incluant des cycles de nettoyage et une exposition thermique, seront nécessaires pour valider la durabilité et l'applicabilité des revêtements étudiés. Ces conclusions offrent un cadre pour optimiser les revêtements protecteurs, améliorant ainsi la fiabilité et la sécurité des composants tels que les vannes dans le traitement des huiles lourdes, garantissant des performances constantes dans des environnements de plus en plus exigeants.

ABSTRACT

Fouling remains a persistent challenge in the petrochemical industry, driven by the dynamic nature of feedstock composition and harsh operating conditions. During heavy oil processing, elevated temperatures and high sulfur content significantly accelerate fouling, primarily through sulfidation and coke deposition. The unpredictability of feed composition complicates the development of universal solutions, as the fouling scales formed are constantly changing. Maintaining the integrity and functionality of critical components such as valves is essential to ensure process safety by preventing leaks and ensuring proper sealing. Materials used in valve applications must possess a balance between strength, ductility, thermal stability, and fatigue resistance. While nickel-based alloys like Inconel 718 offer excellent mechanical properties, they are highly susceptible to sulfidation and lack adequate wear resistance, necessitating the use of protective coatings. In the present work, a phenomenological model was proposed to describe the initial fouling mechanism of Inconel 718 and Wallex 50. This model was later complemented by addressing scale aging based on failure analysis of Ni-containing field samples. In addition, we have developed and implemented an optical imaging method for semi-quantitative assessment of the degree of fouling.

HVOF-sprayed coatings, typically composed of cobalt-based alloys mixed with carbides, have become the industry standard for valves, enhancing wear resistance and providing better sulfidation protection compared to bare nickel alloys. However, these metallic coatings remain susceptible to fouling, which can lead to valve seizing, and operational failure due to increased torque. In response to these challenges, second-generation HVOF coatings were developed as alternatives to current benchmarks. Coatings such as Co-2 and Co-3, after undergoing heat treatment, exhibited significantly reduced surface fouling, making them viable candidates for industrial implementation.

To further enhance fouling resistance, third-generation PVD coatings were explored, offering superior performance compared to HVOF coatings. However, the industrial application of sputtered coatings presents practical challenges, as achieving sufficient thickness on complex geometries for wear resistance is rather difficult. Among these advanced coatings, SiBCN emerged as a promising option due to its amorphous structure and high thermal stability, while improving corrosion resistance with adequate mechanical performance. With a hardness exceeding 15 GPa and relatively adequate adhesion, SiBCN is suitable for certain wear applications, though additional

optimization is required to improve adhesion and long-term performance. TiAlN demonstrated far superior hardness and adhesion, providing effective sulfidation protection, though it was susceptible to increased localized coke deposition. Both SiBCN and TiAlN are identified as promising alternatives for use in valve components, depending on specific operational requirements.

Amorphous alumina showed exceptional anti-fouling properties, but its mechanical performance was insufficient. Annealing the Al_2O_3 coating improved its hardness to over 20 GPa and enhanced adhesion, making it suitable for areas exposed to lower wear conditions. However, the annealing process introduced oxides from the substrate into the coating matrix, reducing its anti-fouling properties. The use of CeO_2 also showed promise, particularly for protecting against sulfidation, though its low hardness and poor adhesion limit its standalone application.

The results emphasize the importance of tailored coating solutions to address both fouling and mechanical performance challenges in petrochemical environments. Long-term testing under real operational conditions, including cleaning cycles and thermal exposure, will be necessary to validate the coatings' durability and feasibility. These findings provide a framework for optimizing protective coatings to improve the reliability and safety of components such as valves in heavy oil processing, ensuring consistent performance in increasingly demanding environments.

TABLE OF CONTENTS

DEDICATION	iii
ACKNOWLEDGEMENTS	iv
RÉSUMÉ.....	v
ABSTRACT	vii
TABLE OF CONTENTS	ix
LIST OF TABLES	xiv
LIST OF FIGURES.....	xvi
LIST OF SYMBOLS AND ABBREVIATIONS.....	xxii
LIST OF APPENDICES	xxviii
CHAPTER 1 INTRODUCTION	1
1.1 Motivation	1
1.2 Problem identification	2
1.2.1 Problem statements	4
1.3 Objectives.....	6
1.4 Scientific contributions	7
1.5 Thesis organization	9
CHAPTER 2 LITERATURE REVIEW	11
2.1 Heavy oil	11
2.1.1 Organic fouling	12
2.1.2 Inorganic fouling	16
2.1.3 Generalized fouling mechanisms	21
2.1.4 Fouling models.....	25
2.1.5 Laboratory scale fouling.....	28

2.2	Materials.....	29
2.2.1	Alloys	29
2.2.2	Microstructure and diffusion.....	34
2.2.3	Surface engineering.....	38
2.2.4	Coatings.....	42
CHAPTER 3 METHODOLOGY.....		53
3.1	Surface preparation	53
3.1.1	Surface preparation for microscopy	53
3.2	Coating deposition.....	54
3.3	Fouling experiments.....	54
3.3.1	Fouling quantification	57
3.4	Reproducibility.....	58
CHAPTER 4 ARTICLE 1 : HEAVY OIL CORROSION FOULING OF NI-BASED ALLOY AND CO-BASED THERMAL SPRAYED COATINGS		59
4.1	Abstract	59
4.2	Introduction	60
4.3	Materials and methods	62
4.3.1	Surface preparation	62
4.3.2	Microscopy.....	64
4.3.3	X-ray diffraction.....	64
4.3.4	Fouling	64
4.4	Results and discussion.....	66
4.5	General discussion and the phenomenological model of fouling	81
4.6	Conclusion.....	84
4.7	Acknowledgements	85

CHAPTER 5	ARTICLE 2 : ENHANCED HEAVY OIL FOULING RESISTANCE OF COBALT-BASED SPRAY-DEPOSITED COATINGS BY ALLOY DESIGN AND HEAT TREATMENT	86
5.1	Abstract	86
5.2	Introduction	87
5.3	Materials and methods	89
5.3.1	Surface preparation	89
5.3.2	Microstructural characterization	90
5.3.3	Mechanical properties	91
5.3.4	Contact angle.....	91
5.3.5	Rheology	92
5.3.6	Fouling	92
5.4	Results and discussion.....	93
5.4.1	Coating microstructure before and after heat treatment.....	93
5.4.2	Mechanical properties	98
5.4.3	Fouling	99
5.4.4	XRD analysis.....	106
5.4.5	Contact angle characterization	108
5.5	Conclusions	111
5.6	Acknowledgements	111
CHAPTER 6	ARTICLE 3 : ALUMINA COATINGS ON NI-BASED SUPERALLOYS: THE IMPACT OF ANNEALING ON HEAVY OIL FOULING	112
6.1	Abstract	112
6.2	Introduction	113
6.3	Materials and methods	115

6.3.1	Surface preparation and coating deposition	115
6.3.2	Coating characterization.....	118
6.3.3	Fouling test.....	119
6.4	Results	120
6.4.1	Alumina deposition optimization	120
6.4.2	Effect of annealing	122
6.4.3	Heavy Oil Fouling on Alumina-Coated Inconel Surfaces	131
6.5	Discussion	136
6.6	Conclusions	138
6.7	Acknowledgements	139
CHAPTER 7 REACTIVELY SPUTTERED TIALN AND SIBCN COATINGS FOR THE PROTECTION OF A NICKEL-BASED ALLOY AGAINST HEAVY OIL CORROSION FOULING		140
7.1	Introduction	140
7.2	Materials and methods	142
7.2.1	Surface preparation	142
7.2.2	Coating deposition.....	142
7.2.3	Microscopy	143
7.2.4	Micro-scratch testing.....	143
7.2.5	Nanoindentation	144
7.2.6	X-ray diffraction.....	144
7.2.7	Contact angle.....	144
7.2.8	Fouling test.....	145
7.3	Results and discussion.....	146
7.3.1	Coatings deposited on Inconel 718	146

7.3.2	Coatings deposited on borided Inconel 718	155
7.4	Conclusions	160
CHAPTER 8 GENERAL DISCUSSION		161
8.1	Limitations	166
8.2	Perspectives and recommendations	167
CHAPTER 9 CONCLUSION		169
REFERENCES		171
APPENDICES		203

LIST OF TABLES

Table 1.1 Publications in peer-reviewed journals.	8
Table 1.2 Presentations at conferences and symposia.....	9
Table 2.1 Atomic lattice structure and packing density.	34
Table 2.2 Key processes altering lattice and defects in alloys.	36
Table 2.3 Surface engineering processes altering lattice and defect structure.	37
Table 4.1 Elemental composition of the IN718 alloy and Wallex 50 coating.	63
Table 4.2 Fouling test reactors dimensions.	65
Table 4.3 Optical image parameters and surface fouling intensity.	69
Table 4.4 Wallex 50 surface map sum spectrum with varying penetration depth.	79
Table 5.1 Elemental composition of the Co-based coatings.	90
Table 5.2 Mechanical properties of the HVOF-sprayed Co-based coatings deposited on IN718 before and after heat treatment (HT).	99
Table 5.3 Surface contact angle measurements on the HVOF-sprayed Co-based coatings deposited on IN718. Arrows symbolize the highest and lowest angles. Correlation with fouling intensity.	110
Table 6.1 Elemental composition of IN718 and IN625 provided by the supplier.	117
Table 6.2 Alumina coating deposited on glass: refractive index (n), n -gradient (%), extinction coefficient (k), and thickness obtained for different oxygen flow values.	121
Table 6.3 Nanoindentation and scratch analysis of the alumina coatings deposited on IN625. The deposition time was increased for a higher O_2 flow rate to account for a lower deposition rate.	122
Table 6.4 Elasto-plastic properties before and after annealing of alumina deposited with an oxygen flow rate of 4 sccm on IN625 and IN718 substrates. The critical load values constitute the cohesive (LC_1) and adhesive (LC_2) strength of the films.	125
Table 7.1 Elemental composition of the bare Inconel 718 substrate.	142

Table 7.2 Surface energy components of the liquids in mJ/m^2	145
Table 7.3 Elasto-plastic properties of the nitride coatings deposited on the Inconel 718.....	148
Table A.1 Elemental composition of the nickel-containing alloys.....	203

LIST OF FIGURES

Figure 1.1 Fouled ball valve used in heavy oil hydrocracking operations. (A) shows a general view of the valve surface, while (B) provides a close-up of scale deposits.....	6
Figure 1.2 Schematic of a ball valve and the challenges to overcome.....	7
Figure 2.1 Comparison of the Ellingham diagram of selected oxides [93], and the Ellingham diagram of selected sulfides [89]. Adapted and reprinted from [89], [93] with permission from Elsevier.....	19
Figure 2.2 Deposition mechanism where the precursor forms in the bulk fluid (Case 1), in the boundary layer (Case 2), or directly on the surface (Case 3). Adapted and reprinted from [69] with permission from Elsevier.	24
Figure 2.3 Types of defects structure in solid materials.	35
Figure 2.4 (a) Wenzel model and (b) Cassie–Baxter model. Where θ_W and θ_{CB} are the Wenzel and Cassie–Baxter contact angle of the liquid droplet. Adapted from [174], under the terms of the Creative Commons Attribution 4.0 License.....	40
Figure 2.5 Comparison map of common coating processes based on achievable coating thickness and substrate temperature during deposition. Adapted from [198], under the terms of the Creative Commons Attribution 4.0 License.....	43
Figure 2.6 Schematic of a typical magnetron sputtering system with a planar target configuration.	48
Figure 2.7 Structure zone diagram (SDZ) applicable to energetic coating deposition. The axes are defined as generalized temperature T^* , normalized energy flux E^* , and in the z-direction, a net film thickness t^* . Reprinted from [238] with permission from Elsevier.....	50
Figure 2.8 Schematic of a high-velocity oxygen fuel (HVOF) deposition system. Adapted and reprinted from [247] with permission from Elsevier; and adapted from [248] under the terms of the Creative Commons Attribution 4.0 License.	52
Figure 3.1 Autoclave reactor used for fouling tests.	55
Figure 3.2 Cross-section of the batch reactor and sample holder	56

Figure 3.3 Sample holder before (A), during (B), and after (C) the fouling experiment.....	56
Figure 3.4 Photography setup designed for capturing and analyzing sample images under controlled lighting conditions.....	57
Figure 4.1 Wallex 50 surface. A) SEM image represents the elemental distribution based on EDS, and B) identifies the phases.....	67
Figure 4.2 Surface of the samples after exposure to heavy oil in the Reactor 1: (A) optical image and (B) after image treatment. The red circle highlights a fouled, delaminated area that was identified as fouling after image processing. The images represent a matrix of 20 x 20 mm.	68
Figure 4.3 Cross-section SEM images and EDS maps of IN718 after fouling at 445 °C for 2 h. The fouled samples are identified as A) Reactor 1 with catalyst (CT), B) Reactor 1, and C) Reactor 2, with the EDS map region marked as a white square.....	71
Figure 4.4 Cross-section SEM images and EDS maps (white square) of IN718 after oxidation in air at 445 °C for 2 h.....	73
Figure 4.5 Cross-section SEM images and EDS maps of Wallex 50 after fouling at 445 °C for 2 h. The fouled samples are identified as A) W50 in Reactor 1 with catalyst (CT), B) W50 in Reactor 1, with EDS map region marked as a white square, and C) W50 in Reactor 2.	75
Figure 4.6 XRD patterns of the Wallex 50 coatings. The magenta dashed lines identify the alloying phases and the symbols of the identified sulfides. The coating patterns are compared before degradation (black) and after degradation in Reactors 1 and 2, with and without catalyst (CT).	77
Figure 4.7 SEM images of Wallex 50 surface fouled in Reactor 2. EDS compositional maps use varying electron beam intensity.	78
Figure 4.8 Phenomenological model describing the corrosion fouling mechanism in dependence of the sulfidation precursor formation rate and concentration: A) high corrosion rate, B) intermediate corrosion rate, and C) low corrosion rate.	82
Figure 5.1 Near-surface region SEM and EDS compositional maps of the as-sprayed Co-based coatings: Co-1, Co-2, and Co-3.....	95

Figure 5.2 SEM images and EDS compositional maps of the near-surface region of the Co-based coatings after heat treatment: Co-1HT, Co-2HT, and Co-3HT.....	97
Figure 5.3 Surface of the samples after exposure to heavy oil: (A) optical image and (B) after image treatment. The images represent a matrix of 20 x 20 mm.....	101
Figure 5.4 SEM images, and EDS and WDS maps on the cross-sections of Co-based coatings after fouling at 450 °C for 2 h. The fouled samples are identified as as-deposited Co-1, Co-2, and Co-3, and after heat treatment, Co-1HT, Co-2HT, and Co-3HT.	105
Figure 5.5 XRD patterns of the sprayed Co-based coatings. The dashed lines follow the identified alloying phases, the black dots represent non-identified patterns after fouling, the open squares are sulfides, and the open circle is graphite. The graphs (A) depict the Co-1 and Co-1HT, (B) Co-2 and Co-2HT, and (C) Co-3 and CO-3HT samples.....	108
Figure 6.1 Internal view of the batch reactor structure, and sample holder.....	120
Figure 6.2 XRD patterns of alumina coatings on IN625 before and after annealing. The dashed lines represent IN625 (black), γ -alumina (blue), and α -alumina (red). The corresponding alumina phases are indicated above the dashed lines. Database: α -Al ₂ O ₃ (ICDD 046-1212) PDF-2, γ -Al ₂ O ₃ (ICDD 002-1420) PDF-2.	123
Figure 6.3 XRD patterns of alumina coatings on IN718 before and after annealing. The dashed lines represent IN718 (black), γ -alumina (blue), α -alumina (red), and chromium oxide (green). The corresponding alumina phases are indicated above the dashed lines. Database: α -Al ₂ O ₃ (ICDD 046-1212) PDF-2, γ -Al ₂ O ₃ (ICDD 002-1420) PDF-2, and Cr ₂ O ₃ (ICDD 038-1479) PDF-2. The dots correspond to Cr ₂ O ₃ (green), and NbCrO ₄ (purple).	124
Figure 6.4 Scratch tracks of alumina coatings deposited on IN625 (a) and on IN718 (b) before and after annealing at 800, 900, and 1000 °C for 2 h. The cohesive failure (LC_1) is marked in red, and the coating adhesion failure (LC_2) is marked in blue.	126
Figure 6.5 SEM images and EDS compositional maps of the surface of alumina-coated IN625 after annealing for 2 h at 1000 °C. EDS maps correspond to the highlighted rectangular area. .	127
Figure 6.6 SEM images and EDS compositional maps of the surface of alumina-coated IN718 after annealing for 2 h at 1000 °C. EDS maps correspond to the highlighted rectangular area. .	128

- Figure 6.7 Surface region showing the FIB cut area in the alumina-coated IN625 (a) and IN718 (b) after annealing for 2h at 1000°C. The surface is angled by 45° to show the correspondence between the surface and coating/substrate interface. It is possible to identify the correspondence of the alumina grain boundary with the grain boundary of the substrate for IN718 (indicative lines), but no correspondence of the surface grain boundary is present for the IN625..... 129
- Figure 6.8 FIB SEM cross-sections and EDS maps of alumina-coated IN625 (a) and IN718 (b) after annealing at 1000°C for 2h. EDS maps correspond to the highlighted rectangular areas. 130
- Figure 6.9 Alumina-coated IN718 after annealing for 2 h at 1000 °C followed by heavy oil fouling for 2 h at 450 °C: a) SEM images of representative areas at different magnifications; b) Magnified SEM image of the rectangular section of (a.3) and corresponding EDS maps. 132
- Figure 6.10 Alumina-coated IN625 annealed for 2 h at 1000 °C followed by heavy oil fouling for 2 h at 450 °C: a) SEM images at different magnifications, and b) Magnified SEM image of region (a.3) and corresponding EDS maps..... 133
- Figure 6.11 SEM images and EDS maps on the FIB-prepared cross-sections of alumina-coated IN718 (a) and IN625 (b) samples after annealing at 1000 °C for 2 h followed by fouling at 450 °C for 2 h. Images a.1 and b.1 show the surface of the cut area, and EDS maps are taken from the highlighted rectangular areas in a.2 and b.2. 134
- Figure 6.12 SEM images and EDS maps on the cross-sections of as-deposited alumina on IN718 (a) and IN625 (b) after fouling at 450 °C for 2 h. The EDS of image (a) is taken from the whole area, and image (b) is taken from the highlighted rectangular area. 135
- Figure 7.1 Cross-section SEM images of the Inconel 718 substrate coated with A) pc-Coating, B) am-Coating, and C) a-Si/am-Coating. The EDS images represent respective elemental maps. 147
- Figure 7.2 Scratch tracks of the am-Coating, a-Si/am-Coating, and pc-Coating systems. The cohesive failure (LC_1) is marked in blue, and the coating adhesion failure (LC_2) is marked in red..... 148
- Figure 7.3 A) Contact angles of the surfaces, and B) Linear fitting of the OWRK model..... 149

Figure 7.4 Cross-section SEM images and EDS maps of the Inconel 718 alloy with A) pc-Coating, B) am-Coating, and C) a-Si/am-Coating after fouling at 450 °C for 2 h.	152
Figure 7.5 XRD pattern of the fouled coatings. The dashed lines identify the Inconel 718 phases. The crystalline structure orientation of is represented, the asterisk marks correspond to oxide. The silicon-based coating (both without and with the a-Si interlayer) remained amorphous.	155
Figure 7.6 Scratch tracks of the am-Coating and the a-Si/am-Coating deposited on borided Inconel 718. The coating adhesion failure (LC_2) is marked in red.	156
Figure 7.7 Cross-section SEM images and EDS maps of the 718 alloy: A) borided, B) borided and coated with the amorphous film, and C) borided and coated with the a-Si/am-Coating system.	157
Figure 7.8 Cross-section SEM images and EDS maps of the Inconel 718: A) borided, B) borided and coated with the amorphous film, and C) borided and coated with the a-Si/am-Coating system after fouling at 450 °C for 2 h.	159
Figure 8.1 Phenomenological model describing the corrosion fouling mechanism, encompassing: A) the high-temperature sulfidation pathway in heavy oil, B) fouling initiation, C) inorganic scale formation, D) evolution and aging of the inorganic scale, and E) aged inorganic scale.	164
Figure A.1 Stainless Steel 321 catalytic support grid. (A) shows the sample sheet and the corrosion on both sides, (B) shows the elemental identification from point ID EDS, and (C) shows the constructed map from point ID EDS measurements.....	205
Figure A.2 Alloy ASTM A638 (Grade 660). (A) shows the sample cut from a seal ring, (B) shows the squared area EDS elemental maps, and (C) shows the amplified sulfide- and oxide-rich areas.....	206
Figure A.3 Scratch tracks of CeO_2 thin film deposited on IN718. The blue mark identifies the cohesive failure LC_2), and the red mark identifies full coating removal (LC_3).....	207
Figure A.4 XRD pattern of the deposited CeO_2 thin film and IN718 substrate. The dashed lines identify the Inconel 718 phases. The crystalline structure orientation of CeO_2 is represented	208

Figure A.5 SEM image and corresponding EDS maps of Inconel 718 coated with CeO ₂ thin film after fouling at 450 °C for 2 h	209
Figure A.6 Internal side view of the reactor modifications. Blue Thermowell, green agitator coupling to magnetic drive and top bearing holder, and purple main shaft body holding the samples represented in black.....	211

LIST OF SYMBOLS AND ABBREVIATIONS

a_2	model constant
A_r	reactor surface area
a_s	surface area per reactor volume multiplier
<i>AEBP</i>	atmospheric equivalent boiling point
<i>AISI</i>	stainless, austenitic chromium-nickel-molybdenum steels
Al_2O_3	alumina
am-Coating	amorphous coating
<i>API</i>	American Petroleum Institute
BCC	body-centered cubic
C_{Ab}	concentration of bulk fluid
C_{As}	concentration on the surface or film
C_b	concentration in the bulk fluid
C_r	concentration of the reactant
C_s	concentration close to the surface,
CA	contact angle
CCR	conradson carbon residue,
CeO_2	cerium oxide
CFD	computational fluid dynamics
CNESST	Commission des Normes, de l'Équité, de la Santé et de la Sécurité du Travail
CT	catalyst
CTE	coefficient of thermal expansion

<i>CVD</i>	chemical Vapor Deposition
<i>D</i>	diffusion coefficient
<i>d</i>	characteristic length of the tube
<i>D_{AB}</i>	mass diffusivity
<i>dm_f</i>	net deposition rate
<i>dt</i>	infinitesimal time change
<i>DC</i>	direct current
<i>DSLR</i>	digital single-lens reflex
<i>ECTFE</i>	ethylene chlorotrifluoroethylene
<i>EDS</i>	energy dispersive X-ray spectrometer
<i>EIA</i>	energy information administration
<i>E</i>	Young's modulus
<i>E_f</i>	fouling activation energy
<i>E_s</i>	surface energy
<i>E_r</i>	reduced Young's modulus
<i>FCC</i>	face-centered cubic
<i>FFKM</i>	perfluoroelastomers
<i>FIB</i>	focused ion beam
<i>FKM</i>	fluoroelastomers
<i>H</i>	hardness
<i>h_D</i>	convective mass transfer coefficient
<i>HT</i>	heat treatment
<i>H₂S</i>	hydrogen sulfide
<i>HCP</i>	hexagonal close-packed

<i>HE</i>	hydrogen embrittlement
<i>HIC</i>	hydrogen-induced cracking
<i>HTSG</i>	high-temperature sol-gel
<i>HVAF</i>	high-velocity air-fuel
<i>HVOF</i>	high-velocity oxygen fuel
<i>ICDD</i>	international centre for diffraction data
<i>IDLH</i>	immediately dangerous to life or health
<i>IN625</i>	Inconel 625
<i>IN718</i>	Inconel 718
<i>J</i>	joule
<i>k</i>	reaction rate order
k_{Di}	mass transfer coefficient
k_f	the thermal conductivity of foulant
<i>LC</i>	critical load
<i>M</i>	metal
<i>m</i>	stoichiometric factor
$\dot{m}_d$	deposition flux rate
$\dot{m}_r$	removal flux rates
<i>MCR</i>	micro-carbon residue
<i>MCT3</i>	micro-combi tester
<i>n</i>	refractive index
<i>NIOSH</i>	national institute for occupational safety and health
<i>NSERC</i>	natural sciences and engineering research council
<i>O.D.</i>	outer diameter

<i>OWRK</i>	Owens–Wendt–Rabel–Kaelble
<i>PAEK</i>	Polyaryletherketone
pc-Coating	polycrystalline coating
<i>PEEK</i>	polyether ether ketone
<i>PEL</i>	permissible exposure limit
<i>PHR</i>	process hazard review
<i>PSI</i>	pound per square inch
<i>PVD</i>	physical vapor deposition
<i>R</i>	universal gas constant
<i>Ra</i>	roughness
<i>R_b</i>	deposit bond resistance
<i>r_{Di}</i>	rate of diffusion or rate of mass transfer in a stagnant film
<i>R_f</i>	fouling resistance
<i>RF</i>	radio frequency
<i>R_g</i>	ideal gas constant
<i>S</i>	elemental sulfur
<i>Sh</i>	Sherwood number
<i>SCC</i>	stress corrosion cracking
<i>SCP</i>	standardized control procedure
<i>SEM</i>	scanning electron microscope
<i>SiBCN</i>	silicon boron carbon nitride
<i>S_s</i>	surface entropy
<i>SSC</i>	sulfide Stress Cracking
<i>SSCC</i>	sulfide stress corrosion cracking

<i>SZD</i>	structure zone diagram
<i>SARA</i>	saturate, aromatic, resin, and asphaltene
<i>t</i>	film thickness
<i>T</i>	temperature
<i>T_s</i>	temperature of the surface
<i>TBC</i>	thermal barrier coatings
<i>TGO</i>	thermally grown oxide
<i>TiAlN</i>	titanium aluminum nitride
<i>TiN</i>	titanium nitride
<i>TSD</i>	thermal spray deposition
<i>U_s</i>	surface internal energy
<i>V</i>	reactor volume
<i>v'</i>	stoichiometric coefficients
<i>v_M</i>	stoichiometric coefficient of the metal
<i>v_S</i>	stoichiometric coefficient of sulfur in the sulfide
<i>VTB</i>	vacuum tower bottoms
<i>W_a</i>	work of adhesion
<i>W50</i>	Wallex 50
<i>WDS</i>	wavelength-dispersive X-ray spectrometer
wt. %	weight percentage
<i>XRD</i>	X-ray diffraction

Greek letters and symbols

α	alpha, Arrhenius pre-exponential term
----------	---------------------------------------

γ	gamma, interfacial free energy
γ_l	total surface energy of the liquid
γ_l^d	dispersive component of the liquid's surface energy
γ_l^p	polar component of the liquid's surface energy
γ_s^d	dispersive component of the solid's surface energy
γ_s^p	polar component of the solid's surface energy
Γ	surface activity
ΔG	Gibbs free energy of formation
θ	angle, contact angle
k	extinction coefficient
ρ_f	foulant density
σ	strength of adhesion
τ	shear stress
ϕ_d	deposition term
ϕ_r	removal term
φ	deposition mass flux
$^{\circ}$	degrees
$^{\circ}\text{C}$	degrees Celsius
$^{\circ}\text{F}$	degrees Fahrenheit
μm	micron meter
$\%$	percentage

LIST OF APPENDICES

APPENDIX A	Failure analysis of industrial samples.....	203
APPENDIX B	CeO ₂ thin film fouling	207
APPENDIX C	Process hazard review.....	210

CHAPTER 1 INTRODUCTION

1.1 Motivation

The increase in demand for crude oil derivatives and the depletion of high-quality light crude represent a substantial growth in the exploration of a broad range of feeds. For refiners around the globe, the conversion of heavy oil remains a significant financial factor. As the world calls for lighter fuels as naphtha and middle distillates of crude oil increase, sources of unusual oil and heavy crude become essential to supply the market. Optimizing the residuum conversion technology to yield a wide range of light and medium distillates is the toughest mission confronting refiners today and depends on the knowledge about the feedstock, products, physicochemical properties, and catalysts tailoring [1]. The expected investment in petroleum-related infrastructure for the next decade is estimated to be over \$1 trillion. The conventional oil production reaches a production plateau, indicating that the investment is mainly destined to unconventional and new oil sources, to overcome technological challenges [2].

Canada is the world's fifth-largest oil producer and has the world's third-largest proven oil reserves [3]. Canadian oil production increased by 16% from 2015 to 2020, and 82% of the volume of crude was exported [4]. According to the Energy Information Administration (EIA) statistics, in 2022, Canada accounted for 60% of the United States' gross crude oil imports [5]. However, oil sands are over 97 percent of Canada's 171 billion barrels of proven oil reserves [6]. Oil sands consist of a complex blend of sand (83%), bitumen (10-12%), water (4%), and clay (3%). Producing synthetic crude suitable for oil refineries requires extensive separation and upgrading processes [7]. Crude oil heavy fractions usually have a sulfur content higher than 2% by weight [8], and bitumen can reach up to 7% of sulfur [9]. Bitumen also contains nitrogen, oxygen, and traces of metals such as vanadium, iron, and nickel [10]. The presence or higher concentration of reactive contaminants, especially sulfur, increases the technological challenges of the materials during all exploration steps [11]. According to NACE International, the cost of corrosion in the United States oil and gas industry is estimated to be \$1.372 billion. These costs and environmental risks are likely to increase in future years from the exploration of unconventional oil [12]. Materials that are simultaneously resistant to corrosion and wear at high temperatures are needed to address the increase in unconventional oil exploration, which exposes surfaces to harsher sulfur-containing environments.

1.2 Problem identification

When processing crude oil, materials are exposed to extreme environments. The operational conditions are harsher when dealing with heavy oil and bitumen, exposing the surfaces to higher sulfur concentrations (> 2 wt. %) and temperatures (> 290 °C). The properties of the oil vary according to the proportion of the main components [13], and that proportion varies from one field to another, from wells in the same field, and even in the same well according to the oil level [8]. The exposed surfaces corrode, forming an inorganic scale, while organic material is deposited, characterizing fouling [14]. Fouling by sulfur aggressive attack and organic fluids from crude oil is a combined effect of reactions, dependent on the stream location of the plant site, oil composition, blending proportion, presence or absence of oxygen, temperature, metal, nature of the acids, pH, etc. [15].

Unlike chemical mixtures, the corrosiveness of sulfur-containing hydrocarbons is not proportional to the sulfur weight percentage. Crude oil, especially the heavy sour fractions, contains a wide variety of sulfur-bearing constituents: elemental sulfur (S), hydrogen sulfide (H_2S), sulfides (SR), disulfides, polysulfides (RS_nR), mercaptans (RSH), sulfide salts, aromatic sulfides, aliphatic sulfides, etc. At high temperatures, some sulfide compounds suffer decomposition (different temperatures and rates), releasing elemental sulfur and H_2S that react with the metal surfaces. Combining the effect of sulfidic corrosion with fouling lead by the same compounds' decomposition, the surface problem intensifies [16]. Although corrosion inhibitor technology has advanced significantly, the corrosion inhibitory effect in sour oil (> 0.5 wt. % sulfur) is limited compared to sweet conditions (< 0.5 wt. % sulfur); it is ineffective or even detrimental for sour conditions [17].

The mechanism behind H_2S corrosion is not fully understood, leaving several open questions regarding how the microstructure of alloys (Fe-, Ni-, and Co-based) and the formed metal sulfide films influence corrosion. Understanding corrosion mechanisms and improving corrosion control, especially for localized corrosion (e.g., pitting corrosion), remains unresolved. General sour corrosion can be estimated based on the theoretical and empirical effects of sulfide scale layers, but reliable localized corrosion mechanisms need to be developed [17]. There is a lack of theoretical understanding about the intergranular cracking mechanism, heat treatment and metallurgy influence, and hydrogen sulfide migration through the alloy [18]. The nuances

involving sulfur-related corrosion need further investigation [16], as the alloying effect of an element and the concentration relationship is not always an obvious, straightforward relationship [19]. The determination of the initiation steps of corrosion is crucial for materials development.

The inherent complexity of the process is one of the reasons that material engineering focuses on studying only how the degradation occurs and how to mitigate it, rather than studying the effects of the reaction. Material selection is a critical factor in the design of a system and requires proper information about the feed composition [20]. However, no standardized data is available for quantitative comparison of material performance. Major efforts to elucidate fouling mechanisms in the gas and oil industry focused on iron alloys and heat exchangers. Several studies have examined the formation of FeS and its contribution as a promoter of carbonaceous fouling, commonly known as coke [17], [18], [19].

Other critical components, such as industrial valves, require investigation of fouling mechanisms. Valves are typically produced with refractory metals or other elements resistant to heat and wear, but for H₂S- and H₂-containing environments, lower-hardness materials are recommended to prevent embrittlement and sulfide stress cracking initiation [18]. At low hardness, the material retains better toughness and ductility, reducing its susceptibility to cracking under tensile stress. NACE Standard MR0175-90 suggests as a good practice to avoid hard valve components to prevent sulfide stress cracking, leading to brittle failure without significant plastic deformation [16]. Complications arise when dealing with the regulations. There is a need to better define limitations from approved and novel materials regarding Sulfide Stress Cracking (SSC). NACE MR-0103 allows the use of some materials that are not included in NACE MR-0175. Some materials have been deleted from ISO 15156/NACE MR-0175, leading to a non-practical replacement of components [18]. The limitations of several useful materials for valves need to be determined, such as metal oxides, nitrides, and borides.

A combination of adequate valve alloys and hard coatings is required to avoid catastrophic failure while maintaining the components' structural integrity and adequate wear properties. However, direct deposit of a harder coating onto a softer substrate can lead to delamination due to the lack of adhesion or thermal expansion coefficient incompatibility, and differences in elastoplastic, and structural characteristics [21]. Together with erosion, fouling can cause significant damage to the

valves within the industrial plant. Fouling is one of the most significant causes that lead to unstable reactor pressure control and valve failure [22].

Valve problems at hydrocracking units represent safety and economic issues since repairing a worn valve is an arduous, lengthy, dangerous, and costly service. The coating solutions proposed to be beneficial in protecting materials against sulfidation have only been shown in ideal conditions. In the context of valve applications, the sealing surface has to remain intact, and even protective scale formation can represent a problem. Thus, the typical protective materials are not suitable, as most of their protection comes from the formation of oxide layers, which are brittle in nature. There are different possible solutions to mitigate the material damage, but some are not realistic or expensive and may require a complete process redesign.

1.2.1 Problem statements

1. As reported by the heavy-oil cracking industry, layers in the material surface induce a mismatch between sealing surfaces, leading to a loss of sealing integrity when the valve is closed (Figure 1.1). In some cases, a significant change in the geometry can increase torque requirement and stroke time, leading to inoperability (seizure) or even fracture of the materials. An isolation valve failure can be defined by inoperability or leakage (failure to seal). Both failure modes can have multiple origins. This work focuses on failures induced by a change in the shape of the ball and seat sealing surfaces due to the formation of a mechanically robust layer. Two scenarios can be explored to solve this challenge: 1) Suppression of the formation mechanism of the detrimental layer, or 2) Minimizing bond strength of the detrimental layer to ease removal when stroking the valve by mechanical or chemical methods.
2. Both strategies can be explored using coating technology. Surface engineering through coating technology is a flexible and cost-effective technique to enhance the performance of existing components. The coating is a barrier preventing environmental interaction with the underlying surface. In an ideal world, the selected coating material must be multifunctional, presenting as many characteristics as possible, like corrosion, oxidation and abrasion resistance, hydrophobicity or hydrophilicity, thermal stability, anti-stick properties, and mechanical toughness.
3. From a general perspective, coke deposition is intimately linked to surface energy, so lowering the chemical activity of the surface should modify the coke-growth kinetic. The

environment is sulfur-rich, and materials that are known not to react with sulfur to form a scale should be prioritized. In addition to the previous requirements, the potential coating solution should resist high temperature (up to 500°C), sulfidic corrosion, long exposure time, and wear under conditions typically found in valve applications.

4. The selection of materials is based on what type of material must be protected for a given application. Here, INCONEL® alloy 718 (IN718) is most frequently used as a substrate material, and the performance of the coatings will be compared to a baseline material used as valves in the industry. The interface can be engineered to improve coating adhesion and create an adequate gradient of properties to accommodate the difference in properties between the coating and substrate (e.g., ion bombardment, boriding, nitriding, and interlayers).
5. The lack of data about the limitations of new materials slows down acceptance for possible field applications [23]. The protection against sulfidic corrosion/sulfidation is strongly linked to the formation of oxides. However, the feed composition is an uncontrollable factor influencing the formation and morphology of the protective oxide scale [24]. Thus, to avoid uneven scale formation, which can lead to poor corrosion protection and significant changes in the geometry of the protected component, a direct deposit of a protective layer is suggested instead of promoting oxide-forming elements.
6. Non-metallic components have been extensively used for corrosion applications [25]. However, they are limited to material incompatibility (e.g., environment chemicals, adhesion, temperature, and pressure).
7. Gaps between field and laboratory experimental data are hard to overcome [17]. Standardization in corrosion test protocols and new characterization methodologies for materials selection are needed to compare the performance and corrosion mechanisms, further reducing artifacts and errors in sour corrosion studies.

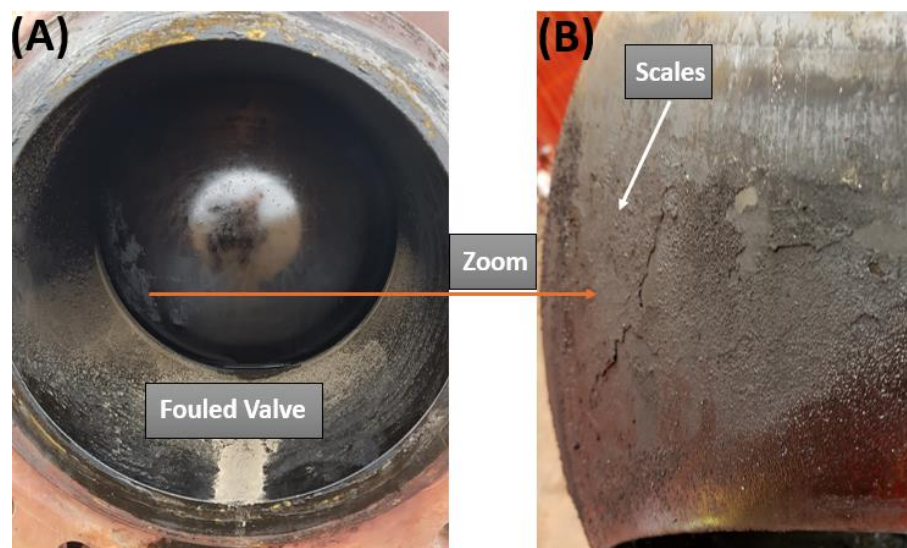


Figure 1.1 Fouled ball valve used in heavy oil hydrocracking operations. (A) shows a general view of the valve surface, while (B) provides a close-up of scale deposits.

1.3 Objectives

The main objective of this thesis is to develop coatings for isolation valves that are resistant to sulfidation and coke formation under high temperature and pressure conditions of crude oil environments (Figure 1.2).

The specific objectives are summarised as follows:

- I. Develop the methodology for the assessment of fouling and sulfidation.
- II. Optimize the performance of sprayed coatings and compare it to the benchmark materials.
- III. Fabricate oxide and nitride coatings with magnetron sputtering and evaluate their performance.

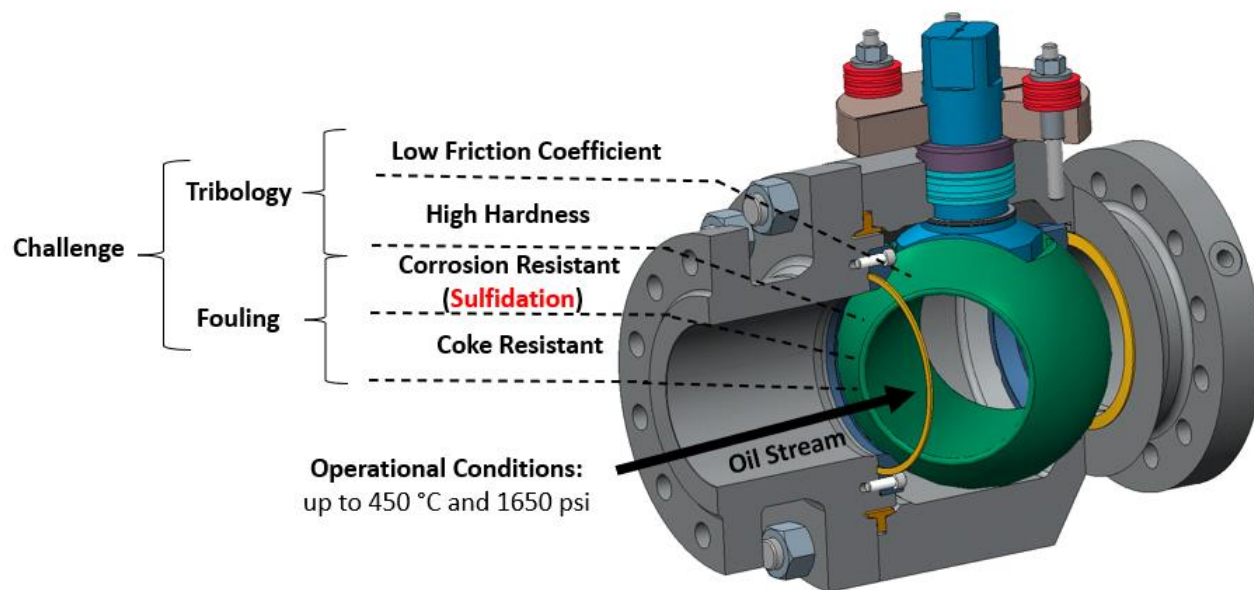


Figure 1.2 Schematic of a ball valve and the challenges to overcome.

1.4 Scientific contributions

The main results presented in this thesis gave rise to publications submitted to peer-reviewed journals. These articles represent the body of this work and address the specific objectives described above (Table 1.1). The results obtained were also presented at conferences (Table 1.2). Failure analysis of industrial components was carried out (Appendix A) and compared to samples produced on the laboratory scale. A Process Hazard Review (PHR) describing the reactor design, modifications, certification, materials compatibility, and risk analysis was produced (Appendix C).

Table 1.1 Publications in peer-reviewed journals.

Fellipy S. Rocha, Pedro R. T. Avila, Fadila Khelfaoui, Luc Vernhes, Gregory S. Patience, Kevin J. Smith, Jolanta E. Klemberg-Sapieha, Ludvik Martinu. “Heavy Oil Corrosion Fouling of Ni-based Alloy and Co-based Thermal Sprayed Coatings.”

Submitted to *Fuel*, 2024.

Fellipy S. Rocha, Pedro R. T. Avila, Oumar Touré, Marwan Azzi, Fadila Khelfaoui, Luc Vernhes, Gregory S. Patience, Jolanta E. Klemberg-Sapieha, and Ludvik Martinu. “Enhanced Heavy Oil Fouling Resistance of Cobalt-based Spray-Deposited Coatings by Alloy Design and Heat Treatment.”

Published in *Surface and Coatings Technology*, SCT, 2024.

Fellipy S. Rocha, Etienne Bousser, Marwan Azzi, Fadila Khelfaoui, Luc Vernhes, Gregory S. Patience, Jolanta E. Klemberg-Sapieha, Ludvik Martinu. “Alumina Coatings on Ni-based Superalloys: The Impact of Annealing on Heavy Oil Fouling.”

Published in *Surface and Coatings Technology*, SCT, 2024.

Table 1.2 Presentations at conferences and symposia.

Fellipy S. Rocha, Marwan Azzi, Luc Vernhes, Fadila Khelfaoui, JE Klemberg-Sapieha, Ludvik Martinu. "Co-Ni-Cr-W Based Coating Surface Sulfidation." 10th International Symposium on Group Five Elements, Montreal, 2023.

Fellipy S. Rocha, Marwan Azzi, Luc Vernhes, Fadila Khelfaoui, Gregory Patience, JE Klemberg-Sapieha, Ludvik Martinu. "Reactively Sputtered Alumina Coatings on Inconel Substrate for Crude Oil Fouling Protection." Canadian Chemical Engineering Conference (CSCChE), Calgary, 2023.

Fellipy Rocha, Luc Vernhes, Fadila Khelfaoui, Gregory Patience, JE Klemberg-Sapieha, Ludvik Martinu. "Protection Against Heavy Oil Fouling and Sulfidation: Comparison of PVD and Thermal Sprayed Coatings." 50th International Conference on Metallurgical Coatings and Thin Films (ICMCTF), 2024.

1.5 Thesis organization

The thesis content is presented in terms of nine chapters and other sections, and it is as follows:

Chapter 1 highlights the challenges the gas and oil industry faces while processing unconventional oil feed. It describes the industrial motivations of the project to improve the performance of industrial valve materials through surface engineering. The chapter also introduces the main problems and outlines the objectives.

Chapter 2 provides a brief literature summary about surface organic and inorganic fouling related to the oil cracking process and an understanding of alloys and materials selection for this application. It also presents a background in surface engineering and techniques for fabricating coatings.

Chapter 3 illustrates the methodologies for testing samples, coating fabrications, and characterization techniques.

Chapter 4 explores fouling on IN718 and Wallex 50 benchmark materials. It aims to enhance our understanding of the early stages of fouling and the morphology of the inorganic scales formed from sulfides and oxides.

Chapter 5 studies the sprayed Co-based coatings, the effect of heat treatment, and the variation of the elemental composition on protection performance.

Chapter 6 describes the fouling protection using alumina thin films, the interaction of the substrate and coating after annealing, and the effects of this interaction on the performance against fouling.

Chapter 7 shows the performance of SiBCN, and TiAlN coatings in protecting against coke formation and sulfidation.

Chapter 8 contains a general discussion of the work with limitations and perspectives.

Chapter 9 describes the conclusions of the presented study.

CHAPTER 2 LITERATURE REVIEW

2.1 Heavy oil

The petroleum complex mixture ranges from 10 000 to 100 000 constituents, with more than 10 000 different elemental compositions identified ($C_cH_hN_nO_oS_s$) [26], encompassing approximately 100 distinct chemical species [27]. The composition varies based on the nature of the organic material, geological properties, temperature, and pressure, leading to changes in physical and chemical properties [28]. The identification of crude oil components is typically categorized into SARA groups: saturated hydrocarbons (alkanes and cycloalkanes), aromatic hydrocarbons, resins (alkane chains with highly polar end groups), and asphaltenes (condensed aromatic rings associated with aliphatic tails). Resins and asphaltenes represent the higher molecular weight fraction and contain the majority of heteroatoms (S, O, and N), forming polycyclic and organometallic compounds, as well as metals. Unsaturated hydrocarbons (olefins) are absent from the mixture, with the highest concentration of hydrocarbons found in the light fraction of crude oil ($< C_{15}$) [29].

The properties of crude oil vary according to the proportions of its main components. Alkanes are the most abundant fractions, consisting of straight (n-paraffins) and branched (isoparaffins) chains in conventional oil. The proportion of saturated hydrocarbons decreases as molecular weight increases [13]. Heavy fractions typically, though not always, contain a sulfur content greater than 2% by weight [8]. Among the SARA fractions, asphaltenes tend to aggregate, contributing to high viscosity values [2], and viscosity increases exponentially with asphaltene concentration [30]. Asphaltenes are responsible for the rheological properties of fossil fluids. The viscosity of heavy oil is related to the concentration, structure, and aggregation of asphaltenes [31]. In addition to categorizing petroleum derivatives based on their physical properties, heavy oils are also arbitrarily defined as those fractions that require thermal stimulation for recovery, such as bitumen from bituminous sands (tar sands and oil sands) [8]. Temperature directly impacts viscosity and is influenced by the volatility or composition of the oil, primarily affecting the heavy fractions [2]. An increase in temperature promotes the dispersion of monomer units through disruption of the macromolecular structures aggregates [32].

The molecular-level characterization of heavy oil was first attempted by Boduszynski [33]. He observed that the variation in heteroatom concentration, hydrogen deficiency, and molecular weight is a function of atmospheric equivalent boiling point (AEBP), based on the hypothesis that

a high boiling point does not necessarily indicate a high molecular weight. The plot of carbon number versus AEBP reveals that for a specific carbon number, a wide range of boiling points exists among petroleum compounds [34]. Boduszynski demonstrated that hydrogen deficiency and heteroatom concentration increase with rising AEBP, and the distribution profile of metals, sulfur (S), and nitrogen (N) suggests that these elements are constituents of the same molecular structures [33].

The processing of heavy oil, bitumen, and vacuum residues forces refineries to handle highly contaminated feedstocks. The large quantity of contaminants leads to catalyst deactivation and reactor fouling [35]. Upgrading heavy feedstocks falls into two main categories: carbon rejection and hydrogen addition processes. Carbon rejection redistributes hydrogen, creating fractions with varying H/C atomic ratios. In contrast, hydrogen addition introduces external hydrogen to increase the overall H/C ratio. These broad categories are further subdivided into specific upgrading technologies [36]. Coking, particularly delayed coking, is the most widely used carbon rejection technology, generating petroleum coke as a byproduct through thermal cracking [37].

Hydrocracking is a representative technology of the hydrogen addition process, operating within a high upper-end temperature range (290–445 °C) and pressure (150–3000 psi) in the presence of a catalyst [38]. The LC-FINING ebullating bed process is particularly well-suited for hydrocracking heavy sand oils, bitumen, and vacuum residuum feedstocks into high-quality transportation fuels and fuel oils, while simultaneously removing sulfur, nitrogen, micro-carbon residue (MCR), Conradson carbon residue (CCR), asphaltenes, and metal-containing species [11].

2.1.1 Organic fouling

The higher proportion of asphaltenes, sulfur, and metals in heavier oils is the primary driver of increased fouling rates [39]. Asphaltenes are a highly diverse structural class of non-hydrocarbon compounds that constitute approximately 15% of heavy oil content, with concentrations that can be even higher in residues [40]. Their molecular weight ranges from 600 to 2 000 000 g/mol, and their density falls between 1.1 and 1.20 g/mL, with an H/C ratio of 1.0 to 1.2 [41]. Asphaltenes consist of condensed aromatic rings linked to aliphatic tails, containing highly polar species [41], or fused aromatic and naphthenic ring core structures with alkyl side chains [34]. Their structure resembles graphene fragments, where interaction and association behavior are governed by the

condensed structure's π - π stacking and the presence of functional polar groups [42]. Some of the various polar functional groups include sulfoxides, carboxylic acids, and amides [27].

Blending crude oil can lead to the precipitation of species due to unstable mixing proportions [39]. The Hildebrand solubility parameter is used to evaluate the compatibility of crude oils and the stability of asphaltenes [43]. This solubility parameter is the most widely accepted empirical thermodynamic approach for describing stability, defined as the square root of cohesive energy density [44]. Wiehe classifies fouling due to asphaltene stability into three modes: nearly incompatible, incompatible upon blending, and incompatible [44]. The presence of additives can alter the structure, mechanism, and kinetics, contributing to the imprecision in crude oil science [30]. Coke deposition progressively forms less stable oil blends, which, in conjunction with corrosion, results in the release of more metal from the surface. The interaction between these processes is attributed to the thermal generation of hydrogen sulfide [44].

Organic fluid fouling is classified into three general classes of reactions: autoxidation, polymerization, and thermal decomposition [45]. Researchers have typically focused on autoxidation because it plays a central role in deposit formation in heat exchangers [46]. Autoxidation involves a complex set of free radical reactions. Thermal condensation cracking is the dominant reaction class in the higher temperature range (250-300 °C) associated with autoxidation. Indeed, autoxidation has been reported as the controlling reaction mechanism for hydrocarbon fluid fouling at low and medium temperatures [47]. At higher temperatures, thermal decomposition reactions, such as cracking, thermolysis, and pyrolysis, become the primary sources of fouling. The thermal decomposition of hydrocarbons generates radicals, making the reaction autocatalytic. However, the fouling pattern of asphaltenes is more challenging to categorize within these three primary cases of organic fouling, and little progress has been made in this area [45].

Thermal destabilization of asphaltenes and coke formation are important mechanisms associated with organic deposition and adhesion to hot surfaces [48]. Due to the complexity of the asphaltene fraction, it is practically impossible to determine which specific compounds are responsible for the fouling process or to measure their individual contributions [49]. When heated above 300 °C, asphaltenes do not melt; instead, they decompose, forming carbon and volatile products that react to form compounds interacting with the surface [41]. At elevated temperatures, the thermal reaction of aliphatic sulfur compounds from heavy crude oil generates hydrogen sulfide [44]. A similar

effect is observed for asphaltene molecules extracted from crude oil when they react in the temperature range of 300 to 500 °C in both air and nitrogen (N₂) atmospheres [50].

The degree of instability of asphaltenes is directly related to the fouling rate, with the dehydrogenation reaction of asphaltenes on hot surfaces leading to coke formation on the walls [44]. There is limited information regarding the processes that result in coke formation from asphaltenes [51]. Coke can form either directly on the surface or in the fluid bulk, and the amount of asphaltene content can determine the formation rate of amorphous, high-adhesive coke [48]. The temperature of 350 °C is considered a threshold for increased coke formation in an oil environment, and the presence of asphaltenes is believed to lower the temperature required to initiate coking. Coke is thought to result from cracking, polymerization, and condensation reactions. It is defined as the toluene-insoluble carbonaceous solids formed under temperature-influenced reactions of carbon-rich materials. The formation of coke is an irreversible process [44].

The complex interaction of coke formation on surfaces is influenced by the surface properties, and sulfur content. The kinetics of catalytic coke deposition are significantly faster on pre-oxidized surfaces compared to reduced ones. For iron surfaces, oxidizing atmospheres produce Fe₃O₄ and Fe₂O₃, which act as coke formation catalysts [52]. Fe₂O₃ decreases crystalline volume, coke strength, aromaticity, graphitization degree, and carbon order [53]. The addition of Fe₂O₃ catalyst promotes the breakdown of heavy aromatic rings, with no triple-bond aromatic rings detected in tar at 600–700 °C [54]. These effects could facilitate the coke removal from the surface.

High concentrations of sulfur-containing additives are given to effectively suppress carbon deposition on metals, whereas sulfur-free catalysts are prone to rapid carbon formation [55]. However, the relationship between sulfur content and coke inhibition is not obvious. For instance, trace levels of H₂S below 1 ppm can exhibit a protective effect against catalytic coke formation on iron, with the oxidative state of the surface playing a role in this behavior [52]. Conversely, H₂S concentrations of 5–10 ppm promote catalytic carbon growth on iron, nickel, or cobalt particles, while 25 ppm of organic sulfides have been shown to reduce catalytically generated carbon [55]. In contrast, aromatic sulfur compounds in jet propellants at 450 °C accelerate coke formation [56].

The inhibitory effect of sulfur on carbon formation is a dynamic phenomenon [57]. The formation of stable metal sulfides is thought to play a key role in suppressing carbon deposition, while the subsequent decomposition of these sulfides may accelerate carbon formation [58]. Although sulfur

can reduce catalytic coke formation, amorphous carbon may still form at very high carbon potentials when sulfur coverage increases [57].

Compounds not naturally present in crude oil, such as olefins, can influence fouling. They are formed during the crude conversion process and serve as feedstock for the petrochemical industry [59]. Olefins are unsaturated carbon compounds characterized by double bonds, referred to as alkenes [60]. Compounds with triple bonds are known as alkynes or biolefins [59]. Olefins are significant in fouling processes because they are more unstable than paraffins and react readily with compounds such as oxygen, halogens, and even with each other [60]. Olefins exhibit a low propensity to cause fouling at surface temperatures below 200 °C; however, in the temperature range of 250 to 325 °C, the polymerization reaction of olefins increases fouling, and temperatures above 350 °C lead to a significant rise in fouling rates. A slow polymerization of olefins is observed at 270 and 300 °C [61]. The reactivity of these molecules can induce hydrogenation and double-bond isomerization reactions. Additionally, associative forms of adsorption (e.g., π -interactions) and metal-carbon bonds are major factors influencing the hydrocarbon adsorption mechanism [62]. Thus, olefins represent another important class of molecules contributing to organic fluid fouling alongside asphaltenes.

Carbonaceous fouling is classified as "acute" when it occurs over short periods of time [63], and is typically associated with the processing of thermally unstable feedstocks [64], often due to the destabilization of particulates or asphaltenes caused by mixing incompatible oils or slop oils [65]. The fouling is referred to as "chronic" when it develops slowly over months or years, resulting from a gradual accumulation of organic materials [63]. Evidence suggests that this "steady state" fouling is a synergetic process involving both sulfidic corrosion and coke formation [66]. The triggers of "acute" inorganic fouling may be linked to elevated concentrations of inorganic precursors or particles, along with other contributing factors. A deposit composition model supports the assumption that the rate of organic material deposition is independent of the behavior of inorganics. Thus, the fouling mechanism may be described as an alternation between chronic organic/inorganic deposition and acute deposition of inorganic materials. Both inorganic and organic deposition rates exhibit similar dependencies on shear and temperature; however, inorganic deposition also relies on other unknown phenomena [14]. To more effectively analyze deposit formation, it is necessary to integrate precipitation, chemical reaction, and corrosion models [67].

2.1.2 Inorganic fouling

The molecular structure of asphaltenes contains varying proportions of inorganic elements such as sulfur (0.3%–10.3%), oxygen (0.3%–4.8%), nitrogen (0.6%–3.3%), and trace amounts of metals (Fe, Ni, and V) in the form of porphyrins [68]. During thermal decomposition, these inorganic elements are released and contribute to non-organic fouling, such as sulfidic corrosion [49]. Nitrogen-containing compounds, like pyrroles and pyridines, can negatively impact hydrocarbon stability, while oxygen promotes oxidation. Sulfur compounds exhibit a more complex behavior. Free sulfur, disulfides, polysulfides, and thiophenol promote sludge formation in storage tanks, whereas diphenyl sulfide, dibenzothiophene, aliphatic mercaptans, and aliphatic sulfides show minimal effects. Thiols, sulfides, disulfides, and condensed thiophenes can decompose thermally to form free radicals. Sulfur heteroatoms in branched structures can also promote the thermal decomposition of alkanes [69]. Interestingly, some sulfur compounds, such as thiophene, may mitigate chronic carbonaceous fouling when added to oil, likely through a preferential adsorption mechanism [66]. Sulfur impurities are also responsible for the polarity of asphaltenes, enhancing their self-association properties and contributing to sulfidic corrosion [70].

The mechanism of inorganic fouling via the sulfidic corrosion process begins with the thermal destabilization and decomposition of sulfur-containing compounds, which form the more stable hydrogen sulfide (H_2S) at temperatures above 230 °C [71]. Up to 95% of the original sulfates (SO_4^{2-}) in the aqueous phase are reduced to H_2S and CO_2 at temperatures around 300 °C. H_2S starts to thermally dissociate into sulfur and hydrogen at temperatures above 350 °C and fully dissociates at 1 700 °C. Free sulfur becomes highly reactive when heated, reacting with hydrogen, oxygen, and metals. Various sulfur-bearing compounds affect the kinetics of H_2S formation differently, with disulfides and mercaptans being the most reactive under thermal stress, followed by aliphatic sulfides and thiophenic compounds. Benzothiophenic compounds are the most stable organically bound sulfur species during the thermal decomposition of crude oil [15]. These reactive sulfur compounds interact with metallic components from the feed, local material surfaces, and upstream piping, contributing to corrosion. Simultaneously, coke is deposited, forming a strongly adherent carbonaceous layer on the surface [71].

Sulfidic corrosion occurs within a temperature range of 230–540 °C in the oil and gas industry [15], presenting a predominant problem between approximately 230 and 450 °C. This type of

corrosion is classified as a uniform corrosion attack in the range of 232–427 °C, especially in environments where liquid or vapor phase oil contains sulfur species, a common occurrence in downstream oil refineries [72]. The sulfidic corrosion rate tends to increase from 230 °C, peaking around 425–450 °C and decreases when the temperature rises above 450 °C until 540 °C. By approximately 425 °C, most corrosive sulfur compounds have likely reacted with metallic surfaces [15]. Some studies suggest sulfidic corrosion starts when the metal temperatures are above 200 °C, with significant activity between 235 °C and 485 °C [16], while others define sulfidic corrosion of steels at temperatures exceeding 450 °C [73]. The variance in temperature ranges and the characterization of sulfidic attack in the oil and gas industry can be attributed to the kinetics of sulfur compound decomposition, sulfur scale formation, and coke deposition. Each of these phenomena is influenced differently by temperature [74], and oil composition also varies based on the reservoir level and location [8].

McConomy and Couper-Gorman curves are widely utilized to predict sulfidic corrosion rates in established iron-based alloys. The modified McConomy curves are typically applied in environments without hydrogen, while Couper-Gorman curves are used for environments containing hydrogen [75]. Despite extensive study, the exact mechanism of metallic sulfidic corrosion remains unclear. It is generally accepted that corrosion progresses through the formation of a metal sulfide film on the surface, which is described as “pseudo-passive.” This means the film is semi-protective but not a tenacious barrier against corrosion [72].

Sulfidic corrosion is also named as sulfidation or high-temperature sulfidic corrosion. It is categorized as a “pure” chemical reaction occurring under “dry” conditions, meaning without the presence of electrolytes, and it proceeds via a non-electrochemical pathway [15]. Unlike typical corrosion reactions that involve water and are governed by electric potentials, sulfidic corrosion does not involve electrical current or potential on the metal surface. Therefore, it cannot be explained using models that rely on electrical potential, such as the Tafel kinetic equation, which is often adequate for other corrosion processes [19].

Although water may not directly influence the sulfidation reaction, it plays a significant and complex role in crude oil fouling processes. Water in crude oil is typically present as a water-in-oil emulsion and plays a critical role in the stability of compounds such as asphaltenes. Under thermal stress, the emulsion equilibrium becomes destabilized, leading to the separation of water

droplets and heavy organic matter, which subsequently precipitate and contribute to particulate fouling [76], [77]. Higher concentrations of dissolved salts (e.g., NaCl and CaCl_2) within the aqueous phase can further promote inorganic fouling [78]. When exposed to heat, these salts may undergo hydrolysis, producing acidic compounds that exacerbate corrosion [79]. Additionally, water can decompose into reactive species and oxygen radicals, which catalyze the formation of fouling precursors and accelerate corrosion, further intensifying surface fouling [80]. Therefore, water content significantly influences fouling mechanisms by precipitating salts and facilitating corrosion reactions (inorganic fouling) while simultaneously destabilizing asphaltenes, triggering precipitation, and promoting polymerization reactions (organic fouling).

Traditional corrosion models describe corrosion rates as being controlled by three types of kinetic reactions: electrochemical activation energy, mass transport, and ohmic resistance [81]. In the context of sulfidation, which is a “pure” chemical reaction, the process is thought to be primarily controlled by mass transport. Since H_2S is a key component driving sulfidic corrosion, its surface interaction can be modeled as a mass flux-controlled reaction. The total mass flux is a combination of three processes: 1) convective diffusion through the mass transfer boundary layer, 2) molecular diffusion through the liquid in the porous outer layer, and 3) solid-state diffusion through the inner sulfide film [82]. Remarkably, even low concentrations of H_2S , as little as 2 ppm, are sufficient to initiate the formation of sulfide scales [83].

Sulfidation can be seen as the “oxidation” caused by sulfur compounds. Wagner’s theory of alloy oxidation is applicable to sulfidation [84], as well as to other processes like carburization and nitridation [85]. The reaction of iron sulfidation has been extensively studied, fitting the Wagner’s theory [86]. The growth of sulfide and oxide scales on alloying elements typically follows a parabolic growth pattern [87], where the thickness of the scale increases over time, but the growth rate slows down. In some cases, sulfidation initially proceeds at a linear rate, governed by the inward diffusion of sulfur rather than the outward diffusion of metal cations, until a certain scale thickness is established [88].

Sulfidation is significantly more destructive than traditional oxidation due to several key factors, including the microstructure of the scales, the thermodynamics of sulfide formation, and the physicochemical properties involved. Sulfur-induced corrosion progresses more rapidly than oxidation, with the rate of the bimolecular gas-phase reaction of H_2S being represented by an

Arrhenius-type equation [89]. The Pilling-Bedworth Ratio of metal sulfides is higher than for oxides [90], leading to an increased volume of the elementary cell. This expansion facilitates faster diffusion, accelerating further corrosion. The continuous sulfide phase on the material surfaces provides alternative pathways for faster ion diffusion [91].

The high concentration of point defects in sulfides, which can reach around 1% in the solid state, is related to the variability in stoichiometry depending on the conditions under which the scales form. Furthermore, the parabolic growth constant of sulfide scales is 2 to 7 orders of magnitude greater than that of oxide scales [87]. The sulfidation rate of metallic elements can be 10^4 to 10^6 times faster than the corresponding oxidation rate, depending on the temperature [92]. The free energy of formation plots for oxides and sulfides (Figure 2.1) indicate that oxides are more thermodynamically stable than sulfides. Additionally, the differences in the free energy of formation among various metal sulfides are smaller compared to those of their corresponding oxides, resulting in lower thermodynamic stabilization. These factors underscore why sulfidation is more aggressive and challenging to manage in industrial environments compared to oxidation.

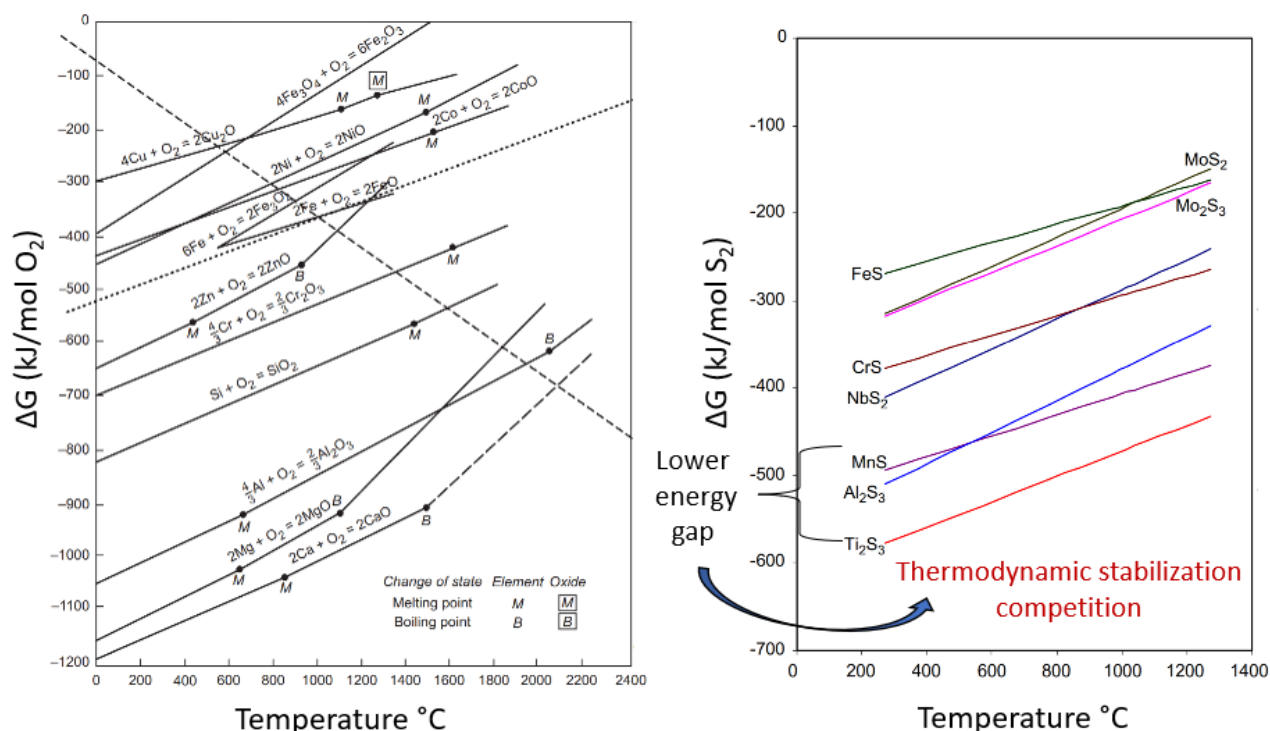
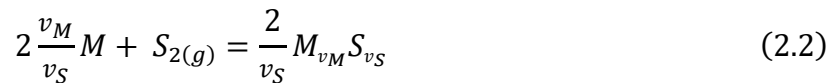


Figure 2.1 Comparison of the Ellingham diagram of selected oxides [93], and the Ellingham diagram of selected sulfides [89]. Adapted and reprinted from [89], [93] with permission from Elsevier.

The sulfide scale formed is fragile and tends to spall and crack more readily than oxides, contributing to higher sulfidation rates. Sulfides and sulfates can be found in a liquid state on metal surfaces, which destabilizes oxides and accelerates corrosion. In an oxygen-free environment (reducing conditions), the metals react with gaseous sulfur and H_2S according to the equations [87]:



Where, M is the metal (e.g., Fe, Ni, Cr, and Al), v' represents the stoichiometric coefficients, $v' = \frac{v_M}{v_S}$ and does not always correspond to a whole number; v_M is the stoichiometric coefficient of the metal and v_S of sulfur in the sulfide. The reaction of one mole of gaseous S_2 free energy varies according to the Ellingham diagram (Figure 2.1), and the normalized equation is written as [87]:



The stability of the sulfide scale is generally associated with the Gibbs free energy of formation, where lower formation energy should result in more stable scales [89]. The free energy of the formation of sulfides is higher than that of oxides with the same stoichiometry, which typically results in sulfides having lower thermodynamic stability and melting points [87]. Although some elements, such as titanium, exhibit lower free energy for sulfide scale formation compared to the examples mentioned above, they are reactive and form a rapidly growing oxide layer that is porous [89], non-protective, and brittle [94]. Refractory metals (e.g., Mo, Nb, Ta, W, and Re) are known to provide protection as they form a slow-growing and stable oxide protective scale [95]. Additionally, the change in Gibbs free energy of formation (ΔG) of sulfides from different metals is similar, leading to a competition for stabilization when dealing with alloys containing multiple elements. For instance, at 600 °C the ΔG (Kj/mol) are: Mo_2S_3 is similar to MoS_2 , -300; NbS_2 , -410, Al_2S_3 , -450; Ti_2S_3 -550 [89].

Beyond sulfidation, H_2S triggers several other forms of corrosion, including: 1) aqueous H_2S -induced corrosion, which forms a solid adherent layer; 2) hydrogen-induced cracking (HIC), which causes blistering of the metal due to the diffusion of hydrogen atoms into the alloy; 3) hydrogen embrittlement (HE), which involves hydrogen absorption and diffusion that leads to localized defects and material failure; and 4) sulfide stress corrosion cracking (SSCC), which results in unexpected sudden failure of materials subjected to tensile stress, typically observed in materials with Rockwell hardness (HRC) above 22 [18]. For this work, we focus on sulfidic corrosion from

sulfur compounds and its interactions with organic fouling mechanisms, due to its relevance to heavy crude oil fouling.

Other corrosion processes are also present in the gas and oil industry, occurring both uniformly and locally, including: acidic corrosion, atmospheric corrosion, dry corrosion, wet corrosion, biocorrosion, carburization, crevice corrosion, dealloying, erosion-corrosion, hydrogen damage, oxidative corrosion, and sour water corrosion [16]. Additionally, acid corrosion is a broad term encompassing all the organic acids found in crude oil, typically associated with naphthenic acids. These compounds are represented by the simple formula RCOOH , as they are carboxylic acids [96]. However, around 3000 naphthenic acids have been identified, along with numerous heteroatom acids (where $\text{R} = \text{C}_x\text{H}_y\text{N}_z\text{S}_v$) [24]. Several ASTM standards exist to quantify these acids. Naphthenic acid corrosion occurs at temperatures ranging from 230 to 400 °C, with a maximum rate observed between 270 °C and 280 °C. Overall corrosion increases when temperatures exceed 340 °C, but this effect is linked to sulfur reactions rather than the acid itself [96]. Furthermore, the formation of the sulfide scale plays a protective role against other forms of corrosion, such as naphthenic acid corrosion, resulting from competitive reactions [97]. Thus, acidic corrosion is not considered in the study presented in this thesis.

2.1.3 Generalized fouling mechanisms

Epstein was the first to categorize and summarize the understanding of fouling in heat transfer engineering processes [98]. Later, other researchers updated the knowledge base concerning the fouling matrix [99], [100], [101]. The fouling mechanisms are classified into five generic types based on the nature of the reactions that lead to fouling [46]: 1) biological fouling is associated with microorganism activity that forms organic films and/or promotes the attachment of macroorganisms; 2) crystallization involves the precipitation and deposition of dissolved salts when they become supersaturated; 3) particulate fouling occurs when suspended particles are deposited on surfaces; 4) chemical reaction fouling pertains to the chemical reactions of one or more reactants in a flowing fluid, resulting in the generation of precursors or direct accumulation on the surfaces; and 5) corrosion fouling is caused by chemical reactions involving a reactant and the metal surface [102].

The fouling mechanisms can be described in five distinguishable steps: initiation or delay period, transport, attachment or deposition, removal, and aging [46]. In theory, fouling can be categorized

into the five mechanisms following the outlined steps; however, in practice, two or more mechanisms often operate in parallel [102]. The evolution of the fouling mechanism varies based on influential factors such as temperature, pressure, surface conditions, fluid composition, and flow velocity. Due to its complex physicochemical processes, crude oil fouling involves an uncertain reaction mechanism. Typically, fouling particulates result from upstream corrosion products [101], and the roughness created by corrosion can influence the fouling mechanism. To simplify, we focus on the formation of a solid on metal surfaces, considering particulate deposition, chemical reactions, and corrosion fouling mechanisms.

The combination of sulfidic corrosion and organic fouling through the decomposition of the same compounds exacerbates the surface problem. Two hypotheses can be proposed: 1) local corrosion followed by organic deposition on the corroded surface, and 2) corrosion occurring beneath the deposits [16]. Sulfidation is primarily considered in three situations: i) the presence of sulfur (in low concentration) in an oxidizing environment; ii) a reducing environment where sulfur is the principal corrosive agent; and iii) sulfate salt environments (hot corrosion) in the presence of alkali [89]. During fouling, the reactant is consumed [102], and if the products of the chemical reaction are not dissolved in the solution following their formation, they can foul the surface. Additionally, pH can be one of the controlling parameters [103]. Non-oxidative conditions are the focus of research concerning oil and gas industry conditions and warrant further investigation [45]. The exclusion of oxygen (whether dissolved or in the air) can significantly reduce fouling based on the oil composition [69], and minimize hydrocarbon autooxidation reactions [45].

It is suggested that thermal fouling, rather than organic fouling driven by chemical reactions, may be more appropriate for defining the mechanisms of foulant formation directly on surfaces through chemical reactions or from the bulk transport of destabilized particulates present in the feed oil [104]. The composition of the deposit may provide crucial insights into the roles of carbon deposition and sulfide scales at temperatures where coke forms in the bulk fluid. The metal content in a feed can be sufficient to result in metal sulfide deposition even in the absence of corrosion. To determine the deposition mechanisms for both non-corroding and corroding surfaces, radial element distribution measurements within the deposit can serve as an important tool [105]. Corrosion layers may induce fouling by enhancing chemical reactions or contribute to the thinning of the viscous sublayer due to mass transfer [74].

Temperature significantly influences the kinetics of fouling, and the mechanism varies depending on whether it occurs above or below the cracking temperature (350 °C) [106]. Below 350 °C, organic fouling arises from asphaltene instability and its tendency to precipitate. Above the cracking temperature, thermal decomposition becomes the primary driver of fouling; as the temperature increases, both sulfidation and coking deposition intensify, with coking occurring at a higher rate. In quantitative terms regarding surface deposit accumulation, organic fouling (coking) predominates at temperatures above 350 °C, while at lower temperatures, fouling due to inorganic factors that form sulfides is more prevalent [74].

Experimental data indicate distinct pathways for foulant formation, transport, and attachment [45], [47]. The chemical reaction typically occurs on the wall, in the bulk, or at the thermal boundary viscous layer (Figure 2.2). Three scenarios are generally accepted for the fouling process: first, a sulfide film is formed through particulate deposition from the bulk or boundary layer onto the hot metal surface, and afterward, coke deposition may occur at an accelerated rate; second, sulfides are produced via surface reactions, and at low temperatures, the deposited coke may inhibit further sulfidation, thereby protecting the metal; and third, coke and sulfides are simultaneously generated through the decomposition of metallic salts in the feed oil, with sulfide formation occurring independently of coke presence [74]. These scenarios have been extensively studied regarding the formation and contribution of FeS as a carbonaceous fouling promoter on the surfaces of heat exchangers [71], [74], [105], [107]. However, studies that consider the interaction of coke and sulfides from other metals under hydrocracking conditions are lacking.

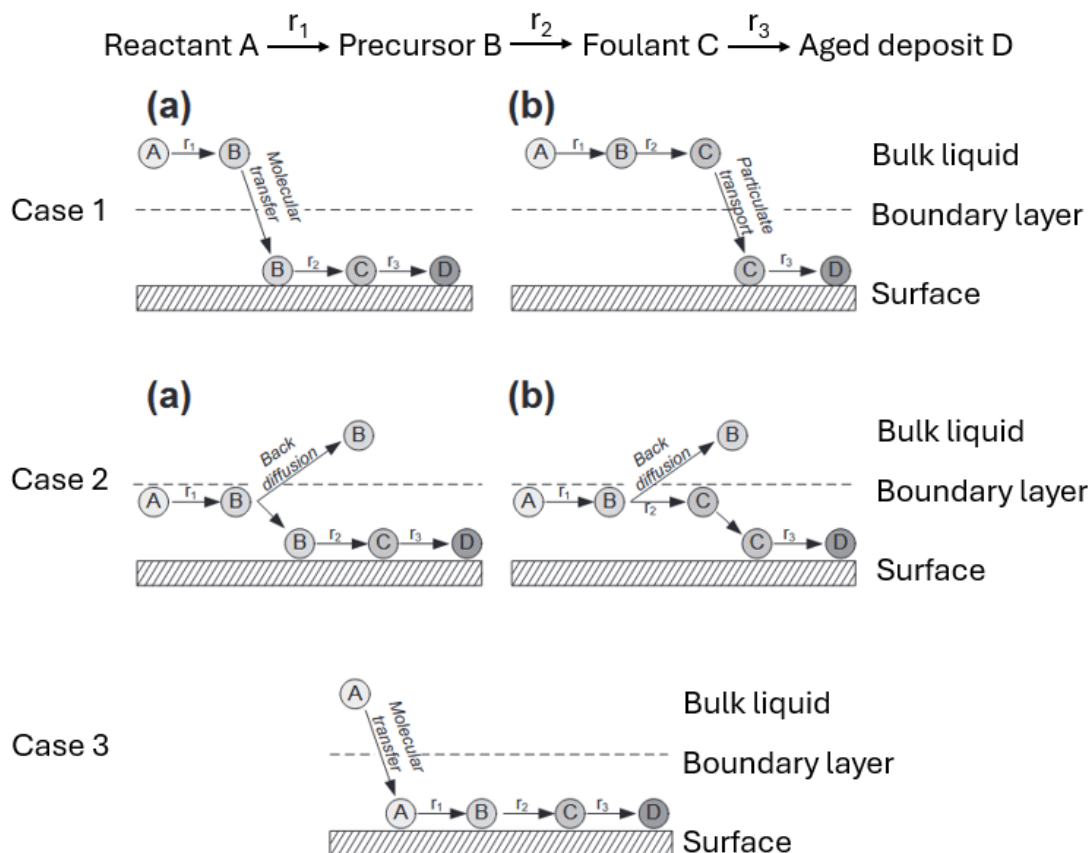


Figure 2.2 Deposition mechanism where the precursor forms in the bulk fluid (Case 1), in the boundary layer (Case 2), or directly on the surface (Case 3). Adapted and reprinted from [69] with permission from Elsevier.

There are still several disagreements regarding the mechanisms responsible for forming deposits, the foulant precursors, and the locations where the reactions occur. A consensus has not been reached about the constituents and chemical structures of the deposits [69]. The composition of the deposits can provide insights into the predominant mechanisms underlying crude oil fouling. High concentrations of unexpected elements may indicate corrosion of upstream components or result from added chemical reactions. The hydrogen-to-carbon (H/C) ratio is significant for determining the nature of the coke; when the ratio is > 0.95 , it suggests partial molecular degradation, < 0.8 indicates hardened material due to heat flux exposure, and < 0.7 is associated with exposure to higher temperatures. The sulfur content can be quantified using the ASTM standard D4239, which provides important information regarding the association of elements based on the metal and sulfur molar ratio. However, for crude-related deposits, the percentages of C, H, N, S, and other metals

rarely add up to 100%. This inaccuracy is attributed to the non-homogeneity of the samples and the presence of oxygen-forming oxides [108].

2.1.4 Fouling models

The complex nature of crude oil and the lack of reproducibility in creating fouling deposits present significant challenges to developing accurate models. Several models have been proposed based on the location and type of reaction driving the fouling mechanism. To simplify, most models are constructed with several assumptions: 1) changes in surface roughness over time are neglected; 2) only one type of fouling is considered; 3) physical properties of the fluids are assumed to be constant; 4) variations in flow velocity and cross-sectional area due to fouling are disregarded; 5) the fouling layer is assumed to be homogeneous; and 6) the size and shape of deposits are ignored. Additionally, most studies typically focus on concentration, temperature (both wall and bulk), flow velocity, and time. The fundamental fouling process balance equation, idealized by Kern and Seaton, is given as [103]:

$$\frac{dm_f}{dt} = \dot{m}_d - \dot{m}_r \quad (2.3)$$

Where, $\frac{dm_f}{dt}$ is the net deposition rate, $\dot{m}_d$ and $\dot{m}_r$ are deposition and removal rates. The surface local deposition flux $\dot{m}_d$ is related to the transport and can be expressed by [103]:

$$\dot{m}_d = h_D(C_b - C_s) \quad (2.4)$$

Where, C_b is the concentration in the bulk fluid, and C_s is the concentration close to the surface, and h_D is the convective mass transfer coefficient obtained from Sherwood number (Sh), which is a flow and geometry-dependent parameter expressed as [103]:

$$Sh = \frac{h_D d}{D} \quad (2.5)$$

The Sh number can be obtained from the Nusselt number given a heat and mass transfer analogy [109]. The simple general equation from Kern and Seaton serves as the foundation for understanding fouling mechanisms. To develop specific mechanisms, it is essential to consider additional parameters such as kinetics for chemical reactions, temperature for thermal decomposition, and crude oil properties for threshold mechanisms. Several mechanisms have been proposed in the literature [39], [46], [101], [103], [109].

In reality, the fouling models can be described as being controlled by: 1) transport (diffusion), 2) back diffusion, 3) adsorption, 4) desorption, 5) chemical reactions in the bulk fluid, 6) chemical reactions in the film or on the surface, 7) corrosion in the bulk, 8) corrosion in the film and on the surface, and 9) asphaltene precipitation [109]. The dynamic process of fouling can be represented by a fouling resistance curve, which illustrates the resistance over time. The fouling resistance R_f is the standard measurement for fouling on heat exchanger surfaces [69]:

$$\frac{dR_f}{dt} = \phi_d - \phi_r \quad (2.6)$$

Where the fouling rate $\frac{dR_f}{dt}$ is a function of the deposition ϕ_d and removal ϕ_r [101], and the R_f can also be calculated from a relationship between temperature and heat flux [46]. These equations represent general fouling models, and a chemical reaction model should consider the kinetics of the reaction. Assuming that chemical reaction fouling occurs on the surface, an Arrhenius kinetic model can be used to represent the fouling process as a function of temperature:

$$\phi_d = \alpha \exp\left(-\frac{E_f}{R_g T_s}\right) (C_r)^k \quad (2.7)$$

Where the ϕ_d is the deposition term, α is the Arrhenius pre-exponential term, E_f is the activation energy of the fouling reaction, R_g is the ideal gas constant (can be substituted by Boltzmann constant), T_s is the temperature of the surface, C_r is the concentration of the reactant and k represent the reaction rate order. The removal term ϕ_r is a function of the shear stress τ and the deposit bond resistance R_b , and a_2 is a model constant [101] :

$$\phi_r = a_2 \frac{\tau}{R_b} \quad (2.8)$$

The fouling models have evolved to account for coke deposition, considering both kinetics and mass transfer. Subsequently, they were further extended to include foulant convection back into the fluid bulk. It was observed that kinetics primarily controls the fouling rate at low temperatures and high mass flow, while precursor diffusion becomes the controlling mechanism at high temperatures and low mass flow. However, the definition of the removal term represents a conceptual challenge due to the re-entrainment of particles. Additionally, the deposit bond resistance term, represented by ϕ_r , is a parameter that is difficult to estimate [101].

Crittenden et al. [67], [69], [110], [111] developed a transport-chemical reaction model that incorporates back-diffusion to predict fouling in refineries. This model, which accounts for two fouling mechanisms, is more rigorous than models that focus solely on chemical reactions [46], and excludes the problematic removal term. Crittenden model fouling resistance was defined as:

$$\frac{dR_f}{dt} = \alpha \exp\left(-\frac{E_f}{R_g T_s}\right) \quad (2.9)$$

Their calculated E_f for light crude oil was 33 kJ mol⁻¹, indicating a mixture of chemical and physical mechanisms. For heavy crude oil, the E_f was 21 kJ mol⁻¹, suggesting the predominance of a physical mechanism. Activation energy values below 40 kJ mol⁻¹ indicate that chemical and physical phenomena are important for the deposition [67]. Low apparent activation energy indicates that the fouling process is dominated by physical phenomena. The apparent activation energy for crude oil fouling strongly depends on velocity, becoming independent of velocity at the isokinetic temperature. Beyond this threshold, at temperatures exceeding the isokinetic point, the fouling rate increases with rising velocity. For Maya crude oil, the isokinetic temperature is 274°C. Oils with lower asphaltene content typically exhibit higher isokinetic temperatures, whereas more complex oils are expected to have lower isokinetic temperatures [112].

Epstein proposed a model for the initial chemical reaction fouling rate based on the proportionality of the residence time of the fluid at the surface and the surface attachment, assuming that a longer residence time increases the probability of a chemical reaction occurring. The initial fouling rate is expressed as a function of mass flux as follows [46]:

$$\left[\frac{dR_f}{dt}\right]_{t=0} = \frac{m\varphi}{k_f \rho_f} \quad (2.10)$$

Where, m is the stoichiometric factor, φ is the deposition mass flux, k_f is the thermal conductivity of foulant, and ρ_f is the foulant density. The difference in concentration in the bulk and close to the wall is the driving force. Epstein's model exhibits a good fit to Crittenden's data for initial fouling rates [46].

The corrosion models arise from the interaction of active sulfur species with dissolved metal species (bulk reaction) or with dissolved sulfur in the fluid interacting with steel surfaces. The fouling equations governed by corrosion are analogous to the equations of corrosion in the film

[109]. The activation energy calculated based on film energy is higher than that based on the surface temperature [39]. It is assumed that the rate of corrosion fouling per unit surface area is equal to the rate described by the fundamental Kern and Seaton diffusion equation per unit surface area [109]:

$$r_{Di} = k_{Di}(C_{Ab} - C_{As}a_s) = \frac{ShD_{AB}}{d} \left(C_{Ab} - C_{As} \frac{A_r}{V} \right) \quad (2.11)$$

Where, r_{Di} is the rate of diffusion or rate of mass transfer in a stagnant film, k_{Di} is the mass transfer coefficient, C_{Ab} is the concentration of bulk fluid and C_{As} is the concentration on the surface or film, a_s is the surface area per reactor volume multiplier, which can be expressed by the quotient of the reactor surface area A_r and the reactor volume V . Sh is the Sherwood number, d is the characteristic length of the tube and D_{AB} is the mass diffusivity [109]. Parameters that are typically neglected in the models are surface related (e.g., materials), equipment design, operational fluctuations, properties of the foulant stream, and the nature of the process [103].

2.1.5 Laboratory scale fouling

One of the major drawbacks related to fouling experimental research is that the operational conditions are often chosen arbitrarily. Researchers have not reached a consensus on systematic procedures and guidelines to address the issue. Various experimental setups have been reported in attempts to establish the mechanisms and characteristics of crude oil fouling [39]. The complexity of crude oil chemistry involves several factors that influence the fouling process, making it challenging, and in many cases impossible, to predict sulfidation based solely on the physicochemical composition [113].

Producing relevant data on a small scale is one of the challenges in experimental fouling research. It is difficult to replicate the volume, and the time required to compare crude fouling with that observed in refineries. Consequently, small-scale experiments are often designed to accelerate the fouling process, primarily by employing higher temperatures than those found in the field. The goal of laboratory-scale experiments is not necessarily to reproduce actual conditions in the refinery unit, but rather to isolate and identify the variables that contribute to deposition and to enable the comparison of different crude samples under identical or well-defined conditions [111]. Conducting studies on a small scale provides the opportunity to understand crude oil behavior,

deposition kinetics, interactions with surface materials, and how to leverage these insights to develop suitable surfaces for application.

There are several different types of experimental apparatus designed to produce fouling, including: i) once-through units, ii) coiled wire probes, iii) thermal fouling testers, iv) tubular systems, v) annular systems, vi) autoclave systems, and vii) stirred tank systems [46], [114], [115], [116], [117]. Some of these reactors are commercially available for purchase. There are notable differences in reactor operation, even among the simplest options, such as stirred batch reactors. Computational Fluid Dynamics (CFD) simulations serve as a valuable complement to experimental data, especially since it is often deemed impossible to experimentally analyze flow rate contributions [110].

2.2 Materials

2.2.1 Alloys

The alloy design strategy aimed at developing alloys resistant to sulfur attack is similar to the approach used for high-temperature oxidation. The goal is to create alloys that form a slow-growing, stable, and protective thin film on their surface. The available standards for sulfidic corrosion are summarized in the NACE International report series and by the American Petroleum Institute (API) guidelines. NACE publications 34103, MR-0103, and MR-0175 provide an overview of materials that exhibit resistance to sulfidic corrosion in petroleum refining environments. Additionally, the API Recommended Practice 939-C offers guidelines to prevent sulfidation failures in oil refineries operating in the temperature range of 230-540 °C. A significant portion of the information contained in these documents is derived from practical observations in the industry based on non-publishable data [16]. Unfortunately, the information available regarding materials' performance under realistic conditions is limited and inconsistent, with a broad range of specifications [95]. The degree of material degradation is typically assessed through qualitative classification and is generally related to the chromium content in the Fe, Ni, and Co-based alloy chemistries [118].

Carbon steel is the standard material commonly used in the gas and oil industry; however, it is particularly vulnerable to corrosion, especially at temperatures exceeding 230 °C [119]. According to NACE publication 34103, the maximum allowable operating temperature for carbon steel is limited to 260 °C. This limit can be extended to 343 °C with the addition of 5 wt. % chromium and

further increased to 400 °C with 9 wt. % chromium. Chromium steels have the advantage of forming a more protective sulfo-spinel layer (FeCr_2S_4) compared to the less effective Fe_{1-x}S defective layer. In addition, chromium can poison the decomposition of sulfur compounds prior to their incorporation into the scale; however, the presence of hydrogen promotes this decomposition, counteracting the beneficial effects of chromium. The mechanism related to these effects has not been established yet [72]. For environments that contain hydrogen, 304 stainless steels (18/8 Cr/Ni) are recommended for use at temperatures above 260 °C [72].

Interestingly, the corrosion rate of carbon steel can be slightly higher in alloys containing 5% chromium compared to the bare alloy. This phenomenon can be attributed to the complex nature of the reaction environment [72]. Additionally, sulfidic corrosion failures in carbon steels are often linked to low silicon content. Steels containing 0.15% to 0.30% silicon have shown superior performance in certain environments compared to those with less than 0.1% silicon [16]. When exposed to crude oil at 300 °C, AISI-316 stainless steel exhibits a non-linear decreasing corrosion behavior, which is likely due to a concentration gradient of the scale film formed by the continuous cycle of formation and detachment of the low adherent second layer of iron sulfide (FeS) [120].

The relationship between alloying elements and their concentrations in alloys is complex and not always linear. For instance, Fe-Al systems tend to show greater resilience to sulfidation compared to Fe-Cr alloys [89]. When examining the behavior of binary Fe-Al and ternary Fe-Al-Cr alloys, particularly those combined with elements like molybdenum (Mo), niobium (Nb), zirconium (Zr), and yttrium (Y), unexpected results emerge when subjected to H_2S - H_2 environments at temperatures between 500 °C and 800 °C. Specifically, when the aluminum concentration exceeds 40%, and chromium is present at 4%, the behavior of the ternary alloy aligns closely with that of the binary Fe-Al alloy. In addition, higher chromium content can disrupt the initial formation of the protective Al_2O_3 layer, which is critical for corrosion resistance. Interestingly, the addition of molybdenum can counteract the disruptive effects of chromium on protection. Zirconium and yttrium show minimal impact on the scale morphology, but they do enhance scale adhesion. In general, lower chromium alloys tend to exhibit better corrosion resistance in gaseous environments, while alloys with higher chromium content provide improved resistance against sulfur-bearing acids [121]. This nuanced understanding underscores the importance of selecting alloying elements and understanding their interactions to optimize performance under specific corrosive conditions.

In high-temperature gaseous sulfidation conditions ($T \approx 800\text{ }^{\circ}\text{C}$), Fe-Al alloys containing 10-20% aluminum develop a duplex scale characterized by the presence of defective Fe_{1-x}S and Al_2S_3 phases. As the aluminum concentration increases, the hexagonal FeAl_2S_4 phase is formed. Continuous exposure to sulfidation leads to the precipitation of a non-protective internal Al_2S_3 layer, which fails to inhibit the outward diffusion of metallic cations and the inward diffusion of sulfur. This process results in the development of a new Fe_{1-x}S layer beneath the precipitated Al_2S_3 . Additionally, both Al_2S_3 and FeAl_2S_4 can hydrolyze upon contact with air, generating hydrogen sulfide (H_2S) and forming non-protective, spalling hydrated alumina [89]. The effectiveness of aluminum additions in nickel alloys appears to be even lower, complicating the formation of a continuous alumina layer [89]. The thermodynamic conditions that favor oxide formation over sulfide scales remain uncertain, suggesting that a pre-oxidation step may be a viable strategy for achieving aluminum-rich scales, as demonstrated in FeCrAlY alloys [95].

Nickel-based alloys are widely applied to mitigate corrosion. When combined with chromium, Ni is the most effective element in controlling carburization [16]. However, it has been well established that H_2S promotes cracking in nickel-base alloys [122], forming deleterious non-protective sulfide scales, which act as a catalyst to form H_2S in an H_2 -rich environment [16]. Independently of the reaction temperature in the range of 600-900 $^{\circ}\text{C}$ the sulfidation rate of nickel alloy with 2% Cr in sulfur vapor is faster than pure nickel, but when the alloy contains over 20% Cr, the corrosion rate is lower than that of pure Cr [123]. The sulfidation of a Ni-20Cr alloy in the temperature range of 700-750 $^{\circ}\text{C}$ showed that Ni_3S_2 and NiO were predominantly formed, with sulfur detected within the NiO grains [124]. The sulfidation of Ni-Cr-Mo alloys at 700 $^{\circ}\text{C}$ formed distinct structures composition and microstructure based on the alloying content. The formed scales are a combination of Cr_3S_4 , Cr_2S_3 , $(\text{Cr},\text{Mo})_3\text{S}_4$, $(\text{Cr},\text{Mo})\text{S}_2$, MoS_2 , Mo_2S_3 , NiS, and Ni_3S_2 . The best protection was achieved when the ternary additions were above 10% [125].

High levels of Mo, Al, Nb, and/or Mn are necessary to protect iron and nickel-based materials from sulfidation [89]. The presence of significant quantities of refractory metals (e.g., Mo, Nb, Ta, W, and Hf) in the intermetallic phase leads to the formation of a slow-growing and more stable scale [95]. Additions of Nb create an inner sulfide layer that reduces the diffusion of Fe and Ni. Simultaneously, Nb and Ti dissolve oxygen, resulting in the formation of non-protective porous oxides. Mn sulfide alters the stoichiometry of other elements' scales, though its benefits are not fully understood. Mo and W react to form volatile compounds [89]. Mo and Al preferentially form

the spinel $\text{Al}_{0.55}\text{Mo}_2\text{S}_4$, which provides significant sulfidation resistance; however, MoS_2 and other refractory metal sulfides possess a layered crystal structure that allows for the migration of ions similar in size to those of the base alloys. Transition metal ions can diffuse relatively quickly through the Van der Waals gaps of the octahedral holes, which separate the loosely bound regions between Mo and S. Nb and Mo form sulfides at rates comparable to chromium oxidation under similar conditions, and each element interferes with the formation rate of the other [92]. Therefore, high amounts of alloying elements are widely employed, but they represent a compromise between mechanical properties and sulfidation resistance [126].

Nickel alloys can withstand dry sulfur dioxide attack up to 370 °C; however, in the presence of contaminants, nickel experiences significant sulfur corrosion even at low temperatures [127]. Within typical refinery settings, Inconel 625 (IN625) represented a substantial improvement under both oxidizing and reducing sulfidation conditions, resulting in reduced acidic corrosion, stress corrosion cracking (SCC), and chloride SCC [128]. Inconel 718 (IN718) is a mechanical evolution of IN625 and is the preferred alloy due to its adequate fracture toughness and high strength (above 120 ksi), along with its resistance to general and localized corrosion from both sulfide stress cracking and anodic stress corrosion cracking [129]. Inconel 718 is suitable for use in safety valves rated for pressures of 15,000 to 20,000 psi; however, its application was limited to sour service at moderate temperatures (~180 °C) and in conditions where free sulfur is absent [130]. According to NACE MR0175, IN718 is appropriate for environments with free sulfur only at temperatures below 135 °C [131]. The microstructure, composition, and heat treatment of IN718 have been optimized to minimize hydrogen embrittlement and stress corrosion failures [132]. To address severe corrosive environments at higher temperatures (~260 °C), alloys with increased molybdenum content, such as Alloys 725 and 925, were developed [130].

The natural evolution from nickel-based alloys to cobalt-based alloys occurs because the sulfidation rate of cobalt is significantly slower than that of nickel and iron. This is generally attributed to the lower diffusivity of cobalt ions in sulfides, the higher melting point of cobalt and cobalt sulfide, and evidence indicating a smaller molar volume for cobalt sulfide formation [133]. Nickel sulfides have a lower melting point, with the Ni-Ni₃S₂ eutectic forming at approximately 645 °C, while Co-Co₄S₃ forms at 880 °C [134]. At the eutectic formation temperature, the deviation from the ideal crystal spacing in nickel sulfide is much greater than that in other sulfides. The lattice strain of nickel sulfide ranges from -0.188 to 0.222, whereas cobalt lattice strain varies from 0 to

0.07 [89]. This wide range of lattice strain for nickel sulfides indicates lower stability and higher atomic mobility within the lattice, which enhances the corrosion rate. Therefore, substituting nickel with cobalt mitigates the risk of faster liquid corrosion in higher-temperature applications. Liquid corrosion products tend to rapidly deplete the alloy, making them highly undesirable. Additionally, it is possible to control the formation of liquid sulfides by increasing the iron or chromium content, which raises the melting temperature of sulfide scales. Alloys containing nickel concentrations below 20% and chromium levels above 25% can prevent liquid sulfide formation [92].

Thermodynamics alone is inadequate to explain the higher corrosion rate of nickel compared to cobalt. Additional physical, chemical, and mechanical properties are essential for developing the alloy and scale [92]. Other mechanisms must dominate to account for the greater corrosion of nickel in the presence of sulfur below the eutectic formation temperature. Cobalt sulfides are more stable thermodynamically, exhibiting better adherence and a lower tendency to spall compared to the rapidly reacting nickel alloys. In Ni-Co alloys, when the Ni mass ratio approaches unity, the lattice interaction between the two metals decreases their availability for sulfidation [135]. The microstructure of the alloy and the scale can significantly influence the degradation rate. For instance, a cobalt alloy with a fine-grained dendritic pattern provides sulfur diffusion channels, which increases corrosion, whereas the nickel alloy forms a more protective coarser dendrite structure [136].

Sulfur scales exhibit unpredictable behavior, and the simultaneous formation of oxides may account for the variability in scale formation and corrosion resistance. The tendency to form oxides is not uniform across the surface, leading to areas with differing levels of protection. The lack of protectiveness can be attributed to the poor adherence of the scales to the alloy surface [24]. Even a continuous sulfide phase on the material surface can create alternative, faster diffusion pathways for ions [91]. Sulfide systems are complex, and there is a lack of information regarding the diffusion properties of sulfides, the nature of defects, and the microstructure. Material selection is a critical factor in the design of a system [20], yet no alloy meets the fundamental requirements to fully protect the surface from scale growth [92]. Therefore, to mitigate the risks inherent in the heavy oil hydrocracking process, new strategies must be developed to manage, control, and prevent fouling. Additionally, the synergistic contribution of inorganic and organic fouling must be addressed [107], particularly since the presence of coke may seal diffusion pathways and/or influence the rate of precursor formation.

2.2.2 Microstructure and diffusion

Diffusion is the mass transport from one region to another, driven by concentration gradients [137]. It is a structure-sensitive property influenced by the atomic arrangement of the material [138]. Fick's two laws govern diffusion: the first states that the diffusion rate is proportional to the concentration gradient, which serves as the driving force, while the second ensures mass conservation. The mathematical solutions to these laws depend on the specific system configuration, such as a thin film or a surface [138]. The diffusion rate is generally slower in amorphous materials than in crystalline ones. However, the complex behavior of diffusion in amorphous materials and the challenges of direct comparison make it highly material- and condition-dependent [139]. The rate of diffusion is also inversely proportional to atomic packing density (Table 2.1).

Table 2.1 Atomic lattice structure and packing density.

Lattice Structures [140]	Packing Density	Void Space	Diffusion Rate
Body-centered cubic (BCC)	~68%	High	Fast
Face-centered cubic (FCC)	~74%	Medium	Moderate
Hexagonal close-packed (HCP)	~74%	Medium	Slow/Moderate [141]

The microstructure of materials, typically ranging in scale from 1 to 1000 μm [142], plays a critical role in engineering designs aimed at improving performance [143]. Microstructure strongly affects diffusion, which tends to increase proportionally with lattice irregularities. Defects in solid materials are classified into four categories based on their dimensionality [144]: point defects (0D), line defects (1D), planar defects (2D), and volume defects (3D) (Figure 2.3). The distribution of alloying elements, whether deliberate or accidental, can create microstructural defects that impact material properties [145].

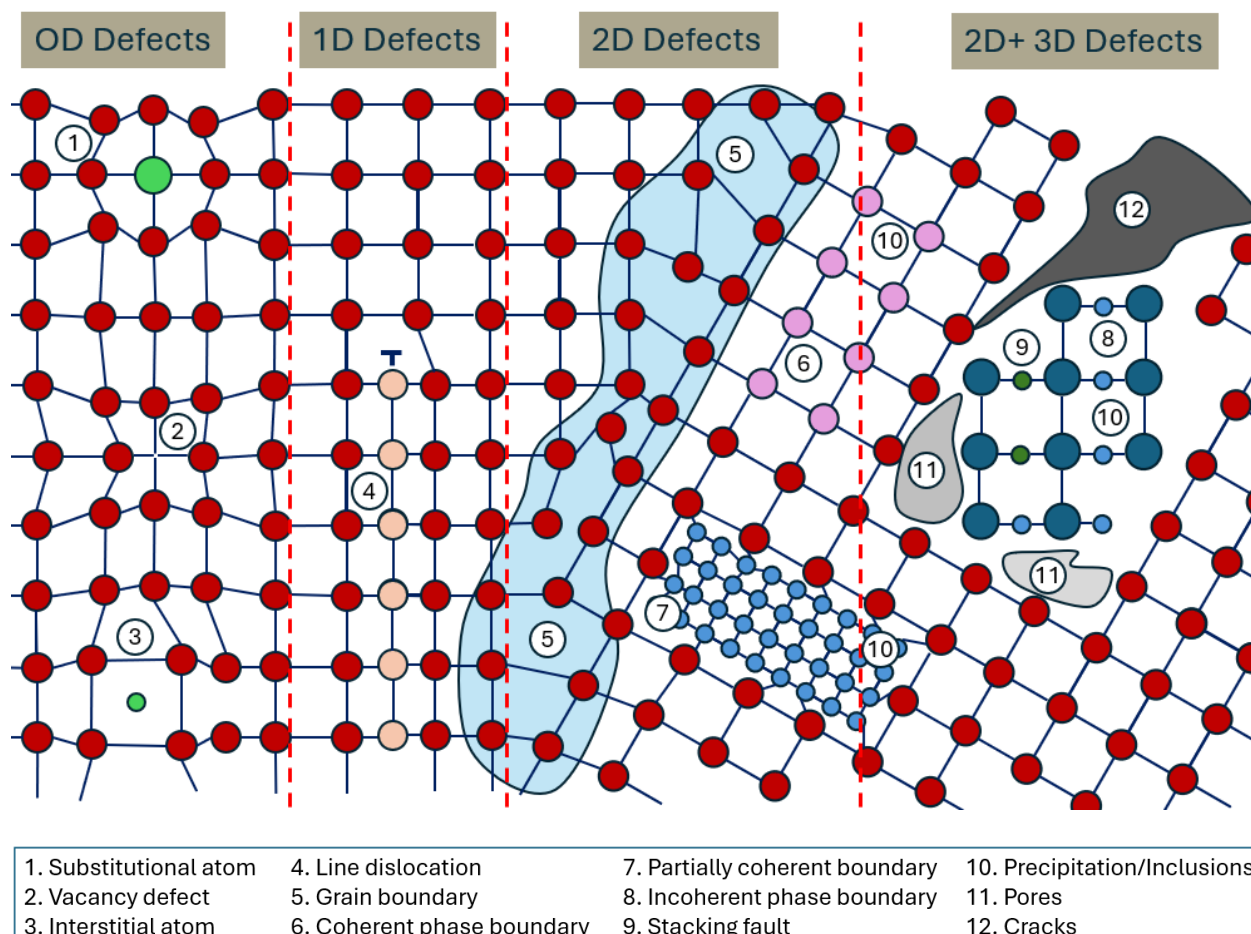


Figure 2.3 Types of defects structure in solid materials.

Diffusion through microstructural irregularities, known as short-circuit diffusion, can be several orders of magnitude faster than lattice diffusion, even at a crystal's melting temperature. The melting temperature and the crystal lattice structure influence lattice diffusion in metals. At lower temperatures, the impact of short-circuit diffusion becomes more pronounced [146]. Diffusion along free surfaces is significantly faster than through the lattice and is only minimally affected by surface structure and packing [138]. Short-circuit diffusion coefficients are strongly influenced by minor element segregation, dislocations, and grain boundary characteristics. In practical materials, the estimation of these coefficients is particularly challenging due to the presence of alloying elements, impurities, and the history of heat treatments, especially in heat-resistant steels [146].

In cold-worked materials, diffusion rates are higher than in annealed states, although recrystallization tends to mask this difference [138]. Mechanical and heat treatments are the primary processes that modify alloy microstructures and defect distributions (Table 2.2).

Additional treatments that affect lattice structure and defect density are often associated with surface engineering techniques (Table 2.3).

Table 2.2 Key processes altering lattice and defects in alloys.

Process	Defect Reduction	Defect Introduction	Lattice Impact
Annealing [147], [148]	Removes dislocations and reduces defects proportion	Minor formation of 0D defects during diffusion	Restores lattice parameters
Recrystallization [149]	Removes dislocations	Boundary defects in new grains	New grain formation
Grain refinement [150], [151]	Removes large grains	High grain boundary density	Minimal lattice change
Cold working [152]	-	High dislocation density	Distorts lattice
Tempering [153]	Reduces residual stress	Precipitation and inclusions	Partially restores lattice

Table 2.3 Surface engineering processes altering lattice and defect structure.

Process	Defect Reduction	Defect Introduction	Lattice Impact
Plasma/Ion treatment [154]	Relieves surface stresses, reduces surface contaminant and micro-voids	Implant interstitial atom and creates vacancies	Modify surface lattice structure
Optical treatments [155]	Laser shock peening reduces surface defects by introducing compressive stresses	Induce dislocations or phase changes at high energy density	Refine surface microstructure or introduce compressive strain
Electrical treatment [156]	Electropulsing reduces dislocation density and relieves internal stresses	Electromigration induces vacancies and atomic rearrangement	Lattice relaxation or distortion due to atomic rearrangement and local thermal effects.
Chemical treatment [157]	Eliminates surface defects through etching or passivation and reduces grain boundary segregation	8. Introduce interstitial atoms, alters surface chemistry and phase composition	Interstitial diffusion alters surface lattice or forms new phases (e.g., hardened layers)
Coatings (CVD/PVD) [158], [159]	Thin film can cover surface defects, achieving passivation	Introduces residual stresses, 0D and 1D defects during deposition	Alters lattice near the coating interface, and can induce lattice strain

2.2.3 Surface engineering

The imprecision inherent in the process is one of the reasons material engineering focuses primarily on studying how degradation occurs and how to mitigate it, rather than on investigating the effects of the reactions themselves [91]. The general process of surface scale formation can be categorized as a deposition process, where heterogeneous nucleation and growth occur at surface asperities, or as an adhesion process, in which a crystal nucleates in the bulk and adheres to the wall, building up over time. The deposition process predominantly controls the rate of surface scale formation [160]. The removal of adhesive bonds depends on system geometry, elastic properties, and interfacial surface energy. In the case of thin films, the interfacial energy is equivalent to equilibrium values [161].

The strength of adhesion (σ) of a rigid material on an elastic surface is proportional to both the elastic modulus (E) and the work of adhesion (W_a) over a certain film thickness (t) [162]:

$$\sigma = \sqrt{\frac{W_a E}{t}} \quad (2.12)$$

The work of adhesion (W_a) is represented by a relationship of surface free energy of the interacting phases [163]:

$$\sigma = \gamma_1 + \gamma_2 - \gamma_{12} \quad (2.13)$$

Where γ_1 , γ_2 , and γ_{12} are the interfacial free energy [164] for the substrate, the foulant, and the substrate-foulant interface, respectively [162].

There are three surface engineering approaches to reduce the adhesion strength of solids: i) modifications to physical properties, specifically reducing the elastic modulus (E); ii) physical modifications that alter surface contact; and iii) physical and chemical modifications aimed at reducing surface energy W_a . The first approach focuses on lowering the modulus, which decreases the equilibrium barrier for fracture at the adhesive interface during the debonding process. The modulus variation between a soft and a hard surface can differ by up to five orders of magnitude [162]. However, this strategy is insufficient for applications that require materials to possess certain levels of toughness, wear resistance, erosion resistance, and the ability to withstand high temperatures.

The second strategy generally involves controlling surface microtexture through changes in surface roughness and patterning. A hierarchical pattern can create superhydrophobic surfaces, minimizing water contact. The Wenzel and Cassie-Baxter models explain the wettability phenomena observed in rough surfaces [165], [166] (Figure 2.4). The Wenzel model describes a wetting state in which the liquid fully conforms to the texture of the surface, penetrating its roughness. In contrast, the Cassie-Baxter model represents a state where the liquid remains on top of air pockets trapped within the surface roughness. In the Wenzel regime, surface roughness amplifies the intrinsic wettability of the material: hydrophilic surfaces become more hydrophilic, while hydrophobic surfaces become more hydrophobic [167]. Conversely, the Cassie-Baxter regime alters the intrinsic wettability by introducing air entrapment, consistently leading to an enhancement of surface hydrophobicity, regardless of the initial contact angle [168]. This results in an apparent increase in hydrophobicity for hydrophobic surfaces. On hydrophilic surfaces, however, the presence of air pockets may reduce the effective wettability, leading to a lower-than-expected hydrophilicity.

This strategy has been applied to create ice-phobic surfaces that delay ice formation [169], prevent biofouling [170], and design self-cleaning surfaces [171]. Surface texture is a key component in reducing liquid fouling. However, surface roughness is typically detrimental when addressing solid fouling, as it increases surface contact and interlocks particles and surfaces, thereby enhancing adhesion [172]. The introduction of roughness on the surface of alloys has been shown to increase coke formation during heavy oil processing [173]. Additionally, controlling general surface fouling by tuning physical properties is extremely challenging in the oil industry due to the constantly changing feed composition. It is difficult to obtain the modulus of oil components, such as waxes, which can vary between 61 and 250 MPa [162].

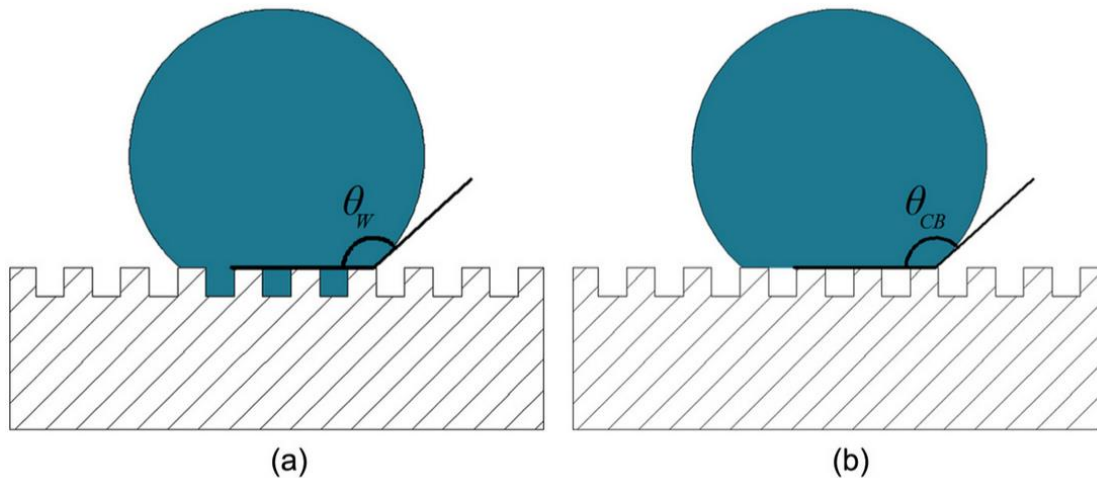


Figure 2.4 (a) Wenzel model and (b) Cassie–Baxter model. Where θ_W and θ_{CB} are the Wenzel and Cassie–Baxter contact angle of the liquid droplet. Adapted from [174], under the terms of the Creative Commons Attribution 4.0 License.

Surface free energy depends on factors such as the arrangement of atoms, crystal orientation, and defects, all of which are influenced by microstructural modifications. Surface mechanical treatments alter surface or subsurface characteristics, including morphology and microstructure [175]. Parameters like surface roughness [176], [177] and annealing [178] can significantly impact the surface energy of alloys. Other surface modification techniques, such as ion implantation, have been shown to effectively reduce surface energy and inorganic fouling on stainless steel in heat exchange applications [179], [180]. Considering that the surface energy E_s , can be expressed as a function of surface internal energy U_s , temperature T , and surface entropy S_s :

$$E_s = U_s - TS_s \quad (2.14)$$

In the case of ion implantation, the introduction of a foreign element increases the surface entropy. If this element possesses higher energy, it can decrease the bonding between atoms on the surface, thereby reducing the internal energy and significantly lowering the total surface energy [181]. A lower surface energy affects scale growth by reducing the number of nucleation sites [182]. Furthermore, the relationship between surface energy and the composition of two-component systems can be expressed as [183]:

$$\Gamma = -\frac{a}{RT} \frac{\delta E_s}{\delta a} \quad (2.15)$$

Where Γ is the surface activity, or surface excess of solute, a is the solute activity, R is the universal gas constant, and E_s is the surface energy. When applied to solids, this equation illustrates that surface energy will be minimized as the activity of the implanted elements in the surface layer increases. Therefore, by implanting reactive elements such as F, C, and O, the surface energy of the alloy is reduced [181]. Other surface techniques, such as nitriding, carburizing, and boriding, are also used industrially to modify the surfaces of alloys.

The surface energy of a typical smooth metal (2.4 mJ m^{-2}) is three orders of magnitude higher than that of the lowest surface energy fluorinated polymers (0.0067 J m^{-2}) [162]. Surface energy can be calculated based on contact angle measurements, with the most common models being the Owens–Wendt–Rabel–Kaelble (OWRK) method [184], the van Oss method [185], and the Wu method [186]. Each method is technically suitable for specific types of surfaces (low surface energy, non-polar, or polar), but the surface properties are often unknown prior to measurement [187]. The OWRK method typically provides intermediate quantitative results compared to the other methods, while the qualitative results of all three methods are equivalent [188]. Therefore, the OWRK method is generally more suitable for surface energy screening:

$$(1 + \cos\theta)\gamma_l = 2 \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right) \quad (2.1.6)$$

Where, θ is the contact angle of the liquid on the solid surface, γ_l the total surface energy of the liquid, γ_s^d dispersive component of the solid's surface energy, γ_l^d dispersive component of the liquid's surface energy, γ_s^p polar component of the solid's surface energy, and γ_l^p polar component of the liquid's surface energy.

Modifying surface energy and roughness parameters does not guarantee that the surface will exhibit adequate antifouling characteristics. A combination of factors related to hydrodynamic effects, process scale formation, and the chemical composition of the scale must be considered to protect surfaces [160]. When fouling is driven by localized corrosion, scales form from the dissolution rate of the alloy's constituent elements. Therefore, surface diffusion control is likely the most critical design parameter for addressing corrosion-driven fouling. In contrast, surface energy and adhesion are more relevant for preventing other types of fouling that depend heavily on the processing feed material, such as particulate fouling and coke deposition. Among the surface engineering strategies,

chemical modifications that minimize surface energy, reactivity, and diffusion hold the highest potential for reducing fouling during hydrocracking.

2.2.4 Coatings

Developing reliable alloys for heavy oil applications is a critical yet complex task that requires significant capital investment. As an alternative, protective coatings for base materials become highly attractive [118], especially when the potential cost of damage due to degradation far exceeds that of applying the coating. Coatings can be applied to simple external surfaces exposed to natural elements or designed to function in more complex environments. The protective layer serves as both a physical and chemical barrier, enhancing the properties of the underlying surface [189]. Alloys are commonly protected by coatings across various industries, including shipping [190], aerospace [191], and petrochemicals [192].

In the oil industry, pipeline anti-corrosion coatings are commonly used as "flow coats." These coatings reduce friction between viscous fluids and the internal pipe walls by decreasing surface roughness. The effective minimum thickness for a flow coat is 40 μm (1.5 mils), while a thickness of at least 135 μm (5 mils) is required to provide a significant corrosion barrier. These values represent the most practical and economical protective barriers for pipelines operating at relatively low temperatures [193]. Non-metallic components have been widely employed for corrosion protection and will continue to play a critical role in oil and gas exploration. Polymers and fluorinated compounds are the primary group of non-metallic coatings [23]. Ethylene chlorotrifluoroethylene (ECTFE) offers an effective and smooth corrosion barrier for gas lines at temperatures up to 150 °C. Polyaryletherketone (PAEK) and polyether ether ketone (PEEK) are anti-wear and anti-creep materials suitable for potential valve applications. Fluoroelastomers or fluorocarbons (FKM) and perfluoroelastomers (FFKM) can withstand harsh environments containing H_2S and CO_2 at temperatures up to 300 °C [194]. The application of these materials requires comprehensive knowledge of the operational conditions to avoid critical failures related to material incompatibility (e.g., environmental chemicals, adhesion, temperature, and pressure) [23].

There is a wide range of coating techniques, each with its own advantages and disadvantages (Figure 2.5). Certain technique variants, such as plasma-enhanced CVD (PECVD), photo-CVD, atomic layer deposition (ALD), and hybrid methods, are designed to operate at milder conditions.

Along with Chemical Vapor Deposition (CVD), Thermal Spray Deposition (TSD) methods offer the greatest range in coating thickness, followed by Physical Vapor Deposition (PVD). These methods can produce a wide variety of coating thicknesses while accommodating fluctuations in operating conditions [195]. The deposition process parameters directly influence the properties of the resulting coating [196]. Material characteristics vary according to the application, guiding the appropriate choice of deposition method. Factors such as substrate composition, size, and geometry have a direct impact on working temperature, bonding mechanism, deposition rate, coating uniformity, thickness control, as well as pre-treatment and post-treatment processes [197].

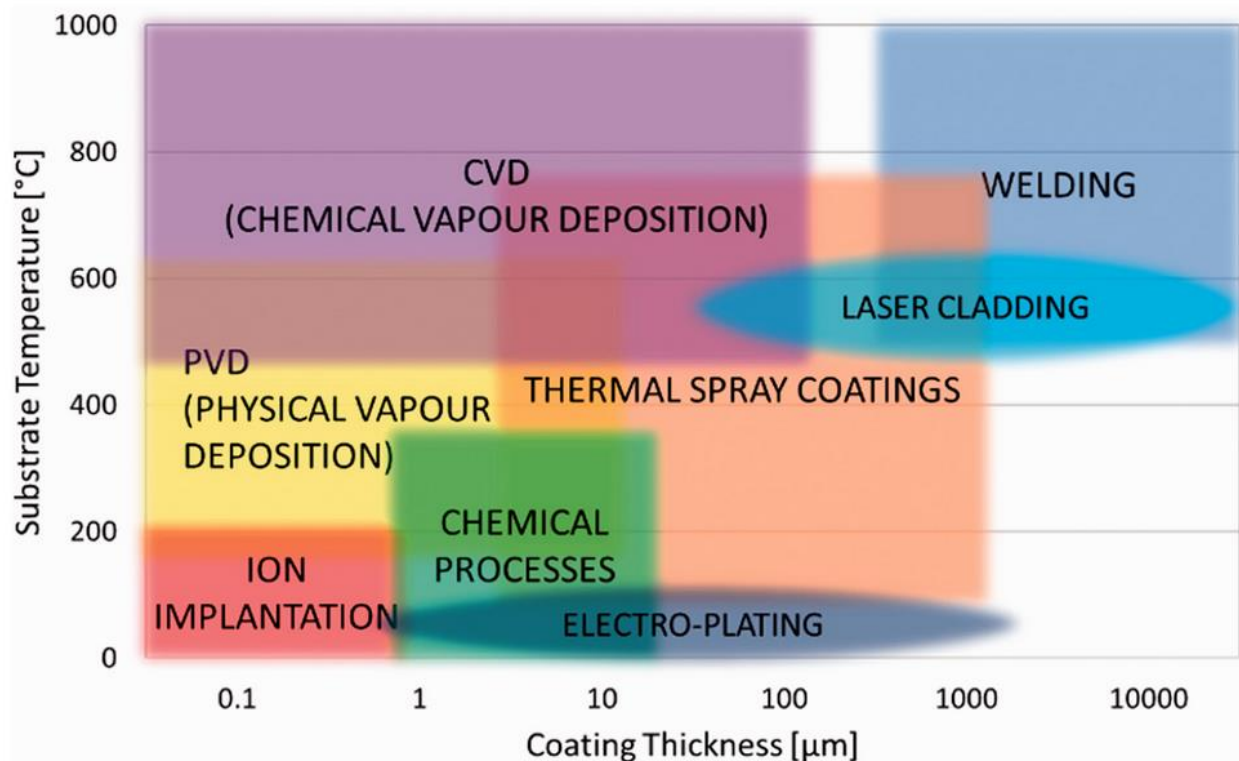


Figure 2.5 Comparison map of common coating processes based on achievable coating thickness and substrate temperature during deposition. Adapted from [198], under the terms of the Creative Commons Attribution 4.0 License.

Coating thickness, microhardness, adhesion strength, porosity, and grain boundary structure are commonly critical characteristics for many applications [199]. Generally, the thickness of the coating and the substrate's limiting temperature are two primary factors in selecting a coating process. While thicker coatings are often preferred for longer service life, reproducibility, along

with mechanical and chemical properties, can sometimes take precedence [195]. The key requirements for a protective coating material system are [200]:

- (1) Selection of coating material and technology – chemical compatibility (chemical stability, wetting angle, adhesion, etc.); thermo-physical compatibility (thermal expansion and thermal stability).
- (2) Diffusion barrier – protection against liquids and gases permeability (O_2 , CO_2 , H_2 , H_2S , etc.); diffusion stability in contact with reactive compounds, minimizing solid solution elements migration and leaching.
- (3) Physical properties – Thickness (high-temperature protection); hardness (wear resistance); porosity and grain boundary (chemical protection).

Other important characteristics include surface energy (which affects the tendency to form deposits), interfacial stress (which impacts cracking and delamination), and intrinsic oxidation (which can either promote or reduce oxide layer formation). These properties vary depending on the application. The most widely used high-temperature protective coatings include: carbides, such as HfC , SiC , TiC , TaC , WC , and ZrC ; borides, like B_4C , HfB_2 , TiB_2 , and ZrB_2 ; oxides including B_2O_3 , HfO_2 , SiO_2 , TiO_2 , and ZrO_2 ; nitrides, like BN , TiN , and Si_3N_4 ; silicides such as $MoSi_2$ and $TiSi_2$; and several combinations, such as $SiC + TaC$, $SiC + Si_3N_4$, $SiC + ZrC$, $SiC + ZrB_2$, and $SiC + B_4C$ [200].

In addition to high-temperature resistance, specific properties are required when developing coatings for extreme environments [201]. For example, porosity is advantageous for thermal barrier coatings (TBC) [202], catalytic coatings [203], and membranes [204]. However, for protective coatings, porosity is detrimental, as it compromises the ability of the system to act as an effective barrier between the substrate and the environment [205]. In the case of alloy corrosion resistance at elevated temperatures, surface passivation is typically the adopted strategy. The choice of deposition technique significantly affects costs, scalability, and protective performance. The sulfidation protection and anti-coking properties of various coatings are discussed below, focusing on relevant deposition techniques for the petrochemical industry and the study presented here.

Packed cementation produces corrosion- and wear-resistant diffusion coatings and relies on a master alloy powder, halide salts for activation, and inert fillers like oxides and carbides [206]. Packed cementation reduced the coking rate of ASTM A297 HP alloy from $0.9 \text{ g/m}^2\text{h}$ to $0.25 \text{ g/m}^2\text{h}$

(Cr-based), 0.44 g/m²h (Cr-Al-based), 0.50 g/m²h (Al-Si-based), and 0.40 g/m²h (Al-Ti-based). The performance of Cr cementation was comparable to that of CVD-deposited TiC + SiC composites, while TiC performed similarly to Cr-Al cementation [207]. Thermal treatment induces the formation of an external oxide layer on the cemented coating, which influences the coking mechanism and the properties of the coke, effectively inhibiting catalytic coke formation [208].

Although coatings produced by the packed cementation method may improve coke resistance, the substrate plays a crucial role in influencing the coating's microstructure and phase. Necessary heat treatment steps to enhance the coating's protectiveness can trigger surface phase transformations in the substrate and promote partial decarburization, along with other microstructural changes. A chromizing-siliconizing (90Cr-10Si) process enhanced oxidation resistance in the austenitic steel alloy 304 and Inconel 800. However, in a coal gasification reducing (sulfidizing) environment at Shell Development, the coating improved the performance of steel but had little impact on the other alloys [209]. Additionally, one of the significant issues with coatings produced by this method is thermo-mechanical fatigue, as cyclic strains caused by temperature gradients can lead to thermal fatigue cracks [210].

Another low-cost deposition technique, such as sol-gel, is employed to develop coatings that enhance sulfidation and coke resistance. The sol-gel process typically produces ceramics, glasses, and composites as coatings. A hybrid organic/inorganic high-temperature sol-gel (HTSG) deposited onto stainless steels demonstrates a lower fouling rate in a crude oil environment containing 4% sulfur at temperatures exceeding 315 °C [211]. Sol-gel deposited SiO₂, CeO₂, CeO₂-SiO₂ multilayers, and Ce-Si composites have been reported to exhibit anti-coking properties. Among these, Ce-Si composites showed the best performance with a 68.7% reduction in coke deposition, followed by CeO₂-SiO₂ multilayers with higher concentrations of CeO₂ [212]. A bilayer derived from sol-gel processes, consisting of CeO₂- α -Al₂O₃, also demonstrates good anti-coke performance. The presence of the passivating oxide hinders the diffusion of reactive elements, thereby minimizing catalytic coke formation and facilitating coke removal. Furthermore, CeO₂ exhibits catalytic activity in oxidation, which helps reduce the decoking temperature [213]. However, sol-gel techniques face several challenges for large-scale industrial production. There is a lack of systematic evaluation regarding adhesion and stability, and their synthesis often requires long processing times, necessitating proper optimization to avoid phase separation, particularly in

hybrid coatings [214]. Moreover, optimizing sol-gel coatings to achieve corrosion and wear resistance in high-temperature applications presents additional challenges [215].

For applications involving high mechanical stress or wear, thermal spray coatings typically outperform packed cementation and sol-gel coatings due to superior adhesion. Thermal spray coating is one of the most significant classes of coatings with various industrial applications. The most notable spraying process is high-velocity oxygen fuel (HVOF) [216]. This technique is generally more expensive than packed cementation and sol-gel methods, as it requires specialized equipment and skilled labor.

When compared to bare 310S alloy, HVOF-deposited Cr-CeO₂ coatings demonstrated anti-coking properties, with higher concentrations of CeO₂ improving performance from 48% to 88.9% for Cr-CeO₂ ratios of 19:1 and 3:2, respectively [217]. WC/CoCr sprayed coatings exhibit high microhardness and maintain their structural and mechanical properties in H₂S-CO₂ corrosive environments [218]. Consequently, this type of coating is widely applied to valves in petrochemical applications, where components must resist sulfidation and wear. However, this technique still produces coatings with defects, necessitating post-treatment processes such as annealing at temperatures close to 1 000 °C. Additionally, their effectiveness against corrosion is often linked to surface scale formation, which carries the limitations previously discussed regarding alloys.

Protecting valves and materials subjected to wear in extreme environments presents a dilemma. Achieving full passivation and corrosion protection requires the formation of a thin film of a dense, defect-free passive layer, typically composed of oxides, on the surface [205]. Passivation helps prevent catalytic coke formation and reduces surface energy, thereby diminishing coke adhesion and facilitating decoking processes. However, the oxide films produced are often brittle and unsuitable for wear applications, while alloying coatings are wear-resistant but still vulnerable to corrosion, albeit to a lesser degree than the base material. Therefore, pseudo-passivation of the surface using nitride or carbide structures emerges as an optimal solution, offering both wear and corrosion resistance.

Few articles demonstrate that nitrides and carbides can be utilized for their anti-coking properties [219], [220], [221], exhibiting performance comparable to alumina [222], [223], and SiO₂ [224] coatings. The effects of these coatings on sulfidic corrosion environments, particularly in heavy oil hydrocracking applications, have seldom been investigated. Typically, these coatings are deposited

using CVD methods to achieve thicknesses greater than 20 μm for wear resistance in harsh conditions. A TiC/Ti(CN)/TiN multilayer coating offers protection against corrosion in H_2S - CO_2 environments at 80 $^\circ\text{C}$ and inhibits the diffusion and penetration of hydrogen into the alloy [225].

The PVD sputtering method provides better control over coating composition and morphology, often resulting in coatings with superior adhesion and finish deposited at lower deposition temperatures compared to the other techniques previously discussed. A 2.5 μm thick AlTiN layer enhanced the oxidation and sulfidation resistance of the TiAlWSi intermetallic material at 850 $^\circ\text{C}$ when exposed to a gas mixture of 90% H_2 and 10% H_2S . Incorporating NbN and CrN in a layered structure further improved corrosion resistance; however, the mismatch in thermal properties led to coating failure after 240 hours of operation [226]. Sputtered TiN and CrN also enhanced the sulfidation resistance of SUS316L alloy when exposed to a mixed gas of H_2O and H_2S at 500 $^\circ\text{C}$, although they resulted in sulfide formation on the surface [227].

Sputtering has its disadvantages, as it is a line-of-sight technique with a low deposition rate, making it less suitable for coating complex shapes and large surfaces. Pre-treatment optimization is essential to enhance adhesion and ensure coating performance. For instance, a study evaluated the fouling resistance of magnetron-sputtered coated surfaces exposed to various types of crude oil. Carbon steel and P91 alloy wires coated with 50 nm of Cr_2O_3 , TiO_2 , and Al_2O_3 were subjected to crude oil at a surface temperature of 350 $^\circ\text{C}$. Although the coatings outperformed the bare alloys, they fell short compared to a pure Cr layer due to poor adhesion [228].

In summary, complex environments exposed to a mixture of hot gases (H_2 , CO , CO_2 , N_2 , and H_2S) create multiple reaction pathways that accelerate the degradation of both the coating and the substrate. The fouling mechanisms are often challenging to interpret accurately and may appear contradictory due to the lack of detailed environmental characterization, which is essential for understanding the underlying processes. There is a pressing need to develop coatings that are corrosion-resistant, minimize foulant deposition, and provide high wear resistance. Each deposition technique offers distinct advantages in corrosion, fouling, or wear resistance, but typically involves a compromise in one of these areas to optimize performance for a specific application. Fine-tuning the deposition process is a crucial step in ensuring the success and durability of the coating in its intended application.

2.2.4.1 Sputtering

In sputtering, energetic ions from a glow-discharge plasma strike the cathode (target), ejecting atoms that are deposited onto a substrate, forming a thin film. The ion impact on the target also releases secondary electrons, which play a role in sustaining the plasma. Magnetrons generate a magnetic field parallel to the target, confining the emitted electrons and significantly increasing the probability of electron–atom collisions [229]. This enhanced ionization efficiency produces a denser localized plasma, improving the sputtering rate and enabling a reduction in operational pressure (Figure 2.6). Lower pressures increase the ions' mean free path, resulting in more energetic deposition and potentially enhancing the film's uniformity, adhesion, and density on the substrate.

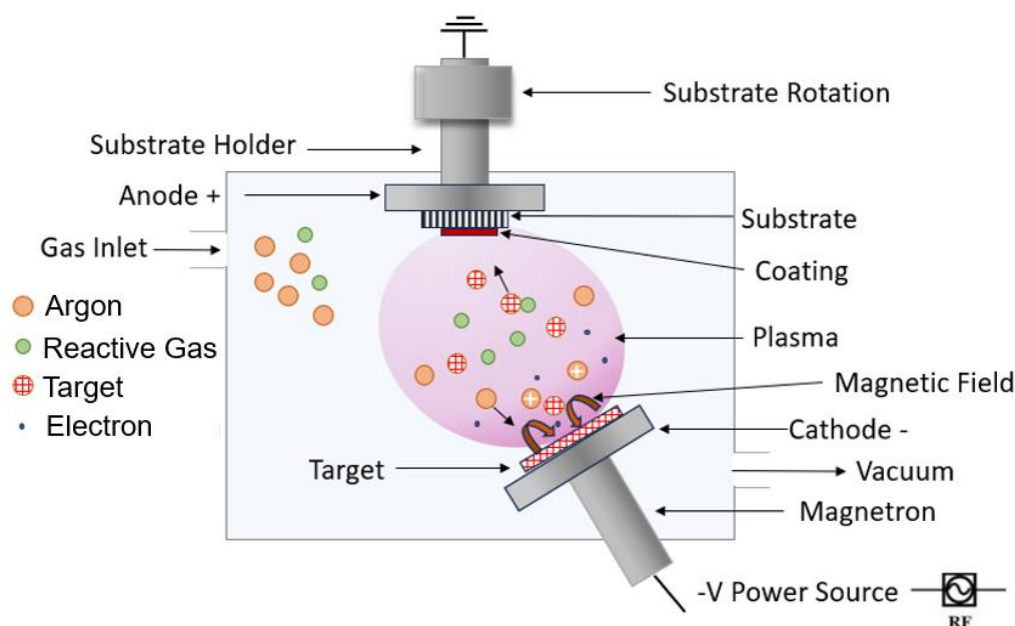


Figure 2.6 Schematic of a typical magnetron sputtering system with a planar target configuration.

Reactive sputtering process involves using metallic targets where an inert gas (e.g., Ar) is mixed with reactive gases (e.g., O₂ and N₂). In reactive magnetron sputtering, three deposition modes can be observed; they are characterized by a hysteresis behavior that displays two stable states of the system (metallic and poisoned), with a transition state between them. The hysteresis is represented as a curve of the cathode voltage and deposition rate versus the reactive gas flow at a constant discharge current [230]. The deposition rate in the reactive mode is lower compared to the pure metallic mode [231]. A high supply of reactive gas allows for stoichiometric deposition; however, it can lead to target surface poisoning, significantly reducing the deposition rate. This indicates that

an optimal balance must be achieved to attain both high deposition rates at proper stoichiometry [232]. Some models, such as Berg's model, were essential to improve the reactive sputtering process [233]. Operating in the transition mode may prevent excessive target poisoning, maintain a more stable plasma, and increase the deposition rate.

In reactive sputtering, insulating films that form on the target surface (poisoned mode) can accumulate charge, leading to arcing, which negatively impacts the quality of the deposited films. To mitigate this issue, suitable power sources are essential. Traditionally, radio frequency (RF) power has been preferred over direct current (DC) power to address these challenges [234]. In RF power mode (typically at 13.56 MHz), the power polarity is alternated [235]. During the negative pulse, plasma ions are attracted to the cathode, sputtering the target atoms, while during the positive pulse, electrons are drawn to the target surface, discharging the cathode and preventing arcing [236]. Although RF improves plasma stability and prevents arcing, the deposition rate is approximately half that of DC power with an equivalent power input [237]. Alternatives such as pulsed DC and mid-frequency AC power are also effective in preventing arcing [234]. All sputtering depositions in this study utilized RF as the power source to minimize process variables. Furthermore, specific microstructure characteristics can be tailored by controlling the deposition parameters. A structure zone diagram (SZD) is a useful tool illustrating qualitatively the common features of thicker films (>100 nm) related to various deposition parameters (Figure 2.7) [238]. The specific deposition conditions of the deposited coatings in this study are detailed in their respective Chapters.

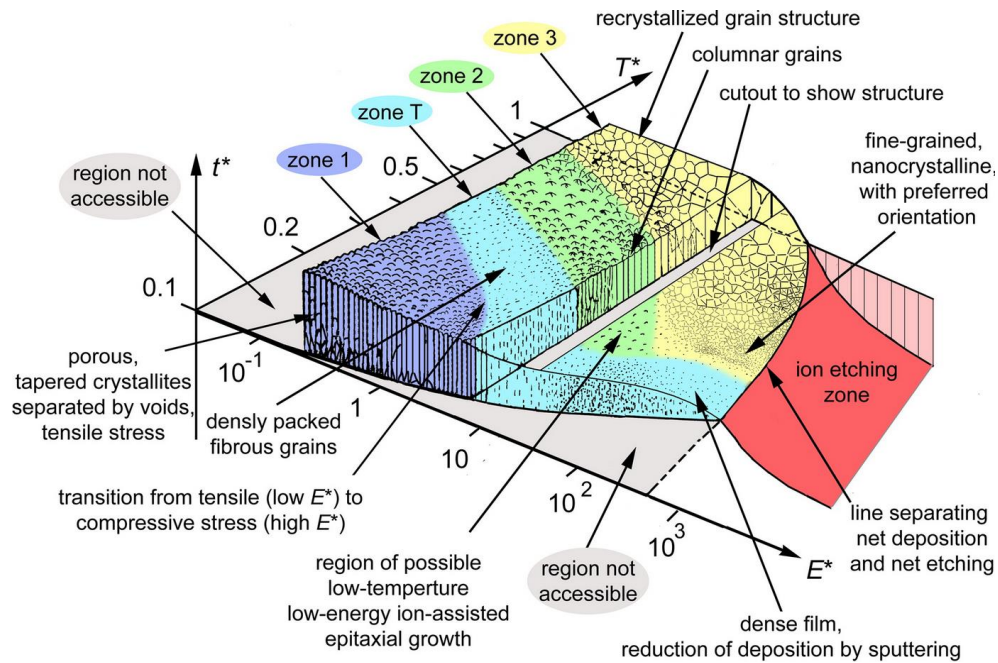


Figure 2.7 Structure zone diagram (SDZ) applicable to energetic coating deposition. The axes are defined as generalized temperature T^* , normalized energy flux E^* , and in the z -direction, a net film thickness t^* . Reprinted from [238] with permission from Elsevier.

2.2.4.2 Thermal Spraying

Thermal Spray Deposition (TSD) encompasses a range of coating processes in which a stream of metallic or non-metallic particles is accelerated using a spraying device or “gun” and deposited onto a substrate to form flattened lamellae, which stack progressively to create a coating [239]. A key advantage of TSD is its ability to deposit a wide range of materials onto diverse substrates. Applications of TSD focus on wear and corrosion resistance, surface functionalization, component repair, restoration, and additive manufacturing [240]. This industrial method is widely employed for surfacing and resurfacing engineered components, enabling the deposition of materials such as metals, alloys, metal oxides, ceramic blends, carbides, wires, rods, and composites on various substrates to form unique microstructures [241].

Among the TSD methods, arc spray, flame spray, and atmospheric plasma spray have been extensively used since the first development in 1917 [240]. Traditional TSD processes exhibit limitations, including porosity, oxidation, and residual stress [242], which can adversely affect the mechanical, electrical, and corrosion resistance properties of the coatings compared to bulk materials [240]. Residual tensile stress arises during the cooling and solidification of molten droplets, as underlying solidified layers remain at lower temperatures. This incremental stress accumulation restricts the maximum coating thickness; beyond a certain point, coatings may crack or detach from the substrate. In contrast, High-Velocity Oxygen Fuel (HVOF) and detonation Gun processes produce coatings with less residual tensile stress or even exhibit residual compressive stress. The high-velocity impact of partially molten particles during these processes creates a ‘peening’ effect, compressing the underlying material and enhancing coating adhesion and density [242].

HVOF involves injecting a mixture of oxygen and fuel into a combustion chamber, igniting it, and expelling the gas at high velocity through a nozzle (Figure 2.8). Powder particles are introduced into this gas stream and propelled toward the substrate. HVOF coatings exhibit low porosity, strong substrate adhesion, and enhanced corrosion and wear resistance [243]. Typical particle velocities at the nozzle exit range from 1525 to 1825 m/s [244]. The high kinetic energy of the particles contributes to dense and well-adhered coatings [245]. However, the success of the process depends on the feedstock powder size, typically between 10 and 40 μm . Particles larger than 40 μm may

not fully melt, while those smaller than 10 μm risk burning or degrading before reaching the substrate [246].

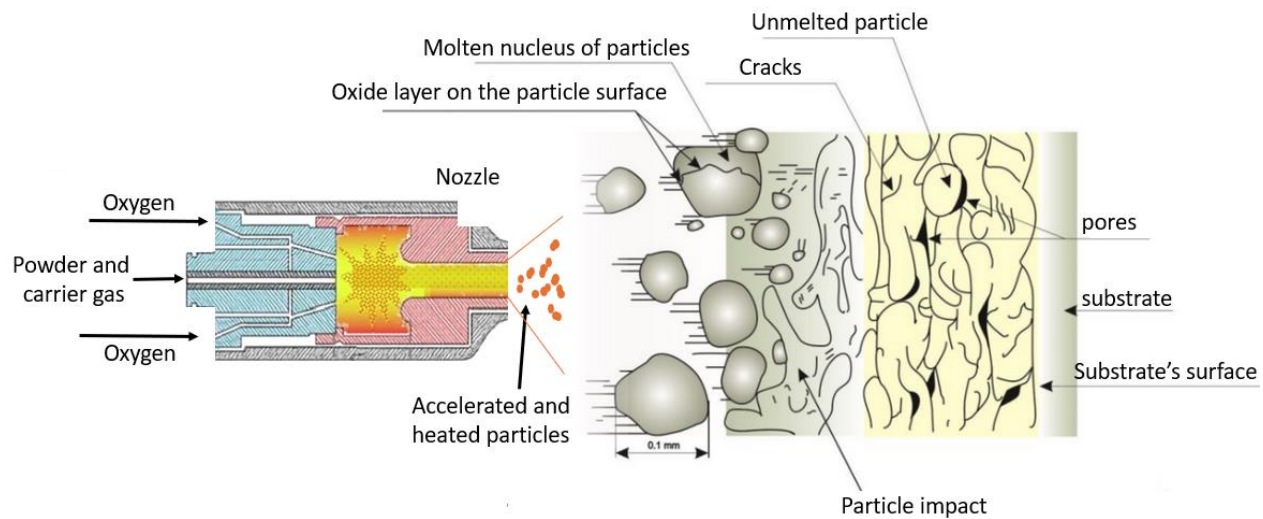


Figure 2.8 Schematic of a high-velocity oxygen fuel (HVOF) deposition system. Adapted and reprinted from [247] with permission from Elsevier; and adapted from [248] under the terms of the Creative Commons Attribution 4.0 License.

Despite its advantages, thermal spray processes, including HVOF, are limited to surfaces directly accessible to the spray stream. Only areas with a direct line of sight to the spray gun can be coated [242]. High-Velocity Air-Fuel (HVOF) technique addresses some of the TSD limitations related to porosity and oxidation. By using air instead of oxygen, HVOF achieves higher jet velocities and lower flame temperatures, reducing powder particle oxidation and maintaining raw material properties. Additionally, HVOF provides a cost-effective alternative to HVOF while producing dense coatings with lower porosity [244].

CHAPTER 3 METHODOLOGY

This chapter outlines the main experimental methodology in this work, including preparing and coating the substrates, fouling experiments, and sample preparation for characterization. The characterization techniques for each coating are detailed in their respective Chapters. These techniques primarily focus on assessing the coatings' mechanical properties and the nature of fouling. Inconel 718 served as the main substrate for the experiments.

3.1 Surface preparation

The surface preparation removes contaminants and influences the surface's ability to develop durable, well-adhering coatings [163]. Substrates ($25 \times 25 \times 3 \text{ mm}^3$) were polished using a Struers LaboPol-5 polishing machine with SiC grinding papers (grit sizes ranging from 100 to 800) under continuous water flow and rotation ($\sim 250 \text{ rpm}$). For finer polishing, an MD-Largo pad was used with a $9 \text{ }\mu\text{m}$ diamond solution to eliminate deeper grooves at a faster rate. Next, the samples were mounted on a mechanical arm with a constant pressure of 30 N and polished using an MD-Dac pad with a $3 \text{ }\mu\text{m}$ diamond solution, followed by polishing with an MD-Floc pad using a $1 \text{ }\mu\text{m}$ diamond solution. The mechanical arm's pressure was then reduced to 15 N, and the samples were polished on a chemical pad with OPS solution (particle size 5 nm) containing 3% by volume of H_2O_2 , achieving a mirror-like finish. Finally, the substrates were cleaned in an acetone ultrasonic bath, followed by an isopropanol ultrasonic bath, for 10 minutes each.

Before coating deposition, the samples underwent a plasma sputter-cleaning process. The coupons were mounted on the sample holder inside the deposition chamber, where an RF-induced negative bias of -650 V generated plasma at 5 mTorr (0.67 Pa) using argon gas. This process removes the native oxide layer from the surface while promoting surface activation [249]. Following this step, the samples remained in the chamber, and thin films were deposited via magnetron sputtering.

3.1.1 Surface preparation for microscopy

The cross-sections were prepared by cutting the samples with an alumina oxide cut-off wheel (model 50A13, Struers) using a PICO-155P precision cutter from Pace Technologies. For fouled samples, the region selected for cutting was the area with the most apparent surface deposits. Additionally, pieces extracted from the fouled samples were coated with a 20 nm gold layer via magnetron sputtering over the fouled area, followed by copper electroplating in a 10 M CuSO_4

solution at 2 V for 20 minutes. This step was essential to differentiate the carbon from the mounting epoxy and the carbon originating from coke. It also facilitated the identification of contamination in the cross-section after the final polishing step, enabling a more precise microscopy analysis.

The samples were placed in a mount, and EpoFix Resin from Struers was poured into it. To fill micro-voids and porosities within the samples, the mount was placed in a vacuum chamber and maintained at 1 mTorr for approximately 5 minutes. After vacuum impregnation, the mount with the samples was allowed to cure for 24 hours. The embedded samples were then polished according to the steps outlined above. Once a mirror-like finish was achieved on the cross-sectional surface, it was sputter-coated with a thin metal layer (< 10 nm of Cr or Au) to minimize charging during SEM measurements.

3.2 Coating deposition

In the context of this work, the coatings deposited by the High-Velocity Oxygen Fuel (HVOF) thermal spray process were acquired through the industrial partner of the project. The other coatings were deposited via magnetron sputtering (CeO_2), or reactive magnetron sputtering (Al_2O_3 , TiAlN, and SiBCN).

The oxide and SiBCN coatings were deposited using a planar target configuration. In contrast, the TiAlN coating was deposited with a cylindrical target and magnetron. The rotating cylindrical magnetron configuration offers several advantages. It allows for more efficient target utilization, improving sputter yield and maintaining plasma stability during reactive sputtering [250], [251]. Additionally, this setup is well-suited for operating at higher power densities [251].

The specific deposition conditions for each coating are provided in their respective chapters.

3.3 Fouling experiments

The reactor (Figure 3.1) is made of SS 316 by Autoclave Engineers. The main chamber features a cylindrical shape and is equipped with a heating source provided by the same manufacturer. The shaft was modified to accommodate the prepared samples, and the sample holder is designed to support coupons measuring 1" x 1" x 1/8". A manifold was designed and built from SS 316 to facilitate the gas connections. Attached to the manifold is a WIKA pressure transmitter model S-20 with a diaphragm seal (M1), a Swagelok relief valve (M2) set to 1800 psi, and a back-pressure regulator (M3) configured to operate at 1650 psi. The outlet piping connects to a Swagelok needle

valve (M4) to equalize pressure in a controlled manner before opening the reactor. Additionally, piping with a ball valve connects an argon bottle to the manifold (M5) for purging and pressurizing the reactor before heating. Another piece of piping connects the manifold to the reactor inlet (M6). The exhaust (E) is linked to particle filters containing activated charcoal (F1) and ZnO (F2). A drain valve (D) is installed to remove liquid from the reactor. A water-cooling system is also attached to the reactor.

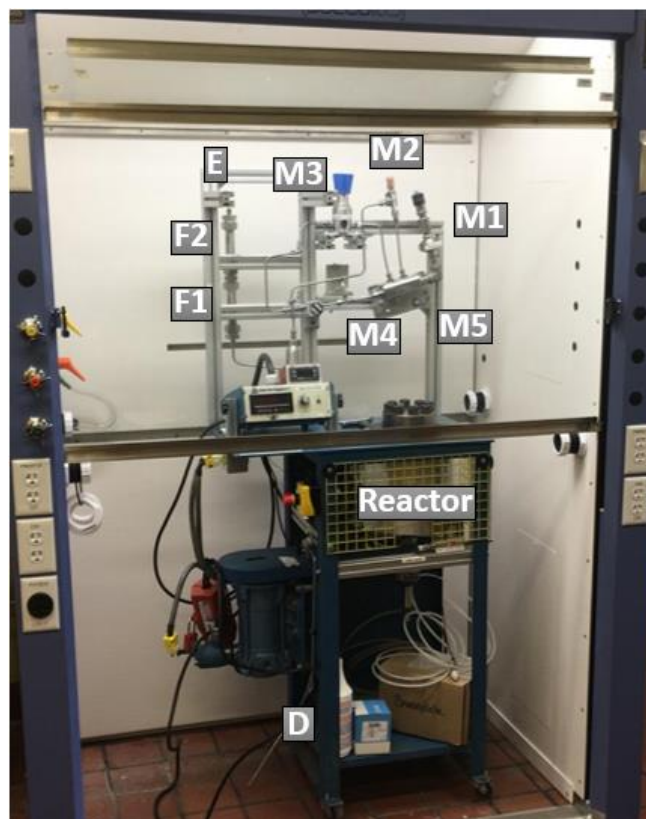


Figure 3.1 Autoclave reactor used for fouling tests.

The samples were placed in the substrate holder and secured within the reactor coupling (Figure 3.2). The sample positioning was intentionally vertical to mitigate gravitational effects that could lead to material deposition due to precipitation. Before heating, the reactor was filled with heavy oil containing 6 wt.% sulfur. The system was pressurized with argon up to 11.3 MPa (1650 psi), regulated by a backpressure regulator, and purged for 5 minutes to evacuate any residual oxygen. The fouling experiments were conducted at 450 °C, followed by a hold time of 2 hours to ensure that all heavy oil was effectively cracked.

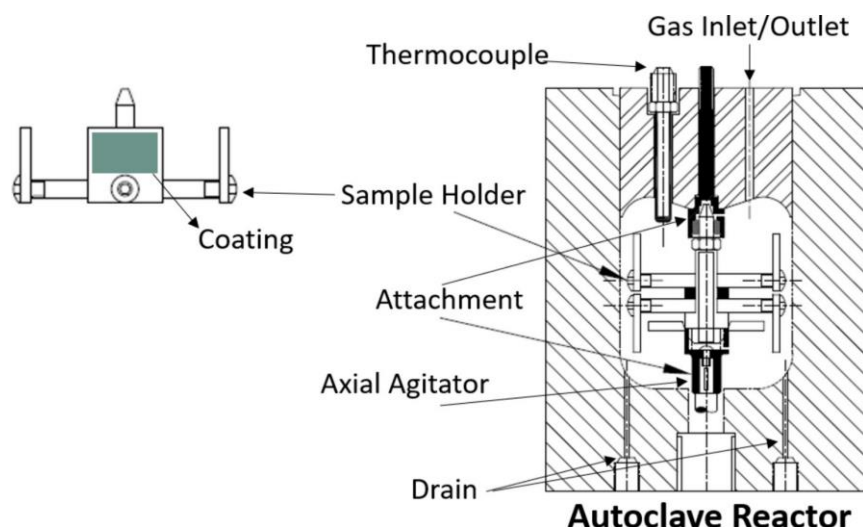


Figure 3.2 Cross-section of the batch reactor and sample holder

After the heating cycle ended, the system was allowed to cool until the following day before depressurizing, opening, and retrieving the samples. The recovered fouled samples (Figure 3.3) were washed with a 50:50 solution of petroleum ether and toluene, followed by a water rinse to remove any non-adherent material. The samples were then air-dried and stored prior to subsequent analyses.

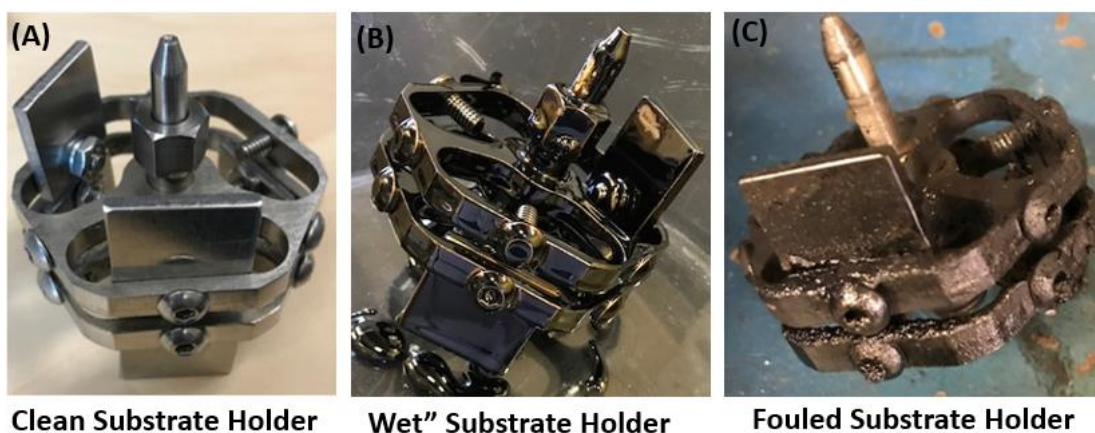


Figure 3.3 Sample holder before (A), during (B), and after (C) the fouling experiment.

For a specific set of experiments, a different fouling reactor and oil were used. In this reactor, the tests were conducted using vacuum tower bottoms (VTB) bitumen containing 5.6 wt.% sulfur, along with hydrogen, a catalyst (FeS), and agitation. Additional experimental details can be found in Chapter 4 and the literature [252]. Due to limitations in the configuration of the second reactor,

the fouling experiments described in Chapter 4 were carried out at a temperature of 445 °C, followed by a holding period of 1 hour.

3.3.1 Fouling quantification

A new optical method was developed to compare the surface fouling of the tested samples (Figure 3.4). Surface fouling was assessed semi-quantitatively using a Nikon D7000 Digital Single-Lens Reflex (DSLR) camera equipped with three Kenko Auto Extension tubes (12, 30, and 36 mm), a 105 mm macro lens, and a Hoya 62 mm NXT Plus Circular Polarizer filter. The camera was mounted on a bridge with vertical adjustment capabilities, and the samples were placed under a dark dome to minimize background reflections. The interior of the dome was illuminated with 58 LED lamps, which were controlled remotely via a LabView program.

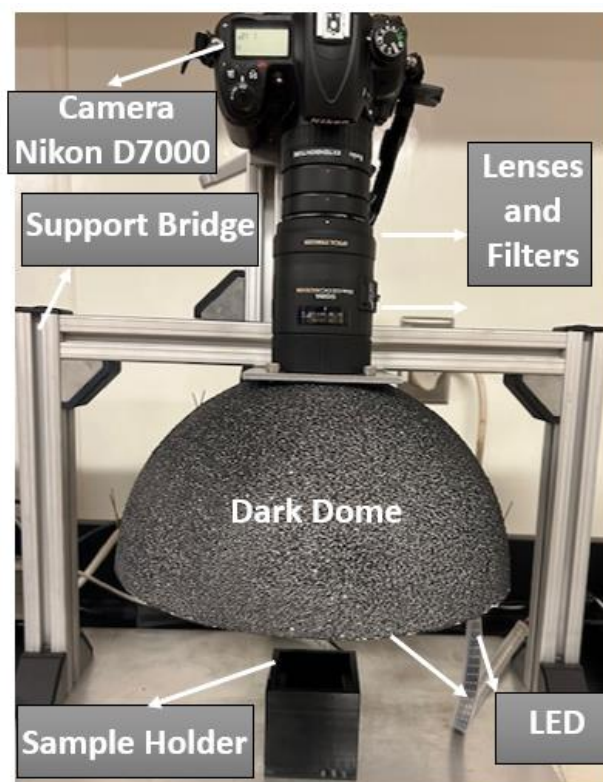


Figure 3.4 Photography setup designed for capturing and analyzing sample images under controlled lighting conditions.

Images were captured with a shutter speed of 1/320 s, an aperture of f/16.0, and a low sensitivity setting ISO 100. These 16-megapixel images were converted to grayscale, with each pixel assigned an intensity value ranging from 0 (black) to 255 (white). A processing algorithm evaluated each

pixel in a loop; if its intensity fell below the chosen threshold value of 50, it was designated as a dark pixel, indicating fouling. The threshold was chosen as the value where the sample with higher surface fouling had an intensity close to 100%. In cases with highly reflective fouled surfaces, a reflection threshold value of 55 was established, where pixels above this value were also classified as dark pixels. The algorithm then calculated the percentage of dark pixels relative to the total pixel count, providing a semi-quantitative measure of surface fouling.

3.4 Reproducibility

To ensure the reproducibility of results, all fouling experiments were conducted using one polished IN718 sample alongside other samples placed in the fouling reactor for a given reaction. The fouled IN718 sample was then compared to those obtained in previous batches to validate the consistency of the reaction. Additionally, at least two samples were analyzed for each material tested.

Microscopy images were collected following a thorough scan of the entire analyzed area. For samples exhibiting a high degree of fouling, images were taken from regions that represented the average fouling for that sample, with areas of maximum and minimum fouling previously identified to ensure representativeness. In contrast, for samples with minimal fouling, such as PVD-deposited coatings, SEM images focused on the areas showing the worst fouling observed during the scan.

CHAPTER 4 ARTICLE 1 : HEAVY OIL CORROSION FOULING OF NI-BASED ALLOY AND CO-BASED THERMAL SPRAYED COATINGS

Fellipy S. Rocha^{1,2}, Pedro R. T. Avila¹, Fadila Khelfaoui³, Luc Vernhes³, Gregory S. Patience², Kevin J. Smith⁴, Jolanta E. Klemberg-Sapieha¹, Ludvik Martinu¹

¹Department of Engineering Physics, Polytechnique Montréal, Montreal, QC H3T 1J4, Canada

²Department of Chemical Engineering, Polytechnique Montréal, Montreal, QC H3T 1J4, Canada

³Velan Inc., 7007 Côte-de-Liesse, Montreal, QC H4T 1G2, Canada

⁴Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

The article was submitted to the *Fuel* on October 27, 2024

Thesis author contribution:

Fellipy S. Rocha, Jolanta E. Klemberg-Sapieha, and Ludvik Martinu jointly conceived the research idea. Fellipy S. Rocha took the lead in developing the methodology, conducting the experimental investigations, curating and validating the data, and preparing the initial manuscript draft. All co-authors reviewed and edited subsequent versions collaboratively.

4.1 Abstract

Nickel-based alloys are used in the oil and gas industry due to their advantageous mechanical properties, but they are susceptible to sulfidation. Co-based alloys are resistant to corrosion, but they offer less attractive mechanical properties at high temperatures. This work identifies possible sulfidation mechanisms of Inconel 718 (IN718, Ni-based) and Wallex 50 (W50, Co-based) as a function of heavy oil hydrocracking operating conditions, including the presence of hydrogen, catalyst, and agitation at high temperature (445 °C) and high pressure (>11 MPa). The main fouling mechanisms are chemical reactions from the sulfur precursors in the case of IN718, and mass transfer in the case of W50.

4.2 Introduction

The only consensus concerning crude oil fouling is that a better understanding of the science behind the problem is needed [69]. Experimental data identify distinct routes for foulant formation, transport, and attachment [45], [47]. Inorganic and organic fouling may occur together or separately, with interactions or independently, in parallel or series. Species react on the surface, in the bulk, or on the thermal boundary viscous layer. Deposits comprise inorganic compounds (sulfides, oxides, and salts), and organic carbon (coke) [74]. However, visually distinguishing the deposited materials is burdensome as they are all black. Disagreements persist about the mechanisms forming deposits, and a unified understanding of these deposits' constituents and chemical structures remains elusive [69].

There are five recognized generic types of fouling mechanisms (crystallization, particulate, chemical reaction, corrosion, and biological), which are divided into five distinguishable steps (initiation or delay period, transport, attachment or deposition, removal, and aging) [39], [46]. In theory, the five fouling mechanisms occur separately, each following the sequential steps. However, in practice, two or more mechanisms often combine and occur with steps in parallel. Understanding the fouling mechanisms and the influential factors is essential to developing appropriate fouling models [39].

Sulfidation and coke deposition are main concerns in the oil and gas industry. The fouling mechanism is distinct when it occurs above or below the cracking temperature (350 °C). Below 350 °C, asphaltene instability and precipitation lead to organic fouling. Above the cracking temperature, both sulfidation and coking deposition increase, with the latter increasing at a higher rate [106]. H₂S is one of the most important components of the sulfidation/sulfidic corrosion rate, and its surface interaction can be assumed as a mass flux-controlled reaction. The total flux is a combination of 1) convective diffusion through the boundary layer; 2) molecular diffusion through the liquid in the porous outer layer; and 3) solid state diffusion through the inner sulfide film [82]. Even low concentrations of H₂S (>2 ppm) are enough to form iron sulfide scales rapidly [83]. The diffusion coefficient increases with temperature and depends on the surface activation energy and gas molecular weight. Other factors, such as pressure and viscous flow, are important to the diffusion rate [253].

One of the challenges of experimental fouling research is to produce relevant data with small-scale reactors. It is problematic to mimic the volume of samples and time necessary to compare the crude fouling produced in experimental reactors with the level of fouling observed in industrial relevant conditions like refineries. Laboratory scale experiments intend to isolate and identify the variables that play a role in the deposition and to compare the behavior of various crude samples, under identical or different well-defined conditions [111]. The small-scale study opens the possibility of understanding not only crude oil behavior and deposition kinetics, but also the interaction with surface materials and how to exploit them to develop materials with adequate surface properties for a long-lasting protection strategy.

Several types of experimental apparatus produce fouling on a laboratory scale; among them are once-through units, coiled wire probes, thermal fouling testers, tubular systems, annular systems, autoclaves, and stirred tanks [114], [115], [116], [117]. Some of these are commercially available. Even the simple stirred batch reactors have a wide variability in their construction and operating windows [46]. Computational fluid dynamics (CFD) simulations complement the experimental data to identify the contribution of the flow rate [110]. Operating conditions directly impact the surface interactions – gas/liquid phase reactions, corrosion, erosion, mechanical wear due to metal-metal contact – influencing the fouling mechanisms. Often, the mechanisms describe the fouling layer growth rate and thermal properties, but little attention is given to the influence on the materials. Comparing different operating conditions and reactors might help elucidate the mechanisms influencing microstructural changes in the materials and possible improvements.

The study of iron alloys is extensive since most of the work done to rationalize the fouling mechanism in oil and gas was carried out to study heat exchangers, as fouling affects the heat transfer properties of the materials and presents safety and environmental risks. The FeS formation and its contribution as a carbonaceous fouling promoter has been well documented [71], [74], [105], [107]. The mechanism of the fouling process initiates via the decomposition of sulfur-containing molecules, forming elemental sulfur and hydrogen sulfide (H_2S), which reacts with the alloy surface and metal coming from the corrosion of upstream piping. In addition, coke is deposited, forming a strongly adherent carbonaceous layer and a FeS brittle film on the alloy surface [71]. Sulfidation induces localized corrosion, characterized by an intense attack only in a particular metal zone, while the rest of the material remains unaltered (e.g., pitting corrosion).

Localized corrosion creates weak spots by selectively removing a specific alloy element from the exposed surface, and is hard to detect [16].

Nickel-based superalloys are used in the petrochemical industry due to their superior mechanical properties under stress at high temperature [254]. However, these alloys are susceptible to sulfidation [122], and/or act as a catalyst to form H_2S in H_2 -rich environments [16]. Critical reactor equipment, including severe-service isolation valves, necessitates exceptional material toughness at high temperature. To achieve this, nickel alloys are often employed for key components, particularly for sealing elements. Inconel 718 (IN718) is typically coated to reduce the coefficient of friction between sealing surfaces that must slide against each other during valve cycling. Additionally, the coating enhances the surface resistance of IN718 to abrasion, erosion, and corrosion, thereby improving its performance under these grueling conditions. Coating technology offers a cost-effective and flexible alternative to improve the materials' surface properties [255]. High-velocity oxygen fuel (HVOF) [216] is a commercially available thermal spray coating technique used to coat valves in petrochemical applications. Wallex 50 (W50) is a self-fluxing sprayable cobalt-based alloy powder, applied on isolation valves. Self-fluxing alloy coatings contain boron and silicon, which lower the melting point, enhance fluxing (fluidity) and wettability during deposition, and act as deoxidizers to protect the material from oxidation [256]. Tungsten carbide coatings are also applied to valves in steam boilers and furnaces, among others [257].

There is a lack of data concerning fouling and the mechanisms that characterize this phenomenon, particularly for materials in critical components in petrochemical applications. This work explores possible sulfidation mechanisms of IN718 and Wallex 50 under various operating conditions and proposes a relevant phenomenological model describing the surface reactions.

4.3 Materials and methods

4.3.1 Surface preparation

The samples consisted of bare IN718 (25x25x3 mm³) and IN718 industrially coated by HVOF with 2 mm thick Wallex 50 (W50) film. The coated samples were heat-treated over 1000 °C for 10 min, creating a metallurgical bond at the coating/substrate interface. Subsequently, they were annealed for over 10 h below 800 °C to recover the toughness of the IN718 substrate. Samples surfaces were mirror polished using SiC papers with varying grit sizes (100 to 800), followed by diamond particle suspension (from 3 μm to 1 μm) varying Struer's magnetic pads, finishing with colloidal alumina

suspension. IN718 possesses a high concentration of Ni (52.9 wt.%) compared to 18 wt.% in W50. The latter alloy has about 45 wt.% of Co, while IN718 is virtually Co-free. Both alloys have about the same concentration of Cr (see Table 4.1).

Table 4.1 Elemental composition of the IN718 alloy and Wallex 50 coating.

Chemical composition, [wt. %]		
Element	Wallex 50	IN718
Co	Balance	0.23
Ni	18	52.9
Cr	19	19.4
W	10	-
B	3.5	-
Si	2.75	0.15
Fe	1	Balance
C	0.8	0.04
Mo	-	2.93
Mn	-	0.17
Ti	-	0.93
Al	-	0.44
Nb+Ta	-	5.09

A Bruker ContourGT-K white-light interferometer was used to measure the surface morphology at optical magnifications of 5x and 20x, corresponding to scan areas of $1268 \times 951 \mu\text{m}$ and $317 \times 237 \mu\text{m}$, and lateral sampling values of $1.98 \mu\text{m}$ and $0.495 \mu\text{m}$, respectively. The Gwyddion [258] open source software was used to trace the surface profile via Laplace interpolation correcting points with non-meaningful data (intensity = 0 or 100%), followed by tilt removal via mean plane subtraction.

4.3.2 Microscopy

The coating topography, microstructure, and elemental composition were assessed with a scanning electron microscope (SEM, JEOL JSM-7600F) equipped with an energy dispersive X-ray spectrometer (EDS), and an Oxford Instruments X-Max detector. The electron beam energy was varied from 5 keV to 30 keV. Before mounting the cross-sections in epoxy, a 20 nm thick gold layer was sputtered on the coated surfaces, followed by copper electroplating in a 10 M CuSO_4 solution at 2 V for 20 min.

4.3.3 X-ray diffraction

X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Discover X-ray diffractometer in Bragg-Brentano geometry with $\text{Cu K}\alpha$ radiation (8.04 keV) using a LynxEye 1-D detector. The incident beam optics configuration consisted of a Gobel mirror and 0.6 mm divergence slit, while automated slits were used in diffracted beam optics. The range of the 2θ scans was from 20 to 90 degrees with a step size of 0.0103° . The XRD data was processed with the Bruker DIFFRAC.EVA V4.3 that included background subtraction and $k\text{-}\alpha_2$ stripping.

4.3.4 Fouling

Two reactors were used to conduct the degradation experiments (Table 4.2). All samples were placed vertically to avoid gravitational deposition on the surface. After the reaction, the samples were washed with a 50:50 petroleum ether and toluene solution, followed by a water rinse to remove excess solvent and non-adherent material. The samples were then dried in air before subsequent analyses.

4.3.4.1 Reactor 1

An 80 g sample of vacuum tower bottoms (VTB) bitumen containing 5.6 wt.% sulfur was introduced into an autoclave-type reactor together with the samples to be tested. 4.1 MPa of H_2 and 3 wt. % of catalyst (FeS) was introduced into the reactor to promote hydrocracking. The stirrer operated at 700 rpm to ensure mixing and simulate turbulent flow past the surface. Upon heating, the pressure increased to 12.4 MPa at 445 °C, and the temperature was kept for 1 h, simulating the cracking environment. After the 1 h reaction, the reactor was rapidly cooled with internal water-based cooling coils before depressurizing, opening, and retrieving the samples. Further experimental details are available [252].

4.3.4.2 Reactor 2

An 80 g sample of VTB bitumen containing 6 wt.% sulfur was introduced to an autoclave-type reactor together with the samples to be tested. The reactor was purged with argon at 11.3 MPa for 5 min to minimize the oxygen concentration and then heated to 445 °C for 1 h to simulate the cracking environment. It cooled overnight before depressurizing, opening, and retrieving the samples [259].

Table 4.2 Fouling test reactors dimensions.

Dimensions (mm)	Internal Diameter	External Diameter	Internal Height	Blade Diameter	Shaft Diameter
Reactor 1	46	59	183	20	12.5
Reactor 2	51	76	48	-	-

4.3.4.3 Fouling quantification

The surface fouling was semi-quantitatively assessed using a previously described method [260]. 16 Megapixel images were taken under a dark dome with a Digital Single-Lens Reflex (DSLR) Nikon D7000 camera equipped with 3 Kenko Auto Extension tubes (12, 30, and 36 mm), 105 mm Macro lens, and Hoya 62 mm NXT Plus Circular Polarizer filter mounted on a bridge. The images

were captured with a shutter speed (exposure time) of 1/320 s, an aperture f/16.0, and a low sensitivity ISO 100. The images were converted to a grayscale, and every pixel was attributed to an intensity value, from black (0) to white (255). A processing algorithm evaluated every image pixel in a loop; if the pixel intensity was lower than the selected threshold value of 50, the pixel was defined dark pixel; if the pixel intensity was above the selected reflection threshold value of 55, the pixel was defined dark; the pixels in between both threshold values were considered white pixels. The addition of the reflection threshold increased the accuracy of the measurements. After defining all pixels, the algorithm calculated the percentage of dark pixels over the total number of pixels which represents the surface fouling.

4.4 Results and discussion

After polishing the bare IN718 substrate, the Arithmetic Roughness, Ra , was approximately 12 ± 3 nm, and the Ra of the W50-coated samples was approximately 117 ± 40 nm. The W50 coating microstructure and composition determined by SEM and EDS showed a complete separation between regions containing Cr and W (Figure 4.1). Ni is mainly concentrated in the area containing W. The EDS analysis identified WCoNi, CrCo, and CoNi phases (Figure 4.1B). No major oxidation is observed, and the oxidized area is correlated with the Si elemental map, indicating the formation of Si oxides.

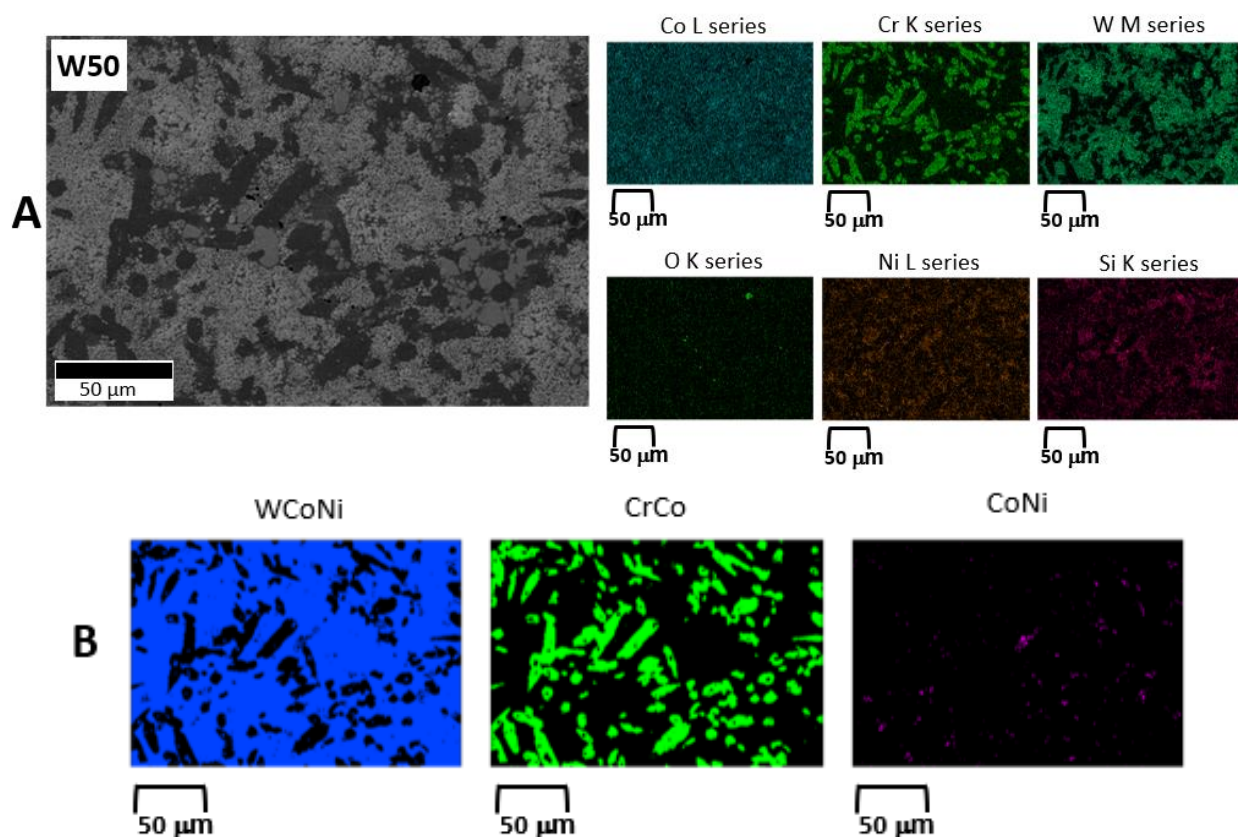


Figure 4.1 Wallex 50 surface. A) SEM image represents the elemental distribution based on EDS, and B) identifies the phases.

Fouling is exhibited by the appearance of carbonaceous materials on the surface. The ability of the different samples to reduce fouling is illustrated in Figure 4.2. The presence of a catalyst during the hydrocracking reaction reduces the amount of fouling accumulated on the material's surface. The IN718 substrate had the highest amount of surface fouling, followed by the as-deposited W50. The polished W50 exhibited the best performance. The reflection threshold for the polished Wallex 50 sample exposed to fouling with catalyst had to be adjusted due to a higher brightness when compared to the samples with a higher fouling content (Table 4.3). The image processing considered a delaminated area marked with a red ellipse (Figure 4.2) as fouling. All samples had a fouling intensity above 90%, except the polished W50 in the presence of catalyst, which had a fouling intensity around 36%, showing the influence of the catalyst and the lower surface roughness. Asphaltene-rich feed, like heavy oil, forms more coke on nickel alloy, affecting the coke structure. The feed and reaction conditions influence the thickness and structure of the layer [173].

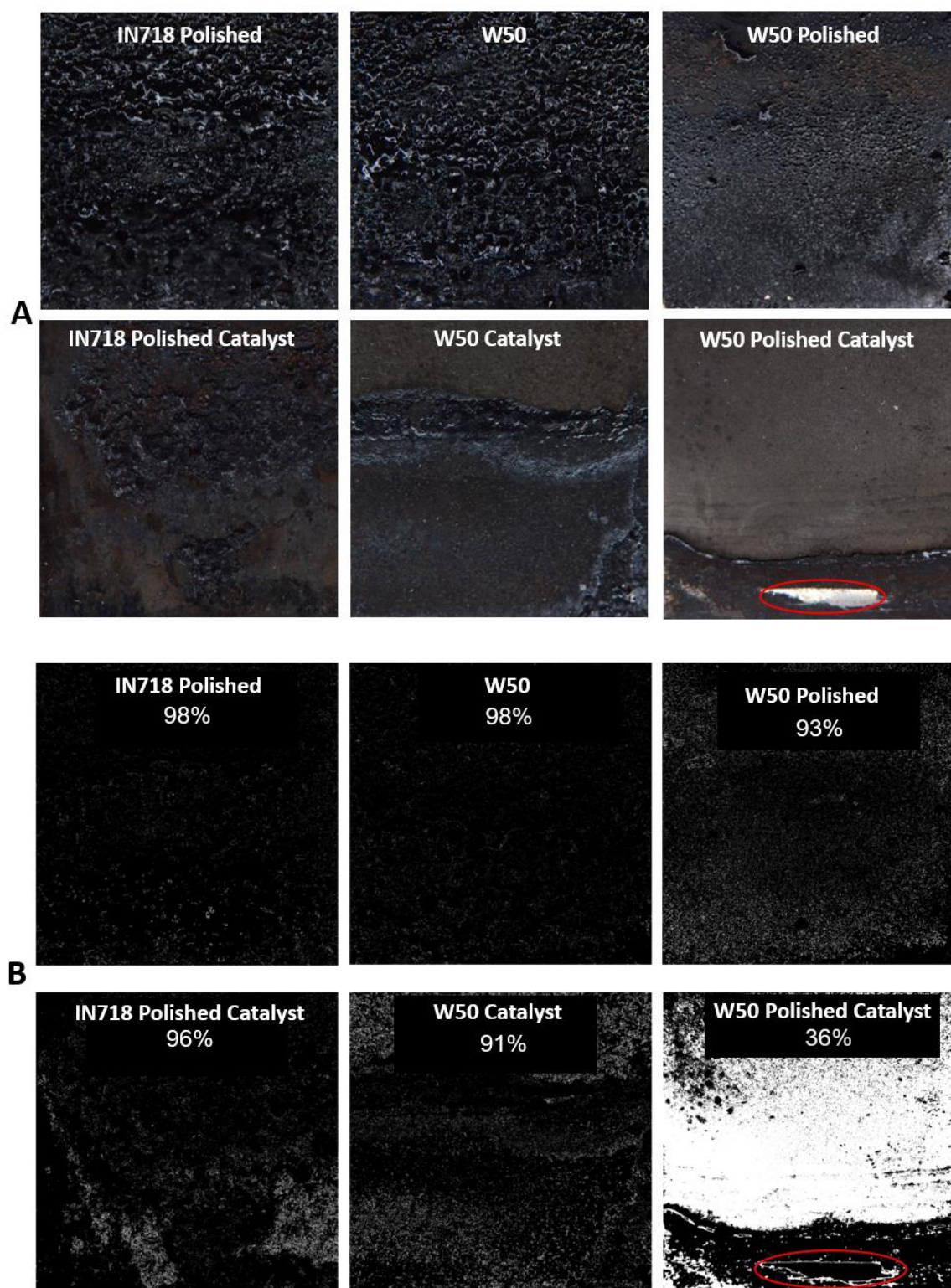


Figure 4.2 Surface of the samples after exposure to heavy oil in the Reactor 1: (A) optical image and (B) after image treatment. The red circle highlights a fouled, delaminated area that was identified as fouling after image processing. The images represent a matrix of 20 x 20 mm.

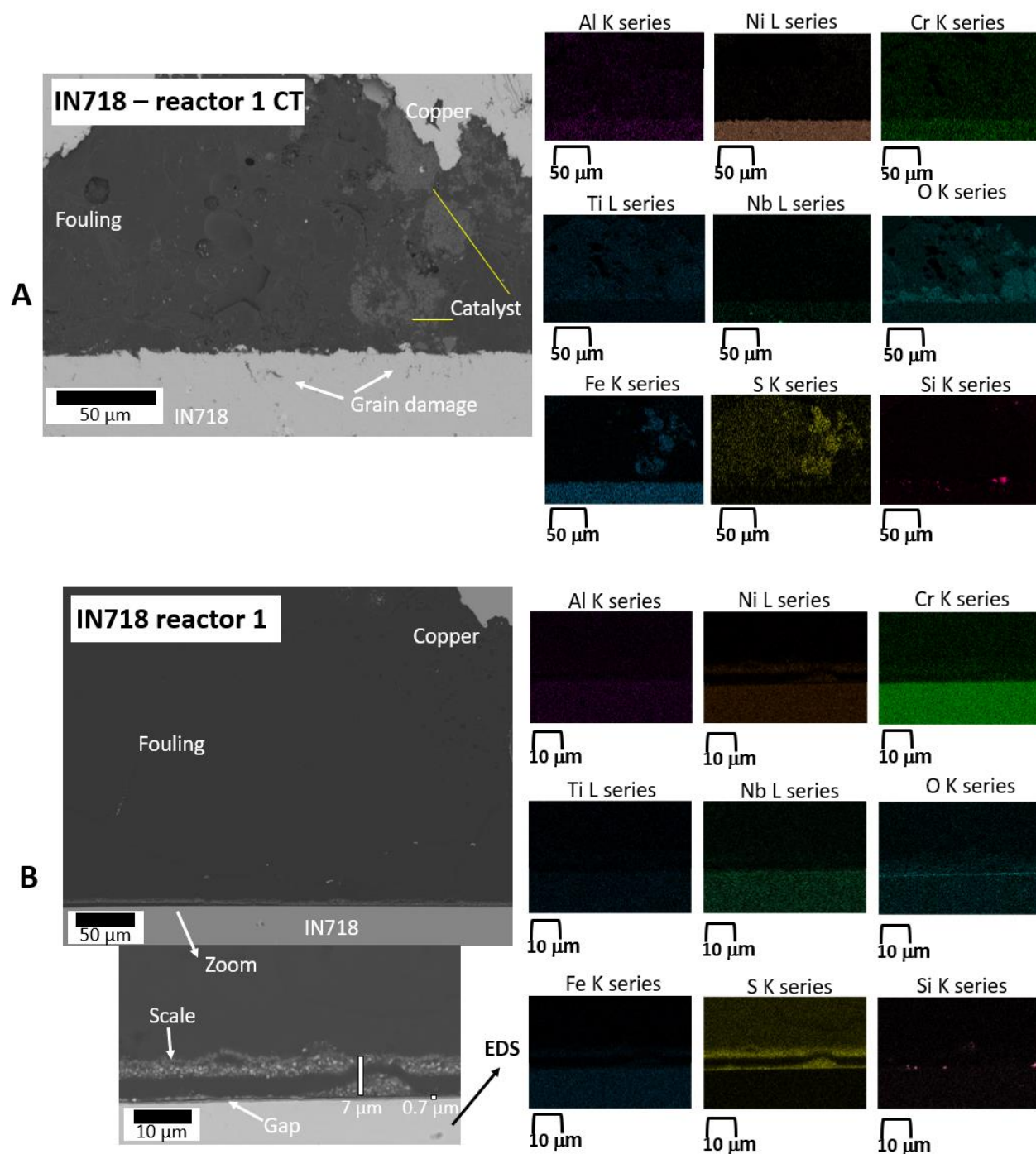
Table 4.3 Optical image parameters and surface fouling intensity.

Sample	Reflection Threshold	Fouling Threshold	Fouling Intensity
Polished IN718	55	50	98%
Polished IN718 with Catalyst	55	50	96%
W50 (as-deposited)	55	50	98%
W50 (as-deposited) with Catalyst	55	50	91%
Polished W50	55	50	93%
Polished W50 with Catalyst	110	50	36%

The cross-section SEM images (Figure 4.3) reveal details of the interaction between the heavy oil and the sample's surface. EDS maps indicate the elemental composition. The analyzed cross-section area was chosen to represent the regions with the highest amount of fouling on the samples. Figure 4.3A shows the IN718 substrate fouled in the presence of the catalyst in Reactor 1, exhibiting a thick layer of coke on the surface. Oxides and sulfides are present throughout the whole fouled region. Oxides are more concentrated closer to the alloy surface and are correlated with Ti and Cr elemental maps. Sulfur has a higher concentration where iron is observed, which characterizes the FeS catalyst.

Figure 4.3B represents the IN718 fouled in Reactor 1 without the catalyst. To gather the whole fouling thickness in Figure 4.3B, the magnification was decreased when compared to Figure 4.3A, showing a higher coke formation in the absence of the catalyst. The region close to the alloy surface in Figure 4.3B was magnified to collect details of the inorganic scale and EDS data. The SEM image shows two layers of inorganic scales separated by a coke layer, in which the scale layer closest to the alloy surface presents signs of delamination by the presence of a gap. A thin oxide layer was formed close to the IN718 surface. Sulfur is concentrated in the scale region and strongly correlated with Ni. Other elements, such as Nb, Ti, Cr, and Fe, have a faint signal in this region.

Figure 4.3C represents the IN718 material fouled in Reactor 2, where the average thickness of the coke layer is similar to the samples in Reactor 1 without the catalyst. In Figure 4.3C, three distinct areas are identified. The region closest to the alloy is about 3 μm thick, rich in oxygen, and the presence of Ti, Al, Nb, Si, and Cr suggests metal oxides formation. The area above the oxides is approximately 10 μm and rich in sulfur. The third region is predominantly composed of carbon.



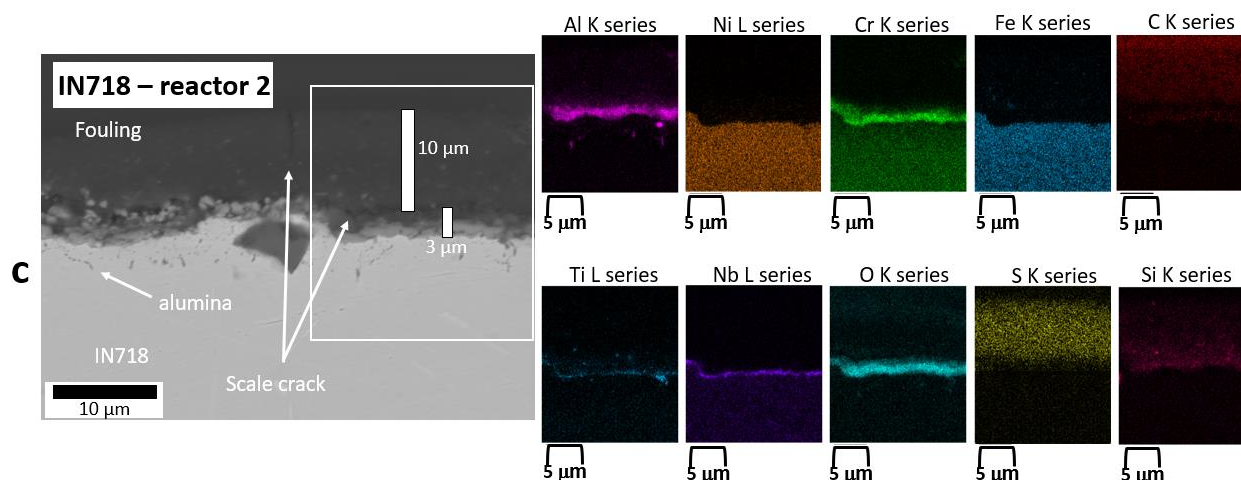


Figure 4.3 Cross-section SEM images and EDS maps of IN718 after fouling at 445 °C for 2 h. The fouled samples are identified as A) Reactor 1 with catalyst (CT), B) Reactor 1, and C) Reactor 2, with the EDS map region marked as a white square.

The fouling experiments were conducted at 445 °C, which is above the cracking temperature [106], with sufficient energy to induce thermal cracking of the hydrocarbon, forming reactive species and precursors that contribute to the surface inorganic and organic fouling. Crude oil fouling has an uncertain reaction mechanism due to the complex physico-chemical processes. Corrosion layers may induce fouling by enhancing the chemical reaction rate or contribute to viscous sublayer thinning due to mass transfer [74].

When considering the IN718 substrate alone (Figure 4.3), the presence of catalyst, hydrogen, and agitation influenced the fouling process. Figure 4.3A shows a high degree of oxidation in the fouled region, with no clear inorganic scale formation. The high concentration of Al and Ti in the oxide region indicates a preferential removal of these alloying elements, as the alloy has less than 1% of Al and Ti (Table 4.1). The surface has clear signs of deterioration induced by corrosion, with increased roughness. The alloy detachment from the bulk is visible on the surface and throughout the fouled layer. Instead of corroding homogeneously, the material is eroded from the surface through localized grain boundary corrosion.

Grain boundary and bulk diffusion alone are insufficient to explain nickel's rapid diffusion. It was suggested that the diffusion rate is related to the microstructure of the scales during corrosion with oxygen and sulfur. Ni diffuses through nickel sulfide networks in the scale, accelerating the diffusion rate [124]. For comparison, with a long exposure at 700 °C for 1100 h, failure analysis of

an IN718 coal gasifier burner showed grain boundary-induced corrosion. Areas with extensive damage and crack propagation showed nickel removal from the alloy and Ni-S interconnected channel in the aged scale [90]. Failure analysis of Incoloy 800HT operating at 160-690 °C revealed intergranular corrosion cracking with sulfur accumulation at the grain boundaries [261].

The IN718 fouling without the catalyst in Figure 4.3B does not present surface damage as in Figure 4.3A. The formation of a 0.7 μm protective oxide layer on the surface reduces the grain boundary attack, preserving the alloy structure. The presence of Ni, Fe, Cr, and Nb in the scales (Figure 4.3B) indicates that the corrosion process without the catalyst is more homogeneous. The catalyst accelerates the formation of reactive species that increase the degradation rate of the alloy. Ti and Si are also in the scale, but no grain boundary damage was observed. The absence of bulk deterioration may be explained by the reduced reaction rate, which corrodes the alloy homogeneously, and the complete detachment of the corroded scale layer. The inorganic scale delamination from the alloy surface can result from the turbulent flow driven by agitation. The constant removal of the scale creates an environment with continuous corrosion of the alloy surface. The degradation rate without the catalyst should be lower than the degradation from the system with the catalyst, once the formation of the oxide layer protects the surface between scale removal cycles.

Figure 4.3C represents the third condition of IN718 fouling, i.e., without hydrogen, agitation, or catalyst. Notably, a 3 μm oxide layer is formed, about four times thicker than the oxide layer in Figure 4.3B. The lack of catalyst and hydrogen reduced the reaction rate of fouling precursor formation, consequently reducing the corrosion rate. The removal of agitation helped the formation of a thicker oxide scale on the surface, without signs of delamination. The EDS maps suggest the presence of Al and Ti oxides in the grain boundaries. Nb and Ti form a thin oxide layer close to the IN718 surface, while Al, Cr, and Si constitute the remaining oxide layer. Ti, Fe, and Si traces are identified above the oxidation, indicating sulfide formation. The sulfur-rich area exhibits a brittle nature with observable cracks, which may lead to the removal of that layer. The oxide formation during the fouling reaction (Figure 4.3C) provides a diffusion barrier limiting sulfidation. More stable sulfides, for example, those of aluminum and niobium, tend to congregate in the inner scale regions, reducing the sulfidation by a factor of 10 [133]. The accumulation of Si, Ti, Nb, and Al was observed in the inner regions.

To verify the formation of oxides on the surface of IN718, the alloy was oxidized for 2 hours at 445 °C in air. The oxidation step confirmed a 1.8 μm thick layer at the surface due to the oxides of Al, Ti, Cr, and Nb (Figure 4.4). When compared to the oxidation observed in Figure 4.3C, the oxidation during the fouling experiment produces a thicker oxide layer more rich in Al.

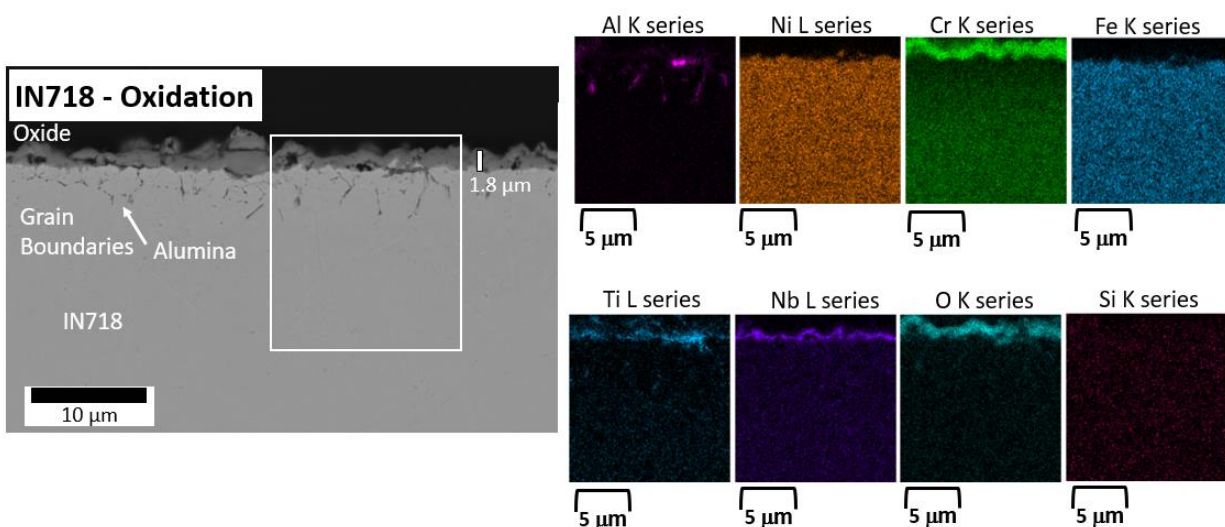


Figure 4.4 Cross-section SEM images and EDS maps (white square) of IN718 after oxidation in air at 445 °C for 2 h.

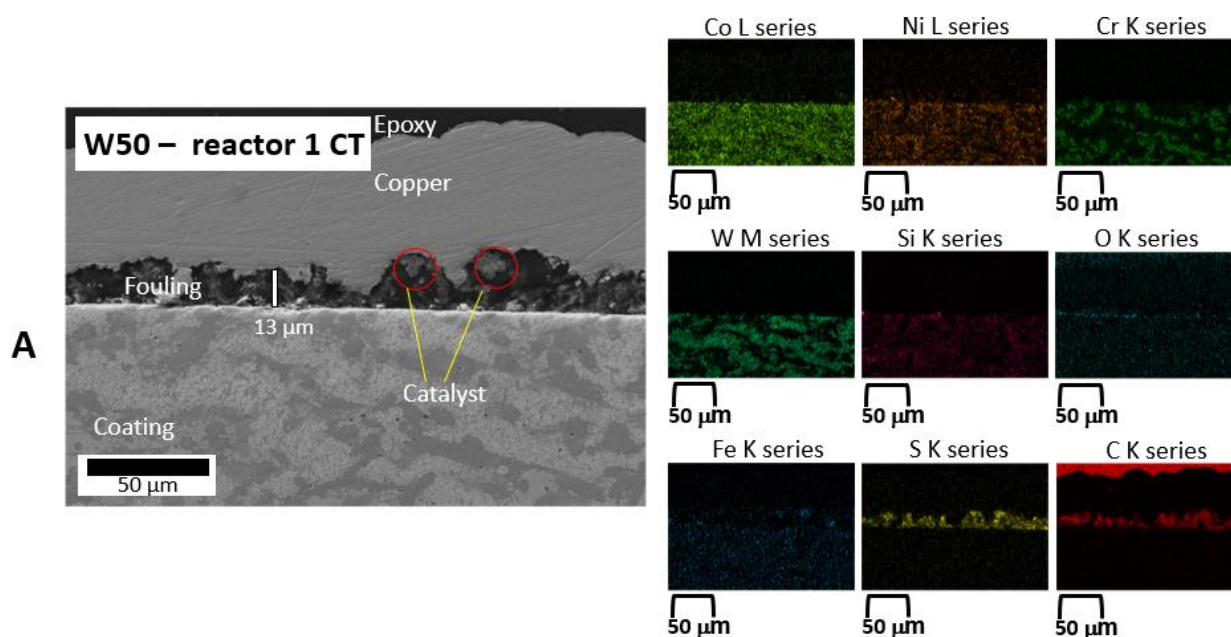
The sulfidation rate of metallic elements is 10^4 to 10^6 times higher than the corresponding oxidation rate, depending on the temperature [92]. Sulfide scales present more defective structures than oxides, providing alternative faster diffusion pathways for the cations [91]. Thus, the sulfide scale is first formed and later oxidized, creating a more stable structure and protection on the surface. However, the oxides formed from sulfides originate within defective structures and should be less protective than the oxides formed directly from the alloy. The oxides formed during the cracking reaction (Figure 4.3C) are granular, and the oxides formed during pure oxidation are more homogeneously distributed (Figure 4.4).

The corrosion rate by sulfur is generally faster than the corresponding oxide, with the bimolecular gas-phase reaction of the H_2S rate constant expressed by an Arrhenius-type equation [89]. The growth constant of Ni, Co, Fe, and Cr sulfides and oxides is known to be parabolic [87]. The observed IN718 oxidation (Figure 4.4) agrees with the literature, where the outer layer is characterized by Nb-rich Cr oxides with some voids and microcracks, a discontinuous Al_2O_3 phase, and various (Ti_xNb_y) C-type carbides. Al_2O_3 growth is observed along the grain boundaries through

inward oxygen diffusion. Ti is also oxidized internally and at the scale-alloy interface [262]. Pre-oxidation of IN718 has been used as a strategy to reduce the surface catalytic activity and inhibit carbon deposition [263].

Figure 4.5 shows the cross-section of the Wallex 50 fouled samples. The thickness of the coke on the W50 surface is reduced compared with IN718 (Figure 4.3). Figure 4.5A represents the W50 fouled in the presence of the FeS catalyst in Reactor 1. Oxides are concentrated close to the alloy surface, and an EDS signal of Si suggests the formation of Si oxide. Minimal coke is formed together with the sulfur-rich scale. FeS catalyst is observed in the inorganic layer that is 13 μm thick.

Figure 4.5B represents the W50 sample fouled in Reactor 1 without the catalyst. In the absence of the catalyst, an increase in coke formation was observed for W50. A thin oxide layer is observed in the coating interface, and another thin oxide layer is observed above the inorganic scale of 13 μm . The latter oxide layer is correlated with Si and Cr. The oxidation pattern embedded in the coke above the scale region suggests delamination of the oxide layers. Sulfur is concentrated in the scale region, strongly associated with Ni and Co. Figure 4.5C represents the W50 fouled in Reactor 2 with a coke thickness comparable to that of Figure 4.5B. In Figure 4.5C, the oxidation is correlated with Si and it mainly occurs at the coating interface. The sulfur inorganic scale is about 8 μm thick, and only coke is observed above the scale.



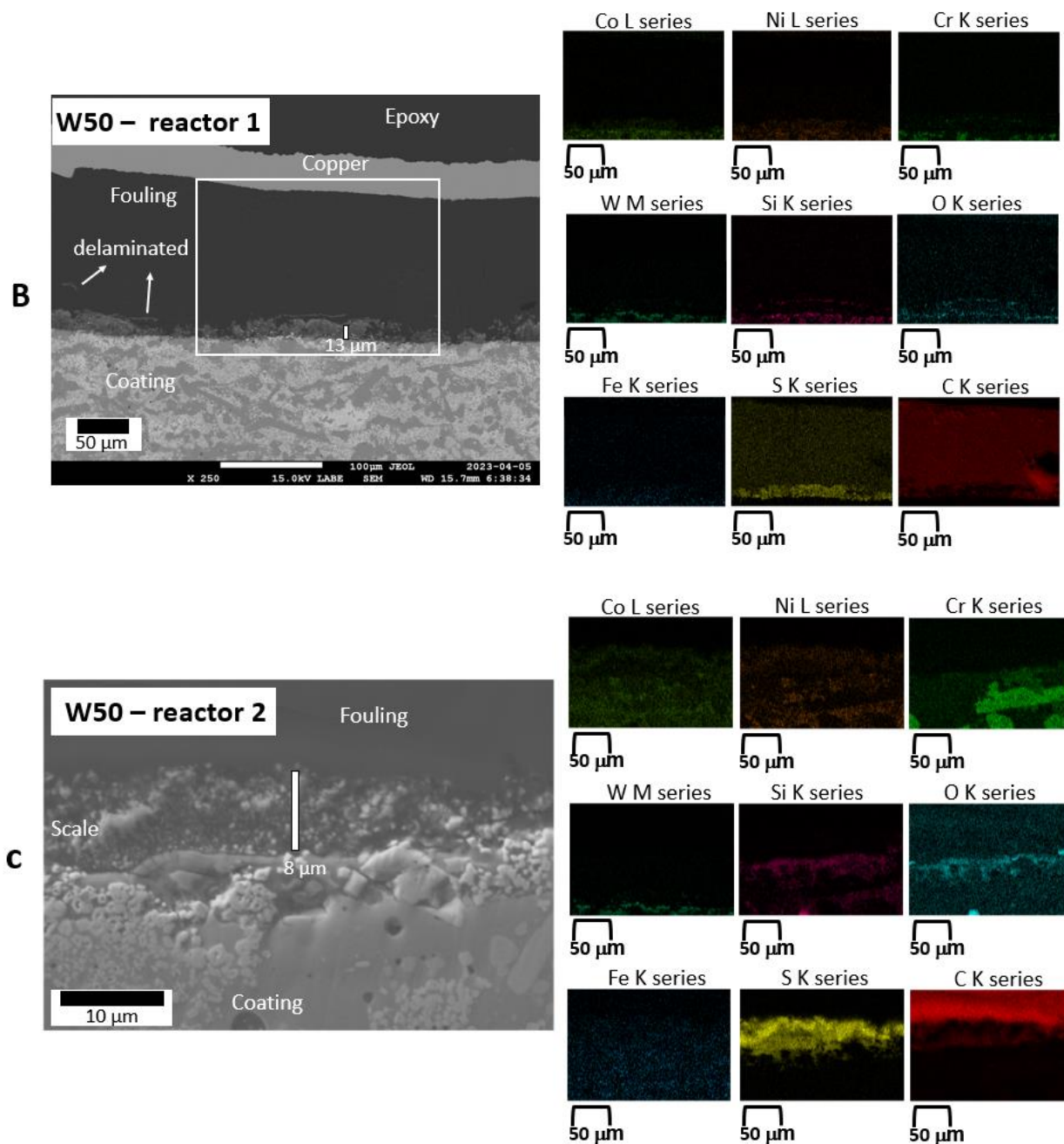


Figure 4.5 Cross-section SEM images and EDS maps of Wallex 50 after fouling at 445 °C for 2 h. The fouled samples are identified as A) W50 in Reactor 1 with catalyst (CT), B) W50 in Reactor 1, with EDS map region marked as a white square, and C) W50 in Reactor 2.

The surface of Wallex 50 demonstrates a different fouling behavior when compared to IN718. For the fouling condition with catalyst (Figure 4.5A), no significant difference is observed on the surface besides the coke and sulfidation simultaneous formation without a thicker coke layer above the sulfur-containing scale. In comparison with the reaction without the catalyst (Figure 4.5B), the

sulfide scale layer tends to have the same thickness of 13 μm on average. The increase in coke concentration without the catalyst allowed one to visualize the oxide scales delamination from the surface and its elemental composition identification. The catalyst only influenced the reduction of coke formation for W50. Following reactions without agitation and hydrogen (Figure 4.5C), the total amount of inorganic scale formation was reduced to 8 μm .

The EDS maps indicate the presence of Ni, Co, and Fe in the sulfur-rich scale region. Si oxide is present on the surface and deeper in the coating. The formation of silicon oxide in the bulk is related to the annealing before the fouling reaction. Silicon oxide is formed in the pores and defects of the coating [260]. In Figure 4.5C, sulfur infiltrated the surface of the coating in the Si-rich porous region. Since a higher amount of defects in the coating surface compared to the alloy has been observed, one would anticipate W50 to have a higher degradation rate. However, the results suggest that different corrosion mechanisms control the fouling of IN718 and W50, where the nickel alloy degrades in a faster way, while outward ion diffusion controls the sulfidation of alloys in H_2S , and the Co diffusion rate is lower than for Fe or Ni [264].

The microstructure of the near-surface region of the W50 samples before and after fouling was further investigated by XRD (Figure 4.6). Inorganic scale formed on W50 at all conditions, which was ideal for comparing the corrosion product composition in different fouling conditions. Identifying XRD patterns of multi-element materials is generally challenging due to an overlap of several possible candidate phases. The degraded samples without the catalyst presented carbon-related amorphous broad scattering at 25.5° . Co, Ni, and Fe sulfides were identified, corroborating with the SEM cross-section (Figure 4.5). The identified phases correspond to indexed peaks with above 30% intensity in the ICDD database.

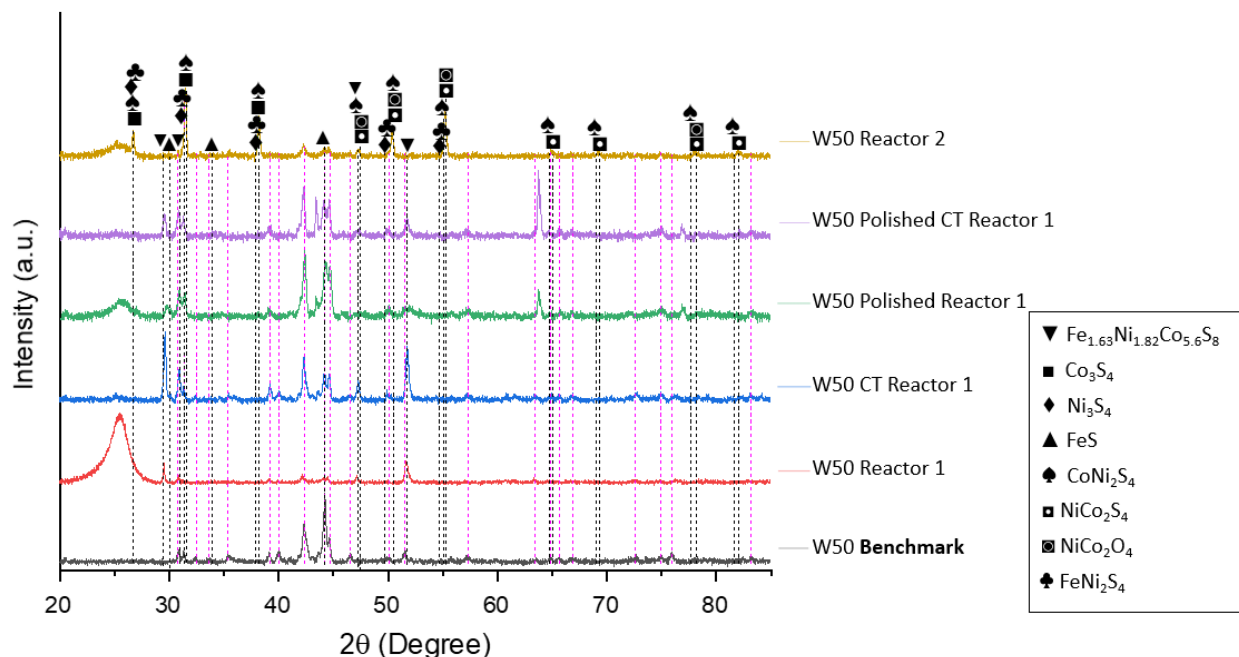


Figure 4.6 XRD patterns of the Wallex 50 coatings. The magenta dashed lines identify the alloying phases and the symbols of the identified sulfides. The coating patterns are compared before degradation (black) and after degradation in Reactors 1 and 2, with and without catalyst (CT).

Figure 4.6 shows a complex XRD pattern, where typically, the peaks with higher intensity in the region from 40° to 50° represent the benchmark material before degradation. The identified $\text{Fe}_{1.63}\text{Ni}_{1.82}\text{Co}_{5.6}\text{S}_8$ was the best match with the ICDD database, with the main peak at about 29.5° and considerable intensity variation between samples. The intensity variation was attributed to the orientation of the crystalline phases related to the normal of the sample's surface and the heterogeneity of the formation of sulfides in the scale layer. All other identified sulfides are Co, Ni, or Fe derivatives, and did not suffer significant peak intensity variation between samples. Ni and Co formed oxides. Other possible sulfides were considered, SiS_2 , WS , and Cr_2FeS_4 , but they could not be confirmed due to the convolution of peaks. Iron, nickel, and chromium are known to form porous, fast-growing iron-rich Fe-Ni-Cr sulfides [228].

To identify the non-homogeneity of the fouling, the surface fouling of Wallex 50 in Reactor 2 was analyzed in the transition zone of the coke formation (Figure 4.7). The areas with more coke are smoother and present cracks. Different electron energy levels were used to verify the elemental composition in different interaction volumes. Lower energy levels show the elemental composition

of the fouling top layer, while higher energy reaches significant contributions deeper in the inorganic scale.

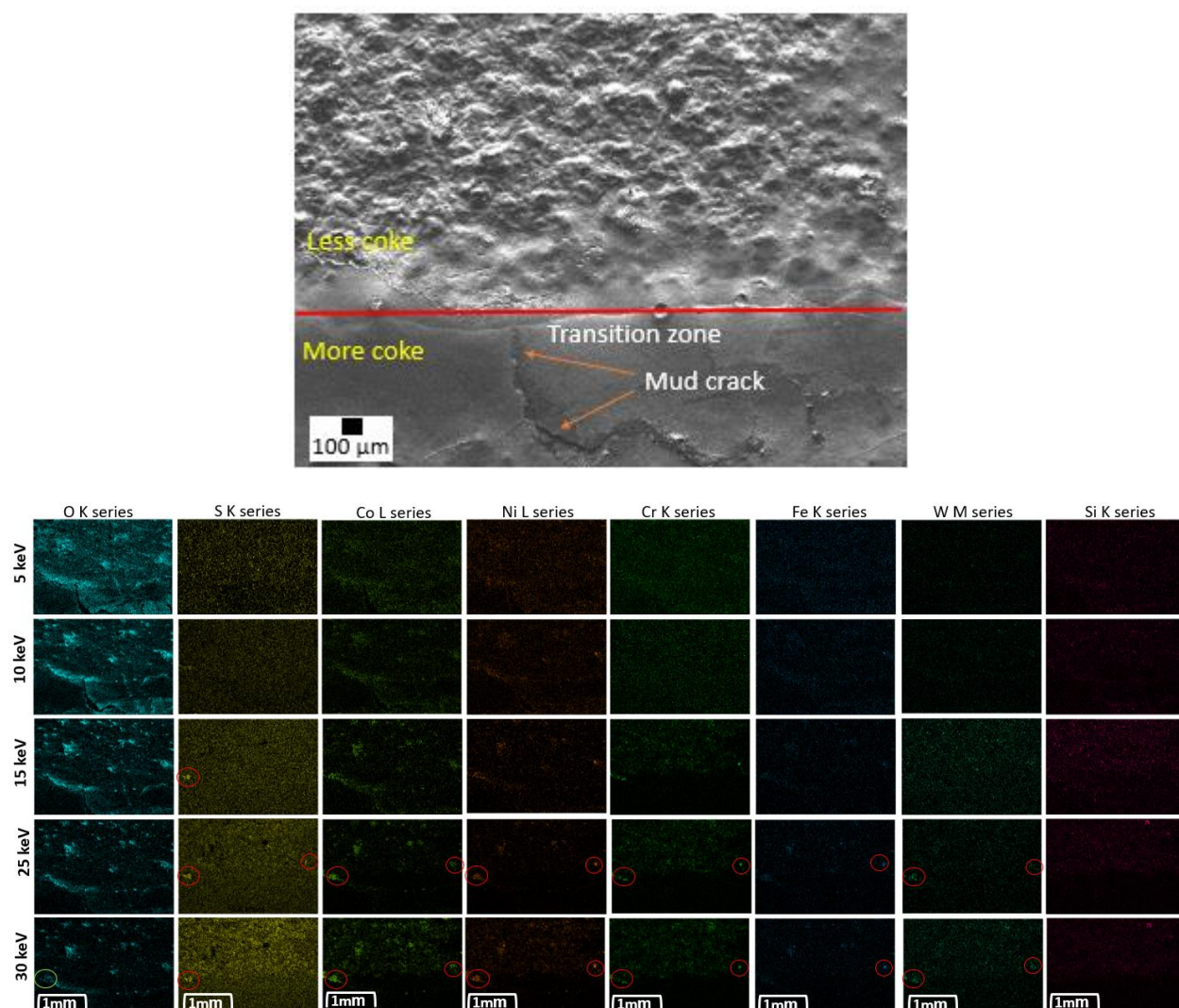


Figure 4.7 SEM images of Wallex 50 surface fouled in Reactor 2. EDS compositional maps use varying electron beam intensity.

Ni and Co are prevalent at all energy levels. Fe, Cr, and W present a higher definition in small areas at 25 and 30 keV. At higher energy, the metallic signal is correlated with the sulfur signal (red ellipses), indicating the formation of sulfides. At 30 keV, the oxygen signal diminishes in a region (green ellipse) with a brighter sulfur spot and a high correlation with Ni, Co, W, and Cr. Table 4.4 shows the calculated elemental distribution for each energy level. The fouling layer is mostly composed of carbonaceous deposits. Thus, the interaction volume was considered for a layer of 100% carbon and calculated using the Kanaya-Okayama formula [265]. The interaction

volume is lower for elements with higher atomic numbers. The calculated values were considered the maximum penetration depth, showing that the beam does not interact with the substrate.

Figure 4.7 confirmed the heterogeneity of the sulfide distribution on the surface, which can drastically affect the XRD measurements. Localized corrosion was accompanied by an intense attack on the carbon layer's defects, confirming the coke's protective behavior on the surface. The selective alloying element removal from the exposed surface is hard to detect [16]. When using lower beam energy, the EDS maps are dominated by oxides. With the increase in electron penetration, the observed oxides tend to appear in the regions with cracks in the coke structure. At the same time, the sulfur signal intensifies predominantly in the area with a lower amount of coke. The EDS maps signals, marked with ellipses, strongly suggest the formation of Cr and W sulfides, which XRD did not confirm due to their scarcity and localized nature.

Table 4.4 Wallex 50 surface map sum spectrum with varying penetration depth.

[wt.%]	5 keV	10 keV	15 keV	20 keV	25 keV	30 keV
Carbon	64.3	75.6	79.3	-	78.3	80.4
Oxygen	15.4	11.6	11.3	-	12.7	10.2
Sulfur	3.3	4.3	4.6	-	4.9	4.7
Cobalt	8.4	4.3	2.3	-	1.5	1.8
Nickel	3.5	1.8	1.3	-	1.0	1.2
Chromium	1.9	0.8	0.3	-	0.6	0.8
Iron	1.2	0.9	0.4	-	0.2	0.2
Tungsten	-	-	-	-	0.1	0.1
Silicon	0.5	0.3	0.3	-	0.3	0.3
Max Depth	0.31 μm	1.46 μm	3.51 μm	6.53 μm	10.40 μm	15.17 μm

The Table 4.4 elemental distribution confirms a higher proportion of sulfides closer to the surface than oxides. Cobalt and nickel are the elements with the highest concentration on the scale, which coincides with the identification of several Co and Ni sulfides in the XRD patterns. This indicates that the sulfidation mainly occurs closer to the coating interface, and sulfur diffusion is the controlling mechanism. Initially, in the presence of a porous defective non-protective scale, the kinetic rate is linear and depends on the inward sulfur diffusion rather than the outward diffusion of metal cations [88]. The higher concentration of oxides closer to the scale surface, such as in Table 4.4, also suggests that at this early stage of corrosion, the outer layer of the scale is older, in agreement with the suggested initial sulfur diffusion control mechanism.

In fact, this process of superalloy sulfidation and subsequent oxidation was shown at 700-900 °C [266]. Double-layered inorganic scales were observed with a compact outer layer and porous inner layers [267]. The alloying elements could impact the adhesion of the inner layer [133], [268]. The corrosion rate is slowed with the scale evolution, the metallic cations diffusion becomes significant to the control mechanism, and the sulfidation rate is further reduced. The sulfidation kinetics of Co and Ni alloys were found to be approximately parabolic in the presence of protective scales [88].

In W50, the cobalt mass ratio is about 2.5 times that of nickel (Table 4.1). Near the W50 coating/scale interface, the scale is sulfur-rich, and the Co:Ni ratio is 1.5 (Table 4.4), indicating that the sulfidation rate of Ni is faster than that of Co. The proportion of Co and Ni is similar to the W50 ratio at the outer oxide-rich scale layer. Considering that close to the operating temperature of 445 °C, the Gibbs free energy of the formation of Co and Ni oxides are similar, the observed proportion of nickel and cobalt in the scale outer layer is close to thermodynamic equilibrium. Thus, these results also indicate that sulfides are initially formed at the W50 coating/scale interface, and the scale aged forming oxides close to thermodynamic equilibrium. The evidence suggests that sulfidation initially occurs at the alloy interface driven by sulfur diffusion. When an adherent scale is formed, cations diffusion dominates the corrosion rate. The corrosion rate decreases as a function of the protective role of the formed scale.

4.5 General discussion and the phenomenological model of fouling

For each run, Reactor 1 with catalyst, without catalyst, and Reactor 2 (without catalyst), the recovered coke yield per gram of bitumen was 35.3, 42.7, and 45.1% (i.e., more than 1/3 of the bitumen fed to the reactor formed coke). The FeS catalyst increases the hydrocracking rate of the VTB, converting the heavy hydrocarbon chains into other fractions and reducing the coke formation. More coke forms in Reactor 2 due to the absence of hydrogen, which reduces the proportion of reactive unsaturated hydrocarbon chains after thermal cracking. In addition, the lack of agitation in Reactor 2 may also contribute to the increased coke formation. The linear impeller speed for the agitated Reactor 1 was about 0.7 m/s, which is at a high fouling rate regime for the temperature used. According to the Ebert-Panchal semi-empirical approach to quantify the effects of temperature and flow velocity on the fouling rate, at 445 °C, a flow rate up to 5.2 m/s induces fouling, and lower speeds favor a higher rate of formation [269], [270].

Based on the experimental observations, we propose a phenomenological model of the fouling mechanism that relies on several assumptions: 1) Corrosion fouling dominates – reactions between the metal surface and compounds in the fluid phase and/or precursors generated (H_2S , elemental sulfur, and other sulfur species) in the fluid phase; 2) temperature is considered constant in the surface and fluid bulk; 3) the fouling inorganic layer is assumed to have the same thickness over the surface; 4) corrosion rate is independent of the deposit shape; 5) the differences in the equipment design and operation fluctuations are considered negligible. Finally, we propose that corrosion of W50 is mainly affected by mass transfer, and IN718 exhibits a complex corrosion mechanism driven by chemical reactions and mass transfer, which alter the surface corrosion depending on the reaction conditions (see Figure 4.8). This phenomenological description supports the processes and effects discussed below.

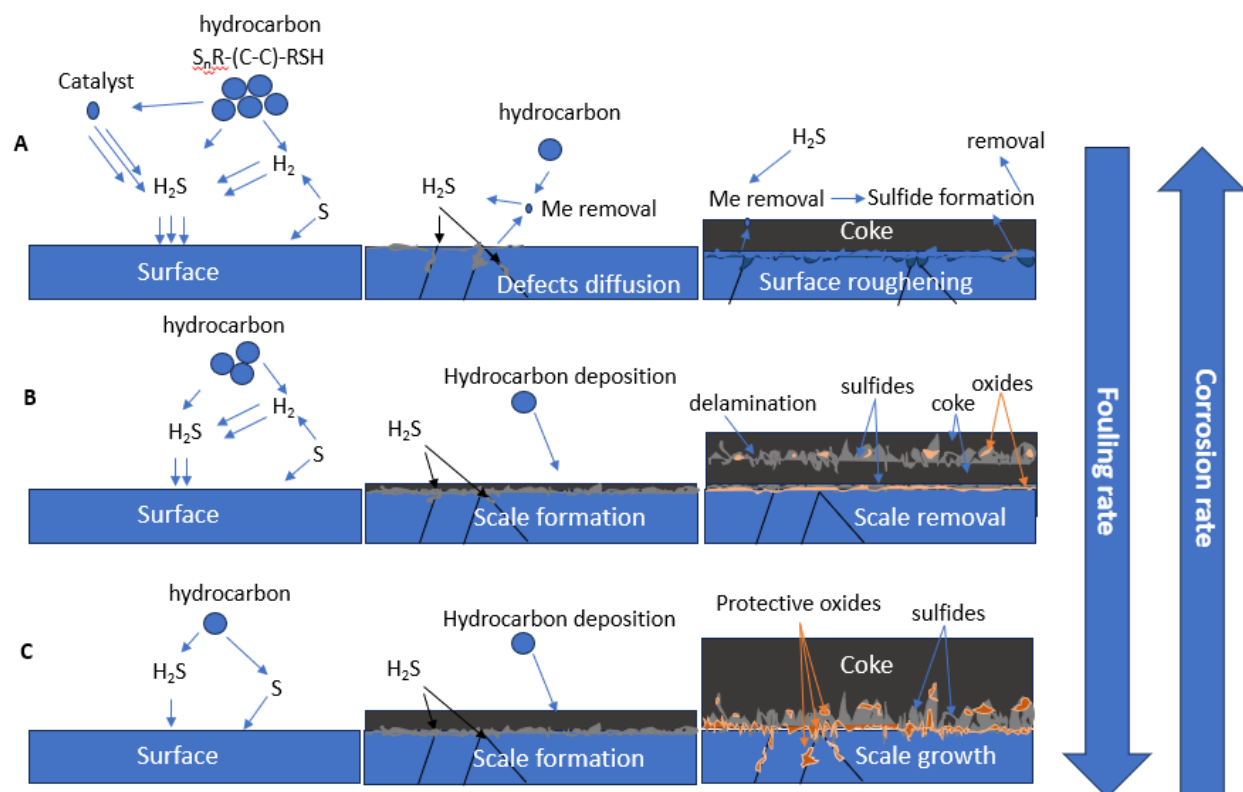


Figure 4.8 Phenomenological model describing the corrosion fouling mechanism in dependence of the sulfidation precursor formation rate and concentration: A) high corrosion rate, B) intermediate corrosion rate, and C) low corrosion rate.

Preferential corrosion through the grain boundary is accelerated with a high concentration of sulfidation precursor, leading to the removal of alloying elements, and increasing surface roughness (Figure 4.8A). For IN718, the catalytic reaction increased the precursor formation rate, consequently maintaining a higher local precursor concentration, and a higher corrosion rate, evidenced by the increase in surface roughness and grain damage (Figure 4.3A). The roughness created by the corrosion can induce other fouling mechanisms. The corrosion reaction products catalyze the formation of more precursors locally [103]. Fe, Co, Mo, W, and Ni sulfides act as catalysts for hydrocracking [271]. Thus, the corrosion products increase the decomposition rate of hydrocarbons locally, raising the sulfur concentration and the sulfidation rate in the inorganic scale. The higher precursor formation rate induces faster sulfidation through grain boundaries, while increasing the alloy surface contact area and promoting chemical reactions and more intense corrosion. The high Ti concentration in the fouled layer and grain damage are evidence of the grain boundary preferential corrosion. The catalytic hydrocracking also reduces the amount of adherent carbon formed.

When IN718 is fouled without catalyst (Figure 4.3B), the corrosion precursor formation and sulfidation rates are reduced, allowing corrosion to occur not only in the grain boundaries, but also on the bulk surface. The mechanism indicated in Figure 4.8B shows that with a slower rate of precursor formation, the reduced corrosion rate gave rise to inorganic scales. The formed sulfides catalyze the hydrocracking reaction, locally increasing the sulfidation rate, and leading to the delamination of the scales. With the consumption of precursors through corrosion, their concentration is lowered, enabling a gradual formation of an oxide-containing layer at the interface between the alloy surface and the scale, reducing the number of defects on the scale and becoming more protective.

The IN718 fouling condition without agitation (Figure 4.3C) shows a thicker inorganic scale on the surface. A low sulfidation rate (Figure 4.8C) allows the early formation of oxides and scale evolution, creating a more adherent protective layer. The thicker and denser layer of coke formed above the scale decreases the diffusion rate of reactive hydrocarbons, minimizing direct sulfidation and the catalytic effect of the sulfides formed in the scale, and further reducing the precursor formation rate. However, the sulfides are self-catalytic, and the sulfidation could continue without further sulfur supply. Metal sulfides are further oxidized, releasing sulfur back, increasing the partial pressure, and accelerating diffusion, facilitating the formation of inner sulfides [90], [272]. Provided the right conditions of oxygen and sulfur partial pressures, the sulfur species react with the metal oxides to form metal sulfide locally [273]. The self-catalytic scenario induces sulfidation even at low concentrations of precursor. H_2S is the most important precursor formed, and mass flux controls its surface interaction.

For W50, the condition in Figure 4.5A, the presence of the catalyst induces a higher formation rate of fouling precursors than the condition in Figure 4.5B. However, the observed inorganic scales had the same thickness under both conditions, indicating that the increased chemical reaction rate forming the precursor did not significantly affect the corrosion and fouling rate. The coke layer formed on the surface in Figure 4.5B was not significant in reducing the sulfidation rate under agitation conditions. The W50 reaction in Figure 4.5C, without agitation, formed inorganic scales with the same morphology as the other fouling conditions, but with lower thickness. In addition, this fouling condition had signs of sulfur infiltration in the coating, which may be explained by an initial higher sulfidation rate. The W50 formed adherent scales following the mechanism observed

in Figure 4.8C without a direct dependence on the precursor concentration and rate of formation. The agitation was the main factor contributing to a higher sulfidation rate for W50.

In oil corrosion, when an oil bulk chemical reaction contributes to the corrosion control mode proposed in [39], the flow velocity is inversely proportional to the corrosion rate, as a higher Reynolds number reduces the chemical reaction volume by minimizing the fouling precursor formation. However, if the fouling is controlled by mass transfer, a higher flow rate will increase the mass transfer from the fluid bulk to the surface, consequently increasing the fouling rate. Also, for this gas oil fouling model, the initial surface reaction rate is inversely proportional to the mass flow rate [39].

We assume that the IN718 fouling mechanism is a balance between the deposition and removal rates, and it is controlled by the chemical reaction rate. However, when an adherent scale is formed on the surface, the influence of the mass transfer in the control mechanism is enhanced. For W50, the mass transfer control of ions diffusion should be the predominant corrosion mechanism. The mechanism is dependent on the inherent corrosion resistance of the materials. When the sulfur concentration is above a certain resistance threshold for each material, the corrosion rate is increased, inducing mechanisms described in Figure 4.8A and Figure 4.8B. The corrosion mechanism follows Figure 4.8C when the material is resilient to the corrosive conditions.

4.6 Conclusion

The cracking conditions with varying catalyst content, hydrogen concentration, and agitation level, influenced the surface corrosion and fouling mechanisms of IN718 and W50 depending on the surface properties. The main findings are encompassed in a phenomenological model proposed to explain the corrosion fouling mechanisms of such alloys as a function of sulfidation rate. The catalyst reduced the formation of coke in all cases. XRD measurements performed on W50 identified Co, Ni, and Fe sulfides, while SEM/EDS surface analyses using varying electron beam energy indicated the presence of Co, Ni, Fe, Cr, and W sulfides.

The IN718 fouling mechanism was controlled by the chemical reactions from the sulfur precursors, which alter the formation of the inorganic layer from the fouling scale. The formed fouling layer is more stable without agitation, with a lower precursor reaction rate, allowing one to form a thicker protective oxide layer. The W50 fouling mechanism was controlled by mass transfer; here, the lower concentration of precursor due to the lack of hydrogen exhibited the lowest inorganic layer

thickness. When hydrogen is available for the reaction, the formed inorganic layer is thicker and independent of the higher formation rate induced by the presence of the catalyst.

Previously, very few works explored sulfidation at temperatures below 600 °C. In our present experiments, we demonstrate that already at a temperature of 445 °C, heavy oil cracking has a direct effect on scale formation. The cracked hydrocarbons form coke that protects the surface from corrosion, but release sulfur, hence increasing the sulfidation rate. The alloy and scale microstructure are fundamental for determining the corrosion rate and control mechanism. The inward sulfur diffusion dominates the initial higher corrosion rate. The scale formation, adhesion, and microstructure evolution control the corrosion mechanism. With a more protective scale, the outward cation diffusion governs the corrosion rate.

The differentiation of the degradation mechanisms of critical materials at a microstructural level can help select appropriate operation conditions and/or mitigation strategies to preserve the integrity of the materials and assure reliable function of the equipment components.

4.7 Acknowledgements

The authors wish to thank Mr. Francis Turcot, Mr. Francis Boutet, and Mr. Jean Ghantous for their expert technical assistance. The authors also thank Dr. Philip Wijaya and Dr. Nazanin Aghdam for their assistance with the experimental work at the University of British Columbia. The project was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada through the NSERC-Alliance grant (no. ALLRP 576758 - 22), by Prima Quebec (grant no. R24-13-003), and by Velan Inc.

CHAPTER 5 ARTICLE 2 : ENHANCED HEAVY OIL FOULING RESISTANCE OF COBALT-BASED SPRAY-DEPOSITED COATINGS BY ALLOY DESIGN AND HEAT TREATMENT

Fellipy S. Rocha^{1,2}, Pedro R. T. Avila¹, Oumar Touré¹, Marwan Azzi¹, Fadila Khelfaoui³, Luc Vernhes³, Gregory S. Patience², Jolanta E. Klemberg-Sapieha¹, and Ludvik Martinu¹

¹Department of Engineering Physics, Polytechnique Montreal, Montreal, QC H3T 1J4, Canada

²Department of Chemical Engineering, Polytechnique Montreal, Montreal, QC H3T 1J4, Canada

³Velan Inc., 7007 Côte-de-Liesse, Montreal, QC H4T 1G2, Canada

The article was submitted to *Surface and Coatings Technology* journal on June 19, 2024 [274]

Thesis author contribution:

Fellipy S. Rocha, Jolanta E. Klemberg-Sapieha, and Ludvik Martinu jointly conceived the research idea. Fellipy S. Rocha took the lead in developing the methodology, conducting the experimental investigations, curating and validating the data, and preparing the initial manuscript draft. All co-authors reviewed and edited subsequent versions collaboratively.

5.1 Abstract

Heavy oil hydrocracking fouls critical reactor components, causing premature turnarounds. Developing materials with superior resistance to coking, sulfidation, and wear proves crucial. High-velocity oxy-fuel (HVOF) coating improves materials' properties as an industrial-ready solution. This study explores the effect of alloying elements on the HVOF-sprayed Co-Cr-Mo-Si coating model and their role in protecting against heavy oil fouling. Heat treatment reduced the coatings' inhomogeneity and microstructural defects, substantially improving their protection against fouling. A novel optical image treatment has been developed to semi-quantitatively assess the surface fouling intensity. The study provides insights into the complex interplay between alloy composition, microstructure, heat treatment, and surface energy in optimizing coating protection against heavy oil fouling.

5.2 Introduction

Cobalt and nickel alloys combine corrosion resistance, excellent mechanical properties, and heat resistance [136]. These alloys function in extreme operation conditions and with hazardous materials [275], such as H_2S , SO_2 , CO , volatile organic compounds, polycyclic aromatic hydrocarbons, and heavy metals. Ebullated bed hydrocrackers operate above $350\text{ }^\circ\text{C}$ to process heavy crude oil with high amounts of impurities from various sources, mainly sulfur [276], leading to the deposition of carbonaceous material (coke) and inorganic material [74]. The surface fouling results in premature failure of critical reactor components, inducing unwanted early turnarounds that incur millions of dollars in cost.

Online repair of worn isolating valves is a difficult and dangerous process. Therefore, further development of valves represents a major potential to improve sour oil cracking operations. Specifically, this application requires materials that concurrently resist oxidation, sulfidation, coke deposition, and wear. Resistance of Fe-, Ni-, and Co-based alloys to hot corrosion and sulfidation is typically qualitative and often associated with their chemistry, in particular with the chromium content [118]. However, higher Cr concentration does not necessarily improve H_2S sulfidation resistance; alloying elements, such as Al, Ti, Mo, and Si, provide more effective protection, even at relatively lower Cr concentrations [135].

Advanced nickel-based superalloys, such as IN-792 and CMSX-4, are prone to sulfidation [277], forming deleterious nickel sulfide scales, and can catalyze the hydrogenation of sulfur compounds to H_2S [16]. Nickel superalloys undergo breakaway accelerated corrosion in low O_2 environments with sulfur, while cobalt-containing materials resist sulfidation over a wide range of S_2 partial pressure and temperature, with mixed carburizing gases such as $\text{CO-CO}_2\text{-CH}_4$ [278]. Specifically, Inconel 718 maintains acceptable mechanical properties up to $700\text{ }^\circ\text{C}$, yet it suffers from corrosion, internal sulfidation, and oxidation, causing alloying elements depletion [279]. Ni-Co-based alloys have considerably superior carburization and sulfidation resistance compared to Ni- and Fe-Ni-based alloys. Increasing the cobalt concentration of the Ni-Co alloys to a near unit mass ratio of Ni:Co reduces both nickel and cobalt availability to form relatively low-temperature metal/metal-sulfide eutectics, and improves the sulfidation attack resistance [135]. Cobalt-based alloys are typically more expensive, and their implementation should warrant a considerable lifespan extension [136].

Coating technology offers a cost-effective and flexible alternative to improve material performance [280]. Various coating techniques with individual advantages and drawbacks have been developed [197]. Thermal spray techniques are readily commercially available. The presence of interconnecting porosity and oxide networks restricts the application of thermal spray coatings in corrosion applications [281], [282]. HighVelocity Oxy-Fuel (HVOF) thermal spray can generate denser coatings with minimal oxidation of metallic materials, phase transformation, and degradation [216], with a lower capital expenditure when compared to the vacuum plasma spraying technique [283]. HVOF-sprayed alloy coatings fail to attain completely passive states, owing to the presence of pores, imperfections, and oxide inclusions [284]. Post heat treatment reduces coating porosity and induces diffusion at the substrate-coating interface creating a metallurgical bond, improving both cohesion and adhesion. However, such post-heat treatments are limited to substrates capable of withstanding temperatures exceeding 1000°C and to coatings able to recover from the resulting inherent distortion [285].

In general, HVOF sprayed Co-based coatings improve wear resistance, but carbides, such as WC/Mo-Co, provide similarly low corrosion protection comparable to Inconel 625 and NiAl coatings following the ASTM G75-95 standard slurry test in H₂S and CO₂ atmosphere [286]. Tungsten carbide at most extends valves durability in heavy oil applications through higher erosion resistance when compared to traditional stainless steel and Inconel alloys. Co-Cr-W (Stellite™) [287] has applications in valves, steam boilers, and furnaces among others [257]. Stellite 6 has superior hot corrosion protection with respect to traditional alloys for gas turbines, and its protective effect is attributed to the oxides of Cr, Co, and Si [288]. In coal-gasification environments, Stellite 6 provides superior protection compared to WC-Co, but it is less effective than coatings such as NiCr and Cr₃C₂-NiCr [289]. By contrast, Co-Cr-Mo coatings resist oxidation- and sulfidation up to 600 °C, and are suitable for applications requiring wear resistance [290]. Co-Cr-Mo coatings containing Ni, Si, Al, and Ti are promising for the sulfidation and carburization environments [135]. In CO₂/H₂S conditions, Co-Cr-Fe-Ni-Mo high entropy alloys corrode less than Ni-Cr and Fe-Cr high entropy alloys [291]. Typically, the sulfidation rate-controlling step of alloys in H₂S is attributed to outward ion diffusion, for which the cobalt reaction rates are lower than for Ni or Fe [264]. This may arise from cobalt and nickel formation of eutectic Co-Co₄S₃ and Ni-Ni₃S₂, whereas Co eutectic is more stable, melting at 880 °C compared to nickel eutectic that melts at 645 °C [292].

Material development for demanding multifaceted environments requires an approach tailored to the application. The understanding of the materials degradation is most often only qualitative and precise interpretation of the possible mechanisms is limited. In particular, apparent contradictions arise when dealing with complex alloys. In addition, the coating method and deposition conditions add another layer of complexity, where structural defects also affect the interpretation. In this work, we explore the role of alloying elements on the HVOF-sprayed Co-Cr-Mo-Si coating model and study their role in the protection against heavy oil fouling. In particular, we analyze surface fouling through a newly developed semi-quantitative optical method, and the extent of internal sulfur attack in relation to the heat treatment conditions, the microstructure, and defects.

5.3 Materials and methods

5.3.1 Surface preparation

The samples consisted of IN718 coupons (25x25x3 mm³) coated with three different HVOF industrially sprayed cobalt-based coatings. Their elemental composition varied according to the powder mixture. After the spray deposition, coated samples were heated to about 1000 °C for 10 minutes to create a metallurgical bond at the coating/substrate interface. Following this treatment, the samples were annealed for over 10 h at about 750 °C to recover the industrial desired mechanical properties of the IN718 substrate. The heat treatment protocol was the same for all annealed samples, and the recovery step is protected by IP.

The coatings were at least 400 µm thick. Their surface was polished to reduce roughness and contamination. The polishing consisted of using SiC papers with varying grit sizes (100 to 800), followed by diamond particle suspension (from 3 µm to 1 µm) while varying the Struers magnetic discs, finishing with colloidal alumina suspension. The elemental composition of the coatings studied in this work comprised Co (>35 %), Cr (> 17 %), Mo (>17 %), and several other elements (Table 5.1).

Table 5.1 Elemental composition of the Co-based coatings.

Limiting chemical composition, wt. %			
Element	Co-1	Co-2	Co-3
Co	Balance	Balance	Balance
Cr	17.9	19	17.7
Ni	4	13	0.2
Fe	0.2	0.1	0.3
Mo	22.9	17	28.7
W	2	1	-
Si	3.3	4	3.4
C	0.2	1.5	0.04
B	0.6	3	-

5.3.1.1 Surface roughness

A Bruker ContourGT-K white-light interferometer measured the surface morphology at optical magnifications of 5x and 20x, corresponding to scan areas of $1268 \times 951 \mu\text{m}$ and $317 \times 237 \mu\text{m}$, and a lateral sampling depth of $2 \mu\text{m}$ and $0.5 \mu\text{m}$, respectively. Gwyddion [258] opensource software was used to trace the surface profile via Laplace interpolation correcting points where no meaningful data was obtained (intensity = 0 or 100%), followed by tilt removal via mean plane subtraction.

5.3.2 Microstructural characterization

The coating thickness, topography, microstructure, and elemental composition were assessed with a scanning electron microscope (SEM, JEOL JSM-7600F) equipped with an energy-dispersive X-

ray spectrometer (EDS), a wavelength-dispersive X-ray spectrometer (WDS), and an Oxford Instruments X-Max detector. For preparing cross-sections of the tested samples, the surface was coated by sputtering a 20 nm thick gold layer, followed by copper electroplating in a 10 M CuSO₄ solution at 2 V for 20 min.

X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Discover X-ray diffractometer in Bragg-Brentano geometry with Cu K α radiation ($\lambda = 0.15406$ nm) using a LynxEye 1-D detector. The incident beam optics configuration consisted of a Gobel mirror and 0.6 mm divergence slit, while automated slits were used in diffracted beam optics. The range of the 2θ scans was from 20° to 94° with a step size of 0.0103° and a dwell time of 1 “/step. The processing of the XRD data was made using the Bruker DIFFRAC.EVA V4.3 that included background subtraction and k- α 2 stripping.

5.3.3 Mechanical properties

A Micro Combi Tester (MCT3, Anton Paar, Graz, Austria) with a Berkovich diamond pyramidal tip was used to quantify the elasto-plastic properties of the coatings. We applied linear loading with a 20 N/min loading rate, and a final load force of 10 N held for 5 s before unloading. A matrix of 2 x 3 indentations was performed with a spacing of 1 mm each, with a total of 6 measured areas per coating. The reduced Young's modulus, E^* , and the hardness, H , were calculated using the Oliver and Pharr methodology [293].

5.3.4 Contact angle

The contact angle experiments were carried out with an Attention[®] Theta Optical Tensiometer and measured automatically using spectroscopic-grade water with a dynamic viscosity of 0.89 mPa.s [294] and a cracked heavy oil fraction containing sulfur (0.38 wt.%) with a viscosity of 1.76 mPa.s (1.76 cP). A 4 μ L liquid drop was generated with an automatic pump at the tip of a syringe, and the volume of the drop was controlled and calculated by the software of the tensiometer. The tip was moved until the drop touched the surface, and then removed. The contact angle was measured after 10 s stabilization time. All measurements were carried out at ambient temperature, and the average contact angle was reported. The contact angle (CA) was measured on polished samples with an average Ra of 15 ± 3 nm.

5.3.5 Rheology

The viscosity of the cracked heavy oil fraction was measured with a Haake viscotester iQ. The temperature was kept constant at 25 °C and controlled by a Polystat[®] circulating bath. The measurements were performed in 10 rotation steps with a linear distribution, varying the shear rate from 10 to 2 000 (1/s). The probe used the CC27 DG/Ti – 01160064 measuring geometry with a gap of 4 mm and a total sample volume of 3 mL. The upper and lower limits of viscosity variation measured for the oil were 1.766 mPa·s and 1.757 mPa·s, with an average dynamic viscosity of 1.760 mPa·s. A detailed study of the viscosity of crude oil and emulsion fractions is described elsewhere [295]

5.3.6 Fouling

A 200 g sample of heavy oil containing 6 % sulfur was introduced to an autoclave-type reactor containing the samples to be tested. All samples were placed vertically to avoid gravitational deposition on the surface. The reactor was purged with argon at 11.3 MPa for 5 min to minimize the oxygen concentration and then heated to 450 °C for 2 h to simulate the cracking environment. It cooled overnight before depressurizing, opening, and retrieving the samples. The sample surface was washed with a 50:50 petroleum ether and toluene solution, followed by a water rinse to remove excess solvent and non-adherent material. The samples were then dried in air before subsequent analyses.

5.3.6.1 Fouling quantification

A Digital Single-Lens Reflex (DSLR) Nikon D7000 camera equipped with 3 Kenko Auto Extension tubes (12, 30, and 36 mm), 105 mm Macro lens, and Hoya 62 mm NXT Plus Circular Polarizer filter was mounted on a bridge allowing adjustments in the vertical direction. The samples were placed under a dark dome, minimizing background reflection. 58 LED lamps were fixed underneath the dark dome and remotely controlled via a LabView program to illuminate the samples. The camera settings were controlled with digiCamControl open-source software. The images were captured with a shutter speed (exposure time) of 1/320 s, an aperture f/16.0, and a low sensitivity ISO 100.

The 16 Megapixel images were converted into a grayscale image where every pixel is attributed to an intensity value, from black (0) to white (255). A processing algorithm evaluated every image

pixel in a loop. If the pixel intensity is lower than a selected threshold value, the pixel is defined as a dark pixel. The threshold was chosen as the value where the sample with higher surface fouling had intensity values close to 100%. All samples were treated with the threshold value of 50. After defining all pixels, the algorithm calculates the percentage of dark pixels over the total number of pixels to obtain the absolute percentage of darkness, which semi-quantitatively represents the level of surface fouling.

5.4 Results and discussion

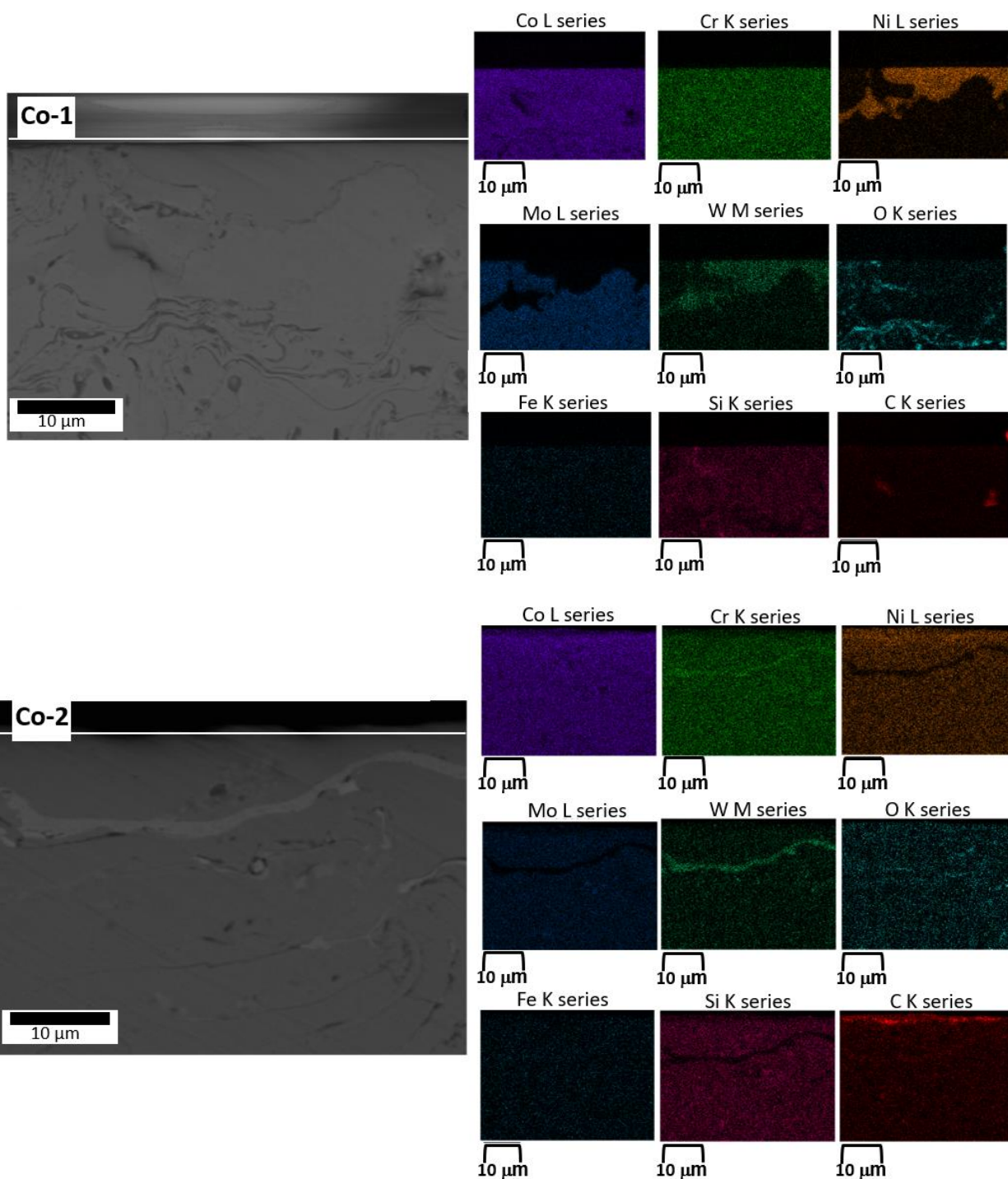
5.4.1 Coating microstructure before and after heat treatment

The surface of the Co-1, Co-2 and Co-3 samples (Table 5.1) before and after heat treatment exhibited the typical HVOF microstructure [296], [297] of partially melted spherical particles scattered over the surface, with fairly porous structure in the near-surface region, with an average roughness (R_a) greater than 5 μm . After polishing, R_a was approximately 15 ± 3 nm. The thickness of the as-deposited coatings varied from 180 to 435 μm , and after polishing, it varied between 160 and 400 μm . Hard sprayed coatings with a thickness greater than 150 μm are well suited for corrosive environments because of their dense structures with fewer defects, as the impact of the newly deposited layer peens the previous layer, and the new layers flatten more efficiently as they impact a much harder surface [298].

A low percentage of W is present on the Co-1 and Co-2 coatings that exhibit a microstructural difference (Figure 5.1). For Co-1, tungsten originates from the Ni-Cr-W particles, while for Co-2, it comes from the WC-Co-Cr particles. The SEM reveals lamellae formation with oxide stringers between them, indicating oxidation of the molten particles during deposition. EDS shows the samples' chemical inhomogeneity, where Co-1 has substantial oxidation in the regions without tungsten, while Co-2 oxidation is scattered over the cross-section, intensifying around the W-containing lamella. Co-3 does not include W in its composition and contains random regions with increased non-specific oxidation. A small lamella of Ni-Cr indicates a low concentration of Ni in Co-3. The Co-1 and Co-3 microstructures are closely related to Co-Mo-Cr-Si HVOF-sprayed coatings [299] and TribaloyTM [300] morphology, while Co-2 corresponds more to StelliteTM [301], [302].

The lamellae formation indicates high-velocity impact from semi-molten droplets creating splat morphology, and their external oxidation protects them against further degradation [303]. The

observed chemical heterogeneity of the sprayed coating might arise from the mass transfer of the semi-melted particles during their in-flight motion, and the external gas flow convection velocity, inducing chemical segregation during the splat solidification [304].



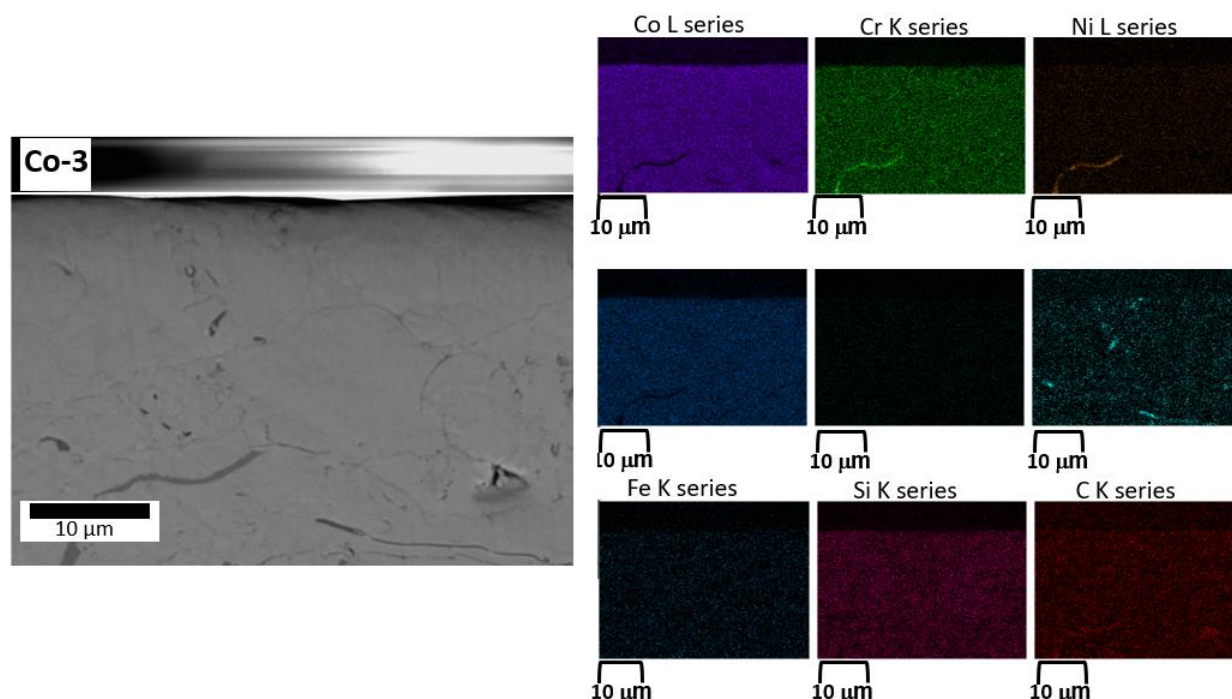
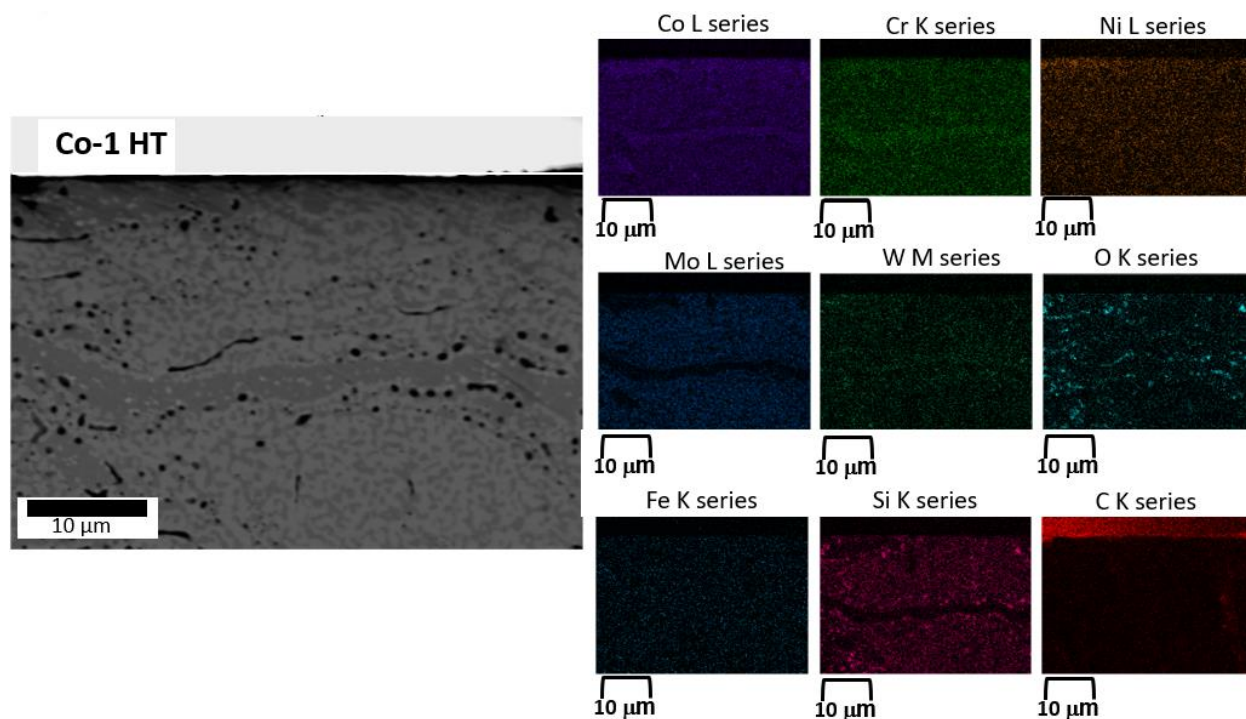


Figure 5.1 Near-surface region SEM and EDS compositional maps of the as-sprayed Co-based coatings: Co-1, Co-2, and Co-3.

Figure 5.2 confirmed the interdiffusion of elements during post-processing heat treatment that increased the overall homogeneity of the coatings underlined by no signs of splats, while different metallic and laves phases were formed. Oxidation is concentrated in regions with high Si content. It indicates that the Co-3HT coating with less Ni exhibits a more apparent oxidation. The oxides were formed preferentially in the areas with more porosity and a larger influx of oxygen due to facilitated diffusion, especially in Co-3HT that preserved the lamellae structure. The high concentration of Si oxides indicates that the coatings achieved thermodynamic equilibrium after heat treatment, since Si oxides have the lowest Gibbs free energy of formation from the elements in the coatings, followed by W and Mo [305].

Sample Co-3HT (Figure 5.2) exhibits a typical lamellae microstructure of heat-treated Co-Mo-Cr-Si HVOF-sprayed coatings with micro-sized and coarse laves phases distribution [306], [307]. The Co-1HT sample has less predominant lamellae structures when compared to Co-3HT, and larger areas rich in Co-Cr with an apparent absence of molybdenum. The Co-2HT SEM image shows a granular morphology absent of clear lamellae formation (Figure 5.2), analogous to a microstructural effect seen in Stellite 6 when 6 % of Mo was added [308]. Co-2HT EDS maps indicate the formation of Cr carbide in zones rich in Cr where Co and Ni are absent. Although Mo,

W, and Cr are known to stabilize the hcp structure of Co-alloys [309] and have a strengthening effect by forming carbides [287], only chromium carbide was later confirmed by XRD for the Co-2HT sample (see below), and no carbides were identified for the other coatings. Owing to their low carbon content, the formation of carbides in Co-1 and Co-3 was unexpected. For low-carbon alloys, it is known that Mo and W contents contribute to strengthening the solid solution [287].



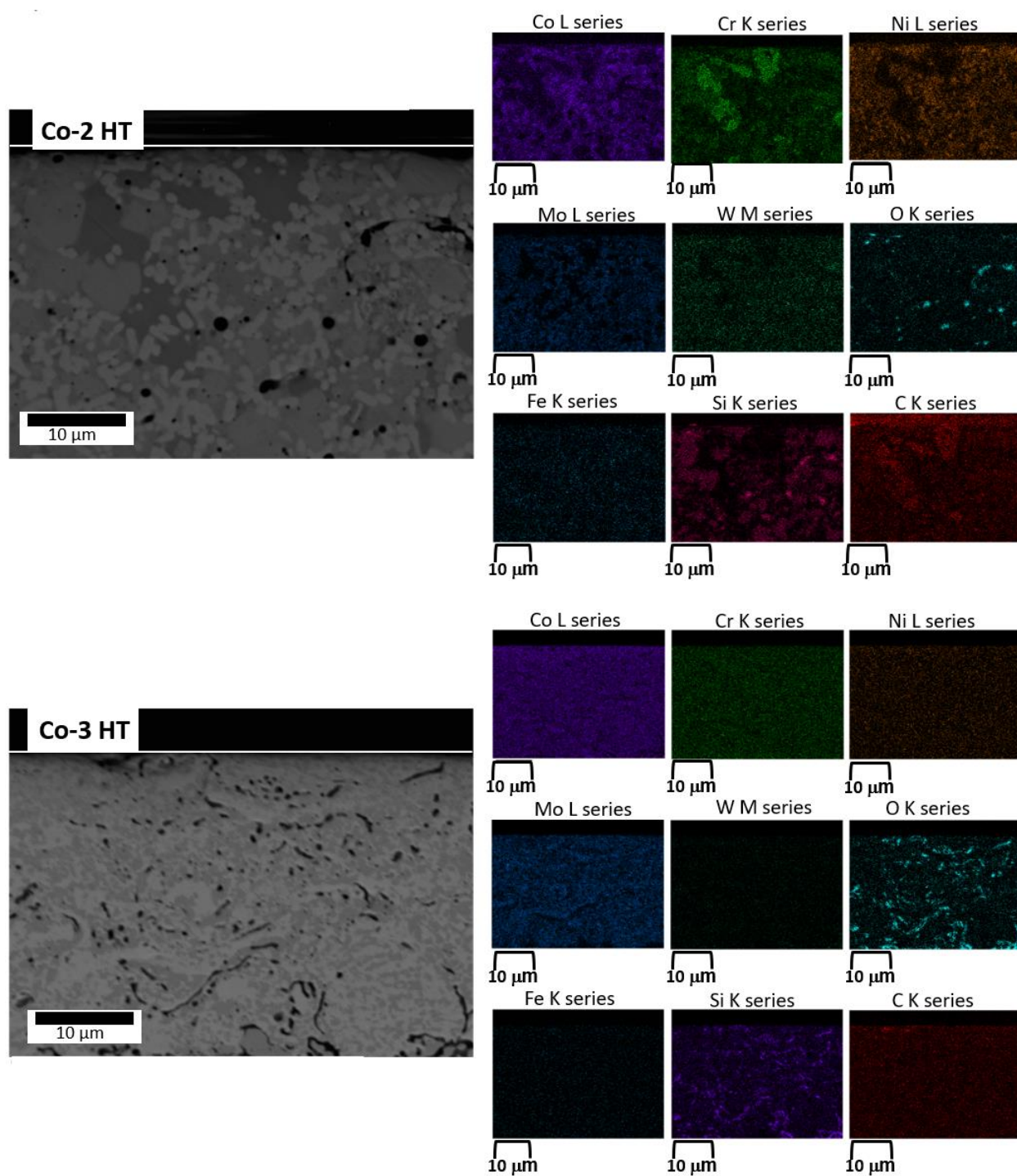


Figure 5.2 SEM images and EDS compositional maps of the near-surface region of the Co-based coatings after heat treatment: Co-1HT, Co-2HT, and Co-3HT.

5.4.2 Mechanical properties

For samples Co-1, Co-2, and Co-3, the microhardness increased by about 18% after heat treatment, while H/E_r decreased by 19% (Table 5.2). The higher hardness for Co-2 and Co-2HT may arise from the presence of chromium carbide. The hardness increases due to the over 10 h heat treatment below 800 °C to age and recover the IN718 strength. In parallel, the first annealing step at over 1000 °C should induce a metallurgical bond with the substrate while increasing the coating toughness and density.

The observed mechanical characteristics are in agreement with the available literature. Low-temperature annealing of Co-based coatings increased hardness and brittleness, while annealing above 750 °C increased toughness [310]. Annealing was observed to reduce porosity [307], and at 1000 °C, it substantially eliminated defects [311]. Co, C, and W diffusion velocity is limited at low heat treatment temperatures, reducing the diffusion between the substrate and the coating interface to promote metallurgical bond. Recrystallization may occur at temperatures around 750 °C, while further increasing hardness and reducing toughness. Higher temperatures around 950 °C induce the brittle metastable phase transformation, and amorphous phases are completely crystallized [310]. Further temperature increase induces Co-phase formation, a higher degree of crystallization, fine crystalline grain enlargement, and densification [311], contributing to achieving the desired microhardness and toughness.

For comparison, the hardness of Co-Mo-Cr-Si HVOF sprayed coatings increased by 31% from 6.7 GPa for as-sprayed to 8.8 GPa after heat treatment at 600 °C [306]. Another study with the same composition and heat treatment methodology reported an increase of 30 % from 7.4 GPa to 9.6 GPa [312]. A lower hardness increase of 13% was reported for Co-Mo-Cr-Si coatings after heat treatment at 800 °C [313]. The hardness of Ni-Mo-Cr-Si coatings was found in a similar range of 6.2 GPa for as-sprayed and 7.4 GPa after heat treatment at 600 °C [312]. Thus, an increase in hardness is achieved when annealing at temperatures below 800 °C, though at the expense of toughness due to the formation of brittle phases. Annealing at higher temperatures is more favorable for preserving the material's integrity and inducing a more uniform distribution of elements and phases by increasing the diffusion rate.

Table 5.2 Mechanical properties of the HVOF-sprayed Co-based coatings deposited on IN718 before and after heat treatment (HT).

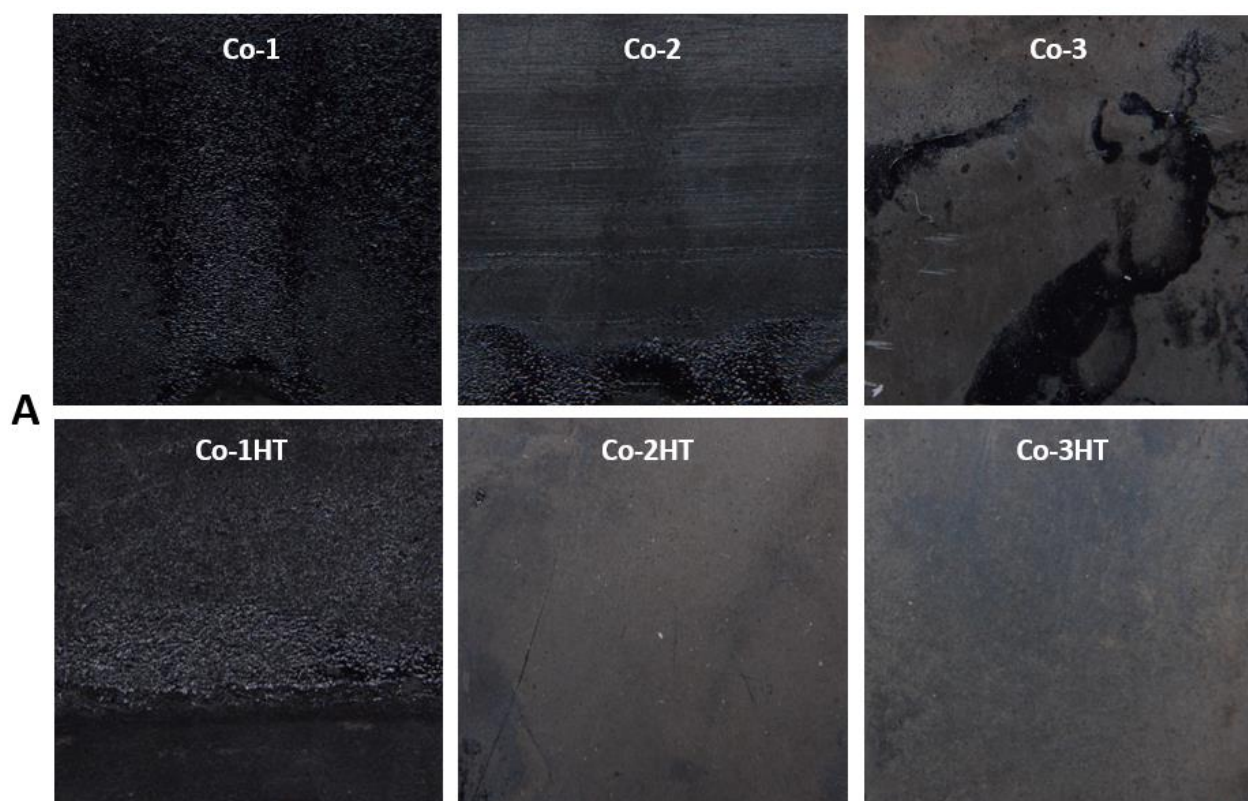
Coating	H (GPa) (ΔH)	E_r (GPa) (ΔE_r)	H/E_r
Co-1	6.1 (0.6)	114 (5)	0.054
Co-2	7.3 (0.9)	119 (6)	0.061
Co-3	6.4 (0.2)	118 (4)	0.054
Co-1HT	7.6 (0.1)	159 (6)	0.048
Co-2HT	8.1 (0.4)	167 (4)	0.049
Co-3HT	7.8 (0.4)	161 (3)	0.048

5.4.3 Fouling

Fouling is exhibited by the appearance of carbonaceous materials on the surface. The samples with higher carbonaceous coverage are Co-1, Co-1HT, and Co-2, respectively, showing a pattern with more carbon in the bottom portion, following the depletion of the oil during the reaction (Figure 5.3A). The effect of oil depletion is more visible for Co-2, where horizontal lines are seen throughout the sample, demonstrating the oil level at a given hydrocracking stage. Fouling is observed on the Co-3 without a specific pattern, while it is highly suppressed on the Co-2HT and Co-3HT samples.

The image treatment shown in Figure 5.3B illustrates the differences in fouling in a more distinct and semi-quantitative way. The reflected light intensity values from the image processing allow one to quantify the degree of fouling. Since the dark carbonaceous layer completely covers sample Co-1, we assign its lowest reflection (or highest darkness) as 100% fouling, and we use it to normalize the fouling (or darkness) values of the other samples, while considering the equivalent metallic mirror finish as the highest reflectance (zero fouling) reference.

The calculated normalized values portray the relative fouling intensity of the samples, varying in descending order from 100, 95, 89, 76, 15% to 3%, corresponding to samples Co-1, Co1HT, Co-2, Co-3, Co-2HT, and Co-3HT, respectively. Thus, the Co-3HT sample exhibits the highest fouling prevention (with 3% fouling), followed by Co-2HT with about 15% of surface coverage. All other samples had a superficial fouling rate above 60%. This optical analysis is valid when all samples meet the same surface criteria before the experiment, such as similar roughness. This approach is valid if the same initial lighting background conditions for image processing are maintained.



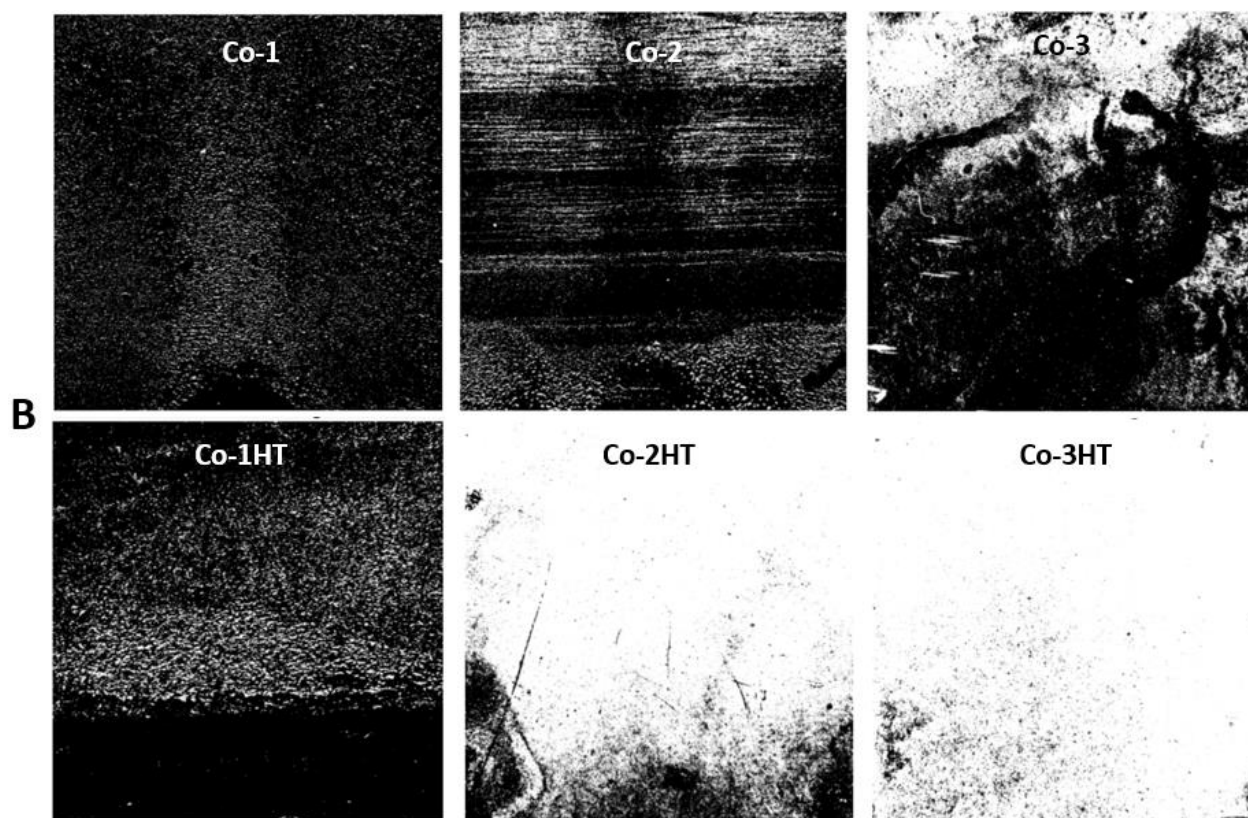


Figure 5.3 Surface of the samples after exposure to heavy oil: (A) optical image and (B) after image treatment. The images represent a matrix of 20 x 20 mm.

To obtain a better insight into the heavy oil surface interactions, we studied the cross-section of the samples using SEM. The EDS maps identified the general elemental composition. In addition, WDS measurements allowed us to deconvolute the Mo and S signals. To improve the quality of the microscopy analysis, gold and copper layers were added on the surface of the sample after the degradation experiment to better distinguish the carbonaceous layer from the oil fouling from the mounting epoxy carbon. Applying these layers also had the benefit of identifying possible polishing artifacts due to the soft nature of the fouled region.

During the fouling experiments, the coatings and substrates are exposed to a complex environment in the test reactor, with a combined effect of hot gases emanating from the oil (H_2 , CO, CO_2 , H_2 , and H_2S) with various reaction pathways. Thus, mass gain quantification was impractical due to the unspecific and uneven fouling formation on the surface and the delamination of the brittle oil-originated scales upon manipulation. The macroscopic observations (Figure 5.3) have been correlated to the SEM microstructural observations. For samples with little surface fouling, namely

Co-2HT and Co-3HT, the analyzed cross-section shown in Figure 5.4 was selected to represent the limited regions where fouling is evident.

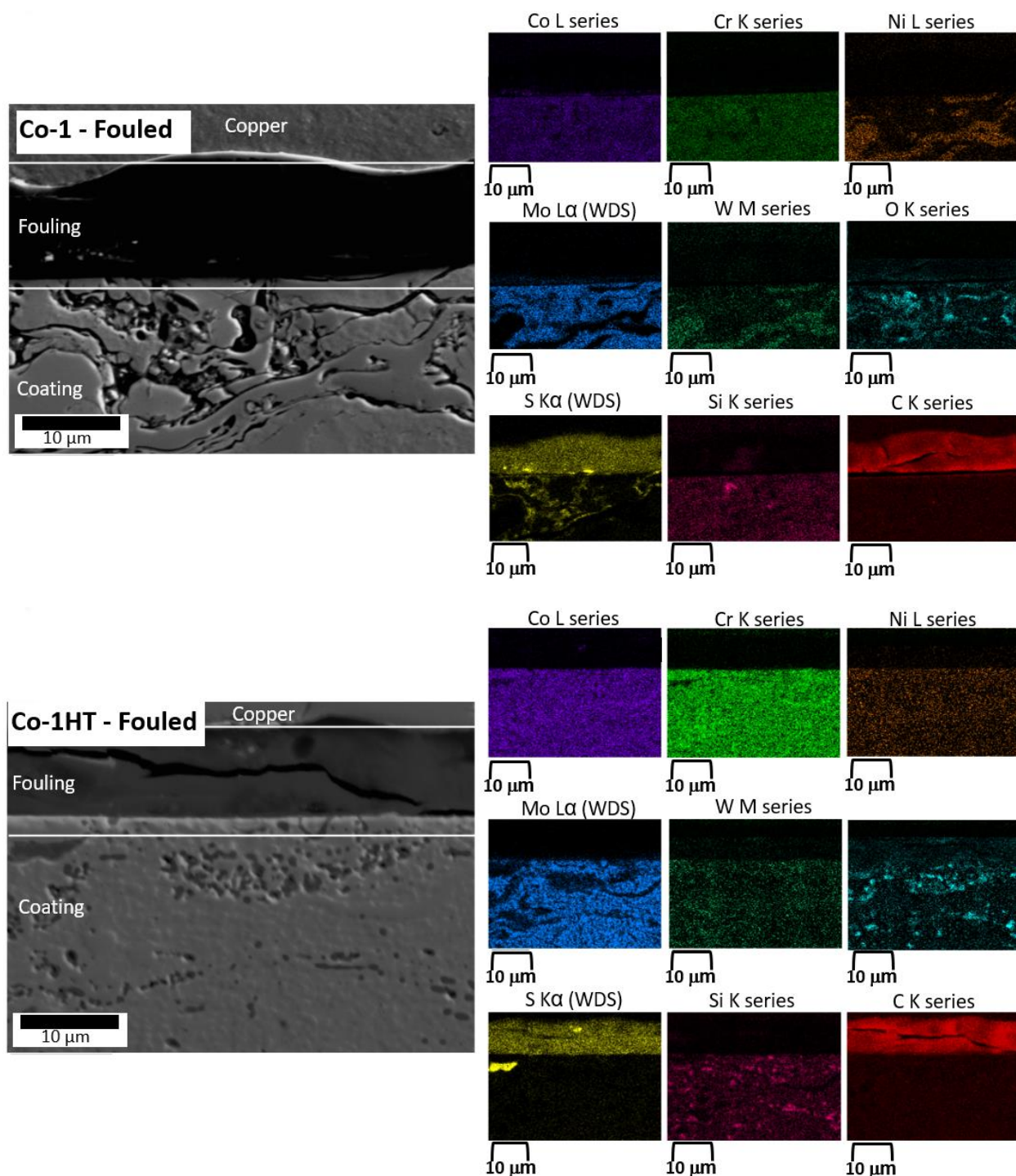
The EDS and WDS maps of the samples cross-section confirm that the fouling region is rich in sulfur and is covered by coke (Figure 5.4). The as-deposited Co-1, Co-2, and Co-3 samples undergo sulfur infiltration in the lamellae structures, evidencing the interconnection of pores with the surface, while the Co-1HT sample experiences sulfur infiltration in larger pockets formed close to the surface. For comparison, sample Co-3HT shows a certain degree of sulfur infiltration in the lamellae, but no sign of internal sulfidation was observed for Co-2HT.

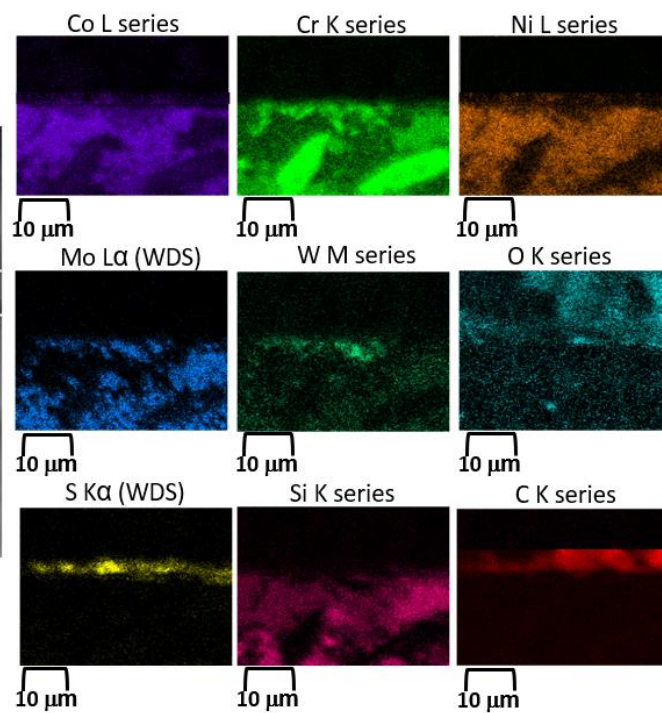
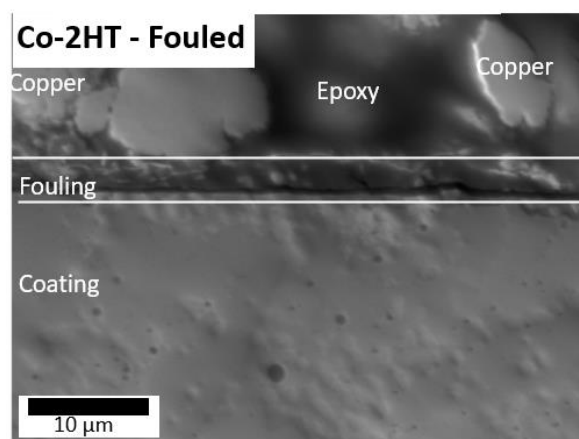
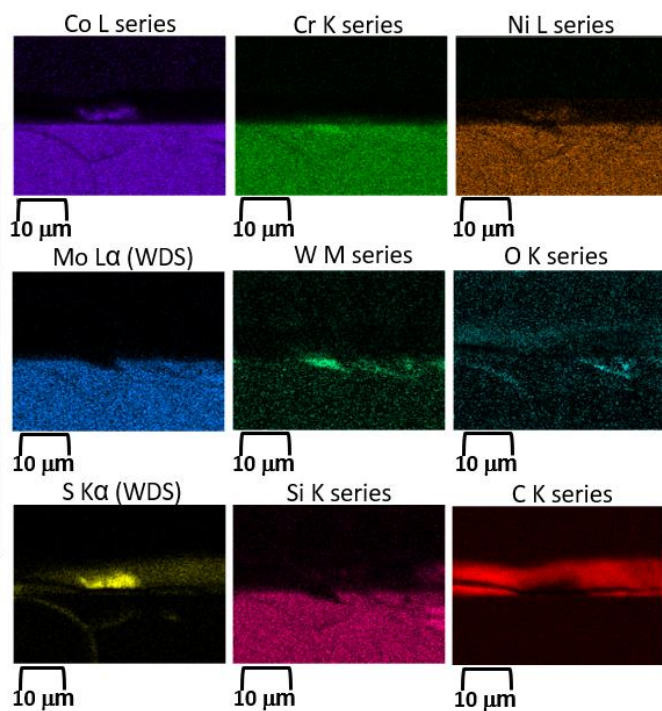
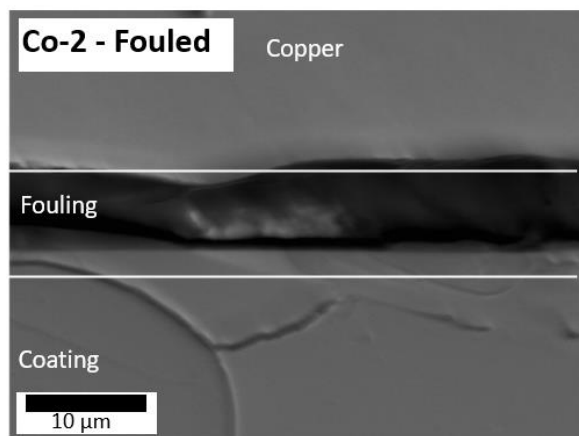
Annealing contributed to the protection of the coatings against sulfur attack. All fouled regions with a higher intensity of sulfur strongly coincide with the position of cobalt, indicating a sulfidation reaction forming cobalt sulfide. For the samples with more nickel, namely Co-2 and Co-2HT, the presence of Ni coincides with the same sulfur-rich regions, suggesting the formation of NiS. The Co-2HT sample with its Cr-rich areas lost the carbon intensity present before the fouling experiment, indicating that the chromium carbides were affected by the fouling process.

In petrochemical plants with an H_2 - H_2S environment, the higher the Ni content in the alloy, the greater the material's susceptibility to corrosion [16]. The alloys tend to form deleterious nickel sulfide, especially in reducing environments [16], which is also the experimental condition of this study. However, in terms of fouling, Co-2, and Co-2HT, which possess 13 wt.% of Ni, accumulated less carbonaceous material than the Co-1 and Co-1HT samples with 4 wt.% of Ni, while behaving like Co-3 and Co-3HT with only 0.2 wt.% of Ni. Similarly, Co-1HT coating with 22.9 wt.% of Mo exhibits a higher fouling rate, while the Co-3HT coating with 28 wt.% of Mo had the lowest fouling rate. For comparison, the Co-2HT sample with 17 wt.% Mo had the second-highest fouling resistance. No direct connection between the fouling rate and the Mo and Ni contents was observed.

After fouling, no specific pattern beyond a higher EDS intensity of S in the fouled region overlapping with Co was observed for the Co-1, Co1-HT, and Co-3 samples (Figure 5.4). However, Co-2 and Co-2HT show a tendency to form scales in the regions with a higher intensity of W near the surface, suggesting that W has an effect on the increased rate of sulfide scale formation, which consequently has a negative effect on the coating performance. As the Co-1 and Co-1HT samples have W in their composition, a similar effect would be expected. However, these coatings are heavily fouled making specific interactions harder to analyze. One should, however,

remember that W from the Co-1 sample is part of the Ni-Cr-W solid solution, while W in the Co-2 sample arises from the carbide in the WC-Co-Cr alloy, which interacts differently during the sulfidation process. Previous studies of sulfidation of the Co-based alloys at 800-1000 °C revealed that tungsten appears in the scale in the same ratio as in the alloy, and it was detected only near the alloy/scale interface [133].





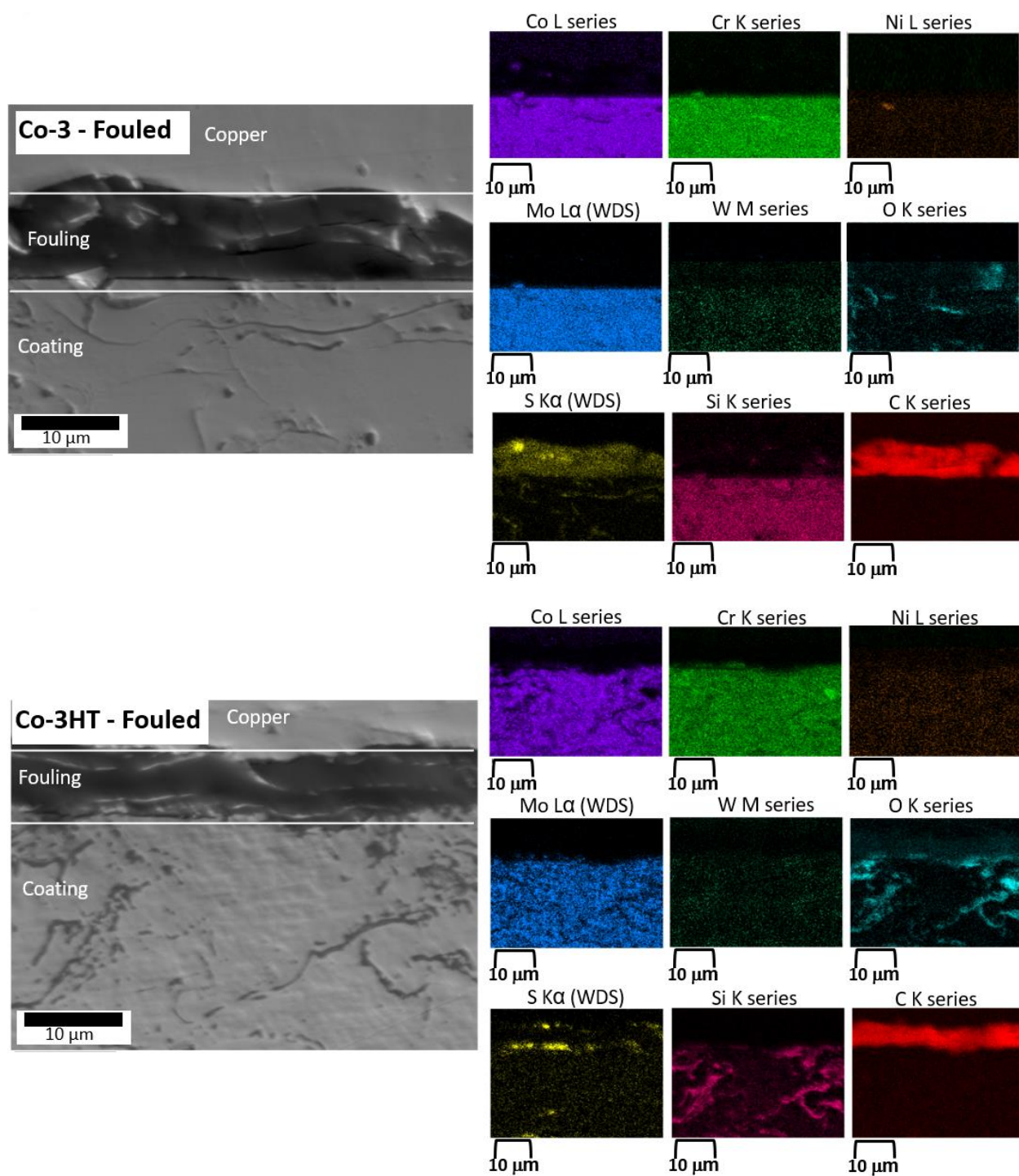


Figure 5.4 SEM images, and EDS and WDS maps on the cross-sections of Co-based coatings after fouling at 450 °C for 2 h. The fouled samples are identified as as-deposited Co-1, Co-2, and Co-3, and after heat treatment, Co-1HT, Co-2HT, and Co-3HT.

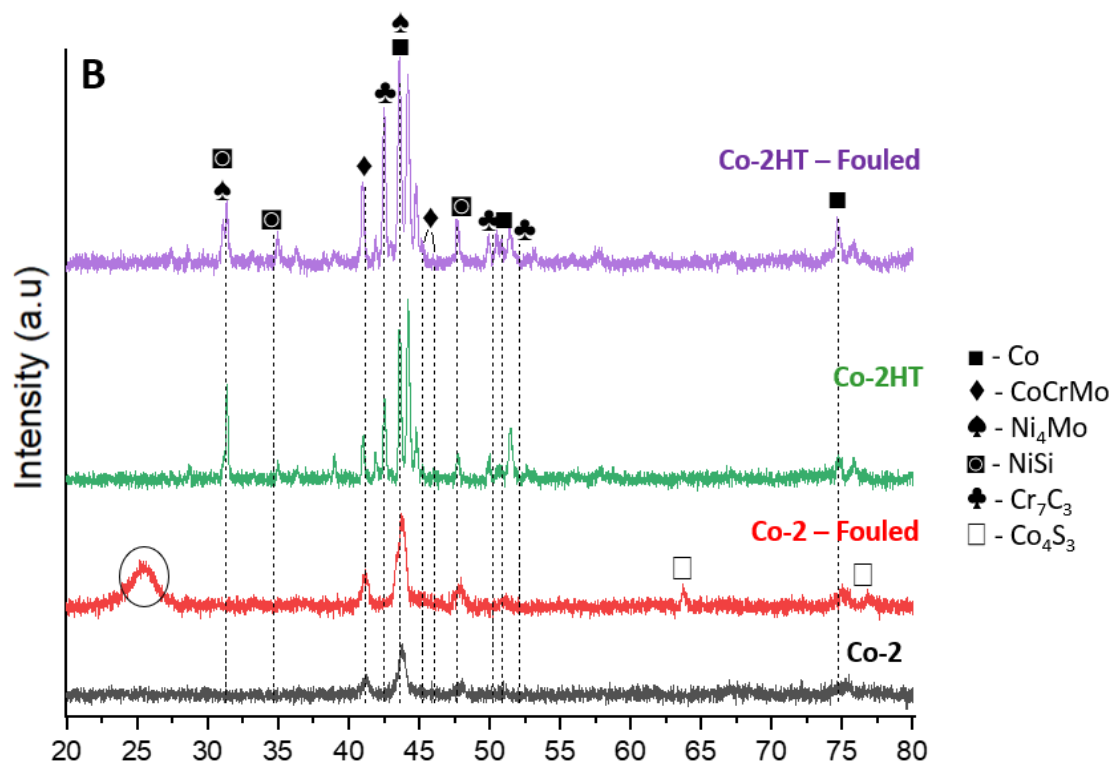
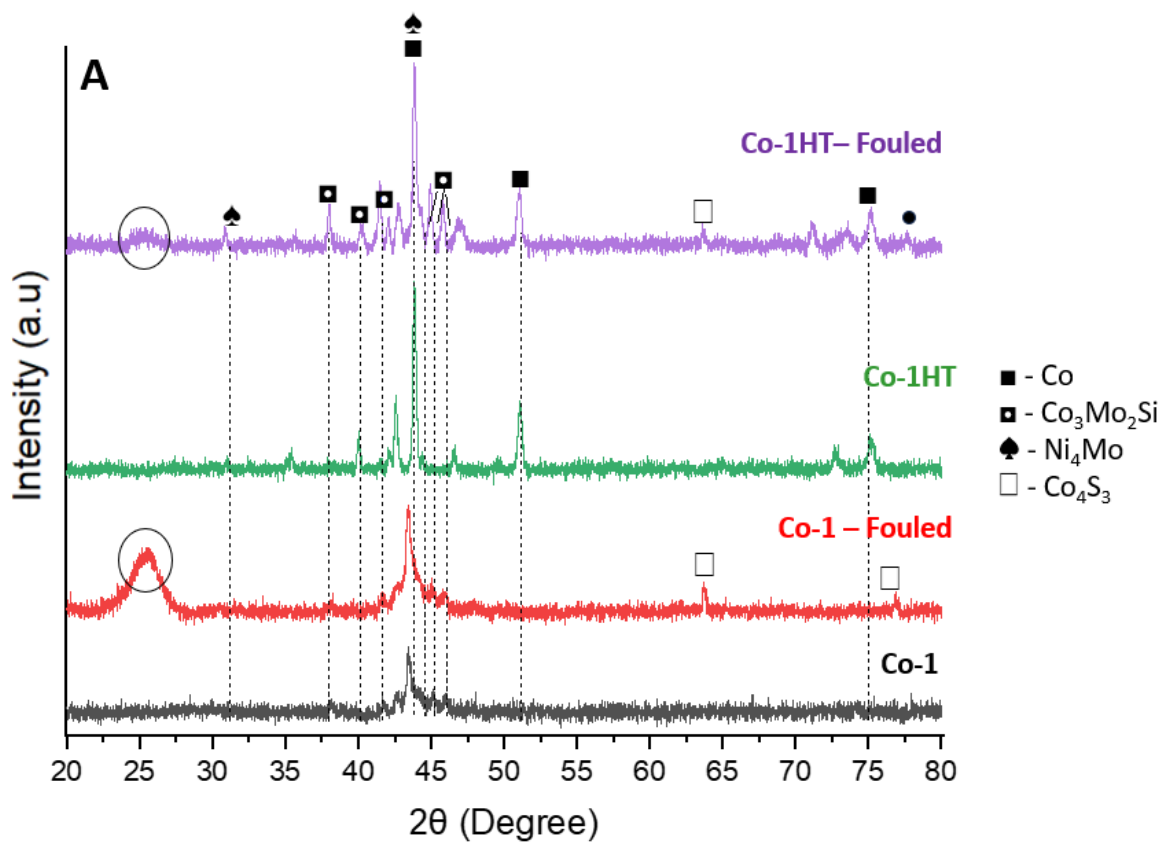
5.4.4 XRD analysis

The XRD diffractograms confirm that after heat treatment, the coatings form new alloying crystalline phases. Specifically, the as-deposited Co-1 and Co-3 samples (Figure 5.5A and Figure 5.5C) show a pattern associated with Co and $\text{Co}_3\text{Mo}_2\text{Si}$ in agreement with [307]. After annealing, Ni_4Mo may be identified in the Co-1HT sample, while Co-3HT shows the formation of SiO_2 corresponding to the relevant EDS maps. The as-deposited Co-2 coating (Figure 5.5B) shows peaks related to Co and Ni. The Co-2HT XRD pattern identifies CoCrMo , Ni_4Mo , NiSi , and Cr_7C_3 phases, which corroborates with the higher concentration of nickel and the presence of chromium carbides also indicated by EDS for the Co-2HT sample (Figure 5.2).

Our results are in good agreement with the published data pertaining to the analyses of heat-treated Co-Mo-Cr-Si materials in which Co, Co_7Mo_6 , Co_3Mo , CoMoSi , and $\text{Co}_3\text{Mo}_2\text{Si}$ phases have been detected, while CoSi was related to the laves formation [306], [307]. Formation of oxides such as Cr_2O_3 , Co_3O_4 , MoO_3 , and CoMoO_4 has also been observed after annealing at 800 °C [313]. With the addition of W and Ni, the presence of NiCr_2O_4 and CoWO_4 has been reported at 600 °C [314].

The amorphous broad scattering at 25° in Figure 5.5 is probably generated by amorphous graphite and correlates well with surface fouling presented in Figure 5.3B. Specifically, the Co-1 sample exhibits the highest graphite intensity followed by Co-1HT and Co-2, in agreement with the highest coke accumulation for the Co-1 sample, and a lower coke formation on the Co-2HT sample. No graphite contribution was detected for samples Co-3 and Co-3HT, corresponding to low coke formation.

Upon fouling, all the samples possessed sulfur on their surface (Figure 5.4), while for some of them, Co and Ni were also distinguished. The XRD analysis confirmed the presence of Co_4S_3 for all samples. Nickel was observed together with sulfur in the cross-sections of the Co-2 and Co-2HT samples (Figure 5.4), which indicates the formation of scales, but no nickel sulfide was possible to detect by XRD (Figure 5.5B). Detached Cr is visible on the fouling layer of the Co-3HT sample (Figure 5.4), but no chromium sulfides or oxides were identified (Figure 5.5C). In general, the unambiguous identification of the reflections in the XRD patterns of the multi-elements sprayed coatings is not trivial. In addition, the fouling layer adds complexity and reduces intensity, making the observation of crystalline phases challenging due to overlapping of different peaks.



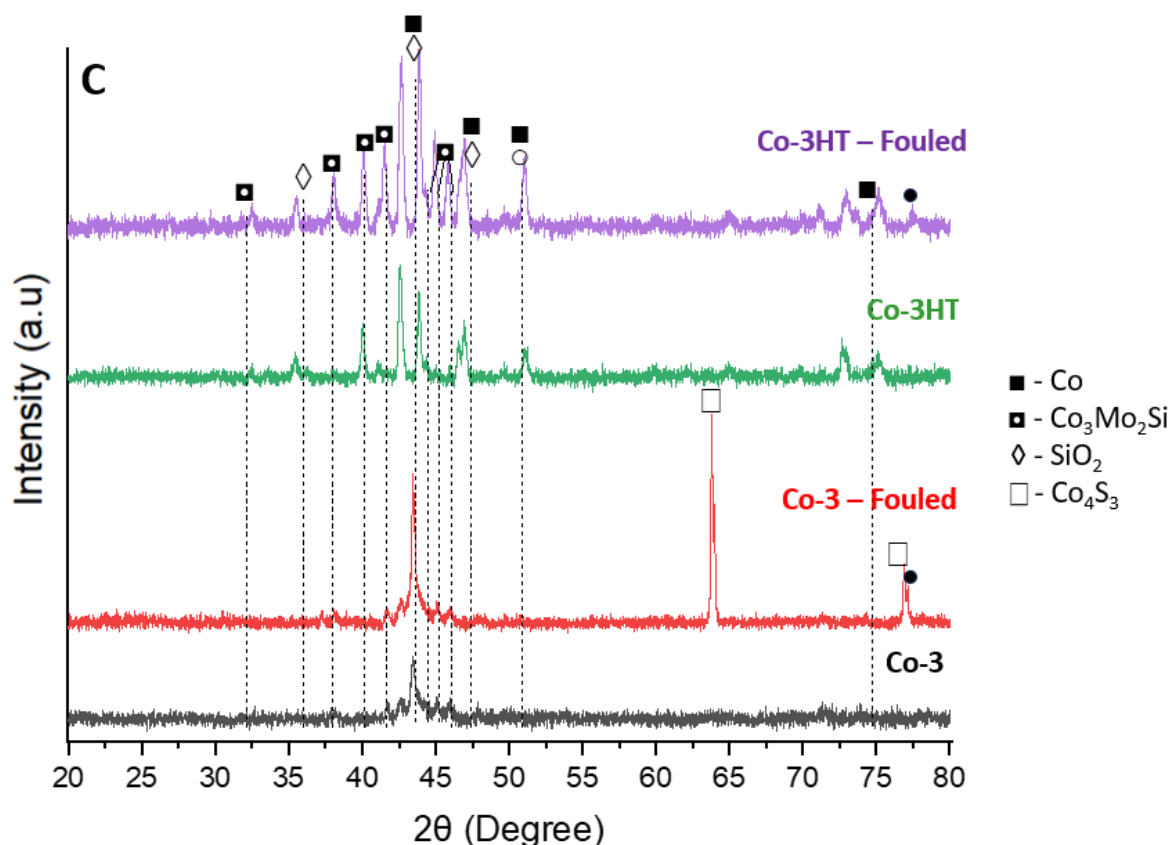


Figure 5.5 XRD patterns of the sprayed Co-based coatings. The dashed lines follow the identified alloying phases, the black dots represent non-identified patterns after fouling, the open squares are sulfides, and the open circle is graphite. The graphs (A) depict the Co-1 and Co-1HT, (B) Co-2 and Co-2HT, and (C) Co-3 and CO-3HT samples.

5.4.5 Contact angle characterization

A reference sample coated with the Co-based alloy Wallex 50 – the current industry standard protective coating for such application – was chosen to study the polishing effect on the CA measurements. In its as-deposited form, this commercial coating has a roughness similar to the coatings analyzed here, and it is applied to isolation valves in hydrocracker units, which is relevant to this study. The as-received Wallex 50 with a R_a value of $5.3 \pm 0.3 \mu\text{m}$ had a significantly higher water CA. After polishing, its R_a was $117 \pm 40 \text{ nm}$, and the CA decreased (Table 5.3) to a value close to that of the other polished samples, underlining that roughness plays a significant role in the coatings' hydrophobicity. The influence of roughness on contact angle measurements was shown on surfaces manufactured on a wide range of engineering materials, including alloys, plastics, and ceramics [315].

Typically, liquid rests on smooth surfaces, whereas on rougher surfaces, it adopts either the Wenzel's or Cassie-Baxter's states, depending on both the surface chemistry and roughness [316]. Wenzel homogeneous regime occurs when the rough surface is completely wet. Thus, surface roughness decreases the contact angle on a hydrophilic surface and increases the contact angle for a droplet on a hydrophobic surface. The Cassie-Baxter regime takes place when the rough surface creates an air pocket between the substrate and the droplet. Such heterogeneous wetting makes contact angles within the hydrophobic range possible on surfaces that are inherently hydrophilic [317]. Scaling down roughness to the micron- or submicron scales induces superhydrophobicity while increasing environmental stability [318]. Although the control of roughness seems to be a good strategy to optimize wettability and surface interaction, the irregular surface impacts the deposition of particles, which quickly fill the surface irregularities. In addition, the entrapped particles may act as catalysts and nucleation sites to induce faster fouling rates.

The contact angle (CA) measurements for water and oil (Table 5.3) were carried out on the polished samples possessing a Ra value of 15 ± 3 nm. This allows one to suppose that the differences in CA values can be primarily attributed to the chemical composition and its homogeneity of the surface. In addition, polishing also removes any surface carbon contamination that impacts hydrophobicity and influences CA [319]. All samples exhibited very low contact angles for the oil droplets, indicating a high degree of oil wettability. CA reduction following the HT, either with water or oil, was primarily controlled by surface chemistry changes. HT increased the elemental homogeneity of the samples (Figure 5.2), while inducing the formation of new crystalline phases and oxides (Figure 5.5), consequently altering the surface composition. This agrees with the observations by other authors who showed that HT increases surface energy by introducing complex oxides [319], and enhances crystallinity and grain growth [316], directly affecting and reducing the CA.

In our measurements, we found a close correlation between the water CA and the coating oil protectiveness. Higher CA indicates a higher fouling rate when comparing coatings within the group: (i) as-deposited, and (ii) heat-treated (HT) (Table 5.3). The HT samples exhibited an overall lower CA and surface fouling than the as-deposited ones, suggesting that other factors played a significant role in surface protection. The HT samples fouling reduction can primarily be attributed to the reduction of pores and other structural defects due to densification during HT. This occurs together with the chemical changes on the surface, leading to passivation, which reduces the surface catalytic effect of cracking, coking, polymerization, and auto-oxidation of the heavy oil. This is

consistent with the predominant fouling mechanisms under hydrocracking conditions, which are chemistry- and corrosion-driven. In addition, reducing chemical fouling consequently reduces the corrosion fouling that is typically aggravated in scenarios under chemical-reaction fouling conditions [320]. Surface energy impacts the particulate and crystallization fouling mechanisms [321], and plays a role in the build-up of chemical fouling [322].

Table 5.3 Surface contact angle measurements on the HVOF-sprayed Co-based coatings deposited on IN718. Arrows symbolize the highest and lowest angles. Correlation with fouling intensity.

Material	Water	Oil	Fouling Intensity
Co-1	70 °	11 °	100 %
Co-2	92 °	21 °	89 %
Co-3	99 °	19 °	76 %
Co-1HT	42 °	6 °	95 %
Co-2HT	89 °	13 °	15 %
Co-3HT	89 °	8 °	3 %
Wallex 50 (as-received)	104 ° ↑	2 ° ↓	-
Wallex 50 (Polished)	91 °	16 °	-
IN718 (substrate)	96 °	5 °	-

5.5 Conclusions

The protection against surface fouling and internal sulfur attack in the Co-Cr-Mo-Si HVOF-sprayed coatings varies according to the alloying elements and heat treatment. The compared coatings have a similar surface roughness and are composed of over 35 % Co, 17% Cr, 17% Mo, and 3% Si. Specifically, Co-1 contains 4% Ni and 2% W, Co-2 contains 13% Ni and 1% W, while Co-3 includes 0.2% Ni and no W. In addition, only Co-2 possesses a significant amount of carbon.

The key findings are summarized as follows:

- Heat treatment promoted interdiffusion, improving the homogeneity of the coatings. Oxidation concentrated in the lamellae and porosities, where silicon accumulated. The coatings exhibited lamellae structure after annealing, suggesting that heat treatment optimization could further enhance the homogeneity and protectiveness.
- Heat treatment increased the surface energy of the samples, as seen in the reduction of contact angle (CA). However, the surface fouling of heat treat coating was significantly reduced. Specifically, the Co-2HT and Co-3HT samples showed the lowest fouling rates, at 15% and 3%, respectively. Thus, the microstructure refinement and reduction of structural defects promoted by the heat treatment were more significant to protect against fouling than the surface energy.

EDS analyses have shown that all samples accumulated sulfur on their surfaces, and the XRD measurements confirmed the formation of sulfides. Samples tend to form surface scales in regions where W is present, suggesting that tungsten negatively affects the coating fouling protection performance. Sulfur infiltrated deep into the coating through interconnected lamellae structures, and heat treatment reduced the degree of sulfur penetration.

5.6 Acknowledgements

The authors wish to thank Mr. Francis Turcot, Mr. Francis Boutet, and Mr. Jean Ghantous for their expert technical assistance. The project was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada through the NSERC-Alliance grant (no. ALLRP 576758 - 22), by Prima Quebec (grant no. R24-13-003), and by Velan Inc.

CHAPTER 6 ARTICLE 3 : ALUMINA COATINGS ON NI-BASED SUPERALLOYS: THE IMPACT OF ANNEALING ON HEAVY OIL FOULING

Fellipy S. Rocha^{1,2}, Etienne Bousser³, Marwan Azzi¹, Fadila Khelfaoui⁴, Luc Vernhes⁴, Gregory S. Patience², Jolanta E. Klemberg-Sapieha¹, Ludvik Martinu¹

¹Department of Engineering Physics, Polytechnique Montréal, Montreal, QC H3T 1J4, Canada

²Department of Chemical Engineering, Polytechnique Montréal, Montreal, QC H3T 1J4, Canada

³Centre for characterization and microscopy of materials, (CM)², Polytechnique Montréal, Montréal, QC H3T 1J4, Canada

⁴Velan Inc., 7007 Côte-de-Liesse, Montreal, QC H4T 1G2, Canada

The article was published in *Surface and Coatings Technology* journal on August 23, 2024 [323]

Thesis author contribution:

Fellipy S. Rocha, Jolanta E. Klemberg-Sapieha, and Ludvik Martinu jointly conceived the research idea. Fellipy S. Rocha took the lead in developing the methodology, conducting the experimental investigations, curating and validating the data, and preparing the initial manuscript draft. All co-authors reviewed and edited subsequent versions collaboratively.

6.1 Abstract

As the sweet crude oil reserves decline, refiners must treat sulfur-rich heavy oil, requiring harsher operating conditions, which are detrimental to process equipment. Application of coatings on critical components protects surfaces against sulfidation, corrosion, and fouling, extends the equipment's lifetime, and reduces the frequency of costly turnarounds. In the present work, we coated Inconel 625 and Inconel 718 substrates with amorphous alumina thin films at room temperature using reactive RF magnetron sputtering. Annealing of the deposited coatings at 800, 900, and 1000 °C increased hardness, improved adhesion, and generated crystalline polymorphs, predominantly γ -Al₂O₃ at lower temperatures, while α -Al₂O₃ was present at 1000 °C. The annealed

substrates formed thermally grown oxides (TGOs), which interacted with the alumina coatings. The TGOs followed grain boundaries in the case of IN718 and a crater-like pattern on IN625. Annealed substrate precipitates generated columnar-like protrusions responsible for inducing crack propagation, which presented TGO formation. After 2 h exposure to heavy oil (containing 0.06 g g⁻¹ sulfur) at 450 °C and 11.3 MPa the as-deposited amorphous alumina presented no clear sign of adherent fouling, while the 1000 °C annealed crystalline alumina surfaces presented evidence of fouling.

6.2 Introduction

Nickel-based superalloys are the predominant choice for extreme environment applications involving high temperatures, and high mechanical stress [254], such as the petrochemical industry, aerospace, and power generation. Despite representing an evolution in applications at elevated temperatures, and being corrosion and creep resistant [324], the IN625 and IN718 alloys have been pushed to their operational limits, and their degradation is a significant concern in harsh environments. In the petrochemical industry, the alloys are subjected to fouling, a combined effect of reactions caused by sulfur and organic components from crude oil [74]. The deposition rate of either inorganic or organic material on the alloy surface depends on shear and temperature [14]. Temperature and reaction time rule the fouling reaction, which is the most significant cause of unstable reactor pressure control and valve failure [22]. With the depletion of conventional crude, heavy fractions are required to sustain the demand, which increases the amount of impurities and, consequently, sulfur content in the feed. Ebullated bed hydrocrackers are the most suitable reactors for processing this residual portion at temperatures above 350 °C, due to the catalyst replacement simplicity during operation [276]. Because of the extreme conditions, the fouling rate in these three-phase reactors is increasing, so materials with superior resistance to sulfidation and coke deposition are required.

Nickel-based alloys, especially when combined with chromium, control corrosion [16]. However, it has been well established that these alloys are prone to sulfidation, while H₂S promotes their cracking [122]. The formed deleterious metal sulfide scales may act as a catalyst to form more sulfides in H₂-rich environments [16]. The continuous sulfide scales on the material surface have more defective structures when compared to oxidation. Thus, sulfidation rates are many orders of magnitude higher with faster diffusion pathways for the metallic cations [91]. Currently, there is

no standardized quantitative data available for material comparison, hence the classification of material hot corrosion or sulfidation is typically qualitative and is often associated with the chromium content and chemistry of Fe-, Ni-, and Co-based alloys [118].

There is a need to achieve realistic simulated experimental conditions to validate the performance with respect to heavy oil fouling of candidate alloys and/or coatings. Unfortunately, the information available about materials performance under real-life conditions is scarce and sparse with a wide range of specifications [95]. The results are often difficult to interpret precisely, and they present apparent contradictions in understanding the possible mechanisms [325]. Thin film technology represents a promising solution to the challenge of protecting the surface of superalloys while maintaining their bulk properties. A coating composition can be chosen exclusively for the desired environmental protection, without the constraints of designing alloys to preserve the structural integrity under extreme conditions [87]. Physical Vapor Deposition (PVD) offers an environmentally friendly and safe deposition process. More precisely, magnetron sputtering allows for effective control of the coating composition, thickness, grain size, and orientation. Thus, it is possible to achieve high hardness, chemical resistance, low porosity, good adhesion and relatively high deposition rates [326]. In the context of protection against oxidation, sulfidation and fouling, oxides are typically considered to decrease surface reactivity.

Alumina (Al_2O_3) has many metastable polymorphs that are categorized as face-centered cubic (FCC) and hexagonal close-packed (HCP) structures. Alpha alumina (corundum) is a thermodynamically stable form and is arranged in an HCP trigonal lattice [327]. Based on aluminium-containing alloy results, Al_2O_3 is expected to provide the best possible protection against sulfur corrosion [89]. However, the formation of a continuous layer of alumina from alloy oxidation requires a higher aluminum content [89]. Direct deposition of thin alumina films on metallic substrates has been reported using various PVD methods. Generally, the thin film is amorphous at a temperature lower than 500 °C, while higher substrate temperatures during deposition, and post-deposition annealing favour metastable polymorphs [328]. To create an alumina crystalline phase by reactive magnetron sputtering (e.g., radiofrequency (RF) sputtering), higher substrate temperatures are required: 500 °C to obtain $\gamma\text{-Al}_2\text{O}_3$, and 700 °C to obtain $\alpha\text{-Al}_2\text{O}_3$ [329]. Crystalline alumina, especially α -alumina, provides a barrier against the direct migration of metallic elements (e.g., Fe, Ni, and Cr) from the substrate alloy to the surface at elevated temperatures [213]. Crystalline alumina is best suited for applications related to wear, as it tends

to be harder than the amorphous phase. Although significant progress has been made in fabricating crystalline alumina by PVD, the simplest approach to produce the alpha phase is a deposition of an amorphous alumina layer at room temperature followed by annealing above 900 °C.

Annealing is prohibitive for many temperature-sensitive substrates inducing unwanted microstructural changes, delamination due to incompatible coefficients of thermal expansion (CTE), and permanent macro deformation of the components. Moreover, while considering thin film technology, one must always keep in mind substrate effects, especially for high-temperature applications where diffusion of the substrate material into the coating matrix is expected. Investigation of alumina coating performance with the influence of the substrate is very important with the aim to develop a dense, defect-free, amorphous coating that would protect the substrate by limiting sulfur diffusion, which occurs mainly through grain boundaries and porosity, along with superficial sulfide scale formation [72]. Besides the surface chemistry and microstructure, the coating thickness is an important factor in providing protection [199]. Previous studies demonstrated that an ALD-deposited alumina passive layer of 5 nm was sufficient to protect against heavy oil fouling at 350 °C. However, the Al_2O_3 layer delaminates after heavy oil fouling tests at high pressure and 350 °C [50]. Above 350°C, the fouling process initiates via the decomposition of sulphur-containing molecules forming hydrogen sulphide (H_2S), which reacts with metals, and coke forms a strongly adherent carbonaceous and brittle metal-sulfide film on the surface [71].

This article focuses on investigating the performance of alumina thin films deposited at room temperature using the RF reactive magnetron sputtering technique as a fouling resistant coating. We study the effect of annealing on the microstructure of amorphous alumina on IN625 and IN718. Different metastable polymorphs of alumina are formed, with $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ being the predominant crystalline phases. We show that the fouling resistance varies with the alumina microstructure, while its amorphous phase exhibits the best performance, with no clear sign of adherent fouling. Unlike other published studies, in this work, we did not observe any coating delamination after fouling up to 450 °C.

6.3 Materials and methods

6.3.1 Surface preparation and coating deposition

Surface preparation affects the surface's ability to form durable well-adhering coatings as it removes weak boundaries and contamination [163]. It consisted of two steps:

Substrate polishing: IN718 and IN625 coupons (25 x 25 x 3 mm) were polished using SiC paper (grit sizes from 240 to 800), followed by diamond particle suspension (from 9 μm to 1 μm), and finally a colloidal alumina suspension. Before deposition, the substrates were sequentially cleaned in acetone and then isopropanol ultrasonic bath. The elemental composition of IN625 and IN718 is presented in Table 6.1.

Sample mounting and pre-treatment: The coupons were mounted on a 150 mm diameter sample holder. A plasma sputter-cleaning process was applied for 30 min in Ar at 5 mTorr (0.67 Pa) and an RF-induced negative bias of -650 V. This step removes the native oxide layer from the surface, while also promoting surface activation and consequently chemical reactivity [249].

The deposition system consisted of a 30 L vacuum chamber evacuated by mechanical and turbomolecular pumps. The magnetron head holding a 50 mm diameter Al target (99% purity) from Kurt J. Lesker was connected to a Seren RF power supply. Another Seren RF power supply was connected to the sample holder (150 mm diameter) to control the bias voltage, which was applied to the substrate only during the pre-treatment step. The alumina was deposited at various oxygen flow rates (4, 5, and 6 sccm) while keeping the Ar flow rate constant (35 sccm). The chamber pressure during deposition was 5 mTorr.

After pre-treatment, Ar plasma was ignited at the magnetron, while the shutter was closed, to clean the target until the bias voltage generated by the plasma stabilized. Oxygen was then introduced into the chamber, and the shutter was kept closed until the bias stabilized again, signaling that the target had reached a suitable composition (due to poisoning). Deposition started when the target bias stabilized and the shutter was opened. The substrate temperature was maintained at ambient without the application of external heating or cooling, and the substrate rotation speed was set at 55 rpm. The total RF power applied to the target was 300 W for the deposition on both metal substrates. The coatings on the Inconel substrates had a thickness of approximately 1.5 μm .

After deposition, the coated samples were annealed in a Carbolite furnace in air at 800 $^{\circ}\text{C}$, 900 $^{\circ}\text{C}$, and 1000 $^{\circ}\text{C}$, for 2 hours, at a heating rate of 60 $^{\circ}\text{C}/\text{min}$. Following annealing, the samples were let to cool down in the furnace after the power was interrupted, and they were retrieved the next day.

Table 6.1 Elemental composition of IN718 and IN625 provided by the supplier.

Limiting chemical composition, [wt.%]		
Element	IN718	IN625
Ni	50.0-55.0	58.0 min
Cr	17.0-21.0	20.0-23.0
Fe	Balance	5.0 max
Nb + Ta	4.75-5.50	3.15-4.15
Mo	2.80-3.30	8.0-10.0
Ti	0.65-1.15	0.40 max
Al	0.2-0.8	0.40 max
Co	1.0 max	1.0 max
C	0.08 max	0.10 max
Mn	0.35 max	0.50 max
Si	0.35 max	0.50 max
P	0.015 max	0.015 max
S	0.015 max	0.015 max
B	0.006 max	-
Cu	0.30 max	-

6.3.2 Coating characterization

6.3.2.1 Ellipsometry

Variable angle spectroscopic ellipsometry was used to assess the coating thickness and the refractive index changes throughout the thickness for films deposited on soda-lime glass. The RC2 ellipsometer from the J.A. Woollam Co. is equipped with two rotating compensators. The measurements were performed at several angles of incidence 45° , 55° , 65° , and 75° in a wavelength range from 200 nm to 1700 nm. An optical model was created based on the Tauc-Lorentz and Gaussian oscillators using the CompleteEase software. The refinement of the optical model provided information about the thickness and surface roughness of the layer, refractive index dispersion curves, and the possible presence of anisotropy.

6.3.2.2 Microscopy

A scanning electron microscope (SEM, JEOL JSM-7600F) equipped with an Oxford Instruments X-Max energy dispersive X-ray spectroscopy (EDS) detector was used to assess the film thickness, microstructure, topography, and elemental composition. Focused Ion Beam (FIB) system (Hitachi FB-2000A) with Ga^+ ions was used at 30 kV to prepare cross-sections of the coated samples after annealing. The trench produced by FIB enabled one to observe the microstructure by SEM at a 45° angle. The real dimensions of the observed microstructures on the FIB-prepared samples are smaller than those on the micrographs because of the 45° cut angle.

6.3.2.3 X-ray diffraction

X-ray diffraction (XRD) measurements were carried out using a Bruker Discover D8 X-ray diffractometer in a grazing angle geometry with $\text{Cu K}\alpha$ radiation (8.04 keV) in a parallel beam configuration with a Gobel mirror (incident beam optics) and Soller slits (diffracted beam optics). The selected grazing angle was $\alpha = 1.0^\circ$ for all measurements, and the range of the 2θ hkl scans was from 20 to 90 degrees.

6.3.2.4 Micro-scratch testing

A Micro Combi Tester (MCT3, Anton Paar, Graz, Austria) equipped with a 200 μm radius Rockwell diamond tip was applied to measure the adhesion of alumina films. The test consisted of a progressive load increasing from 0.03 to 20 N over a scratch length of 3 mm at a speed of 6

mm/min. The critical load 1 (LC_1), which corresponds to a cohesive tensile failure, was determined as the normal force where the first crack occurred. The coating adhesion or critical load 2 (LC_2) was associated with the load at which the coating delaminates. The scratch tracks were observed post-mortem by optical microscopy. The LC_1 and LC_2 values were identified following the ASTM C1624 standard. At least two scratches were performed for each sample to ensure reproducibility. The results presented in the paper show the most representative data.

6.3.2.5 Nanoindentation

A depth-sensing indentation instrument (Hysitron Inc. – Bruker TriboIndenter) equipped with a Berkovich pyramidal tip was used to determine the hardness (H) and reduced Young's modulus (E_r) of the coatings. The area function of the tip was calibrated using a fused silica standard. All measurements were performed with multicycle progressively increasing load indentations with loads ranging from 1 to 200 mN. Each sample was tested using a 4 X 4 indentation matrix and the properties were calculated from a minimum of 25 indentations per spot. Each unloading cycle was analyzed using the Oliver and Pharr method [330], while coating hardness and modulus were determined using the methodology proposed in the ISO 14577-4 standard. The H and E_r values are extracted from a plateau region independent of the penetration depth and the indentation tip effects.

6.3.3 Fouling test

For the fouling tests, the samples were positioned vertically to mitigate gravitational effects in an autoclave-type reactor (see Figure 6.1) filled with 200 g of heavy oil containing 6 wt,% sulfur. The system was pressurized with argon up to 11.3 MPa controlled by a backpressure regulator and purged for 5 min to evacuate any oxygen. The temperature cycle in the vessel consisted of 2 h of temperature increase to reach an internal temperature of 450 °C, followed by a hold time of 2 h to ensure that all heavy oil cracked, after which the system was allowed to cool until the next day before depressurizing, opening, and retrieving the samples. The recovered samples were washed with a 50:50 solution of petroleum ether and toluene, followed by a water rinse to remove non-adherent material. The samples were dried in the air and stored before subsequent analyses.

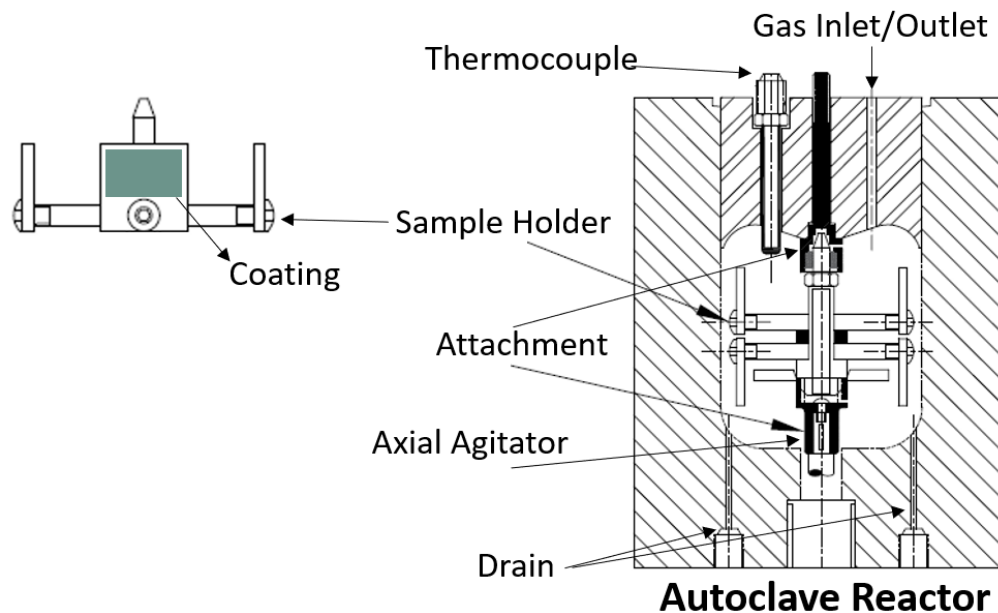


Figure 6.1 Internal view of the batch reactor structure, and sample holder.

6.4 Results

6.4.1 Alumina deposition optimization

In the first series of experiments, amorphous alumina films were prepared on glass and IN625 substrates using argon and varying oxygen flow rates in the hysteresis transition zone with a deposition time of 30 min. Hysteresis is a non-linear change in operation conditions caused by poisoning due to compound formation on the target during reactive magnetron sputtering [331]. Hence, there is a need for optimization, which was achieved through monitoring the films' optical (Table 6.2), and elasto-plastic (Table 6.3) properties.

Table 6.2 Alumina coating deposited on glass: refractive index (n), n -gradient (%), extinction coefficient (k), and thickness obtained for different oxygen flow values.

Power (W)	O₂ flow (sccm)	n	n- gradient (%)	k	Thickness (nm)	Deposition time (min)
300	4	1.65	0.7	0.004	695	30
300	5	1.73	16	0.016	434	30
300	6	1.74	17	0.023	317	30

The refractive index (n) slightly increased with higher O₂ flow rate and power (between 1.65 and 1.74 @ 550 nm), while the extinction coefficient (k) varied between 0 and 0.02, pointing out the near-stoichiometry of the deposited alumina layers. The stability of the growth process has been assessed based on the refractive index (n) gradient throughout the coating. The variation of n ranged from 0% to 17% throughout the coating thickness. The alumina films deposited with an O₂ flow of 4 sccm possessed the lowest n -gradient, signifying the highest level of homogeneity. At this condition, the obtained thickness was also higher, indicating a higher deposition rate, characteristic of a sputtering process regime at the boundary between the metallic and poisoned modes [332].

EDS measurements confirmed a slightly sub-stoichiometric composition of the as-deposited films (oxygen concentrations of 61%, 62%, and 63% for 4, 5, and 6 sccm of O₂, respectively). These values are not affected by the substrate since the complete volume of interaction is within the 1.5 μm thick coating; in fact, the used electron acceleration voltage of 10 kV corresponds to a volume of interaction determined by a penetration depth of $\sim 0.85 \mu\text{m}$ for a reference Al₂O₃ layer using the Kanaya-Okayama formula [265].

Analysis of the elasto-plastic properties (Table 6.3) indicates that the hardness and the H/E_r ratio slightly increased while Young's modulus slightly dropped when increasing the oxygen concentration. The LC_1 and LC_2 values from the micro-scratch test (Table 6.3) confirm that the film deposited with 4 sccm of O₂ is more scratch-resistant and adheres better. In addition, this film also possesses the lowest n gradient, suggesting that higher coating homogeneity is indicative of better adhesion performance.

Table 6.3 Nanoindentation and scratch analysis of the alumina coatings deposited on IN625. The deposition time was increased for a higher O₂ flow rate to account for a lower deposition rate.

O₂ flow (sccm)	<i>H</i> (GPa) (σ)	<i>E_r</i> (GPa) (σ)	<i>H/E_r</i>	<i>LC</i>₁ (N)	<i>LC</i>₂ (N)
4	10.7 (0.9)	193 (16)	0.055	0.67	2.54
5	11.4 (0.5)	188 (19)	0.060	0.53	1.52
6	11.6 (0.8)	186 (12)	0.063	0.37	0.56

6.4.2 Effect of annealing

6.4.2.1 Film crystallinity

In the second series of experiments, conducted after the process and amorphous alumina coating optimization, we deposited films for the subsequent annealing study at a flow rate of 4 sccm of oxygen. This choice was based on better homogeneity, higher deposition rate, and superior adhesion and cohesion. It should be noted that indexing XRD patterns from annealed multi-element alloys is challenging because multiple candidate phases can overlap. In general, the oxidation of nickel-based alloys gives rise to chromium oxides, delta-phase (Ni₃Nb) precipitates, inner oxides, voids, and pores [333]. However, in the case of the diffractograms presented below, the alumina allotropes gave the highest confidence results.

The as-deposited coatings are amorphous, as the XRD diffractogram at room temperature only shows peaks due to the substrate IN625 (Figure 6.2), and IN718 (Figure 6.3). After annealing IN625 at 800 °C, the main peaks correspond to γ -Al₂O₃ formation. The latter peaks further sharpen at 900 °C, while the peaks at 37° and 61° disappear, and the peak at 32° shifts to the left, which represents the formation of additional alumina transition phases, possibly δ and θ [327]. Finally, the sample annealed at 1000 °C exhibits peaks corresponding to α -Al₂O₃. However, the peaks from γ -Al₂O₃ are still visible, and the peak at 32° is now narrower, slightly shifted, and more prominent. Similar to IN625, films on IN718 also confirm the formation of γ -Al₂O₃ at 900 °C (Figure 6.3). However, when annealed at 1000 °C, all γ -Al₂O₃ peak heights are drastically reduced, and the

peaks corresponding to α - Al_2O_3 become dominant. In addition, peaks ascribed to the formation of Cr_2O_3 are now visible, indicating a higher degree of diffusion of chromium into the alumina film. This enhances the formation of α - Al_2O_3 since Cr_2O_3 is a known template to induce alpha alumina formation due to their lattice compatibility [334].

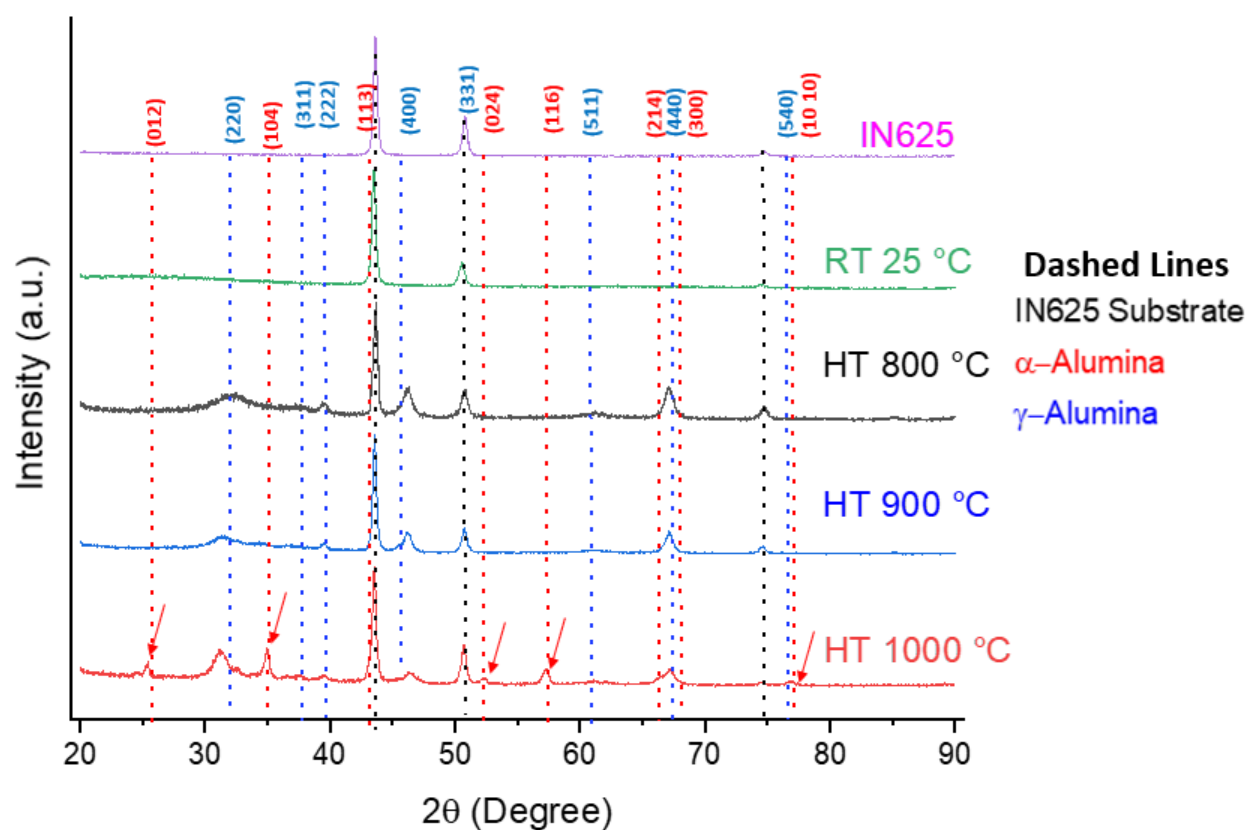


Figure 6.2 XRD patterns of alumina coatings on IN625 before and after annealing. The dashed lines represent IN625 (black), γ -alumina (blue), and α -alumina (red). The corresponding alumina phases are indicated above the dashed lines. Database: α - Al_2O_3 (ICDD 046-1212) PDF-2, γ - Al_2O_3 (ICDD 002-1420) PDF-2.

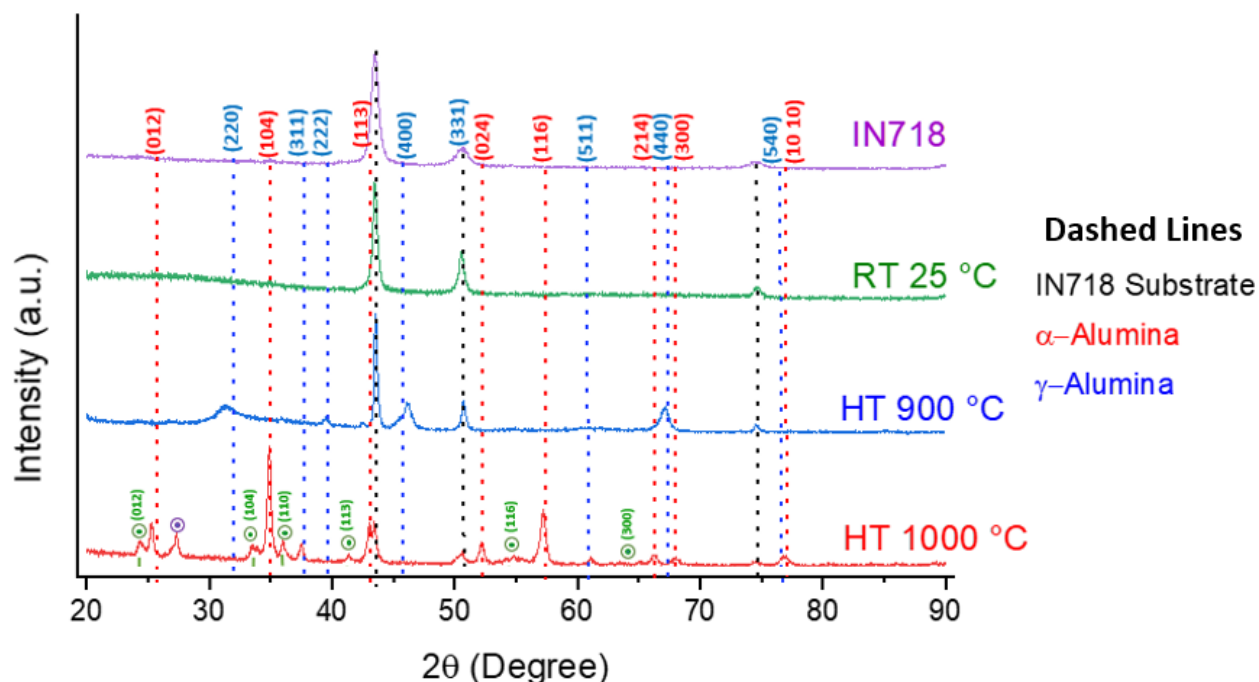


Figure 6.3 XRD patterns of alumina coatings on IN718 before and after annealing. The dashed lines represent IN718 (black), γ -alumina (blue), α -alumina (red), and chromium oxide (green).

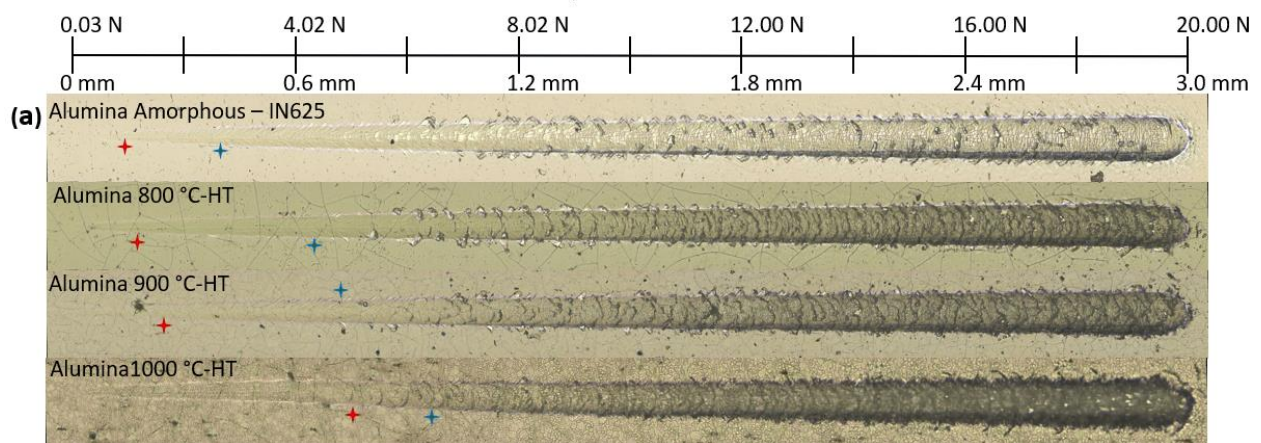
The corresponding alumina phases are indicated above the dashed lines. Database: α - Al_2O_3 (ICDD 046-1212) PDF-2, γ - Al_2O_3 (ICDD 002-1420) PDF-2, and Cr_2O_3 (ICDD 038-1479) PDF-2. The dots correspond to Cr_2O_3 (green), and NbCrO_4 (purple).

6.4.2.2 Mechanical properties

The mechanical properties of the alumina coatings before and after annealing are summarized in Table 6.4. The hardness has approximately doubled after annealing due to crystallization, with a maximum value over 21 GPa for the coatings deposited on IN625 and IN718 and annealed at 900 °C. The H values became slightly lower (20.6 GPa) for samples annealed at 1000 °C. The results of the micro-scratch testing suggest that the cohesive properties and adhesion improve after annealing the films for both substrates (see Figure 6.4 and Table 6.4). The LC_1 values for alumina on IN625 are systematically higher than those on IN718. The LC_2 results for alumina on IN625 are initially higher, but they are equivalent to 6.3 N for both substrates after annealing at 1000 °C.

Table 6.4 Elasto-plastic properties before and after annealing of alumina deposited with an oxygen flow rate of 4 sccm on IN625 and IN718 substrates. The critical load values constitute the cohesive (LC_1) and adhesive (LC_2) strength of the films.

Substrate	Annealing Temperature	H (GPa)	Stdev H	E_r (GPa)	Stdev E_r	LC_1 [N]	LC_2 [N]
IN625	as-deposited	10.7	0.9	192.5	15.7	0.82	2.54
	800 °C	21.1	1.0	265.5	12.4	1.09	4.23
	900 °C	21.7	2.2	262.8	22.3	1.56	4.70
	1000 °C	20.6	1.7	247	19.9	4.92	6.32
IN718	as-deposited	11.1	0.4	198.4	7.6	0.62	2.09
	900 °C	21.2	1.3	256.6	9.8	1.49	4.03
	1000 °C	20.6	2.0	306.3	41.1	4.07	6.33



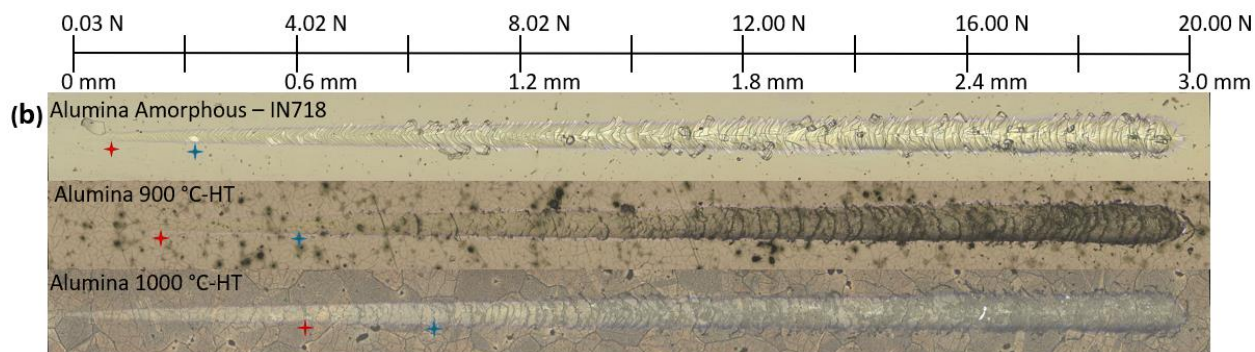


Figure 6.4 Scratch tracks of alumina coatings deposited on IN625 (a) and on IN718 (b) before and after annealing at 800, 900, and 1000 °C for 2 h. The cohesive failure (LC_1) is marked in red, and the coating adhesion failure (LC_2) is marked in blue.

6.4.2.3 Surface analysis

To better understand the effect of annealing on the alumina coatings and the alumina/Inconel systems, SEM and EDS measurements were performed on the surface and cross-sections of samples annealed at 1000 °C. The EDS surface analysis was conducted with a 5 kV accelerating voltage to ensure a superficial analysis and avoid substrate interference. The acceleration voltage during the cross-section EDS analysis was varied from 5 kV to 25 kV. The most revealing imaging conditions were generated at 15 kV; specifically, the images at 15 kV presented a better identification of Ti diffusion and enhanced Cr resolution. At 5 kV, Cr is detectable only by the $L\alpha$ (0.572) line, which can convolute with the O $K\alpha$ (0.525) line, possibly leading to interpretation errors.

As-deposited amorphous alumina films are typically smooth with a roughness on the nanometric scale, in agreement with the literature [335]. The microstructure of alumina coatings on IN625 after annealing at 1000 °C is illustrated in Figure 6.5. The surface appears to be covered by circular crater-like structures with tower-like protrusions inside the craters (see Figure 6.5a), without any clear pattern. Further EDS analysis (Figure 6.5b) indicated that the borders of the crater-like structures are rich in Mn, while the protrusions and the internal part of the craters are rich in Cr, Ti, and Mn. We found that after annealing the alumina-coated IN625 at 1000 °C, only Ni, Mn, Cr, and Ti diffuse (Figure 6.5b), consistent with the previous studies [336].

IN718 has an elemental composition similar to IN625, but with higher concentrations of Ti, Al, and Nb, and lower concentrations of Mn, Si, Mo, Cr, and Ni (see Table 6.1). The annealed alumina

film on IN718 (Figure 6.6a) indicates two types of delimitation lines, a thicker one and a thinner one. The thinner lines are interpreted as cracks, more evident in the higher magnification image, and the thicker lines coincide with grain boundary-like regions, evidenced by the image contrast. The TGO surface pattern matching the substrate grain boundaries is consistent with the literature [336], [337]. The EDS results (Figure 6.6b) of the alumina-coated IN718 after annealing indicate that the thickness of the lines is related to the amount of elemental diffusion. The TGO over the grain boundary region is thicker due to a facilitated diffusion. From the EDS results (Figure 6.6b), we can see a deficit of aluminum in all lines on the surface, while Cr and Ti predominate. The tower-like protrusions are mainly formed by Nb, Ti, and Cr from the substrate material.

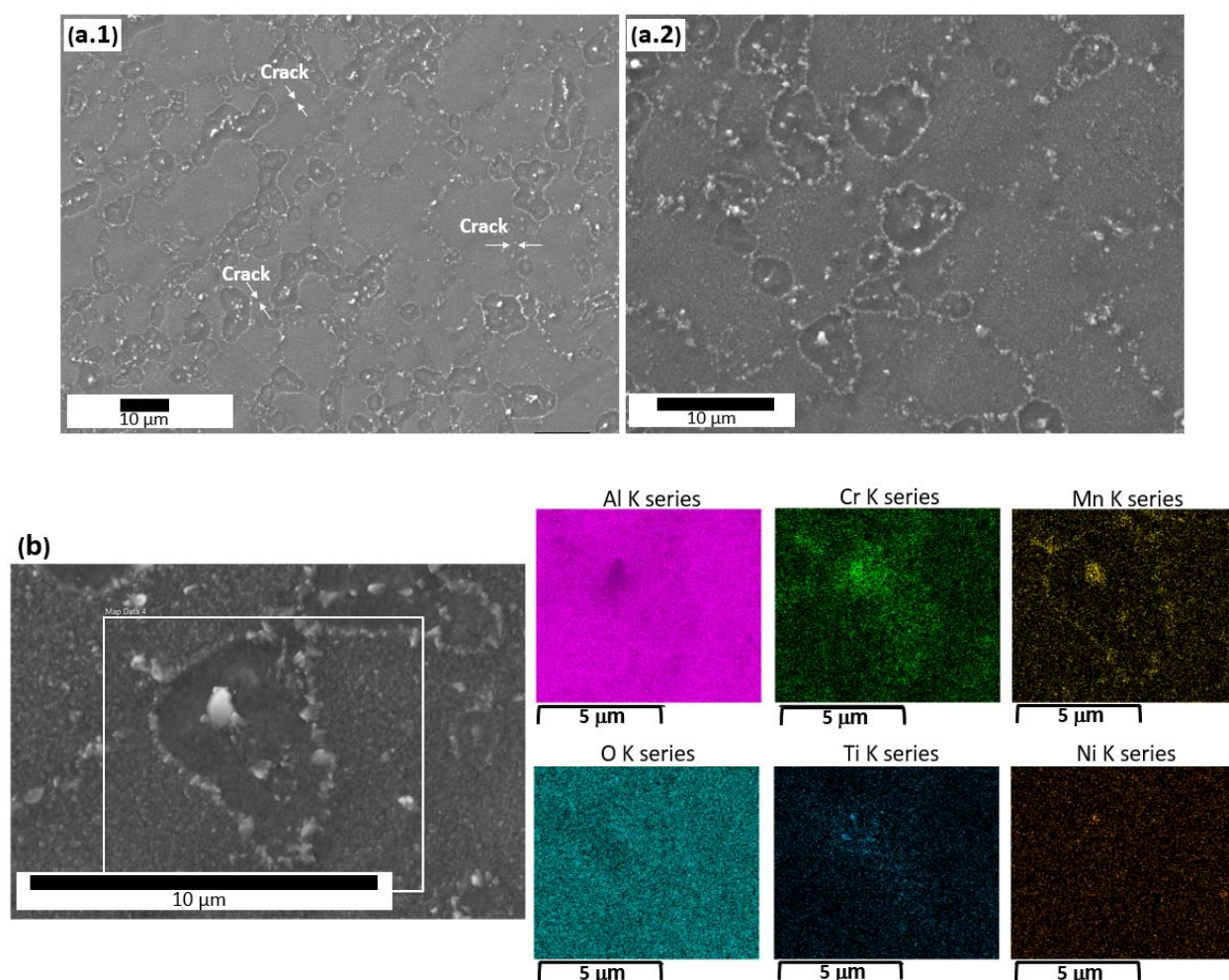


Figure 6.5 SEM images and EDS compositional maps of the surface of alumina-coated IN625 after annealing for 2 h at 1000 °C. EDS maps correspond to the highlighted rectangular area.

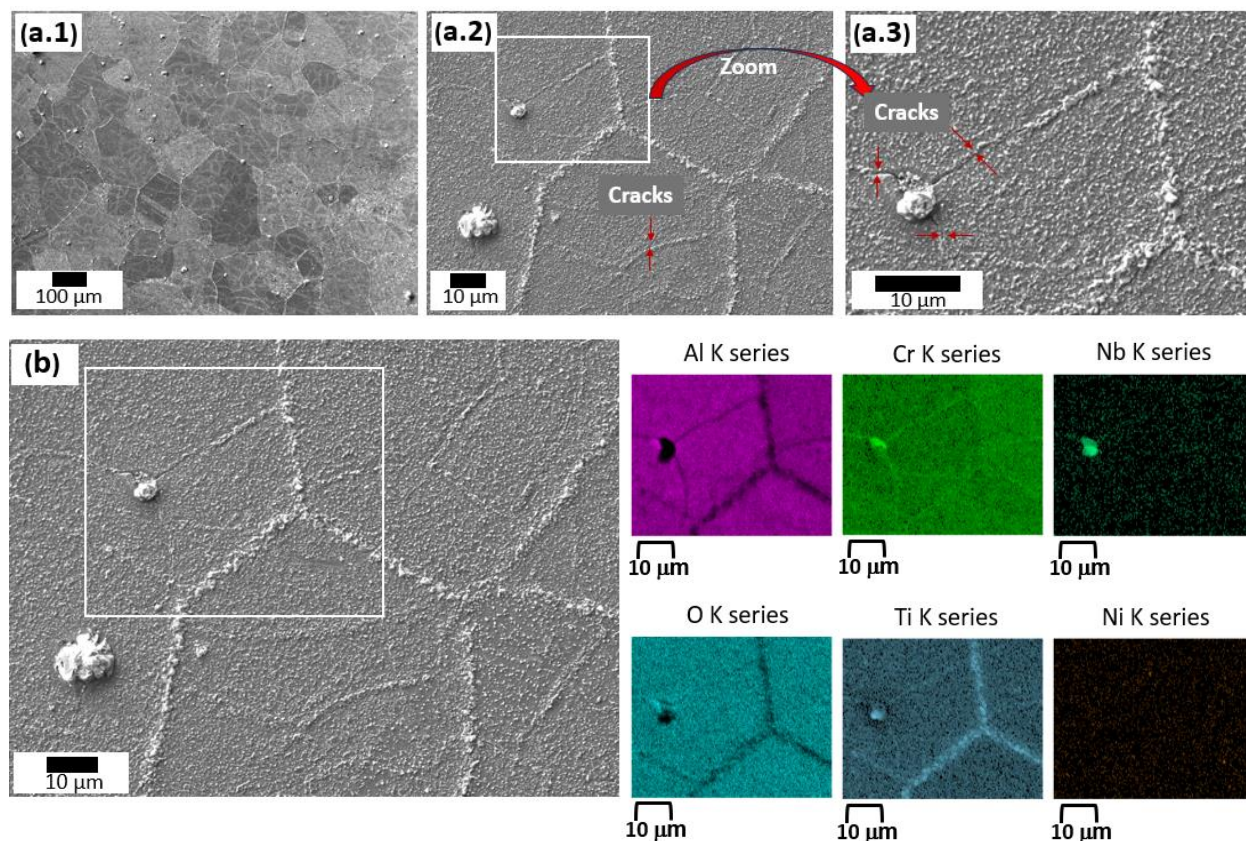


Figure 6.6 SEM images and EDS compositional maps of the surface of alumina-coated IN718 after annealing for 2 h at 1000 °C. EDS maps correspond to the highlighted rectangular area.

6.4.2.4 FIB cross-section analysis

In the following, we performed a detailed analysis of the FIB cross-sections (Figure 6.7 and Figure 6.8) to assess the correspondence of the TGOs seen in the coating surface by SEM in Figure 6.5 and Figure 6.6 and the substrate microstructure. In this case, Figure 6.7 angled images show the area surrounding the FIB cuts. No alignment between IN625 grains and alumina surface structures has been observed; in Figure 6.7a, only the crater-like structures can be detected, together with protrusions and small cracks. In contrast, the grain boundaries of the IN718 substrate are aligned with the thicker lines on the coating surface (see Figure 6.7b) as also indicated in 6.4.2.3.

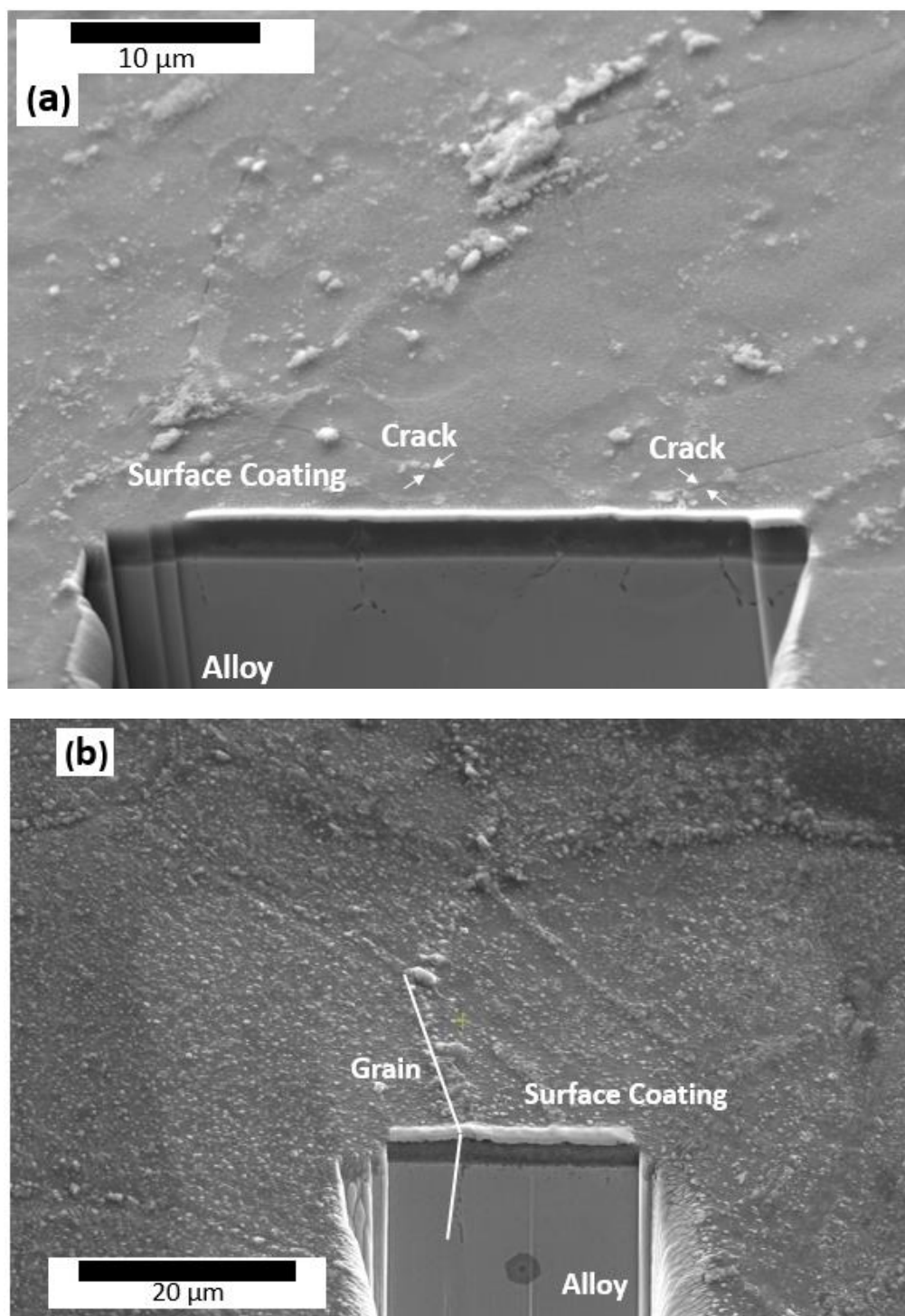


Figure 6.7 Surface region showing the FIB cut area in the alumina-coated IN625 (a) and IN718 (b) after annealing for 2h at 1000°C. The surface is angled by 45° to show the correspondence between the surface and coating/substrate interface. It is possible to identify the correspondence of the alumina grain boundary with the grain boundary of the substrate for IN718 (indicative lines), but no correspondence of the surface grain boundary is present for the IN625.

SEM and EDS analyses of the cross-sections of the alumina-coated IN625 (Figure 6.8a) and IN718 (Figure 6.8b) present a similar behavior close to the substrate-thin film interface. After annealing, the substrate region near the interface exhibits structures characteristic of Kirkendall porosity. This type of porosity represents the removal of alloying elements from the substrate matrix while forming TGOs. Ti and Cr diffuse into the alumina layer and accumulate in the substrate/coating interface, forming a gradient mixed layer, which might be responsible for the adhesion improvement. For Ni–Cr alloys, the voids are due to the simultaneous diffusion of Cr and Ni. Specifically, the diffusion kinetics in the chromium removal zone dictates the formation of voids [338]. Since Cr diffuses faster than Ni and when a net flux of vacancies is established, the condensation of the vacancies contributes to void formation and/or their growth [339].

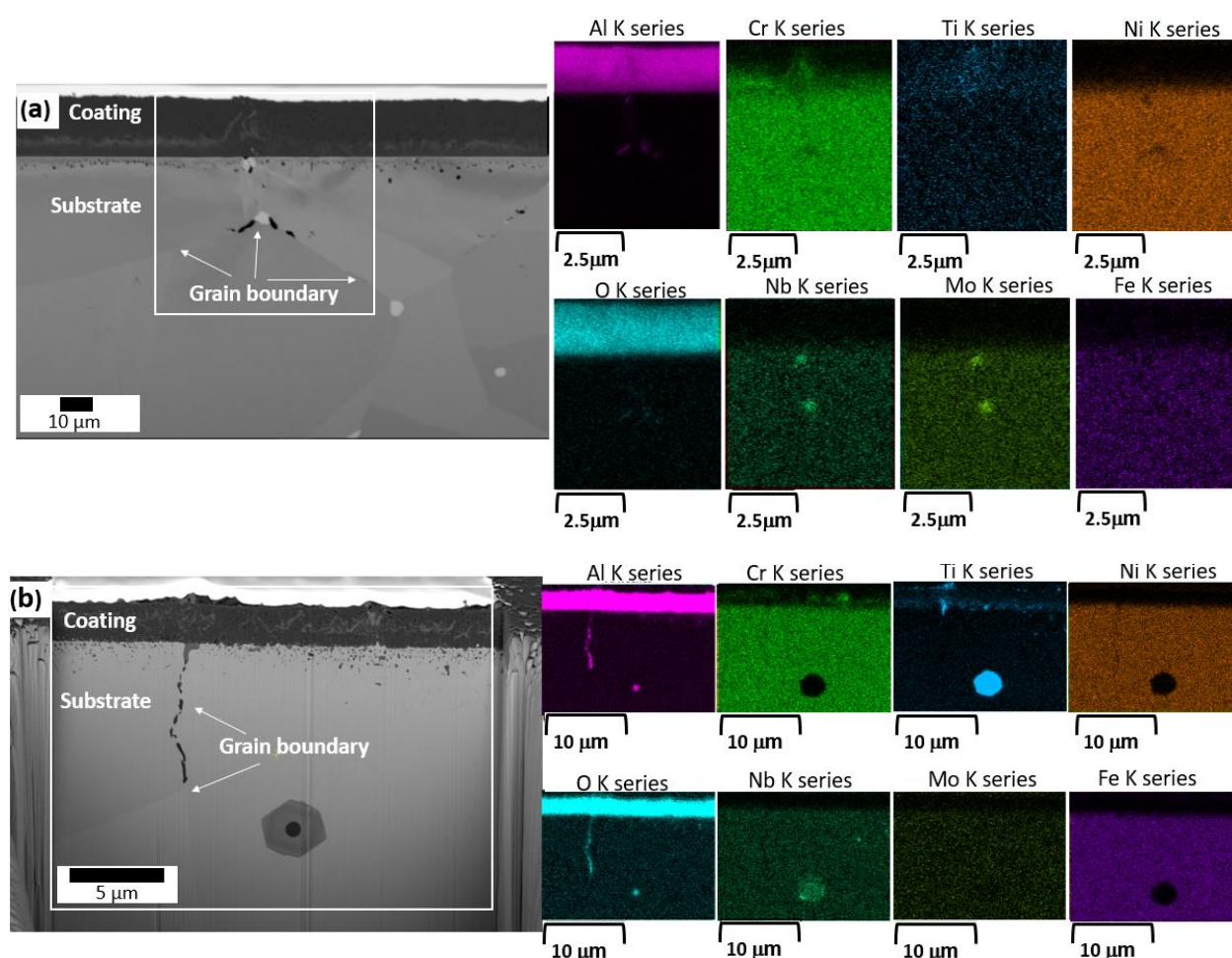


Figure 6.8 FIB SEM cross-sections and EDS maps of alumina-coated IN625 (a) and IN718 (b) after annealing at 1000°C for 2h. EDS maps correspond to the highlighted rectangular areas.

6.4.3 Heavy Oil Fouling on Alumina-Coated Inconel Surfaces

To obtain more insight into the interaction of the heavy oil during the fouling experiments, we studied both types of annealed substrate-coating systems by lower magnification SEM images (Figure 6.9a and Figure 6.10a). The samples exhibited areas with carbonaceous materials in the form of islands with structural differences. For IN718 (Figure 6.9a), outside the area completely covered by coke, the sample is similar to the one without fouling (Figure 6.6a). When analyzing the EDS data from the alumina-coated IN718 after fouling (Figure 6.9b), it is noticeable that the surface is similar to the samples before fouling (Figure 6.6b). Besides this similarity, after fouling, it exhibits a lower concentration of Ti and Cr in the grain boundary regions, leading to a possible interaction of these areas with the heavy oil during the hydrocracking reaction. A small amount of carbon is evenly distributed on the alumina-coated IN718 after fouling. A weak, evenly distributed sulfur signal was detected, which is expected to arise from the sulfur present on the adherent carbonaceous material. No clear sign of sulfidation was detected on the coated IN718.

For IN625 (Figure 6.10) after fouling, the cracks became more visible and deeper, clearly with less TGO than the surface of the IN718 sample (Figure 6.9). In addition, the alumina-coated IN625 surface after fouling (Figure 6.10a) does not indicate the characteristic crater-like structures observed prior to fouling (Figure 6.5). The EDS maps of the cross-section of alumina-coated IN625 (Figure 6.10b) confirm that the cracked region is mainly void, and carbon and sulfur are present in the cracked area.

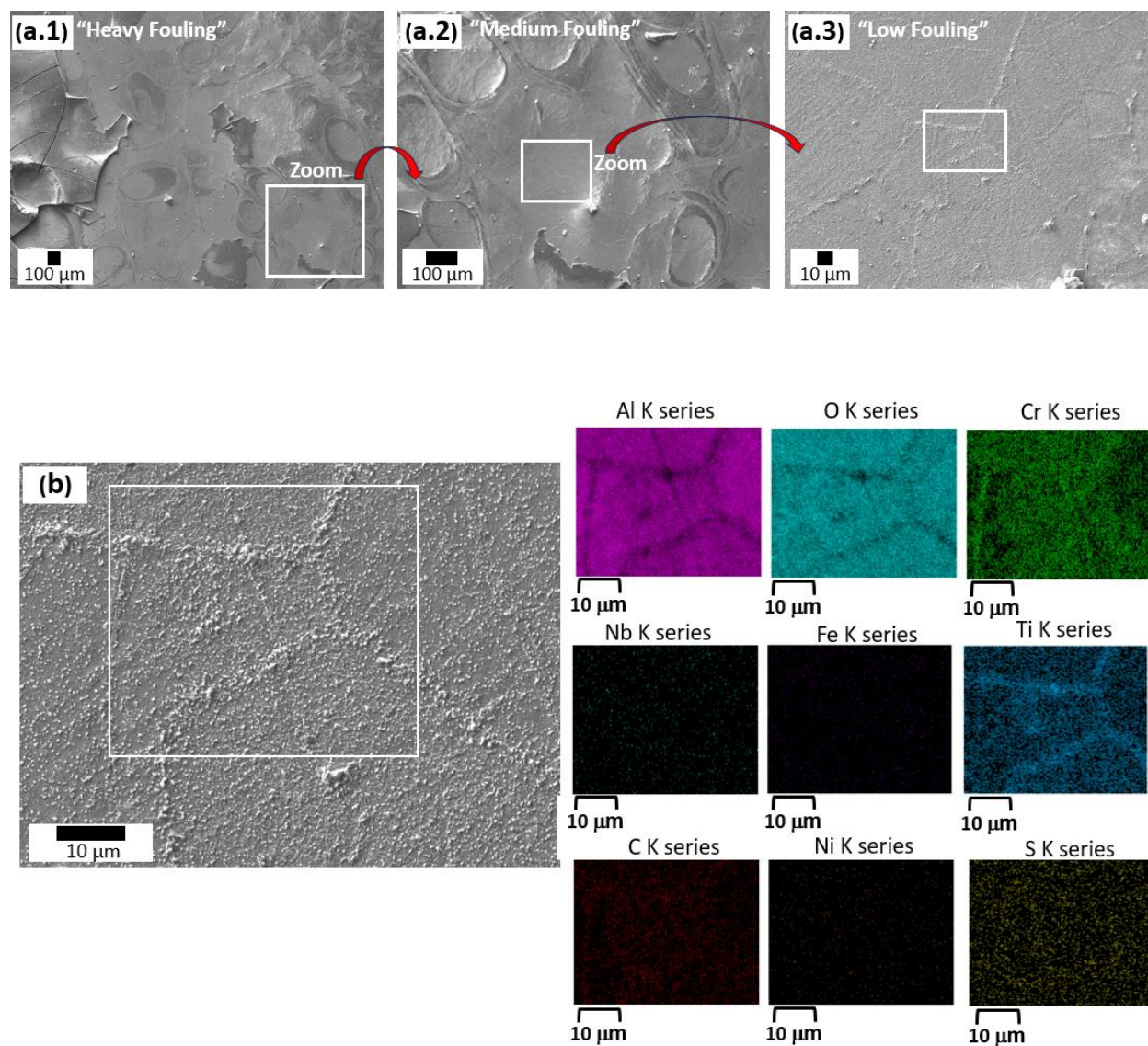


Figure 6.9 Alumina-coated IN718 after annealing for 2 h at 1000 °C followed by heavy oil fouling for 2 h at 450 °C: a) SEM images of representative areas at different magnifications; b) Magnified SEM image of the rectangular section of (a.3) and corresponding EDS maps.

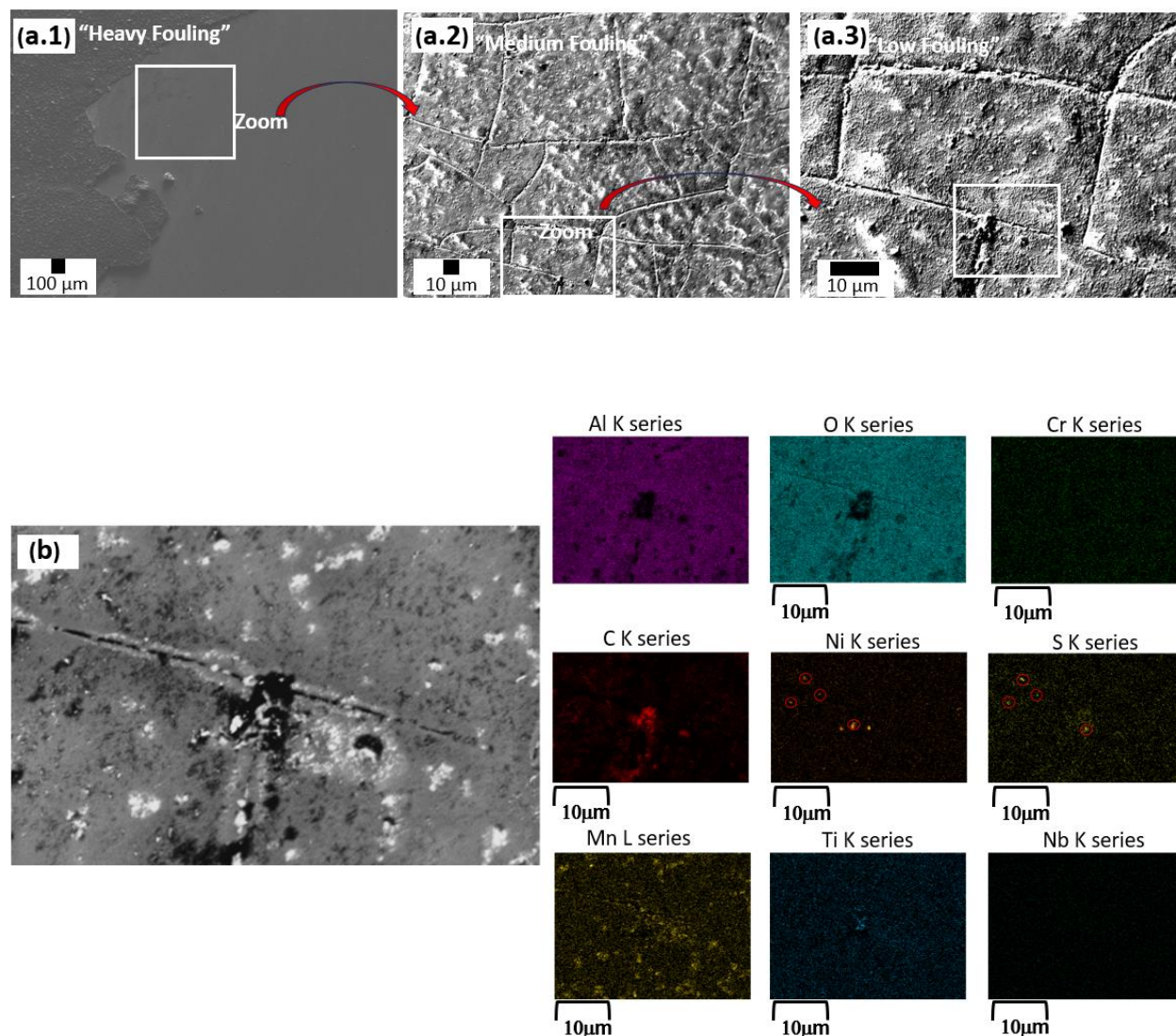


Figure 6.10 Alumina-coated IN625 annealed for 2 h at 1000 °C followed by heavy oil fouling for 2 h at 450 °C: a) SEM images at different magnifications, and b) Magnified SEM image of region (a.3) and corresponding EDS maps.

Analysis of the FIB-prepared cross-sections after fouling provides complementary information about the possible diffusion of sulfur and carbon toward the substrate. For the FIB cut, we chose a location that contained coke islands and visible grain boundaries for IN718 (Figure 6.11a.1), and a crack for IN625 (Figure 6.11b.1). Here, we did not observe any internal diffusion of S or C for either one of the coated substrates. Comparing the EDS results from samples before and after fouling, no differences in patterns of elemental diffusion could be discerned for IN718 (Figure 6.11a.2).

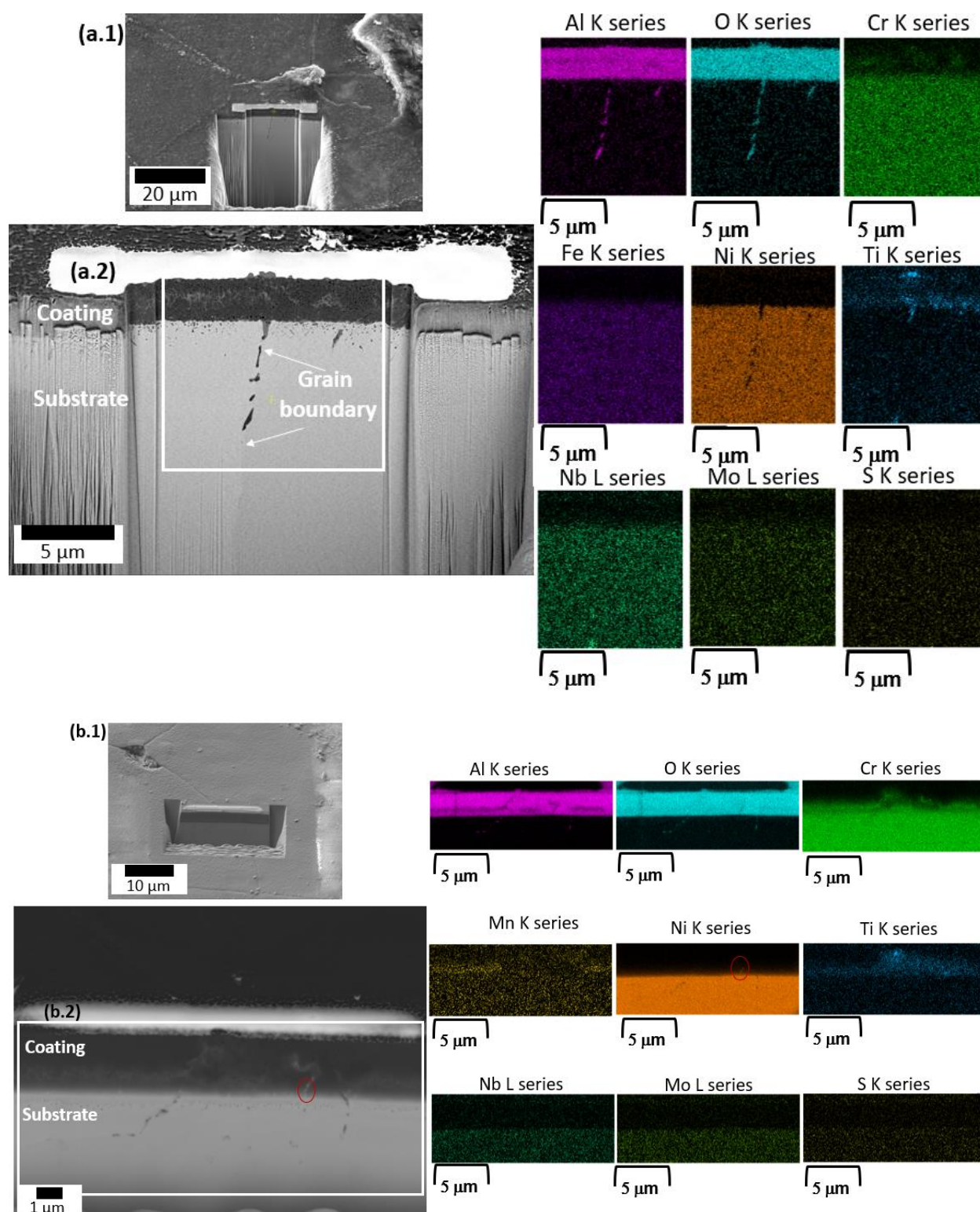


Figure 6.11 SEM images and EDS maps on the FIB-prepared cross-sections of alumina-coated IN718 (a) and IN625 (b) samples after annealing at 1000 °C for 2 h followed by fouling at 450 °C for 2 h. Images a.1 and b.1 show the surface of the cut area, and EDS maps are taken from the highlighted rectangular areas in a.2 and b.2.

The protection against fouling of the as-deposited alumina was also tested. The cross-section of alumina-coated IN718 (Figure 6.12a) and IN625 (Figure 6.12b) shows no adherent layer on their surface. The EDS maps indicate no elemental diffusion from the alloy or sulfur infiltration in the coating matrix. Both as-deposited coating systems effectively protected the surface against the formation of scales and the deposition of carbonaceous material.

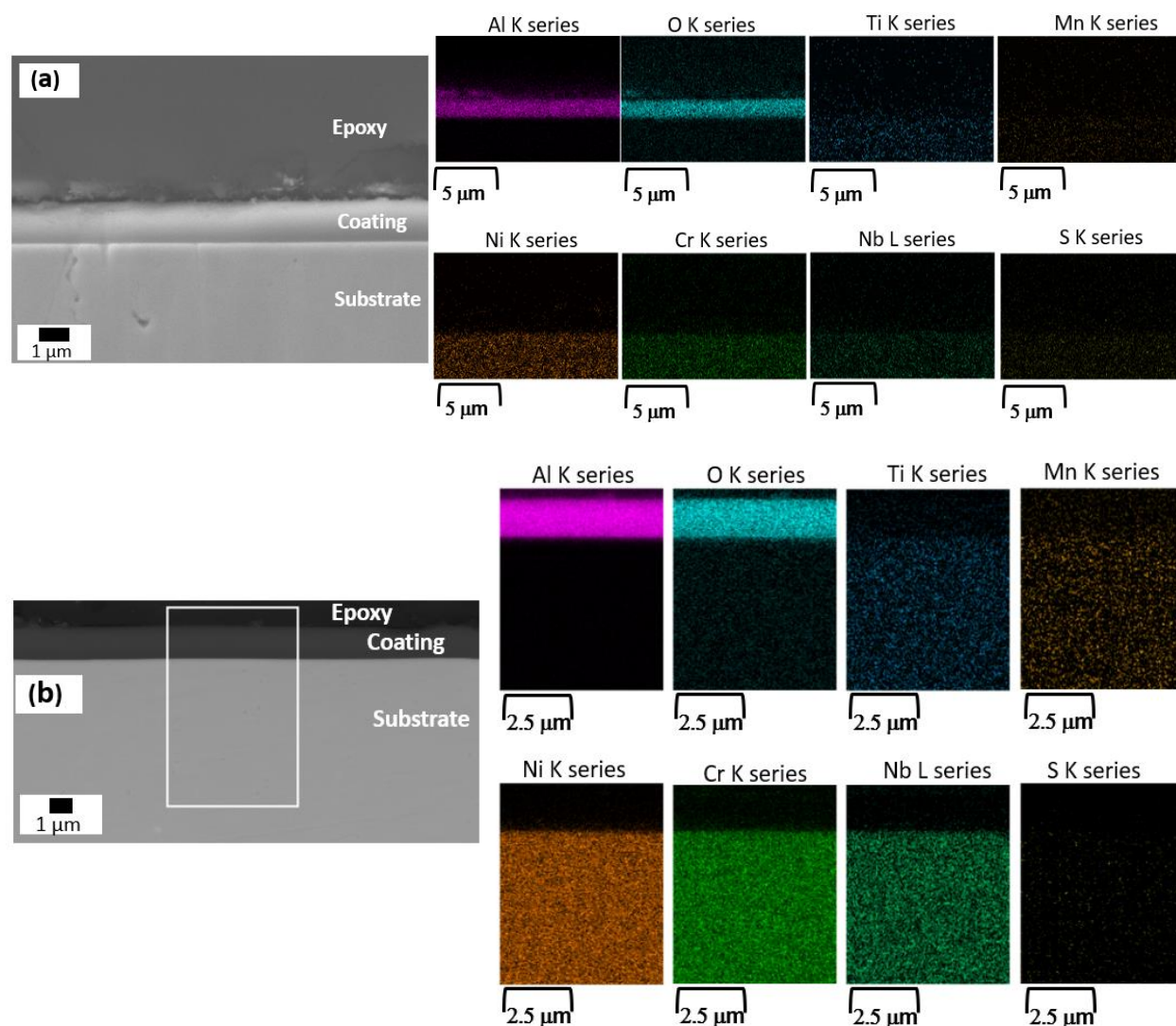


Figure 6.12 SEM images and EDS maps on the cross-sections of as-deposited alumina on IN718 (a) and IN625 (b) after fouling at 450 °C for 2 h. The EDS of image (a) is taken from the whole area, and image (b) is taken from the highlighted rectangular area.

6.5 Discussion

The coatings were optimized and deposited on the nickel alloys in an amorphous state. The properties of the substrates, such as hardness, elastic modulus, and thermal characteristics, also affect the properties of the PVD coatings [340]. The H and E_r values for as-deposited and annealed coatings on IN718 and IN625 are comparable within the experimental error (see Table 6.4). The substrates may cause possible changes in the coating residual stress, affecting the mechanical behavior such as fracture toughness and adhesion [341]. The as-deposited alumina adhesion on IN625 is about 20% higher than the adhesion on IN718. However, the coating adhesion increased on both substrates after annealing, reaching equivalent LC_2 values at 1000 °C, thus increasing 3 times for IN718 and 2.5 times for IN625. The improvement of adhesion after annealing can be related to the formation of TGO at the interface.

The uncoated alloys oxidation is characterized by the formation of Al_2O_3 at the grain boundaries, Ti oxides at the scale-alloy interface, main scale containing Cr, Nb, $(Mn,Cr)_3O_4$ spinel, and metal carbide precipitates [262], [342]. The coating affected the oxidation of the alloys, where the expected Nb oxide layer was not observed, and Mn diffusion was observed only for IN625. Accumulation of Cr and Ti at the substrate-coating interface was observed in both IN625 and IN718 (Figure 6.8). Chromium- and titanium-derived TGO can improve alumina adhesion due to the interface enrichment with Ti and Cr oxide [262]. Ti has a high interaction energy with alumina, and the adhesion energy to separate Cr_2O_3 from Al_2O_3 is higher than the alumina cohesion energy [343]. The titanium concentration on annealed IN718 is prominent, attributable to a higher Ti content (1% in IN718 compared to 0.4% in IN625 – Table 6.1). The possible formation of manganese spinel decreases the evaporation and formation rate of volatile Cr-species [344]. Thus, manganese structures formed on IN625, reducing the Cr_2O_3 formation.

During annealing, the coatings undergo phase transformation and show polymorphism (Figure 6.2 and Figure 6.3). The volume change associated with the alumina phase transformation combined with CTE mismatch generate stress that can relax through defect formation, indicated by the cracks seen in Figure 6.5 and Figure 6.6. For example, the transformation of the γ - Al_2O_3 cubic phase (density, $d = 3.56 \text{ g cm}^{-3}$) to α - Al_2O_3 hexagonal phase ($d = 3.98 \text{ g cm}^{-3}$) results in a volume reduction of approximately 10 % and a large increase in density [345]. The coating thickness, heating rate, and grain size may affect microstructural changes during annealing. Specifically, it

has been shown that the α - Al_2O_3 phase formation at 1000 °C dominates for sputtered coatings over a threshold thickness of 1.2 μm [346]. The annealing of amorphous sputtered films at heating rates above 25 °C/min contributes to the formation of thermodynamically demanding phases [347]. Therefore, in our case, with films of about 1.5 μm and a heating rate of 60 °C/min, the conditions favor the formation of the α - Al_2O_3 phase.

TGO is present on the surface of the coatings and is characterized by a granular microstructure (Figure 6.5 and Figure 6.6). A higher quantity of TGO forms in the coating defect regions, providing a “short-circuit path” through the coating to the surface, enabling faster diffusion. The tower-like protrusion growth induced the formation of more defects in the coating structure. Oxidation of NbC precipitates to Nb_2O_5 has been shown to create tower-like protrusions [337], [348], [349]. In addition, the compressive stress caused by the formation of alumina and other inner oxides in certain regions (such as seen in Figure 6.8) could help induce the material ejection from the grain boundaries and formation of TGO. The formation of aluminum oxides inbetween the grains deep in the IN718 and IN625 alloy matrices has been pointed out by several authors [262], [333], [338].

In our experiments, the sensitivity of the alumina-coated Inconel substrates to fouling has been tested at a temperature of 450 °C over 2h, to induce the thermally-activated reaction of aliphatic sulfur compounds from heavy crude oil that forms hydrogen sulfide. In the fouling testing reactor, complex environments susceptible to the exposure of combined hot gases emanating from the oil (H_2 , CO, CO_2 , H_2 , and H_2S) have an increased number of reaction pathways to degrade the coating and the substrate. The protectiveness of the coating system against fouling depends on surface passivation. Alumina can be considered immune to oxygen environments [350], and has shown to be resistant to sulfidation [50], [89].

Neither the as-deposited alumina nor the annealed system showed signs of delamination after the fouling tests for both substrates. No adherent fouling and internal oxidation were observed on the amorphous as-deposited alumina samples (Figure 6.12). However, annealing introduces other oxides on the surface of the Al_2O_3 coating, which are less protective against fouling. The annealed surfaces accumulated coke (Figure 6.9a and Figure 6.10a). Conversely, the formation of TGO from the substrate material healed the coating defects, closing the short-circuit paths and enhanced the substrate protection. As a result, no internal degradation is observed in the annealed coating

systems. However, after the fouling reaction, the signal of TGO on the surface is reduced in both systems (Figure 6.9b and Figure 6.10b), and the cracks became significantly more apparent with deeper grooves on the IN625 surface. In addition, red ellipses in Figure 6.10b identify S and Ni in the same defective region, suggesting sulfidation through nickel sulfide formation on the IN625 system. Figure 6.11b.2 shows a marked line from the substrate, characterizing heavier element diffusion. A red ellipse indicates nickel in that coating area, suggesting diffusion of this element. The larger grain size of IN718 compared to IN625 should minimize the substrate elemental diffusion, while increasing the protectiveness of the IN718/coating system.

The results indicate that the alumina surface effectively protects against heavy oil fouling; however, the underlying substrate plays a role in the sulfidation and coking propensity. The as-deposited alumina, due to its purity and amorphous nature, is superior in protecting against fouling when compared to alumina annealed at 1000 °C. Even though the annealed alumina has a higher hardness and adhesion that can be beneficial to avoid erosion and wear, the high-temperature annealing step may compromise the integrity of the substrates in practical applications. Therefore, when considering technological applications, one should consider the effect of the underlying substrate on the formation of pores and cracks, and how the substrate interacts with the working environment.

6.6 Conclusions

Near-stoichiometric alumina coatings reactively sputter-deposited on IN718 and IN625 interact with the substrates after annealing and protect the surface against fouling. The key findings are as follows:

1. The refractive index variation through the coating thickness is an indicator of the alumina homogeneity, while a higher homogeneity is related to enhanced adhesion. Annealing up to 1000 °C improved the adhesion on both substrates. LC_2 values indicate that the adhesion of alumina is initially slightly better on IN625 compared to IN718, and is the same after annealing up to 1000 °C.
2. The annealed alumina exhibits polymorphism: γ - Al_2O_3 prevails at 800 and 900 °C, and α - Al_2O_3 is present at 1000 °C. During annealing at 1000 °C for 2 h, mainly Cr and Ti diffuse through the alumina coating, preferentially at grain boundaries and defect areas. For IN625, Mn diffusion is also detected on the surface.

3. Annealed alumina-coated IN718 showed a TGO structure on the surface, which follows grain boundaries and cracks formed in the coating. In contrast, for the alumina on IN625 samples, crater-like structures are present and no relation to the grain boundaries could be established.

Amorphous alumina protects against adherent fouling with no clear sign of coke or sulfidation formation. For the alumina samples annealed at 1000 °C, coke is present on the surface when IN718 is applied, while a higher degree of coke formation and possible sulfidation is detected when IN625 is used as substrate.

6.7 Acknowledgements

The authors wish to thank Mr. Francis Turcot, Mr. Francis Boutet, and Mr. Jean Ghantous for their expert technical assistance. The project was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada through the NSERC-Alliance grant (no. ALLRP 576758 - 22), by Prima Quebec (grant no. R24-13-003), and by Velan Inc.

CHAPTER 7 REACTIVELY SPUTTERED COATINGS FOR THE PROTECTION OF A NICKEL-BASED ALLOY AGAINST HEAVY OIL CORROSION FOULING

7.1 Introduction

The wear of critical components in the petrochemical industry, such as valves, is associated with carbon deposition, particle erosion, and corrosion. When the surfaces are composed of reactive metallic components, such as WC-Ni and WC-Co, selective corrosion may occur when exposed to corrosive environments [351]. Although such structures are generally mechanically resistant, they form a brittle metal-sulfide film on the surface [71]. For high-temperature protection, carbides, borides, nitrides, silicides, and several of their combinations are widely used [200]. Al_2O_3 is anticipated to offer the highest level of protection against sulfur corrosion, according to results related to aluminum-containing alloys [89]. Sputter-deposited amorphous alumina coatings were shown to inhibit coke growth and prevent sulfidation [323]. However, the Al_2O_3 coatings are brittle in nature, and alternatives are sought to prevent corrosion in wear-demanding applications. A strong coating adhesion is fundamental to minimize the diffusion from the environment to the substrate and interfacial diffusion, preserving the integrity of the protective barrier.

Titanium oxides, carbides, and nitrides, which are already wear-resistant, demonstrated their anti-coking properties. Ti nitrides and carbides have superior protection than Ti oxides [220]. TiN/ SiO_2 double-layer coating showed a synergistic effect, indicating anti-coke properties and higher oxidation resistance due to the amorphous nature of the silica layer [352]. Coke growth inhibition by TiN single layer coating was reported to surpass even that of alumina [221]; however, TiN starts to oxidize at around 350 °C [220], forming an under dense rutile TiO_2 top layer [353] which fails to protect the nitride from further oxidation and corrosion compromising its mechanical performance. A way to overcome the limitations of TiN is to add Al as a substitutional atom in the Ti-N lattice. If the ratio of Al/Ti is kept below a threshold (varying from 0.5 to 0.65, depending on the deposition conditions) [354], [355], the TiN structure is preserved in a single FCC phase, leading to solid-solution hardening. At high temperatures in an oxidizing atmosphere, in addition to the TiO_2 , the presence of Al drives the formation of Al_2O_3 on the surface of the coating [356],

which works as a dense and well-adhering passive layer for oxidation and corrosion. Therefore, TiAlN exhibits superior mechanical, oxidation, and thermal damage resistance at higher temperatures compared to TiN [357]. Nonetheless, despite reports of the enhanced performance of TiAlN in preventing the degradation of cutting tools [358], [359], [360], very little is reported on its sulfidation and oil fouling protection. One of the few examples is the study of TiAlN/Nb multilayer coatings, which showed promising sulfidation resistance at temperatures up to 900 °C with reduced oxidation of the protective layer [361].

Preferential grain boundary diffusion occurs during oxidation [362] and sulfidation [261], causing intergranular corrosion cracking. Materials that prevent oxidation should also provide sulfidation protection, as the classical theory of oxidation applies to sulfidation, carburizing, and nitriding [95]. However, it is necessary to consider that the sulfur corrosion rate is typically much faster than that caused by the corresponding oxide [89]. In fact, the sulfidation rate of metallic components is 10^4 to 10^6 times faster [92]. The oxidation protection performance of several titanium- and silicon-based nitrides was compared on silicon-based substrates, showing the superiority of the amorphous silicon nitrides at temperatures up to 1500 °C [363]. For comparison, SiBCN deposited on γ -TiAl alloy substrate was found to exhibit good mechanical properties, stable amorphous structure, and high oxidation resistance at 800 °C [364].

Hydrocracking of heavy sour oils requires materials that are resistant to severe conditions. Operating temperature above 400 °C increases the diffusion coefficient, requiring surfaces with lower reactivity to minimize corrosion. The present work explores two types of polycrystalline and amorphous nitride thin films deposited by Physical Vapor Deposition (PVD), namely reactive sputtering, as passive layers to protect the Inconel 718 substrates during hydrocracking reactions. Magnetron sputtering applied here enabled precise control over the coating's composition and thickness, while achieving high packing density, high hardness, and good adhesion [326]. Borided Inconel 718 was explored as a standalone solution to minimize fouling, and as a substrate to create a gradient of the elasto-plastic properties from the substrate toward the coatings.

7.2 Materials and methods

7.2.1 Surface preparation

Two types of substrates were applied in this work, namely bare Inconel 718 alloy (Table 7.1), and Inconel 718 diffused with boron (25x25x3 mm³). Boron was diffused industrially into the Inconel 718 through a thermochemical surface hardening process. The substrate surface was mirror-polished using SiC papers with varying grit size (100 to 800), followed by diamond particle suspension (from 3 µm to 1 µm) varying Struer's magnetic pads, finishing with colloidal silica suspension.

Table 7.1 Elemental composition of the bare Inconel 718 substrate.

	Ni	Cr	Fe	Nb+Ta	Mo	Ti	Al	Co	Si	C
[wt.%]	52.9	19.4	Balance	5.09	2.93	0.93	0.44	0.23	0.15	0.04

7.2.2 Coating deposition

The coatings were prepared in a multi-target sputtering system consisting of a 700 liters volume stainless steel vacuum chamber turbomolecularly pumped to a base pressure of 3×10^{-6} Torr. The sputtering system featured two magnetron configurations, namely (i) two planar circular magnetrons (10 cm diameter) [364], and (ii) a cylindrical magnetron (Robeko and Sputtering Components) with a 550 mm length and a 152 mm outer diameter.

7.2.2.1 Polycrystalline metal nitride film deposition (pc-Coating)

The substrates were first sputter-cleaned in Ar plasma at 3 mTorr and a bias voltage of -60 V for 30 min while heated at 350 °C. Using the cylindrical magnetron, the TiAl cylindrical target rotated at 10 rpm and was powered from a pulsed DC power supply (Rübig MP 120) operating at a frequency of 0.9 kHz, 740 V and a duty cycle of 90%. A 0.5 µm thick metal interlayer was first deposited by sputtering with pure argon at a pressure of 3 mTorr and a bias of -60 V. Subsequently, nitrogen was introduced to reach a total working pressure of 3.5 mTorr. The deposition continued for 2 hours, with no substrate bias applied during the first hour, followed by gradually increasing

the bias voltage from 0 V to -60 V during the second hour. The total film thickness was about 4.5 micrometers.

7.2.2.2 Amorphous silicon-based nitride film deposition (am-Coating)

The amorphous silicon-based coatings (am-Coating) were prepared at a substrate temperature of 450 °C in a confocal configuration using two planar circular magnetrons. The substrate was first cleaned in pure Ar plasma at 13 mTorr for 20 min with a bias voltage of -420 V. Subsequently, in selected experiments, an interlayer of a-Si, about 0.7 µm thick, was deposited using a Si target and a pulsed DC power supply (Rübig MP 120) operating at a frequency of 10 kHz with an 85% duty cycle. The deposition was performed in Ar at 4 mTorr, target power of 250 W, and no substrate bias was applied.

The complete amorphous films were then prepared by co-sputtering from a B₄C target connected to a radio frequency power supply (T&C Power Conversion AG 0613) and the Si target powered from the pulsed DC power supply (Rübig MP 120). The targets were first cleaned for 20 minutes at 4 mTorr in Ar at -525 V (~155 W) for the DC-driven target, and at -160 V (250 W) for the RF-driven target. Subsequently, deposition started after opening a shutter, while introducing nitrogen at an initial partial pressure of 0.1 mTorr. The nitrogen flow was then increased until reaching an Ar:N₂ ratio of 60:40 and a total working pressure at 4 mTorr, while a power of 400 W was applied on each target. The total thickness after 2 hours of deposition was about 2.5 micrometers.

7.2.3 Microscopy

The microstructure and elemental composition of the coating were examined with a scanning electron microscope (SEM, JEOL JSM-7600F) equipped with an energy dispersive X-ray spectrometer (EDS), and an Oxford Instruments X-Max detector. The electron beam energy was 15 keV. Prior to embedding the cross-sections in epoxy, a 20 nm thick gold layer was sputtered on the coated surfaces, followed by copper electroplating in a 10 M CuSO₄ solution at 2 V for 20 min. The gold and copper layers were added to best separate the fouling from the epoxy.

7.2.4 Micro-scratch testing

A Micro Combi Tester (MCT3, Anton Paar, Graz, Austria) equipped with a 200 µm radius Rockwell diamond tip was employed to measure the adhesion of the thin films. A progressive load from 0.03 to 20 N was applied over a 3 mm scratch length at a rate of 6 mm/min. The scratch tracks

were analyzed according to ASTM C1624 standards using optical microscopy. The identified critical loads (LC_1 and LC_2) correspond to coating cohesive and adhesive failure, respectively, leading to delamination. At least two scratches were performed for each sample ensuring reproducibility.

7.2.5 Nanoindentation

The hardness (H) and reduced Young's modulus (E_r) of the coatings were measured with a depth-sensing indentation instrument (Hysitron Inc. – Bruker TriboIndenter) equipped with a Berkovich pyramidal tip. A fused silica standard was used to calibrate the area function of the tip. The measurements used multicycle indentations with progressively increasing loads from 1 to 200 mN. Each sample underwent testing with a 4x4 indentation matrix, and properties were calculated from at least 25 indentations per spot. Coating hardness (H) and modulus (E_r) values were obtained from a plateau region unaffected by penetration depth or tip effects. The values were determined using the methodology proposed in the ISO 14577-4 standard, and the unloading cycles were analyzed using the Oliver and Pharr method [330].

7.2.6 X-ray diffraction

X-ray diffraction (XRD) measurements were performed with a Bruker D8 Discover X-ray diffractometer in grazing angle geometry with Cu K α radiation (8.04 keV) using a scintillator detector. The incident beam angle was kept at 5° for all samples. The incident beam optics included a Gobel mirror and 0.6 mm divergence slit, while diffracted beam optics utilized automated slits. The 2 θ scans were conducted over a range of 20 to 90 degrees with a step size of 0.0103°. The XRD data was processed using Bruker DIFFRAC.EVA V4.3 software, which included background subtraction and k- α 2 stripping.

7.2.7 Contact angle

Contact angle experiments were performed using an OCA 15EC contact angle measuring and contour analysis system from Neurtek Instruments. The measurements were conducted at ambient temperature, using a 4 μ L droplet of distilled water, glycerol, and oleic acid as reference liquids. The syringe tip carefully transferred the droplet onto the surface, and the contact angle was measured after a 10-second stabilization period. The reported contact angles represent the average of 3 to 5 measurements.

The surface energy was calculated based on contact angle measurements, with the Owens–Wendt–Rabel–Kaelble (OWRK) method [184]. This method allows one to obtain intermediate quantitative results [188]. In order to determine the solid's surface energy dispersive and polar components, the OWRK equation (2.1.6) can be rearranged in a linear correlation [365] following the equation:

$$\frac{\gamma_l(1 + \cos\theta)}{2(\gamma_l^d)^{1/2}} = (\gamma_s^p)^{1/2} \frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}} + (\gamma_s^d)^{1/2} \quad (7.1)$$

Plotting $\frac{\gamma_l(1+\cos\theta)}{2(\gamma_l^d)^{1/2}}$ against $\frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}}$ produces a linear correlation. The total surface energy of the liquid along with its dispersive and polar components are known (Table 7.2). In such case, the linear regression allows determining the γ_s^d , and the γ_s^p as the square of the intercept and the square of the slope, respectively [366].

Table 7.2 Surface energy components of the liquids in mJ/m².

Liquid	γ_l^p	γ_l^d	γ_l
Distilled Water	51.0	21.8	72.8
Glycerol	30.0	34.0	64.0
Oleic Acid	2.0	30.0	32.0

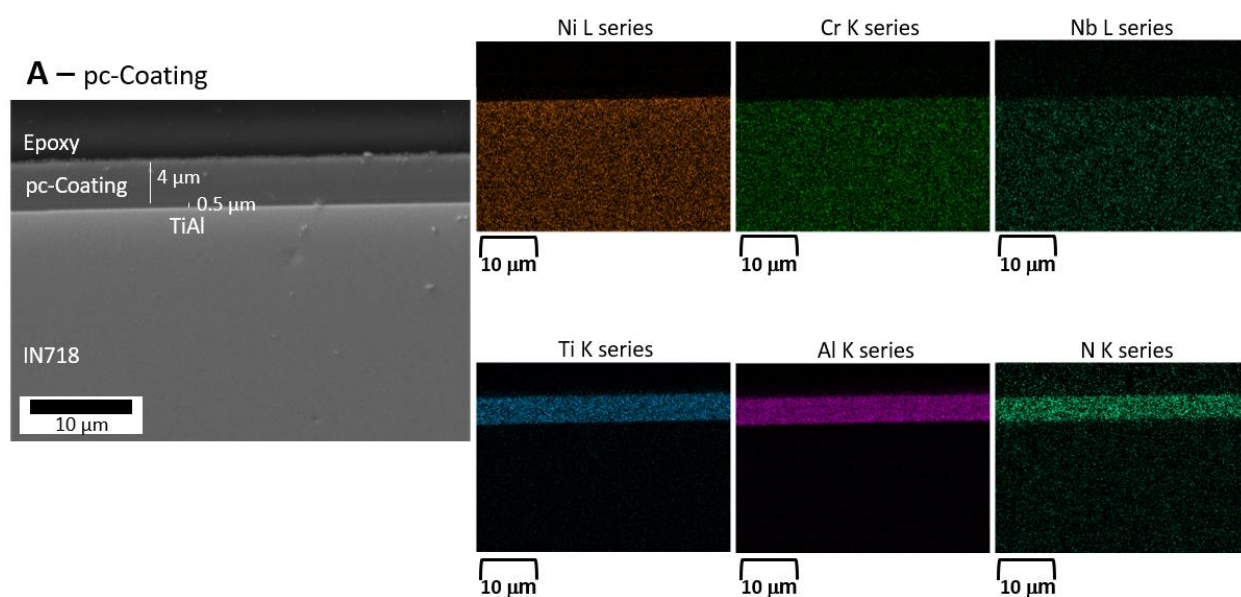
7.2.8 Fouling test

The samples were placed vertically in an autoclave reactor containing 200 g of heavy oil with 6 wt.% of sulfur. The reactor, described in more detail elsewhere [323], was pressurized with argon to 11.3 MPa and purged for 5 minutes to remove oxygen. The temperature was raised to 450 °C and held for 2 hours to ensure complete cracking of the heavy oil. The reactor has been left to cool down overnight before depressurizing it and retrieving the samples. The samples were then washed with a 50:50 mixture of petroleum ether and toluene. Water was used to rinse the samples removing solvent traces. Finally, they were air-dried and stored for further analysis.

7.3 Results and discussion

7.3.1 Coatings deposited on Inconel 718

The coating morphology and composition were determined by SEM and EDS and the results are presented in Figure 7.1. The first coating system consists of a 4 μm thick pc-Coating layer and a 0.5 μm thick TiAl interlayer. In both layers the Ti:Al ratio is close to that of the target. The second am-Coating system consists of a 2.5 μm thick layer and a 0.7 μm thick a-Si interlayer when the latter one is present. The am-Coating deposition conditions were optimized for their best performance corresponding to a high N content and a high Si/C ratio as described in our previous work [364]. Specifically, as confirmed by EDS, a higher concentration of Si is observed closer to the substrate. No interdiffusion of substrate alloying elements and the coating elements has been detected.



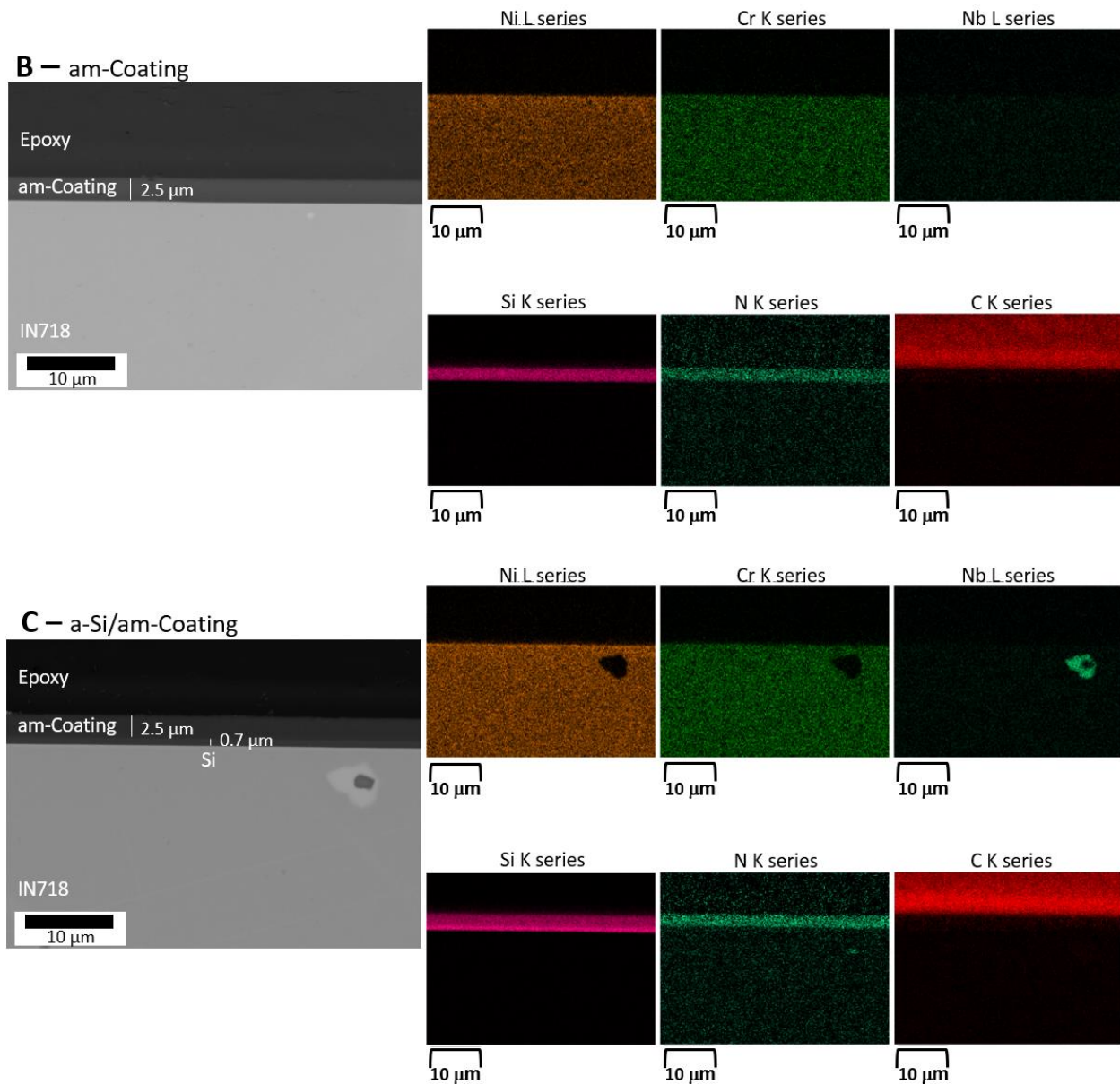


Figure 7.1 Cross-section SEM images of the Inconel 718 substrate coated with A) pc-Coating, B) am-Coating, and C) a-Si/am-Coating. The EDS images represent respective elemental maps.

The mechanical properties of the nitride coatings are summarized in Table 7.3. The pc-Coating exhibits a high hardness of 27 GPa, which is generally related to its excellent tribological performance such as wear resistance. However, very high hardness should not be prioritized at the expense of significant elastic property mismatch between the coating and the substrate. The formation of an interlayer provides the necessary elasto-plastic properties gradient, avoiding adhesive failure. The H/E_r ratio is associated with the material's elastic strain-to-failure; in fact,

higher values are expected to be an indicator of high wear resistance [367]. In this context, the am-Coating and a-Si/am-Coating systems possess a very high H/E_r ratio.

In addition, other aspects, such as coating adhesion, play a crucial role in the performance. The critical loads were derived from the scratch analysis (Figure 7.2). The LC_1 was identified in the first forward chevron tensile crack, and LC_2 , when buckling and wedging spallation, were observed. The pc-Coating scratch track after LC_1 showed a conformal crack pattern without adhesive failure even at the maximum load tested of 20 N. As seen in Table 7.3, the LC_1 and LC_2 critical load values indicate that the addition of an a-Si interlayer increased the coating cohesion by 23.8% and adhesion by 13.6%.

Table 7.3 Elasto-plastic properties of the nitride coatings deposited on the Inconel 718.

	H (GPa)	E_r (GPa)	H/E_r	LC_1 [N]	LC_2 [N]
TiAl-TiAlN	27 ± 1.9	330 ± 36	0.082	6.12 ± 0.03	>20
SiBCN	17.5 ± 1.3	186 ± 13	0.094	3.99 ± 0.23	7.28 ± 0.16
Si-SiBCN	15.5 ± 1.1	164 ± 21	0.095	4.94 ± 0.06	8.27 ± 0.38

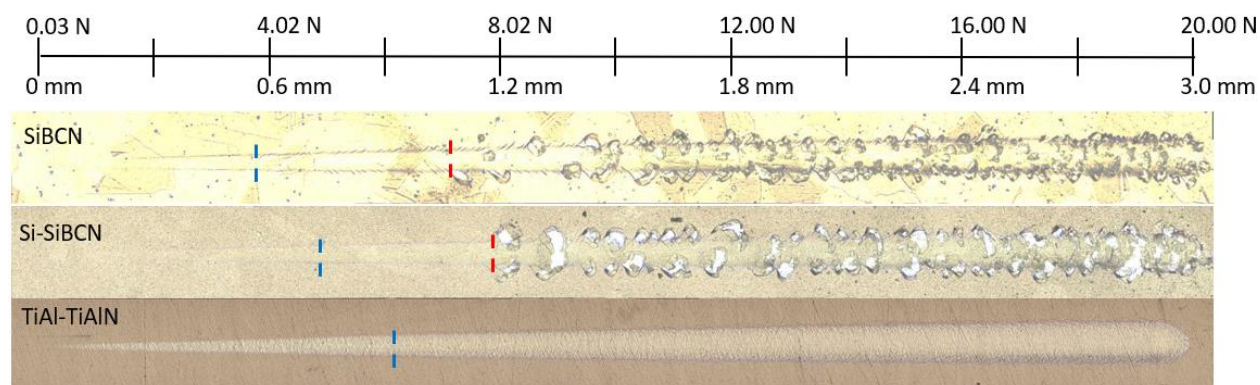


Figure 7.2 Scratch tracks of the am-Coating, a-Si/am-Coating, and pc-Coating systems. The cohesive failure (LC_1) is marked in blue, and the coating adhesion failure (LC_2) is marked in red.

The contact angle measurements (Figure 7.3A) illustrate the interaction between the liquids and the surfaces. For water, the polar component dominates, while for oleic acid, the dispersive component is predominant. Glycerol serves as an intermediate liquid, with nearly equal contributions from its polar (γ_l^p) and dispersive (γ_l^d) components. The contact angle measurements reveal that the pc-Coating exhibits hydrophobic behavior, with a water contact angle greater than 90° [368], whereas the am-Coating does not display hydrophobic characteristics.

Dispersive contributions arise from Van der Waals interactions, while polar contributions are associated with hydrogen bonding [369]. Notably, the electrodynamic interactions – comprising London dispersion forces, Debye forces, and Keesom dipole interactions – are considered long-range forces and collectively categorized as Lifshitz-Van der Waals (LW) interactions. In contrast, hydrogen bonds are classified as short-range (SR) interactions [370].

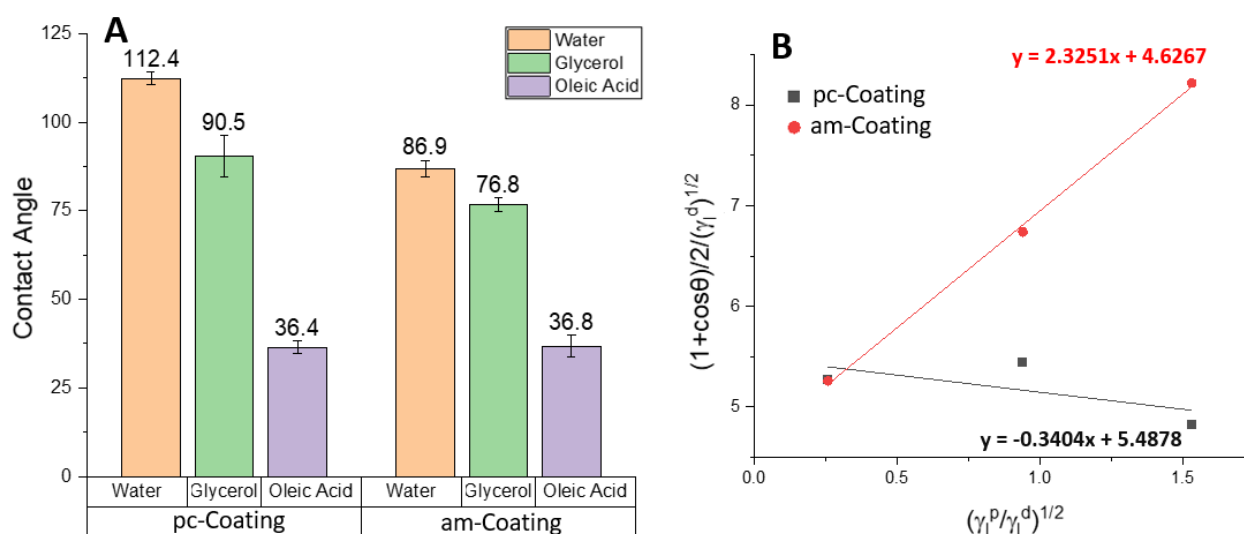


Figure 7.3 A) Contact angles of the surfaces, and B) Linear fitting of the OWRK model.

Figure 7.3B shows linear fitting of the contact angle data using the OWRK model. The γ_s^d , and γ_s^p values of the solids' surface energy were derived from the slope and the intercept of the linear regression equations. The total surface energy of the pc-Coating was found to be 30.2 mJ/m^2 (γ_s^d : 30.1 mJ/m^2 ; γ_s^p : 0.1 mJ/m^2), and that of the am-Coating 26.8 mJ/m^2 (γ_s^d : 21.4 mJ/m^2 ; γ_s^p : 5.4 mJ/m^2). Surface energy correlates with the energy state and equilibrium of the atomic bonds within a material. Generally, materials with stronger internal bonds exhibit higher associated surface energy [371], though increased thickness may reduce surface energy [365]. Consequently, the

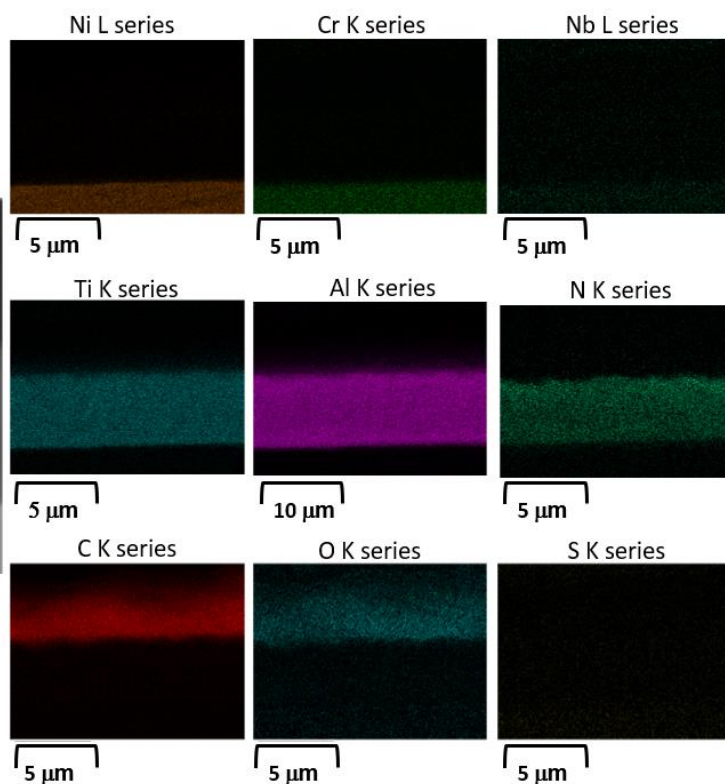
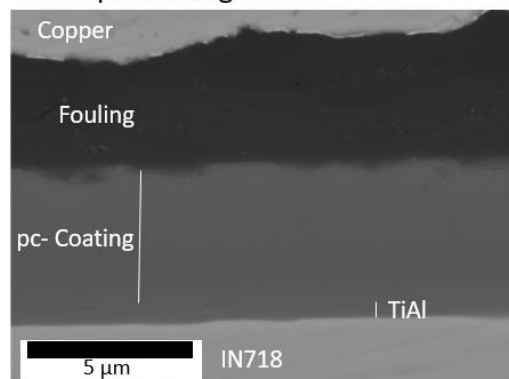
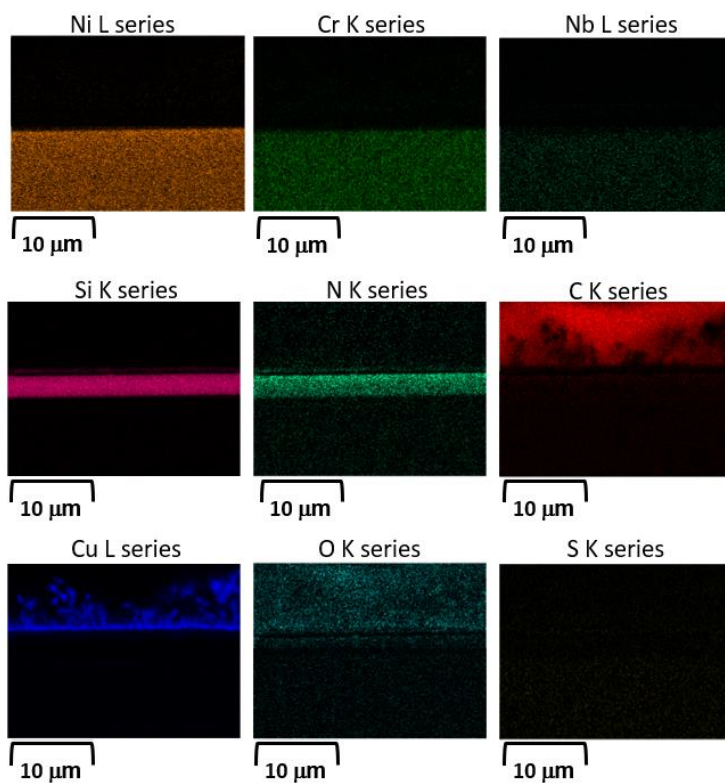
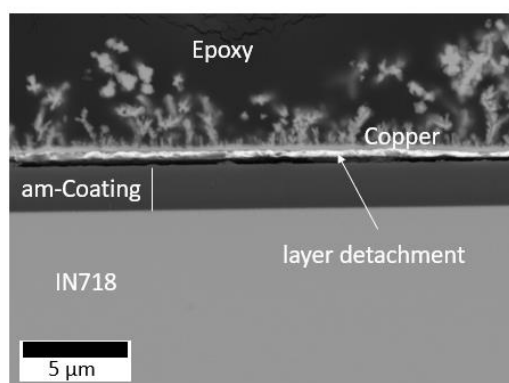
higher surface energy of the pc-Coating could indicate stronger internal bonding, contributing to its superior adhesion and cohesive properties.

7.3.1.1 Fouling

Fouling is characterized by the deposition of unwanted solids on material surfaces, leading to operation challenges in petroleum processing industries. Petroleum fouling occurs through two main mechanisms: physical fouling, where low-solubility materials precipitate, and chemically induced fouling [372]. The vertical arrangement of the samples in the reactor of this study helps mitigate gravitational effects and, consequently, physical fouling. The experimental temperature of 450 °C is above the hydrocracking temperature [106] and in the upper range of vacuum tower furnace processing of heavy oil fraction, strongly inducing coke formation [71]. The oil type influences the structure and mechanism of the fouling [173]. The same type of vacuum tower bottom feed used in the experiments presented in this study generated fouling on the Inconel 718, forming adherent coke, oxides, and sulfides.

The coated Inconel 718 samples were subjected to the fouling test. The SEM cross-section images in Figure 7.4 illustrate the interaction between the surface of the samples and the heavy oil. The cross-section was prepared in the area that showed more signs of fouling. The EDS maps monitor the main elements involved in the substrate corrosion, namely Ni, Cr, and Nb [262], sulfur for sulfidation, and oxygen for oxidation. The other elements on the EDS are pertinent for each tested coating.

No sulfidation or internal oxidation was observed in all samples. The sample coated with the am-Coating without an a-Si interlayer (Figure 7.4B) showed signs of oxidation forming a delaminating layer containing silicon, nitrogen and oxygen above the coating. Virtually no fouling was observed on am-Coating samples with the a-Si interlayer (Figure 7.4C). Besides increasing adhesion, the a-Si interlayer enhanced the am-Coating's cohesive strength, which contributed to avoiding coating oxidation and superficial layer detachment during hydrocracking. For comparison, a layer of about 4 μm of coke formed on the surface of the pc-Coating system (Figure 7.4A). As the coating systems are either amorphous or polycrystalline, we attributed the higher coke formation on the pc-Coating surface to the presence of grains and grain boundaries. Both coatings performed better than the bare Inconel 718, as shown in our previous study.

A – pc-Coating**B – am-Coating**

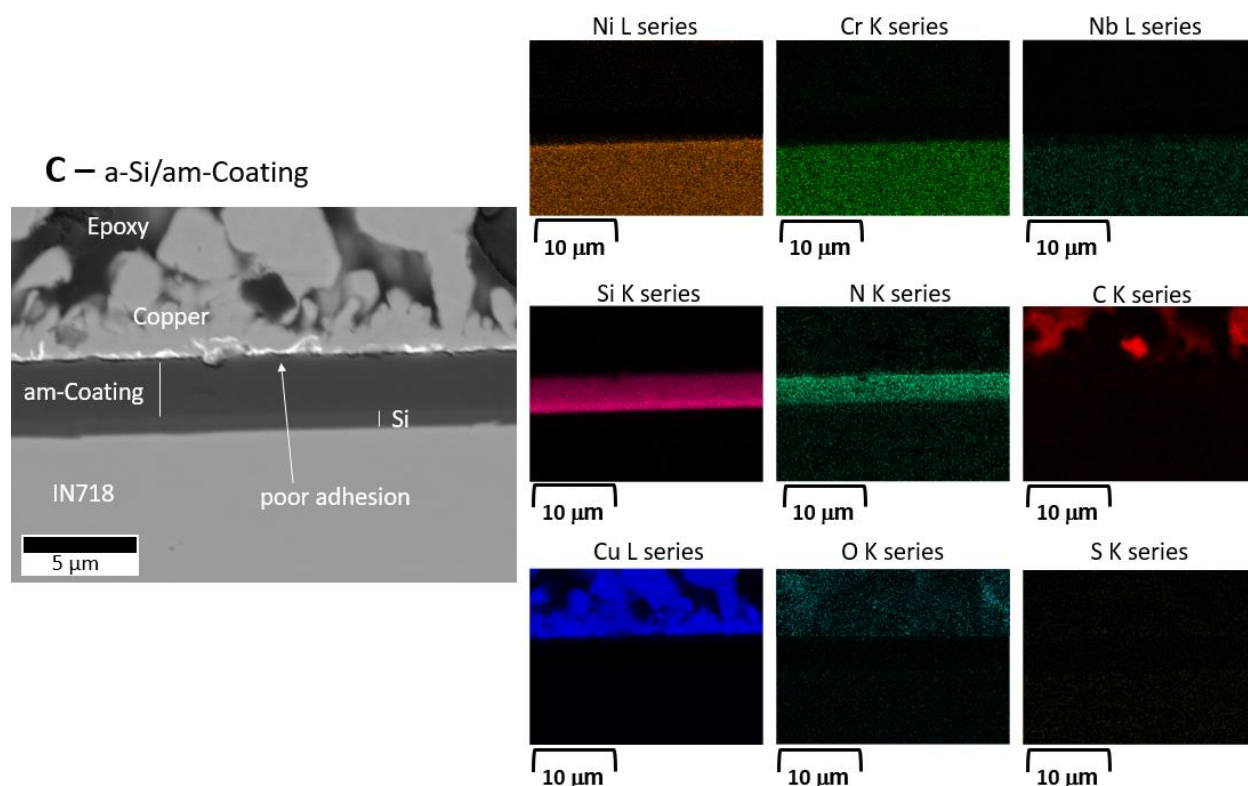


Figure 7.4 Cross-section SEM images and EDS maps of the Inconel 718 alloy with A) pc-Coating, B) am-Coating, and C) a-Si/am-Coating after fouling at 450 °C for 2 h.

The complex physicochemical reactions during crude oil fouling lead to uncertain mechanisms, and they depend on the materials' surface properties. The pc-Coating showed significantly more coke formation on its surface. Physical-mechanical anchoring can be disregarded since the surfaces possess comparable roughness with mirror finishing. Once no diffusion through the coatings has been detected, this phenomenon can also be neglected. Chemical bonding may be the key binding force of coke on the passivated surfaces. A gap between the am-Coating surface and the fouling (coke) layer (Figure 7.4B and Figure 7.4C) suggests that the unwanted fouling layer has poor adhesion.

At the same time, the observed coke layer on the top of the pc-Coating seems to be adherent (Figure 7.4A). Even though more coke is present on the polycrystalline surface as detected by EDS, the XRD showed (Figure 7.5) an amorphous broad scattering at about 25° characterizing carbon only for the amorphous coating without the a-Si interlayer, suggesting formation of different types of coke. In addition, the am-Coating with the a-Si interlayer provided an even better coke protection, and did not form an oxide film on the surface. Often, the surface chemistry from passivating

coatings was overlooked in relation to coke adhesion variation [373]. For comparison, in previous studies, TiN and amorphous SiO₂ surfaces demonstrated distinct coke-inhibiting properties [352]. The difference between TiN and SiO₂ coking resistance is related to coke adhesion, while coke precursor chemisorption on TiN crystalline structure leads to coke strongly bonded to the surface [373].

Amorphous materials such as SiBCN coatings have been shown to exhibit excellent thermal stability [364], retaining its structural integrity even in oxidizing conditions above 1000 °C [363]. Upon oxidation, they form an amorphous SiO₂ layer, which is highly stable and acts as a protective barrier [374]. Generally, silicon-based materials such as borides, carbides, and nitrides demonstrate exceptional chemical inertness at elevated temperatures, offering strong resistance to sulfur attack [375]. While silicon can form sulfides [376], its strong affinity for oxygen leads to the formation of stable SiO₂ [377]. Silicon sulfides are typically formed only under highly reducing conditions with elevated sulfur partial pressures [376], but even then, they tend to decompose or volatilize rather than persist as solid phases [378]. In our case, during heavy oil hydrocracking, a continuous SiO₂ layer is observed on the surface of the am-Coating, even at relatively low temperatures of around 450 °C (Figure 7.5B). Incorporation of the silicon interlayer enhanced the coating's cohesion, thereby indirectly improving its chemical stability and resistance to oxidation (Figure 7.5C).

In contrast to amorphous SiBCN, pc-Coatings such as TiAlN are typically considered less thermally stable, oxidizing at temperatures around 800 °C [379]. This is attributed to the higher reactivity of its metallic components, titanium and aluminum, in both reducing and oxidizing environments. The oxidation of TiAlN has a substantially higher activation energy compared to TiN, with its oxidation resistance largely relying on the formation of Al₂O₃ [380]. While the formation of Al₂O₃ provides better protection than SiO₂, the concurrent generation of TiO₂ affects its protective behavior [381]. TiO₂ tends to form more readily, but is typically porous and less protective, disrupting the development of a continuous Al₂O₃ layer [382]. Additionally, thermodynamic competition between aluminum and titanium during oxidation often results in sub-stoichiometric oxides or defective microstructures, which are less effective in protecting the coating under reducing conditions. When exposed to sulfidation, reactive metallic components form stable sulfides, making them more susceptible to degradation at high temperatures in aggressive environments [383]. However, during hydrocracking at 450 °C, such as in our present

case, no oxidation or sulfidation of the pc-Coating was observed (Figure 7.4C), suggesting its stability under the specific testing conditions corresponding to the real-life operating conditions.

Surface energy plays a role in providing protection against fouling. The comparatively lower total surface energy of the am-Coating, as opposed to the pc-Coating, diminishes surface interactions and significantly reduces coke adhesion. The higher dispersive surface energy (γ_s^d) of the latter one reflects its greater affinity for the organic phase in the heavy oil environment. On the amorphous surfaces, the fouling layer exhibits signs of detachment, whereas coke on the polycrystalline surfaces remains strongly adhered. Additionally, surface energy influences the propensity for inorganic scale formation and deposition, further highlighting the enhanced performance of the amorphous coating in environments prone to fouling.

The crystallographic plane orientation of the pc-Coating shown in Figure 7.5, namely (111), (200), (220), and (311), align with similar TiAlN layers deposited by CVD [384], ion beam sputtering [385], and reactive magnetron sputtering [386], [387]. TiAlN possesses a cubic NaCl B1 structure [385], [387]. In addition, cubic titanium oxide was identified using the ICDD database. This oxide phase overlapped with the other identified ones, confirming possible oxidation of the coating, which had not been detected through SEM analysis. The applied bias of -60 V during deposition was favorable for forming the (111) plane in agreement with a beneficial effect of bias between -40 and -70 V reported elsewhere [385]. The (111) plane is frequently linked with high microhardness and adhesion [388], and is directly related to the good mechanical properties comparable to those presented in Table 7.3. Higher bias is expected to support formation of the (200) texture [385], while reducing the hardness [387]. On the other hand, preferentially formed (111) orientation led to improved mechanical properties, that also has a positive effect on coke adhesion. In fact, for TiN, the (111) and (110) planes were found to undergo strong chemisorption of the coking precursors [373].

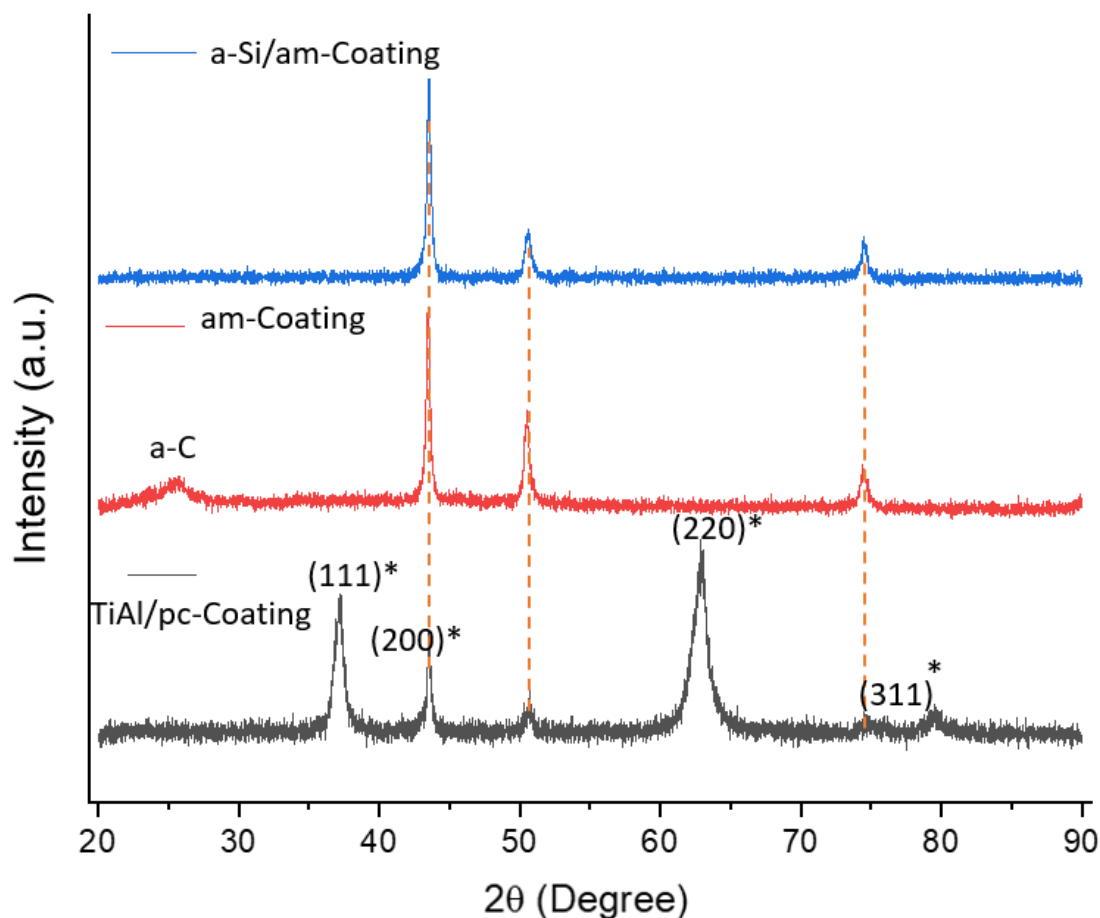


Figure 7.5 XRD pattern of the fouled coatings. The dashed lines identify the Inconel 718 phases. The crystalline structure orientation of is represented, the asterisk marks correspond to oxide. The silicon-based coating (both without and with the a-Si interlayer) remained amorphous.

7.3.2 Coatings deposited on borided Inconel 718

The hardness of the commercial Inconel 718 varies from about 2 GPa when in the solution annealed state to over 4.5 GPa when cold-worked and aged, while the modulus remains fairly consistent at around 200 GPa. To reduce the elastic property mismatch between our amorphous coating (Table 7.3) and the substrate, in an attempt to improve the mechanical properties of the system, boron was diffused industrially into the Inconel 718. The borided Inconel 718 reached a hardness of 14 ± 2.9 GPa with a modulus of 267 ± 70 GPa. The elasto-plastic properties calculated for the borided Inconel 718 are in the range expected for this alloy [389]. However, after the deposition of the amorphous coatings on borided substrate, the coatings exhibited poor adhesion and a weak interface (Figure 7.6). During scratching, removal of the coatings from the borided surface revealed the metallic nature of the substrate, which occurred already at a force as low as 0.1 N

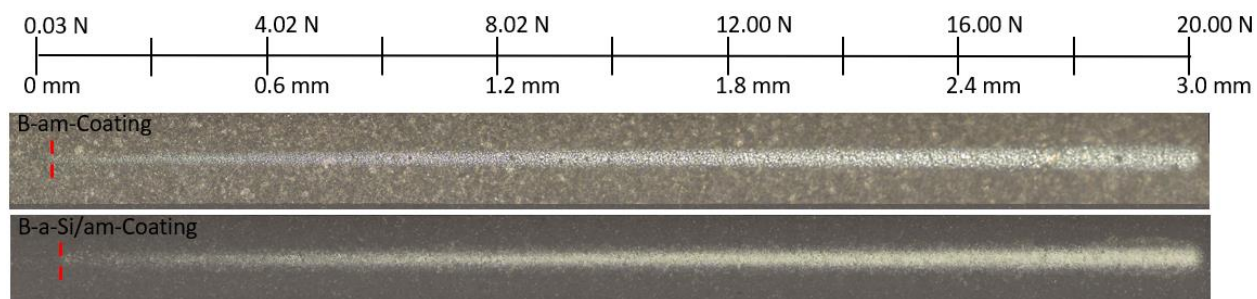


Figure 7.6 Scratch tracks of the am-Coating and the a-Si/am-Coating deposited on borided Inconel 718. The coating adhesion failure (LC_2) is marked in red.

After boriding, Inconel 718 exhibited a modified, about $9\ \mu\text{m}$ thick, layer on its surface containing Nb and Mo carbides embedded in a dendritic matrix (Figure 7.7A). A channel with growing dendrites is observed from the surface until deeper in the alloy bulk. Voids with carbon accumulation are present. After the substrate was covered with an amorphous coating, the visible area affected by diffusion was about $25\ \mu\text{m}$ (Figure 7.7B and Figure 7.7C).

The nickel from the substrate migrated to the alloy surface, forming a boride layer rich in Ni. Chromium was not concentrated in the regions where nickel had a stronger EDS signal. The microstructure of the boride layer has been previously characterized as a mixture of borides with different amounts of boron randomly distributed along the depth of the layer, forming zones [389]. The coating morphology was affected by the boride layer, independently of the Si interlayer, showing structural irregularities with an irregular columnar growth pattern (Figure 7.7C) induced by defects on the borided substrate. The substrate defects at the interface with the amorphous coatings drastically reduced the adhesion, leading to a failure already at $0.1\ \text{N}$ of applied force.

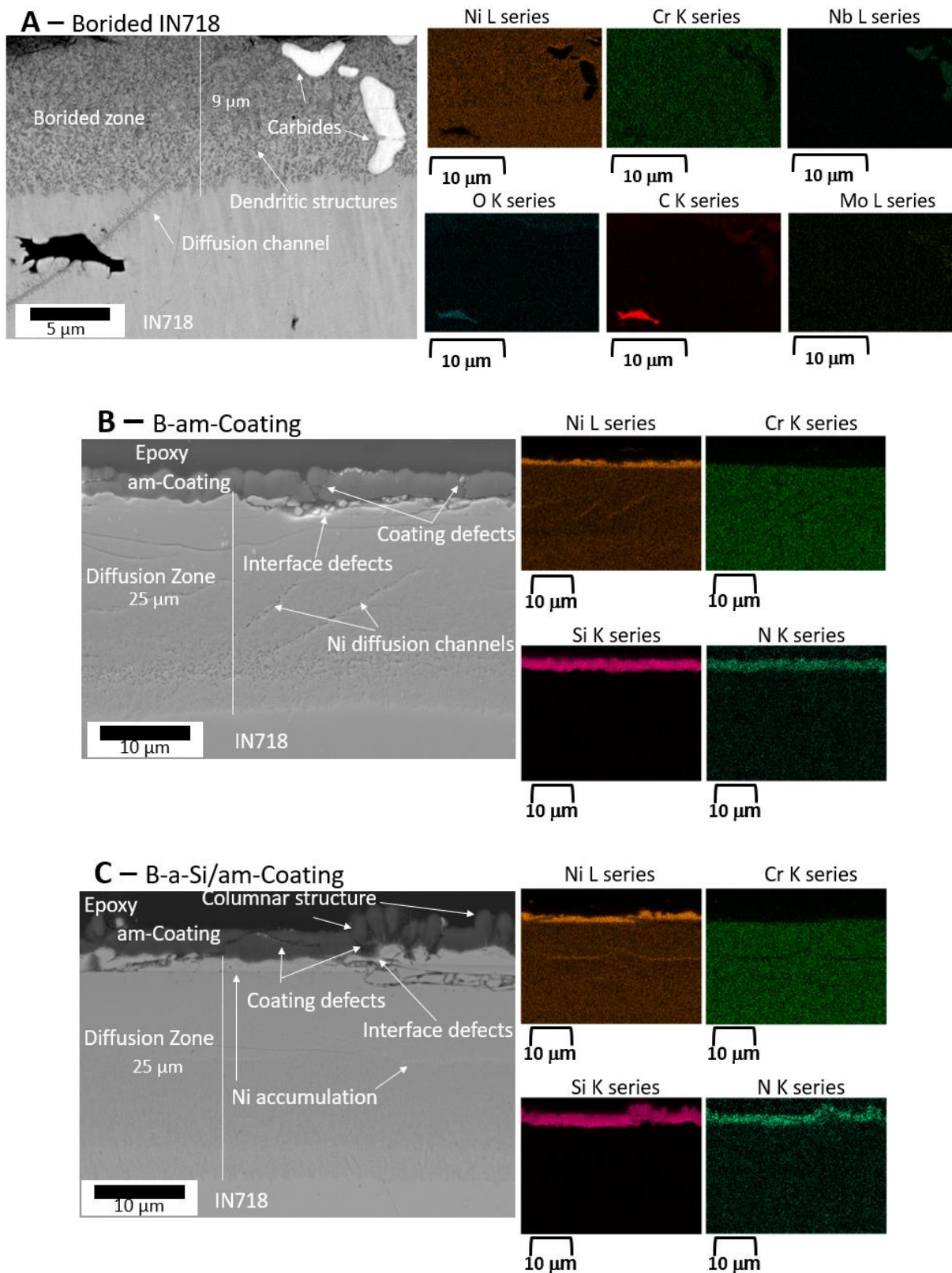
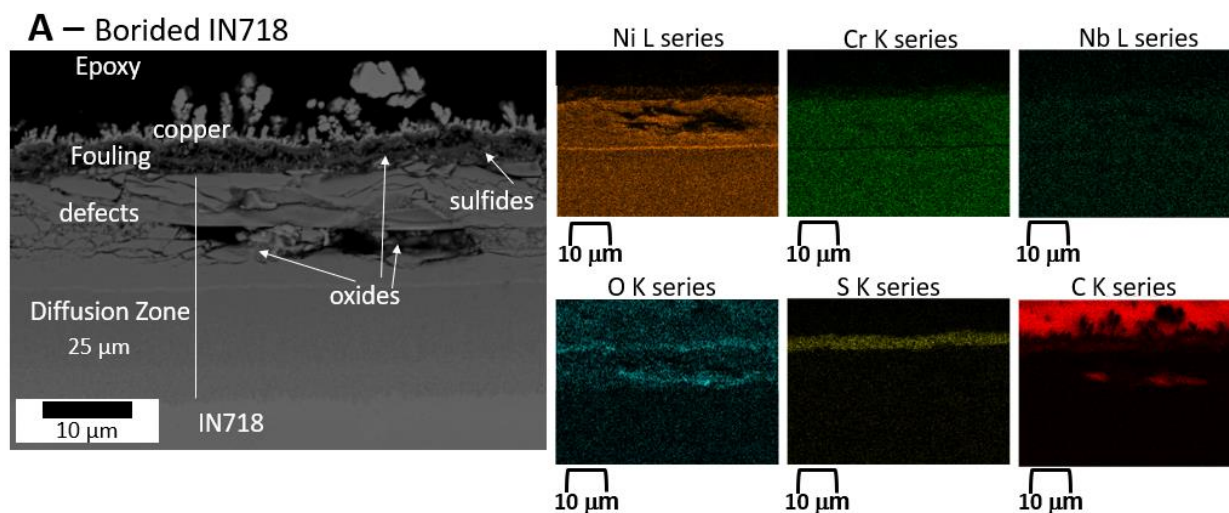


Figure 7.7 Cross-section SEM images and EDS maps of the 718 alloy: A) borided, B) borided and coated with the amorphous film, and C) borided and coated with the a-Si/am-Coating system.

7.3.2.1 Fouling on the amorphous coating on the borided Inconel surface

Boron diffusion into nickel alloys, such as the Inconel 718, has been proven to increase hot corrosion resistance at 800 °C [390], and enhance tribocorrosion at room temperature in a solution containing sulfate and chloride [391]. Borided alloys had higher performance and no structural degradation in sulfidizing environments, operating over 500 hr, at 500 °C and 1 atm [392], [393]. Therefore, boriding Inconel 718 may lead one to expect enhanced performance against sulfidation in hydrocracking conditions.

In fact, the above statement turned out not to be valid for the fouling conditions used in the present work. The bare borided IN718 and the counterparts coated with the amorphous films were subjected to fouling, and extensive degradation was observed (Figure 7.8). The extra roughness introduced on the substrate after the boriding process might also have impacted the protection against fouling.



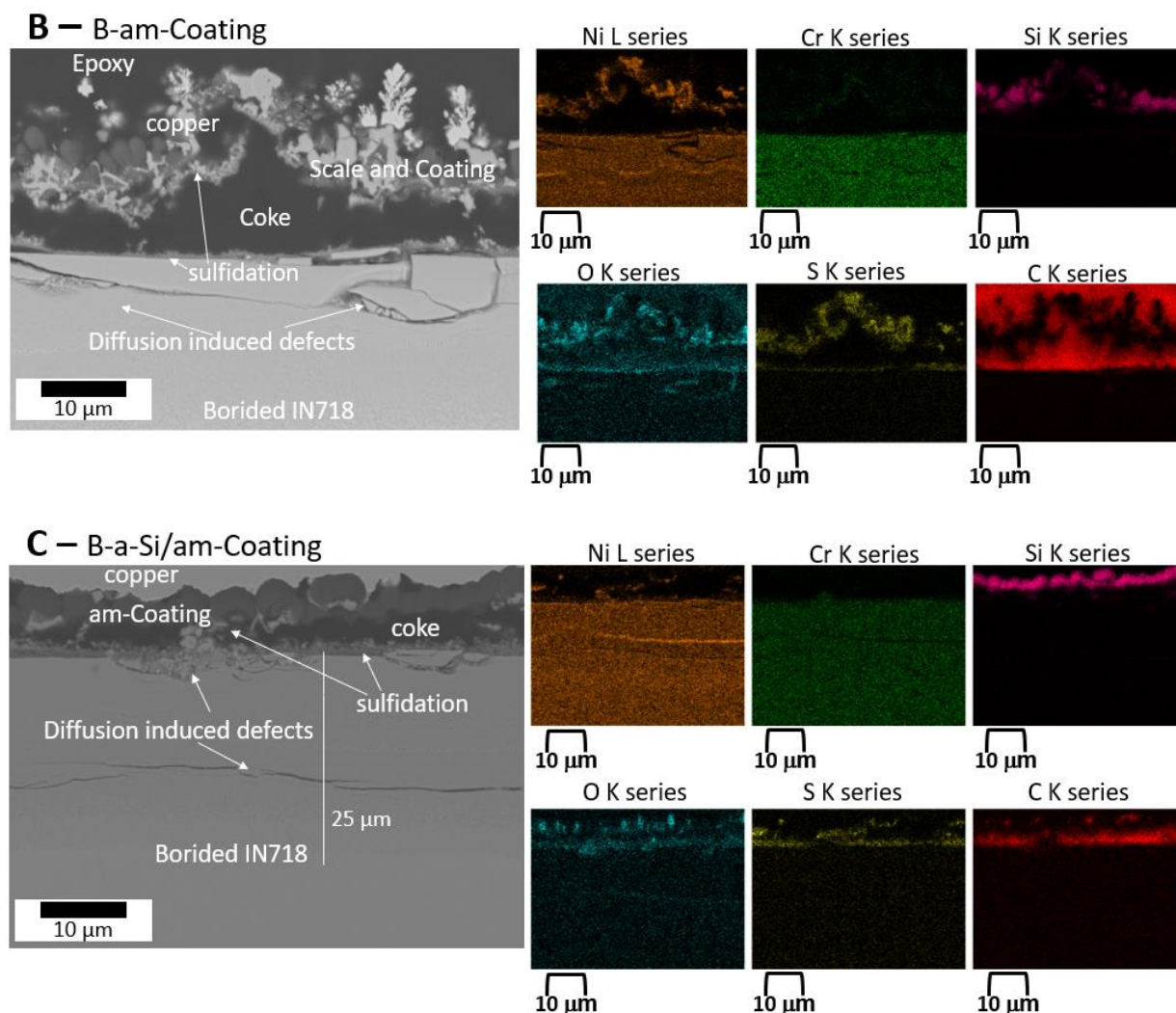


Figure 7.8 Cross-section SEM images and EDS maps of the Inconel 718: A) borided, B) borided and coated with the amorphous film, and C) borided and coated with the a-Si/am-Coating system after fouling at 450 °C for 2 h.

The borided Inconel 718 (Figure 7.8A) exhibits Ni and Cr diffusion to the surface, where sulfur and oxygen are concentrated, suggesting formation of a scale of sulfides and oxides. Oxides are also present deeper in the bulk of the alloy, particularly in the degraded regions. The amorphous coating directly deposited on the borided Inconel 718 delaminated and degraded after the fouling (Figure 7.8B). Ni and Cr sulfides were formed around the degraded coating, and the areas richer in Si were free from sulfur. Coke formed on the alloy surface underneath the coating, and a thin sulfur scale was detected between the alloy and the coke.

On the contrary, when the a-Si/am-Coating system (with the a-Si interlayer) was deposited, the surface integrity was improved, and its degradation was reduced (Figure 7.8C). However, sulfidation and coke adhesion were still observed between the borided alloy and the coating. Thus, boron diffusion was detrimental to the Inconel 718 protection against sulfidation and coke deposition in hydrocracking conditions. In addition, boriding affected the amorphous coating itself, which was more defective and became non-protective, enabling fouling between the coating and the substrate.

7.4 Conclusions

The protectiveness of polycrystalline and amorphous nitride films on a Ni alloy substrate against fouling in hydrocracking conditions was investigated. Although the polycrystalline layers exhibited excellent mechanical properties and adhesion, their higher surface energy and crystallinity led to more coke deposition than on the amorphous coating. The a-Si interlayer improved the adhesion and cohesion, enhancing oxidation resistance, which reduced the coating degradation and its tendency to foul.

These findings suggest that nitrides are promising candidates for heavy crude oil processing applications, where wear, corrosion, and fouling resistance are crucial. Further research on optimizing the crystallographic orientation of polycrystalline nitride films, and the thickness and interfaces in amorphous nitride films could potentially enhance the performance in similar environments. The amorphous coatings exhibited superior anti-coking properties. Despite the fact that boron diffusion increased the corrosion resistance of the Inconel 718 in previous studies, it was detrimental in hydrocracking conditions, causing sulfidation, coking, and damage to the coatings.

CHAPTER 8 GENERAL DISCUSSION

This chapter summarizes the main aspects of fouling, and the results presented in this thesis. The achievements are addressed in relation to the research objectives. The discussion is carried around the previously identified problem statements, which are relevant to the valve industry in petrochemical applications. Limitations are acknowledged, and future perspectives are provided.

Heavy Oil Fouling Process

Fouling phenomena in crude oil processing depend on the feed composition, operating conditions, and material surface characteristics. The feed composition is a parameter that is almost impossible to control and is continuously changing [8]. The composition of the SARA fractions can significantly influence fouling conditions, as asphaltene molecules contain most of the heteroatoms, leading to higher fouling rates [39]. Pressure and temperature can reversibly control asphaltene precipitation, while high pressure enhances solubilization [394]. An increase in temperature may either increase or decrease the precipitation rate [395]. Above 300 °C, asphaltenes decompose, increasing the formation of volatile compounds with reactive heteroatoms [41]. A temperature of 350 °C is considered a threshold that alters the mechanisms and kinetics of crude oil fouling [106]. Beyond 350 °C, both sulfidic corrosion and coking deposition rates significantly increase as a function of rising temperature [61]. Thermal cracking above 350 °C leads to the pyrolysis of asphaltenes [106], resulting in the formation of toluene-insoluble organic deposits [228].

Ebullated bed hydrocrackers operate at temperatures exceeding 350 °C to process heavy crude oil [276]. Despite the evolution of nickel superalloys to withstand sulfidic corrosion conditions, their use is limited to milder temperatures and low sulfur concentrations [130]. Cobalt-based alloys provide superior protection against sulfidation and form a more protective sulfide layer [133]. Protecting reactor components with corrosion-resistant alloys presents challenges, as the alloying elements exhibit a complex interplay [19]. Additionally, the scale formed may be chemically unstable, defective, fragile, and poorly adherent [87], [89], [90], [91], failing to provide complete protection for the surface [92].

Sulfides are more defective than oxide scales, exhibiting a faster rate of formation [91]. Scale formation is somewhat proportional to the partial pressure of H₂S, while the H₂S generation rate depends on the feed composition and overall pressure. An increase in pressure within feed

compositions containing high sulfur content positively affects H_2S generation [396]. Due to surface heterogeneity (e.g., scale formation, alloy composition, and microstructure) and non-isothermal desorption, gas surface diffusion is highly complex. Surface diffusion is a key determinant of the mass transfer of adsorbed gas. The diffusion coefficient increases with temperature and is influenced by the surface activation energy and gas molecular weight. Additionally, factors such as pressure and viscous flows play significant roles in the diffusion rate [253].

Surface engineering strategies can reduce surface energy and, consequently, the adhesion of materials to surfaces [162]. Reducing surface energy is particularly effective in preventing fouling caused by inorganic precipitation and coke formation. It should also facilitate the removal of deposits from the surface. When the scales formed from material corrosion are not protective, minimizing the corrosion rate becomes a more effective strategy to reduce corrosion-driven fouling. Passivating the surface with coatings that limit diffusion is essential, especially for materials that require a tight seal, such as in valve applications. Generally, research is divided into investigations focused on sulfidation protection or coke resistance. The interaction between sulfidic corrosion and coke deposition is rarely explored.

Creating coatings that protect against sulfidation, coke deposition, and wear resistance during heavy oil cracking at 450 °C is extremely challenging. At this temperature range, the thermal cracking energy induces the formation of new reactive precursors, which increases both organic fouling and sulfidic corrosion. Adhesion is one of the primary properties that determine the successful implementation of a coating. In wear-demanding applications, adequate adhesion becomes even more critical, as the material is subjected to soliciting loads that continuously challenge the bond. Research related to the interaction of coking and sulfidation in heavy oil processing environments is primarily focused on alloys in industrial settings. The configuration of the testing apparatus and the composition of the crude oil blend can significantly alter the fouling mechanism. As a result, the findings are often highly variable, frequently qualitative, and difficult to compare.

We proposed to study the fouling effects in the nickel alloy IN718, which serves as the benchmark alloy, and the Co-based thermally sprayed fluxing coating, W50, which is recognized as a benchmark in the valve industry. Failure analysis of industrial samples (Appendix A) was utilized to support the proposed fouling mechanism. Additionally, new HVOF-sprayed and sputtered

coatings were suggested as alternatives to improve anti-fouling properties while maintaining wear resistance.

Benchmark Materials

In this study, we proposed a phenomenological mechanism of fouling for IN718 and W50. The rate of precursor formation governs the corrosion rate for the more corrosion-prone nickel-based alloy, resulting in faster corrosion rates and material removal. Under milder corrosive conditions, a more adherent scale formed, increasing the influence of the diffusion-controlled mechanism. The more corrosion-resistant material, W50, developed an adherent scale in all tested conditions. The presence of a catalyst that induced a higher formation of sulfur-containing precursors did not lead to an increased sulfidation rate, as the scales formed were of similar thickness. Therefore, the total concentration of free sulfur precursors was insufficient to trigger accelerated corrosion, with mass transfer primarily controlling the sulfidic corrosion mechanism. However, in conditions with lower hydrogen concentration and no agitation, the scale on the W50 surface was approximately 40% thinner. This reduction can be attributed to a lack of free hydrogen, which is necessary for H_2S formation, the precursor with higher diffusivity in the gas phase. These experimental conditions also represent different real environments related to oil processing.

We concluded that sulfidation initially occurs through the diffusion of sulfur precursors into the alloy, with the scale evolving from the sulfidation at the alloy/scale interface, thus growing the sulfide scale in that region. During this process, the scale continuously alters its morphology, competing thermodynamically for sulfide stabilization. Concurrently, the older sulfide ages and oxidizes, primarily in the outer layer. As the scale evolves, it can become denser and more protective, minimizing further corrosion and preventing delamination (Figure 4.8).

Industrial Failure Analysis

To improve the understanding of scale formation and evolution, we characterized nickel-containing alloys, namely, stainless steel 321, and ASTM A638 (Grade 660) that had been exposed to a sulfidizing environment at temperatures and pressures similar to those in the current study. The analysis revealed that the samples exhibited two distinct layers: the top layer was richer in sulfur, while the bottom layer was richer in oxides. In the case of the A-286 alloy, which has a higher nickel concentration (25%), we identified a greater concentration of Ni in the sulfide-rich outer layer, supporting the proposed facilitated nickel diffusion through nickel sulfide channels.

Additionally, on the alloy A-286, a small external oxide-rich layer was observed above the sulfide layer, which protects Ni from further leaching within the scale. Based on these findings, we propose a phenomenological model that incorporates the observations regarding the early stages of fouling and the scale aging process (Figure 8.1).

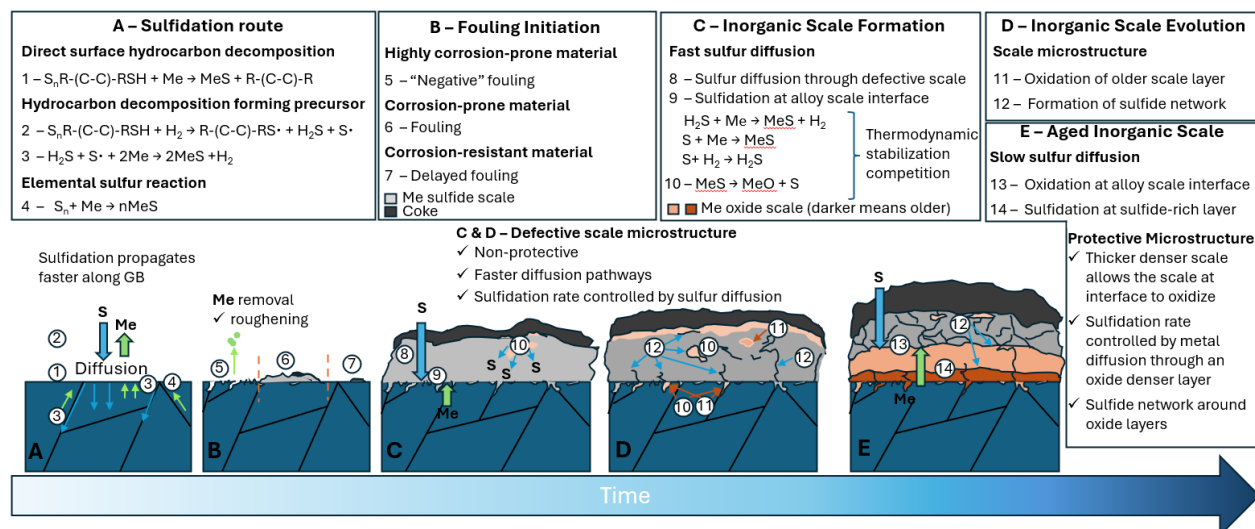


Figure 8.1 Phenomenological model describing the corrosion fouling mechanism, encompassing: A) the high-temperature sulfidation pathway in heavy oil, B) fouling initiation, C) inorganic scale formation, D) evolution and aging of the inorganic scale, and E) aged inorganic scale.

Proposed HVOF coatings

The isolation valve materials used in operating petrochemical plants today are susceptible to fouling. The benchmark coating, W50, is typically deposited on IN718 using the HVOF method. As alternative materials, we proposed three Co-based coating compositions: Co-1, Co-2, and Co-3. These coatings can be prepared using the same methodology as the current benchmark, allowing for an easy adaptation of any promising coating for rapid industrial integration. We demonstrated that post-processing heat treatment is essential for these coatings to reduce defective structures and, consequently, surface fouling. It was suggested that certain alloying elements, such as W and Ni, might be detrimental to sulfidation protection. Additionally, we developed an optical methodology for fast assessing sample surfaces and semi-quantitatively comparing the degree of fouling. The results from this methodology are expressed as fouling intensity, a metric that can expedite the screening of materials without the need for further complex characterization. After heat treatment, the Co-2 and Co-3 coatings emerged as promising candidates, exhibiting only 15% and 3% surface fouling intensity, respectively.

Proposed Sputtered Nitrides and Oxides

The previously proposed second-generation coatings are alloy coatings, which means they will eventually corrode, albeit to a lesser extent than the currently used materials. We proposed using oxides and nitrides as coatings to enhance the protectiveness and prevent the formation of scales. These coatings represent a third generation of coatings deposited by magnetron sputtering. We studied two types of oxides: 1) a full passivation coating of Al_2O_3 , which has been reported to provide the best protection against sulfidation in the literature [89], and 2) an active coating of CeO_2 (Appendix B), which is intended to assist in removing coke from the surface [213]. Two types of nitride coatings have also been tested. The first one was the deposition of a well-known material, TiAlN , which has been shown to be wear- and erosion-resistant [397], [398] as well as corrosion-resistant [399]. The second one was a material that has not been significantly explored, namely SiBCN , which has demonstrated promising results against oxidation at high temperatures [364]. After the fouling experiments, none of the third-generation coatings deposited on IN718 exhibited signs of internal sulfidation, oxidation, or degradation.

The best performance was observed with amorphous alumina, where no scale was detected on the surface of the material after the basic cleaning step to remove non-adherent coke. Although this coating provides protection against sulfidation and coke deposition, it exhibited low hardness and poor adhesion compared to the expected standards for wear applications. For this reason, the alumina coating was annealed at temperatures above 800 °C. The heat treatment improved the hardness to values exceeding 20 GPa, and adhesion was significantly enhanced for alumina annealed at 1 000 °C, and the formation of $\alpha\text{-Al}_2\text{O}_3$ was observed. However, the annealing process also introduced oxides from the substrate into the coating matrix and surface, which diminished the anti-fouling properties of the coating. Thus, while amorphous alumina offers protection against fouling with subpar mechanical properties, annealed alumina demonstrates improved mechanical properties but lower anti-fouling protection.

The second oxide coating approach, CeO_2 (Appendix B), demonstrated good protection against sulfidation, with no sulfur detected near the surface of the material after fouling experiments. However, a layer of coke up to 7.5 μm thick formed on the surface of the coating. Additionally, CeO_2 exhibited a hardness similar to that of amorphous alumina, around 10 GPa, and had poor adhesion, rendering it unsuitable for wear applications. Although the standalone results for CeO_2

were not satisfactory, this material could be utilized to create a composite coating with enhanced properties. A mixture of CeO_2 in low concentrations could improve other oxide coatings, such as Al_2O_3 , by acting as an oxygen donor to regenerate the coating [400]. The incorporation of CeO_2 could enhance the overall fouling resistance of the annealed alumina coatings.

The nitride coatings exhibited superior mechanical properties compared to the oxides. The adhesion of SiBCN and Si-SiBCN was approximately 20% and 30% better than that of the annealed alumina, respectively, while TiAlN demonstrated significantly superior adhesion, with no LC_2 failure observed. The hardness of SiBCN was around 15 GPa, and for the coating with the Si interlayer, it reached 17 GPa, whereas TiAlN hardness was 27 GPa, which is comparable to WC-carbide hard coatings used in extreme wear applications [401]. Although TiAlN displayed excellent mechanical properties and protection against sulfidation, non-continuous islands of adhesive coke formed on its surface. In contrast, SiBCN provided protection against sulfidation and coke deposition close to the performance of the amorphous Al_2O_3 . However, the SiBCN coating without an interlayer developed a detached layer of Si above the coating, indicating potential coating degradation. The addition of a Si interlayer between the substrate and the SiBCN contributed to improve the cohesive strength of SiBCN, thereby preventing the formation of the Si layer on top of the coating.

8.1 Limitations

The fouling apparatus is an autoclave with a limited total volume. While the samples were initially submerged in heavy oil, all the crude was consumed after 2 hours of reaction, making longer-duration tests unfeasible.

The liquids and gases produced after the fouling experiment were not characterized, leaving the nature of the generated precursors unknown and lacking quantitative data on their concentrations. This characterization was not conducted due to safety concerns and logistic limitations. Gas Chromatography with Sulfur Chemiluminescence Detector (GC-SCD) could be utilized to detect sulfur compounds with a sensitivity as low as ppb, providing specific data on H_2S , SO_2 , COS, and mercaptans. Alternatively, Gas Chromatography coupled with Mass Spectrometry (GC-MS) could also detect sulfur compounds, although with lower sensitivity and potential interference from hydrocarbons.

The samples were primarily characterized using microscopy (SEM) along with surface analysis techniques to identify elemental composition (EDS) and structural analysis (XRD). Other methods, such as Electron Backscatter Diffraction (EBSD) and Transmission Electron Microscopy (TEM), could provide deeper insights into the crystallographic structure of the studied materials, particularly when dealing with complex mixtures of alloying elements and scales.

Each deposition technique has its limitations and disadvantages. HVOF coatings are typically thicker but may exhibit a defective structure even after heat treatment at 1,000 °C. In contrast, sputtering is a line-of-sight technique with a lower deposition rate, making it challenging to produce thicker coatings.

The new optical imaging methodology developed to semi-quantitatively assess surface fouling was limited to surfaces with a similar background shade (e.g., metallic surfaces). It could not quantify fouling on the coatings' surfaces, as the coatings caused interference, diffraction, refraction, and scattering of light.

The samples were not subjected to aging or thermal and mechanical cycling, both of which could negatively affect the coating's efficacy. Prolonged exposure to the heavy oil environment at elevated temperatures could result in chemical degradation and microstructural changes, such as grain growth, phase transformations, localized corrosion, and interdiffusion. Thermal and mechanical cycling, could weaken the coating's adhesion due to accumulated stress, potentially leading to detachment from the substrate. Additionally, these processes could make the coating more brittle, increasing its susceptibility to cracking.

8.2 Perspectives and recommendations

The samples could be arranged in sections of a fouling apparatus with a continuous flow [46] to ensure extended exposure times. Samples with the proposed second-generation coatings are scheduled to be installed and tested in an actual heavy oil processing rig, where they will be subjected to longer test durations and thermal cycling.

We propose a co-deposition of alumina and CeO₂ while varying the ratio of the coatings to investigate a possible synergy of fouling protection and coating regeneration after annealing.

An optical image database of fouled surfaces could be utilized to train an algorithm capable of recognizing fouling surfaces through light interference, thereby enhancing the methodology for quantifying fouling on coated surfaces.

The annealing process of HVOF coatings could be optimized to further improve the microstructure of the second-generation coatings. To utilize the proposed third-generation coatings industrially in valve applications, it is essential to optimize the deposition process increasing the coating thickness to over 20 μm , and adapt the deposition system for coating larger components. Furthermore, the developed sputtered coatings could be adapted for use with other techniques, such as CVD or HVOF, to coat larger surfaces effectively.

AI tools can efficiently analyze literature on fouling, sulfidation, and coking in heavy oil environments, including hard-to-access conference papers, uncovering insights often overlooked. By generating a comprehensive database of material performance under varying conditions, AI can resolve experimental contradictions and clarify material behavior. Additionally, AI-driven data extrapolation could be used to predict existing material performance and propose new formulations to mitigate surface fouling.

CHAPTER 9 CONCLUSION

Fouling in the petrochemical industry presents a significant challenge. The constant variation in feed composition makes it virtually impossible to propose a perfect solution against fouling, as the type of scale formed is continuously changing. Specifically, during heavy oil processing, materials must withstand higher temperatures and endure harsher feed conditions. The increased concentration of sulfur is the primary factor contributing to elevated rates of sulfidation of the components. The methodology for assessing fouling and sulfidation was developed (Objective #1), and the proposed phenomenological mechanisms improved the understanding of sulfur migration during the initial stages of corrosion and throughout scale aging in benchmark materials.

When dealing with safety-sensitive materials, such as valves, it is crucial to preserve surface integrity to prevent leaks, ensuring proper sealing and overall process safety. Typical valve alloys must be fatigue-resistant, thermally stable within the operational range, and maintain a balance between strength and ductility while sustaining high tensile and yield strength. Although nickel alloys possess these characteristics, they are not suitable for wear resistance and are highly susceptible to sulfidation. Therefore, coatings are necessary to protect the surface of the nickel alloys.

HVOF coatings are standard in the industry, utilizing carbide mixed with cobalt-based alloys to enhance sulfidation protection and wear resistance compared to the typical nickel alloy used as the base material. However, these benchmark coatings are still subject to fouling and valve seizing, which can lead to operational failures or even delamination due to increased torque when actuating the valve to the desired position. As a response (Objective #2), second-generation coatings based on the HVOF spraying technique have been proposed as a faster alternative to replace the current benchmark coatings. Among the tested HVOF sprayed deposition methods, the coatings Co-2 and Co-3 demonstrated the best performance after heat treatment and could be readily implemented in industrial settings.

The proposed third-generation PVD coatings (Objective #3) demonstrated superior performance against fouling compared to the HVOF-sprayed coatings. However, the implementation of sputtered coatings in this industrial application presents challenges, as the technique is more complex and needs to be adapted for coating complex geometries and larger components with a suitable thickness for wear protection. Among the third-generation coatings, SiBCN exhibited the

second-best fouling protection, following amorphous alumina. Its amorphous nature provides a more homogeneous structure without grain boundaries, contributing to enhanced protection. Additionally, SiBCN possesses a hardness exceeding 15 GPa, which can be considered adequate for certain wear applications. TiAlN offers excellent hardness and adhesion, providing good protection against sulfidation, but it was susceptible to coke accumulation. Therefore, among the materials studied in this work, SiBCN and TiAlN are promising alternatives as third-generation coatings for valve components. Amorphous alumina is suitable for areas not subjected to wear, and its annealed version could also be a viable candidate for valve protection. Further testing of long-term fouling reactions, followed by cleaning and thermal cycles, is necessary to assess the coatings' feasibility over time.

REFERENCES

- [1] J. Liu, X. Fang, and T. Yang, “Novel Ebullated Bed Residue Hydrocracking Process,” *Energy Fuels*, vol. 31, no. 6, pp. 6568–6579, Jun. 2017, doi: 10.1021/acs.energyfuels.6b02937.
- [2] E. Soliman, “Flow of Heavy Oils at Low Temperatures: Potential Challenges and Solutions,” *Processing of Heavy Crude Oils - Challenges and Opportunities*, Dec. 2019, doi: 10.5772/intechopen.82286.
- [3] N. R. Canada, “Crude Oil Industry Overview.” Accessed: Jul. 07, 2024. [Online]. Available: <https://natural-resources.canada.ca/our-natural-resources/energy-sources-distribution/fossil-fuels/crude-oil/crude-oil-industry-overview/18078>
- [4] C. E. R. Government of Canada, “CER – Market Snapshot: Canada’s crude oil exports kept pace with production over the last decade.” Accessed: Jul. 07, 2024. [Online]. Available: <https://www.cer-rec.gc.ca/en/data-analysis/energy-markets/market-snapshots/2021/market-snapshot-canadas-crude-oil-exports-kept-pace-with-production-over-the-last-decade.html?=&wbdisable=true>
- [5] “Oil imports and exports - U.S. Energy Information Administration (EIA).” Accessed: Jul. 07, 2024. [Online]. Available: <https://www.eia.gov/energyexplained/oil-and-petroleum-products/imports-and-exports.php>
- [6] N. R. Canada, “What are the oil sands?” Accessed: Jul. 07, 2024. [Online]. Available: <https://natural-resources.canada.ca/our-natural-resources/energy-sources-distribution/fossil-fuels/crude-oil/what-are-oil-sands/18089>
- [7] N. R. Canada, “Technical Overview.” Accessed: Jul. 07, 2024. [Online]. Available: <https://natural-resources.canada.ca/our-natural-resources/energy-sources-distribution/fossil-fuels/crude-oil/technical-overview/5851>
- [8] J. G. Speight, *The chemistry and technology of petroleum*, Fifth edition. in Chemical industries, a series of reference books and textbooks, no. 137. Boca Raton: CRC Press, Taylor & Francis Group, 2014.
- [9] A. Hung, M. Li, and E. H. Fini, “Effects of Elemental Sulfur on the Aging Trajectory and Adhesion Characteristics of Rubber-Modified Bitumen,” *ACS Sustainable Chem. Eng.*, vol. 9, no. 50, pp. 16918–16925, Dec. 2021, doi: 10.1021/acssuschemeng.1c04798.
- [10] P. Redelius and H. Soenen, “Relation between bitumen chemistry and performance,” *Fuel*, vol. 140, pp. 34–43, Jan. 2015, doi: 10.1016/j.fuel.2014.09.044.
- [11] M. Baldassari and U. Mukherjee, “LC-MAX and Other LC-FINING Process Enhancements To Extend Conversion and On-stream Factor,” *American Fuel & Petrochemical Manufacturers*, p. 16, 2012.
- [12] “Oil & Gas Production - NACE.” Accessed: Jun. 17, 2020. [Online]. Available: <https://www.nace.org/resources/industries-nace-serves/oil-gas>

- [13] E. Stauffer, J. A. Dolan, and R. Newman, "Chapter 7 - Flammable and Combustible Liquids," in *Fire Debris Analysis*, Elsevier, 2008, pp. 199–233. doi: 10.1016/B978-012663971-1.50011-7.
- [14] E. Diaz-Bejarano, E. Behranvand, F. Coletti, M. R. Mozdianfard, and S. Macchietto, "Organic and Inorganic Fouling in Heat Exchangers: Industrial Case Study Analysis of Fouling Rate," *Ind. Eng. Chem. Res.*, vol. 58, no. 1, pp. 228–246, Jan. 2019, doi: 10.1021/acs.iecr.8b04343.
- [15] A. Groysman, *Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry*, 1st ed. 2017. in *Topics in Safety, Risk, Reliability and Quality*, no. 32. Cham: Springer International Publishing : Imprint: Springer, 2017. doi: 10.1007/978-3-319-45256-2.
- [16] J. G. Speight, *Oil and Gas Corrosion Prevention: From Surface Facilities to Refineries*. The Boulevard, Langford Lane, Kidlington, Oxford,: Gulf Professional Publishing [Imprint] Elsevier Science & Technology Books., 2014. Accessed: May 22, 2020. [Online]. Available: <http://app.knovel.com/hotlink/toc/id:kpOGCPFSF8/oil-and-gas>
- [17] J. Kvarekvål and J. Moloney, "6 - Sour corrosion," in *Trends in Oil and Gas Corrosion Research and Technologies*, A. M. El-Sherik, Ed., in Woodhead Publishing Series in Energy. , Boston: Woodhead Publishing, 2017, pp. 113–147. doi: 10.1016/B978-0-08-101105-8.00006-1.
- [18] R. A. King, "11 - Sulfide stress cracking," in *Trends in Oil and Gas Corrosion Research and Technologies*, A. M. El-Sherik, Ed., in Woodhead Publishing Series in Energy. , Boston: Woodhead Publishing, 2017, pp. 271–294. doi: 10.1016/B978-0-08-101105-8.00011-5.
- [19] A. E. Hughes, J. M. C. Mol, M. L. Zheludkevich, and R. G. Buchneit, *Active protective coatings*. New York, NY: Springer Berlin Heidelberg, 2016.
- [20] S.-C. Huang, *Advances in asphalt materials*. Boston, MA: Elsevier, 2015.
- [21] S. Bhowmick, A. N. Kale, V. Jayaram, and S. K. Biswas, "Contact damage in TiN coatings on steel," *Thin Solid Films*, vol. 436, no. 2, pp. 250–258, Jul. 2003, doi: 10.1016/S0040-6090(03)00598-4.
- [22] N. S. Srinivasan and C. A. McKnight, "Mechanism of coke formation from hydrocracked Athabasca residuum," *Fuel*, vol. 73, no. 9, pp. 1511–1517, Sep. 1994, doi: 10.1016/0016-2361(94)90072-8.
- [23] K. A. Esaklul and J. Mason, "27 - Nonmetallics applications in oil and gas production (pipes, liners, rehabilitations)," in *Trends in Oil and Gas Corrosion Research and Technologies*, A. M. El-Sherik, Ed., in Woodhead Publishing Series in Energy. , Boston: Woodhead Publishing, 2017, pp. 627–660. doi: 10.1016/B978-0-08-101105-8.00027-9.
- [24] P. Jin, G. Bota, W. Robbins, and S. Nesic, "Analysis of Oxide Scales Formed in the Naphthenic Acid Corrosion of Carbon Steel," *Energy Fuels*, vol. 30, no. 8, pp. 6853–6862, Aug. 2016, doi: 10.1021/acs.energyfuels.6b01066.
- [25] M. V. Orlov and W. O. Badeghaish, "Advanced Non-Metallic Coatings and Composite Materials for O & G Industry," *J. Phys.: Conf. Ser.*, vol. 1990, no. 1, p. 012001, Aug. 2021, doi: 10.1088/1742-6596/1990/1/012001.
- [26] A. G. Marshall and R. P. Rodgers, "Petroleomics: The Next Grand Challenge for Chemical Analysis," *Acc. Chem. Res.*, vol. 37, no. 1, pp. 53–59, Jan. 2004, doi: 10.1021/ar020177t.

- [27] Dutta Majumdar, Rudraksha}, “A Nuclear Magnetic Resonance Spectroscopic Investigation of the Molecular Structure and Aggregation Behavior of Asphaltenes,” 2015.
- [28] B. P. Tissot and D. H. Welte, *Petroleum Formation and Occurrence*, 2nd ed. Berlin Heidelberg: Springer-Verlag, 1984. doi: 10.1007/978-3-642-87813-8.
- [29] I. M. Cozzarelli and A. L. Baehr, “Volatile Fuel Hydrocarbons and MTBE in the Environment,” in *Treatise on Geochemistry*, Elsevier, 2003, pp. 433–474. doi: 10.1016/B0-08-043751-6/09054-X.
- [30] C. Ovalles, E. Rogel, and J. Segerstrom, “Improvement of Flow Properties of Heavy Oils Using Asphaltene Modifiers,” presented at the SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers, Jan. 2011. doi: 10.2118/146775-MS.
- [31] R. Altoé *et al.*, “Solution behavior of asphaltic residues and deasphalted oil prepared by extraction of heavy oil,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 445, pp. 59–66, Mar. 2014, doi: 10.1016/j.colsurfa.2013.12.082.
- [32] A. P. Szilas, *Production and transport of oil and gas. Part B. Part B*. Amsterdam: Elsevier Science, 1986. Accessed: May 18, 2020. [Online]. Available: <http://www.sciencedirect.com/science/book/9780044499565>
- [33] M. M. Boduszynski, “Composition of heavy petroleums. 1. Molecular weight, hydrogen deficiency, and heteroatom concentration as a function of atmospheric equivalent boiling point up to 1400.degree.F (760.degree.C),” *Energy Fuels*, vol. 1, no. 1, pp. 2–11, Jan. 1987, doi: 10.1021/ef00001a001.
- [34] A. M. McKenna, A. G. Marshall, and R. P. Rodgers, “Heavy Petroleum Composition. 4. Asphaltene Compositional Space,” *Energy Fuels*, vol. 27, no. 3, pp. 1257–1267, Mar. 2013, doi: 10.1021/ef301747d.
- [35] R. Prajapati, K. Kohli, and S. K. Maity, “Slurry phase hydrocracking of heavy oil and residue to produce lighter fuels: An experimental review,” *Fuel*, vol. 288, p. 119686, Mar. 2021, doi: 10.1016/j.fuel.2020.119686.
- [36] A. N. Sawarkar, A. B. Pandit, S. D. Samant, and J. B. Joshi, “Petroleum Residue Upgrading Via Delayed Coking: A Review,” *The Canadian Journal of Chemical Engineering*, vol. 85, no. 1, pp. 1–24, Feb. 2007, doi: 10.1002/cjce.5450850101.
- [37] J. Ramezanzadeh, H. Moradi, J. Ramezanzadeh, and H. Moradi, “Coking,” in *Topics on Oil and Gas*, IntechOpen, 2022. doi: 10.5772/intechopen.106190.
- [38] J. G. Speight, “Chapter 5 - Hydrocracking,” in *Heavy and Extra-heavy Oil Upgrading Technologies*, J. G. Speight, Ed., Boston: Gulf Professional Publishing, 2013, pp. 95–128. doi: 10.1016/B978-0-12-404570-5.00005-3.
- [39] U. B. Deshannava, M. S. Rafeen, M. Ramasamy, and D. Subbarao, “Crude Oil Fouling: A Review,” *J. of Applied Sciences*, vol. 10, no. 24, pp. 3167–3174, Dec. 2010, doi: 10.3923/jas.2010.3167.3174.
- [40] M. Ghanavati, M.-J. Shojaei, and A. R. S. A, “Effects of Asphaltene Content and Temperature on Viscosity of Iranian Heavy Crude Oil: Experimental and Modeling Study,” vol. 27, pp. 7217–7232, 2013, doi: <https://doi.org/10.1021/ef400776h>.

- [41] A. Demirbas, “Deposition and flocculation of asphaltenes from crude oils,” *Petroleum Science and Technology*, vol. 34, no. 1, pp. 6–11, Jan. 2016, doi: 10.1080/10916466.2015.1115875.
- [42] C. Xu *et al.*, “Synthesis of graphene from asphaltene molecules adsorbed on vermiculite layers,” *Carbon*, vol. 62, pp. 213–221, Oct. 2013, doi: 10.1016/j.carbon.2013.05.059.
- [43] R. C. P. Nunes *et al.*, “Model Molecules for Evaluating Asphaltene Precipitation Onset of Crude Oils,” *Journal of the Brazilian Chemical Society*, vol. 30, no. 6, pp. 1241–1251, Jun. 2019, doi: 10.21577/0103-5053.20190019.
- [44] M. Derakhshesh, “Asphaltene Aggregation and Fouling Behavior,” University of Alberta, 2012.
- [45] A. P. Watkinson and D. I. Wilson, “Chemical reaction fouling: A review,” *Experimental Thermal and Fluid Science*, vol. 14, no. 4, pp. 361–374, May 1997, doi: 10.1016/S0894-1777(96)00138-0.
- [46] J. K. Pental, “Design and Commissioning of a Crude Oil Fouling Facility,” Imperial College London, 2011.
- [47] C. B. Panchal and A. P. Watkinson, “Development of an analytical model for organic-fluid fouling,” Argonne National Laboratory, Argonne, IL, USA, 86, 74132, 1994. doi: 10.2172/74132.
- [48] *Heat Exchanger Fouling in the Pre-heat Train of a Crude Oil Distillation Unit. 00016*. London: ESDU International PLC, 2001.
- [49] T. F. Headen, E. S. Boek, G. Jackson, T. S. Totton, and E. A. Müller, “Simulation of Asphaltene Aggregation through Molecular Dynamics: Insights and Limitations,” *Energy Fuels*, vol. 31, no. 2, pp. 1108–1125, Feb. 2017, doi: 10.1021/acs.energyfuels.6b02161.
- [50] P. P. Shetty *et al.*, “Effect of Surface Chemistry and Roughness on the High-Temperature Deposition of a Model Asphaltene,” *Energy Fuels*, vol. 33, no. 5, pp. 4104–4114, May 2019, doi: 10.1021/acs.energyfuels.9b00386.
- [51] B. Avid, S. Sato, T. Takanohashi, and I. Saito, “Characterization of Asphaltenes from Brazilian Vacuum Residue Using Heptane–Toluene Mixtures,” *Energy Fuels*, vol. 18, no. 6, pp. 1792–1797, Nov. 2004, doi: 10.1021/ef049960n.
- [52] F. Ropital and F. Bonnet, “Mechanism of Catalytic Coke Formation and Some Means to Limit it in Refinery Processes,” *Materials Science Forum*, vol. 595–598, pp. 681–688, 2008, doi: 10.4028/www.scientific.net/MSF.595-598.681.
- [53] S. Qiu, X. Yu, Y. Chen, X. Huang, C. Yin, and S. Zhang, “Influence of Fe₂O₃ on the Properties and Structure of Iron Coke,” *ACS Omega*, vol. 8, no. 35, pp. 31946–31953, Sep. 2023, doi: 10.1021/acsomega.3c03730.
- [54] S. Kumar *et al.*, “Catalytic influence of iron oxide (Fe₂O₃) on coal pyrolysis and char combustion at various temperatures,” *Materials Today Communications*, vol. 39, p. 108982, Jun. 2024, doi: 10.1016/j.mtcomm.2024.108982.
- [55] C. D. Tan and R. T. K. Baker, “The effect of various sulfides on carbon deposition on nickel–iron particles,” *Catalysis Today*, vol. 63, no. 1, pp. 3–20, Dec. 2000, doi: 10.1016/S0920-5861(00)00441-7.

- [56] S. Kim, E. Sasmaz, R. Pogaku, and J. Lauterbach, "Effects of reaction conditions and organic sulfur compounds on coke formation and HZSM-5 catalyst performance during jet propellant fuel (JP-8) cracking," *Fuel*, vol. 259, p. 116240, Jan. 2020, doi: 10.1016/j.fuel.2019.116240.
- [57] J. R. Rostrup-Nielsen, "Sulfur-passivated nickel catalysts for carbon-free steam reforming of methane," *Journal of Catalysis*, vol. 85, no. 1, pp. 31–43, Jan. 1984, doi: 10.1016/0021-9517(84)90107-6.
- [58] D. L. Trimm and C. J. Turner, "The pyrolysis of propane. II. Effect of hydrogen sulphide," *Journal of Chemical Technology and Biotechnology*, vol. 31, no. 1, pp. 285–289, 1981, doi: 10.1002/jctb.503310138.
- [59] M. A. Fahim, T. A. Alsahhaf, and A. S. Elkilani, *Fundamentals of petroleum refining*, 1. ed. Amsterdam: Elsevier, 2010.
- [60] R. Sadeghbeigi, *Fluid catalytic cracking handbook: an expert guide to the practical operation, design, and optimization of FCC units*, 3rd ed. Amsterdam ; Boston: Elsevier/BH, 2012.
- [61] Z. Fan, P. Rahimi, T. Alem, A. Eisenhawer, and P. Arboleda, "Fouling Characteristics of Hydrocarbon Streams Containing Olefins and Conjugated Olefins," *Energy Fuels*, vol. 25, no. 3, pp. 1182–1190, Mar. 2011, doi: 10.1021/ef101661n.
- [62] V. Poncet, "Fischer–Tropsch Synthesis and Some Related Heterogeneous Reactions," in *Coal Science*, M. L. Gorbaty, J. W. Larsen, and I. Wender, Eds., Academic Press, 1984, pp. 1–62. doi: 10.1016/B978-0-12-150703-9.50007-X.
- [63] D. I. Wilson and G. T. Polley, "Mitigation of Refinery Preheat Train Fouling by Nested Optimization," presented at the Advances in Refinery Fouling Mitigation Session #46, AIChE, Houston, 2001, pp. 287–294.
- [64] B. L. Yeap, D. I. Wilson, G. T. Polley, and S. J. Pugh, "Mitigation of Crude Oil Refinery Heat Exchanger Fouling Through Retrofits Based on Thermo-Hydraulic Fouling Models," *Chemical Engineering Research and Design*, vol. 82, no. 1, pp. 53–71, Jan. 2004, doi: 10.1205/026387604772803070.
- [65] I. A. Wiehe and R. J. Kennedy, "The oil compatibility model and crude oil incompatibility," *Energy & Fuels*, vol. 14, no. 1.
- [66] T. J. Stephenson, "Corrosion – Fouling on Heat Transfer Surfaces," University of Alberta, Alberta, 2015.
- [67] B. D. Crittenden, S. T. Kolaczowski, and I. L. Downey, "Fouling of Crude Oil Preheat Exchangers," p. 547, 1992.
- [68] T. Tavassoli, S. M. Mousavi, S. A. Shojaosadati, and H. Salehizadeh, "Asphaltene biodegradation using microorganisms isolated from oil samples," *Fuel*, vol. 93, pp. 142–148, Mar. 2012, doi: 10.1016/j.fuel.2011.10.021.
- [69] F. Coletti, B. D. Crittenden, and S. Macchietto, "Basic Science of the Fouling Process," in *Crude Oil Fouling*, Elsevier, 2015, pp. 23–50. doi: 10.1016/B978-0-12-801256-7.00002-6.
- [70] D.-M. Kaimaki *et al.*, "Multiscale Approach Linking Self-Aggregation and Surface Interactions of Synthesized Foulants to Fouling Mitigation Strategies," *Energy Fuels*, vol. 33, no. 8, pp. 7216–7224, Aug. 2019, doi: 10.1021/acs.energyfuels.9b01390.

- [71] W. Wang and A. P. Watkinson, "Deposition from a Sour Heavy Oil Under Incipient Coking Conditions: Wall Shear Stress Effects and Mechanism," in *Proceedings of International Conference on Heat Exchanger Fouling and Cleaning*, Enfield (Dublin), Ireland, 2015, pp. 65–73.
- [72] R. B. Rebak, "Sulfidic Corrosion in Refineries – a Review," *Corrosion Reviews*, vol. 29, no. 3–4, Jan. 2011, doi: 10.1515/CORRREV.2011.021.
- [73] S. Sharifi-Asl, D. R. Chapman, A. Liang, B. Chaloner-Gill, D. Cooke, and A. E. Kuperman, "High Temperature Sulfidic Corrosion of Carbon Steel in Model Oil/Sulfur Compound Blends," presented at the Nace International Corrosion Conference & Expo, 2017, p. 13. [Online]. Available: https://www.researchgate.net/profile/Samin_Sharifi-Asl/publication/316660001_High-Temperature_Sulfidic_Corrosion_of_Carbon_Steel_in_Model_OilSulfur_Compound_Blend s/links/590a4aaaa6fdcc4961776ca9/High-Temperature-Sulfidic-Corrosion-of-Carbon-Steel-in-Model-Oil-Sulfur-Compound-Blends.pdf
- [74] W. Wang and A. P. Watkinson, "Iron Sulphide and Coke Fouling from Sour Oils: Review and Initial Experiments," in *Proceedings of the International Conference on Heat Exchanger Fouling and Cleaning*, Crete Island, Greece, 2011, pp. 23–30.
- [75] J. Hucińska, "Hucińska, Joanna. "Influence of sulphur on high temperature degradation of steel structures in the refinery industry," vol. 6, no. 1, pp. 16–25, 2006.
- [76] A. M. Sousa, H. A. Matos, and M. J. Pereira, "Properties of Crude Oil-in-Water and Water-in-Crude Oil Emulsions: A Critical Review," *Ind. Eng. Chem. Res.*, vol. 61, no. 1, pp. 1–20, Jan. 2022, doi: 10.1021/acs.iecr.1c02744.
- [77] P. Qiao *et al.*, "Fractionation of Asphaltenes in Understanding Their Role in Petroleum Emulsion Stability and Fouling," *Energy Fuels*, vol. 31, no. 4, pp. 3330–3337, Apr. 2017, doi: 10.1021/acs.energyfuels.6b02401.
- [78] Z. He, S. Kasemset, A. Y. Kirschner, Y.-H. Cheng, D. R. Paul, and B. D. Freeman, "The effects of salt concentration and foulant surface charge on hydrocarbon fouling of a poly(vinylidene fluoride) microfiltration membrane," *Water Research*, vol. 117, pp. 230–241, Jun. 2017, doi: 10.1016/j.watres.2017.03.051.
- [79] M. R. Gray, P. E. Eaton, and T. Le, "Kinetics of Hydrolysis of Chloride Salts in Model Crude Oil," *Petroleum Science and Technology*, vol. 26, no. 16, pp. 1924–1933, Oct. 2008, doi: 10.1080/10916460701402412.
- [80] G. S. Frankel, "Fundamentals of Corrosion Kinetics," in *Active Protective Coatings: New-Generation Coatings for Metals*, A. E. Hughes, J. M. C. Mol, M. L. Zheludkevich, and R. G. Buchheit, Eds., Dordrecht: Springer Netherlands, 2016, pp. 17–32. doi: 10.1007/978-94-017-7540-3_2.
- [81] G. P. Gu, J. J. Beaudoin, and V. S. Ramachandran, "12 - Techniques for Corrosion Investigation in Reinforced Concrete," in *Handbook of Analytical Techniques in Concrete Science and Technology*, V. S. Ramachandran and J. J. Beaudoin, Eds., Norwich, NY: William Andrew Publishing, 2001, pp. 441–504. doi: 10.1016/B978-081551437-4.50015-1.

- [82] T. Pehlke, “Studies of Aqueous Hydrogen Sulfide Corrosion in Producing SAGD Wells,” Society of Petroleum Engineers, Banff, Alberta, Canada, 2017. Accessed: Jun. 17, 2020. [Online]. Available: <http://www.onepetro.org/doi/10.2118/188161-MS>
- [83] W. Keogh *et al.*, “Deposition of Inorganic Carbonate, Sulfate, and Sulfide Scales on Antifouling Surfaces in Multiphase Flow,” *Energy Fuels*, vol. 31, no. 11, pp. 11838–11851, Nov. 2017, doi: 10.1021/acs.energyfuels.7b02165.
- [84] D. E. Coates and A. D. Dalvi, “An extension of the Wagner theory of alloy oxidation and sulfidation,” *Oxid Met*, vol. 2, no. 4, pp. 331–347, Dec. 1970, doi: 10.1007/BF00604474.
- [85] P. Cavaliere, G. Zavarise, and M. Perillo, “Modeling of the carburizing and nitriding processes,” *Computational Materials Science*, vol. 46, no. 1, pp. 26–35, Jul. 2009, doi: 10.1016/j.commatsci.2009.01.024.
- [86] D. J. Young, “Chapter 3 - Oxidation of Pure Metals,” in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, D. J. Young, Ed., Elsevier, 2016, pp. 85–144. doi: 10.1016/B978-0-08-100101-1.00003-0.
- [87] D. Landolt, *Corrosion and surface chemistry of metals*. Lausanne, Switzerland: EPFL Press, 2007.
- [88] K. N. Strafford, “The sulphidation of metals and alloys,” *Metallurgical Reviews*, vol. 14, no. 1, pp. 153–174, Jan. 1969, doi: 10.1179/mtlr.1969.14.1.153.
- [89] D. J. Young, “Chapter 8 - Corrosion by Sulphur,” in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, D. J. Young, Ed., Elsevier, 2016, pp. 393–430. doi: 10.1016/B978-0-08-100101-1.00008-X.
- [90] J. Lu *et al.*, “Failure analysis for a dry-pulverized coal gasifier burner made up of Inconel 718 superalloy,” *Engineering Failure Analysis*, vol. 97, pp. 227–233, Mar. 2019, doi: 10.1016/j.engfailanal.2019.01.049.
- [91] D. J. Young, “Chapter 4 - Mixed Gas Corrosion of Pure Metals,” in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, D. J. Young, Ed., Elsevier, 2016, pp. 145–191. doi: 10.1016/B978-0-08-100101-1.00004-2.
- [92] B. Gleeson, “Alloy degradation under oxidizing-sulfidizing conditions at elevated temperatures,” *Materials Research*, vol. 7, no. 1, pp. 61–69, Mar. 2004, doi: 10.1590/S1516-14392004000100010.
- [93] D. J. Young, “Chapter 2 - Enabling Theory,” in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, D. J. Young, Ed., Elsevier, 2016, pp. 31–84. doi: 10.1016/B978-0-08-100101-1.00002-9.
- [94] T. Dudziak, H. L. Du, P. K. Datta, A. P. Ehasarian, C. Reinhard, and P. E. Hovsepian, “Enhanced sulphidation/oxidation resistance of Ti–45Al–8Nb alloy by multilayered coatings at 850°C for up to 675 h,” *Corrosion Engineering, Science and Technology*, vol. 49, no. 7, pp. 590–602, Oct. 2014, doi: 10.1179/1743278213Y.00000000142.
- [95] D. J. Young, “Chapter 14 - Alloy Design,” in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, D. J. Young, Ed., Elsevier, 2016, pp. 685–701. doi: 10.1016/B978-0-08-100101-1.00014-5.

- [96] S. M. Hall, "Chapter 25 - Metallurgy," in *Rules of Thumb for Chemical Engineers (Sixth Edition)*, S. M. Hall, Ed., Elsevier, 2018, pp. 417–430. doi: 10.1016/B978-0-12-811037-9.00025-4.
- [97] R. L. Piehl, "Naphthenic acid corrosion in crude distillation units," *Materials Performance*, vol. 27, no. 1, pp. 37–43.
- [98] N. Epstein, "Thinking about Heat Transfer Fouling: A 5×5 Matrix," *Heat Transfer Engineering*, vol. 4, no. 1, pp. 43–56, Jan. 1983, doi: 10.1080/01457638108939594.
- [99] M. Bohnet, "Fouling of heat transfer surfaces," *Chemical Engineering & Technology*, vol. 10, no. 1, pp. 113–125, 1987, doi: 10.1002/ceat.270100115.
- [100] H. Muller-Steinhagen, M. R. Malayeri, and A. P. Watkinson, "Preface to the proceedings of int. conf. on heat exchanger fouling and cleaning VIII," Schlading, Austria, 2009, p. 3.
- [101] F. Coletti, "Multi-scale modelling of refinery pre-heat trains undergoing fouling for improved energy efficiency," Imperial College London, 2010.
- [102] T. R. Bott, *Fouling of heat exchangers*. in Chemical engineering monographs, no. vol. 26. Amsterdam ; New York: Elsevier, 1995.
- [103] S. N. Kazi, "Fouling and Fouling Mitigation on Heat Exchanger Surfaces," *Heat Exchangers - Basics Design Applications*, Mar. 2012, doi: 10.5772/32990.
- [104] E. D. Bejarano, "A Reaction Engineering Approach to Modelling of Crude Oil Fouling Deposits: Analysis, Monitoring and Cleaning," Imperial College London, London, 2016.
- [105] W. Wang and A. P. Watkinson, "Deposition From a Sour Heavy Oil Under Incipient Coking Conditions: Effect of Surface Materials and Temperature," *Heat Transfer Engineering*, vol. 36, no. 7–8, pp. 623–631, May 2015, doi: 10.1080/01457632.2015.954914.
- [106] S. Ebrahimi, J. S. Moghaddas, and M. K. R. Aghjeh, "Study on thermal cracking behavior of petroleum residue," *Fuel*, vol. 87, no. 8–9, pp. 1623–1627, Jul. 2008, doi: 10.1016/j.fuel.2007.08.015.
- [107] M. Hazelton, T. Stephenson, J. Lepore, V. Subramani, and D. Mitlin, "Sulfide promoted chronic fouling in a refinery: A broad phenomenon spanning a range of heat transfer surfaces and oil types," *Fuel*, vol. 160, pp. 479–489, Nov. 2015, doi: 10.1016/j.fuel.2015.07.074.
- [108] J. Chew, H. M. Joshi, S. G. Kazarian, M. Millan-Agorio, F. H. Tay, and S. Venditti, "Deposit Characterization and Measurements," in *Crude Oil Fouling*, Elsevier, 2015, pp. 95–178. doi: 10.1016/B978-0-12-801256-7.00004-X.
- [109] E. Rammerstorfer, T. Karner, and M. Siebenhofer, "The kinetics and mechanisms of fouling in crude oil heat transfer," *Heat Transfer Engineering*, vol. 41, no. 8, pp. 691–707, Apr. 2020, doi: 10.1080/01457632.2018.1564202.
- [110] M. Yang, A. Young, and B. Crittenden, "Use of CFD to Correlate Crude Oil Fouling Against Surface Temperature and Surface Shear Stress in a Stirred Fouling Apparatus," in *Proceedings of International Conference on Heat Exchanger Fouling and Cleaning VII*, Schlading, Austria, 2009.
- [111] B. D. Crittenden, G. F. Hewitt, M. Millan-Agorio, K. Rostani, S. Venditti, and M. Yang, "Chapter Three - Experimental Generation of Fouling Deposits," in *Crude Oil Fouling*, F.

- Coletti and G. F. Hewitt, Eds., Boston: Gulf Professional Publishing, 2015, pp. 51–94. doi: 10.1016/B978-0-12-801256-7.00003-8.
- [112] B. D. Crittenden, S. T. Kolaczowski, T. Takemoto, and D. Z. Phillips, “Crude Oil Fouling in a Pilot-Scale Parallel Tube Apparatus,” *Heat Transfer Engineering*, vol. 30, no. 10–11, pp. 777–785, Sep. 2009, doi: 10.1080/01457630902744135.
- [113] A. Groysman, “Corrosion problems and solutions in oil refining and petrochemical industry,” *Koroze a ochrana materialu*, vol. 61, no. 3, pp. 100–117, 2017.
- [114] D. A. Muñoz Pinto, S. M. Cuervo Camargo, M. Orozco Parra, D. Laverde, S. García Vergara, and C. Blanco Pinzon, “Formation of fouling deposits on a carbon steel surface from Colombian heavy crude oil under preheating conditions,” *J. Phys.: Conf. Ser.*, vol. 687, p. 012016, Feb. 2016, doi: 10.1088/1742-6596/687/1/012016.
- [115] P. E. Eaton, “Method and apparatus for conducting fouling tests,” US4910999A, Mar. 27, 1990 Accessed: May 27, 2020. [Online]. Available: <https://patents.google.com/patent/US4910999A/en>
- [116] U. B. Deshannavar and M. Ramasamy, “A model to determine maximum heat flux under forced convective heat transfer regime for crude oil fouling studies,” *Applied Thermal Engineering*, vol. 156, pp. 485–493, Jun. 2019, doi: 10.1016/j.applthermaleng.2019.04.091.
- [117] R. Teixeira, A. Pereira, J. Mendes, and L. F. Melo, “Identifying the Nature of Fouling Layers by Online Monitoring of the Propagation of Vibrations Along the Deposition Surface,” *Heat Transfer Engineering*, vol. 35, no. 3, pp. 251–257, Feb. 2014, doi: 10.1080/01457632.2013.825166.
- [118] Z. G. Yang, D. M. Paxton, K. S. Weil, J. W. Stevenson, and P. Singh, “Materials Properties Database for Selection of High-Temperature Alloys and Concepts of Alloy Design for SOFC Applications,” PNNL-14116, 15010553, Nov. 2002. doi: 10.2172/15010553.
- [119] E. Slavcheva, B. Shone, and A. Turnbull, “Review of naphthenic acid corrosion in oilrefining,” *British Corrosion Journal*, vol. 34, no. 2, pp. 125–131, Feb. 1999, doi: 10.1179/000705999101500761.
- [120] Javier Sanabria Cala, Dionisio Laverde Catano, Dario Y. Pena, and Diego Merchan-Arenas, “Influence of temperature and time on the corrosion by sulfidation of aisi-316 steel exposed under transfer line,” *Chemical Engineering Transactions*, vol. 57, pp. 715–720, May 2017, doi: 10.3303/CET1757120.
- [121] J. H. Devan and P. F. Tortorelli, “Oxidation/sulfidation of iron-aluminium alloys,” *Materials at High Temperatures*, vol. 11, no. 1–4, pp. 30–35, Jan. 1993, doi: 10.1080/09603409.1993.11689436.
- [122] J. R. Davis and ASM International, Eds., *Nickel, cobalt, and their alloys*. in ASM specialty handbook. Materials Park, OH: ASM International, 2000.
- [123] S. Mrowec, T. Werber, and M. Zastawnik, “The mechanism of high temperature sulphur corrosion of nickel-chromium alloys,” *Corrosion Science*, vol. 6, no. 2, pp. 47–68, Jan. 1966, doi: 10.1016/S0010-938X(66)80025-2.

- [124] K. Gjønnnes and A. Andersen, "Scale structures during oxidation and sulphidation of nickel and a nickel-chromium alloy," *Ultramicroscopy*, vol. 22, no. 1, pp. 289–295, Jan. 1987, doi: 10.1016/0304-3991(87)90072-6.
- [125] D. L. Douglass and M. Z. Wu, "Sulfidation behavior of Ni-Cr-Mo alloys at 700°C," *Oxid Met*, vol. 22, no. 1, pp. 45–57, Aug. 1984, doi: 10.1007/BF00659248.
- [126] M. J. Schofield, "33 - Corrosion," in *Plant Engineer's Reference Book (Second Edition)*, D. A. Snow, Ed., Oxford: Butterworth-Heinemann, 2002, pp. 33–1. doi: 10.1016/B978-075064452-5/50088-2.
- [127] The International Nickel Company, Inc., "The Corrosion Resistance of Nickel-Containing Alloys in Sulfuric Acid and Related Compounds." INCO-Sterling Forest, 1983. [Online]. Available: https://www.nickelinstitute.org/media/1829/thecorrosionresistanceofnickel_containingalloys insulphuricacidandrelatedcompounds_1318_.pdf
- [128] G. D. Smith, D. J. Tillack, and S. J. Patel, "Alloy 625: Impressive Past/Significant Presence/Awesome Future," in *Superalloys 718, 625, 706 and Various Derivatives (2001)*, The Minerals, Metals & Materials Society (TMS), 2001, pp. 35–46. doi: 10.7449/2001/Superalloys_2001_35_46.
- [129] O. A. Onyewuenyi, "Alloy 718: Alloy Optimization for Applications in Oil and Gas Production," in *Superalloys 718 Metallurgy and Applications (1989)*, The Minerals, Metals & Materials Society (TMS), 1989, pp. 345–362. doi: 10.7449/1989/Superalloys_1989_345_362.
- [130] R. B. Bhavsar, A. Collins, and S. Silverman, "Use of Alloy 718 and 725 in Oil and Gas Industry," in *Superalloys 718, 625, 706 and Various Derivatives (2001)*, The Minerals, Metals & Materials Society (TMS), 2001, pp. 47–55. doi: 10.7449/2001/Superalloys_2001_47_55.
- [131] International Standard, "ANSI/NACE MR0175/ISO 15156-3:2015."
- [132] J. J. deBarbadillo and S. K. Mannan, "Alloy 718 for Oilfield Applications," *JOM*, vol. 64, no. 2, pp. 265–270, Feb. 2012, doi: 10.1007/s11837-012-0238-z.
- [133] S. K. Verma, D. P. Whittle, and J. Stringer, "Sulphidation of cobalt-based alloys," *Corrosion Science*, vol. 12, no. 7, pp. 545–554, Jul. 1972, doi: 10.1016/S0010-938X(72)90063-7.
- [134] S. Mrowec and K. Przybylski, "Transport properties of sulfide scales and sulfidation of metals and alloys," *Oxid Met*, vol. 23, no. 3, pp. 107–139, Apr. 1985, doi: 10.1007/BF00659899.
- [135] S. Soltanattar, "High Temperature Corrosion Behavior of Alloys in Mixed-Gas Environments," University of Pittsburgh, Swanson School of Engineering, 2018.
- [136] C. Mapelli *et al.*, "Comparison of the combined oxidation and sulphidation behavior of nickel- and cobalt-based alloys at high temperature," *Journal of Materials Research and Technology*, vol. 9, no. 6, pp. 15679–15692, Nov. 2020, doi: 10.1016/j.jmrt.2020.11.009.
- [137] A. Díaz, J. M. Alegre, and I. I. Cuesta, "A review on diffusion modelling in hydrogen related failures of metals," *Engineering Failure Analysis*, vol. 66, pp. 577–595, Aug. 2016, doi: 10.1016/j.engfailanal.2016.05.019.

- [138] R. E. Smallman and A. H. W. Ngan, “Chapter 7 - Diffusion,” in *Modern Physical Metallurgy (Eighth Edition)*, R. E. Smallman and A. H. W. Ngan, Eds., Oxford: Butterworth-Heinemann, 2014, pp. 287–316. doi: 10.1016/B978-0-08-098204-5.00007-9.
- [139] D. Lazarus, “Diffusion in Crystalline and Amorphous Solids,” *MRS Online Proceedings Library*, vol. 57, no. 1, pp. 297–311, Dec. 1985, doi: 10.1557/PROC-57-297.
- [140] Z. Wei, J. Yu, Y. Lu, J. Han, C. Wang, and X. Liu, “Prediction of diffusion coefficients in fcc, bcc and hcp phases remained stable or metastable by the machine-learning methods,” *Materials & Design*, vol. 198, p. 109287, Jan. 2021, doi: 10.1016/j.matdes.2020.109287.
- [141] K. Hirata, S. Iikubo, M. Koyama, K. Tsuzaki, and H. Ohtani, “First-Principles Study on Hydrogen Diffusivity in BCC, FCC, and HCP Iron,” *Metall Mater Trans A*, vol. 49, no. 10, pp. 5015–5022, Oct. 2018, doi: 10.1007/s11661-018-4815-9.
- [142] A. P. Mouritz, Ed., “1 - Introduction to aerospace materials,” in *Introduction to Aerospace Materials*, Woodhead Publishing, 2012, pp. 1–14. doi: 10.1533/9780857095152.1.
- [143] A. Madeo, “1 - General Introductory Aspects,” in *Generalized Continuum Mechanics and Engineering Applications*, A. Madeo, Ed., Elsevier, 2015, pp. 1–18. doi: 10.1016/B978-1-78548-032-4.50001-2.
- [144] M. Razeghi, Ed., “Defects,” in *Fundamentals of Solid State Engineering*, Boston, MA: Springer US, 2006, pp. 551–572. doi: 10.1007/0-387-28751-5_14.
- [145] T.-T. Fang, “Chapter 4 - Point Defects in Crystalline Materials,” in *Elements of Structures and Defects of Crystalline Materials*, T.-T. Fang, Ed., Elsevier, 2018, pp. 83–127. doi: 10.1016/B978-0-12-814268-4.00004-7.
- [146] H. Oikawa and Y. Iijima, “7 - Diffusion behaviour of creep-resistant steels,” in *Creep-Resistant Steels*, F. Abe, T.-U. Kern, and R. Viswanathan, Eds., in Woodhead Publishing Series in Metals and Surface Engineering, Woodhead Publishing, 2008, pp. 241–264. doi: 10.1533/9781845694012.2.241.
- [147] X. Tong, H. Zhang, and D. Y. Li, “Effect of Annealing Treatment on Mechanical Properties of Nanocrystalline α -iron: an Atomistic Study,” *Sci Rep*, vol. 5, p. 8459, Feb. 2015, doi: 10.1038/srep08459.
- [148] Z. Chen *et al.*, “Effect of Annealing Conditions on Recovery of Lattice Damage in a High-Energy-Implanted 4H-SiC Superjunction PIN Diode,” *ECS J. Solid State Sci. Technol.*, vol. 11, no. 6, p. 065003, Jun. 2022, doi: 10.1149/2162-8777/ac7351.
- [149] K. K. Alaneme and E. A. Okotete, “Recrystallization mechanisms and microstructure development in emerging metallic materials: A review,” *Journal of Science: Advanced Materials and Devices*, vol. 4, no. 1, pp. 19–33, Mar. 2019, doi: 10.1016/j.jsamd.2018.12.007.
- [150] B. Gwalani *et al.*, “Lattice misorientation evolution and grain refinement in Al-Si alloys under high-strain shear deformation,” *Materialia*, vol. 18, p. 101146, Aug. 2021, doi: 10.1016/j.mtla.2021.101146.
- [151] M. A. Easton, M. A. Qian, and D. H. StJohn, “Grain Refinement in Alloys: Novel Approaches,” in *Reference Module in Materials Science and Materials Engineering*, Elsevier, 2016. doi: 10.1016/B978-0-12-803581-8.03789-9.

- [152] M. N. da S. Lima *et al.*, “Influence of cold deformation on microstructure, crystallographic orientation and tensile properties of an experimental austenitic Fe–26Mn–0.4C steel,” *Journal of Materials Research and Technology*, vol. 19, pp. 7–19, Jul. 2022, doi: 10.1016/j.jmrt.2022.05.020.
- [153] W. Zheng, J. Zhu, and W. Yuan, “Tempering stress relaxation behavior and microstructure evolution of 300 M steel,” *Materials Characterization*, vol. 197, p. 112688, Mar. 2023, doi: 10.1016/j.matchar.2023.112688.
- [154] E. J. Herrera-Jimenez, E. Bousser, T. Schmitt, J. E. Klemberg-Sapieha, and L. Martinu, “Effect of plasma interface treatment on the microstructure, residual stress profile, and mechanical properties of PVD TiN coatings on Ti-6Al-4V substrates,” *Surface and Coatings Technology*, vol. 413, p. 127058, May 2021, doi: 10.1016/j.surfcoat.2021.127058.
- [155] H. M. Dilshad Alam Digonta and A. Fatemi, “Laser shock peening and its effects and modeling on fatigue performance of additive manufactured metallic materials,” *Theoretical and Applied Fracture Mechanics*, vol. 130, p. 104281, Apr. 2024, doi: 10.1016/j.tafmec.2024.104281.
- [156] B. Lu, K. Tang, M. Wu, Y. Yang, and G. Yang, “Mechanism of Electropulsing Treatment Technology for Flow Stress of Metal Material: A Review,” *Alloys*, vol. 3, no. 1, Art. no. 1, Mar. 2024, doi: 10.3390/alloys3010006.
- [157] D. Colombara *et al.*, “Chemical instability at chalcogenide surfaces impacts chalcopyrite devices well beyond the surface,” *Nat Commun*, vol. 11, no. 1, p. 3634, Jul. 2020, doi: 10.1038/s41467-020-17434-8.
- [158] P. Panjan, A. Drnovšek, P. Gselman, M. Čekada, and M. Panjan, “Review of Growth Defects in Thin Films Prepared by PVD Techniques,” *Coatings*, vol. 10, no. 5, Art. no. 5, May 2020, doi: 10.3390/coatings10050447.
- [159] G. Abadias *et al.*, “Review Article: Stress in thin films and coatings: Current status, challenges, and prospects,” *Journal of Vacuum Science & Technology A*, vol. 36, no. 2, p. 020801, Mar. 2018, doi: 10.1116/1.5011790.
- [160] M. M. Vazirian, T. V. J. Charpentier, M. de Oliveira Penna, and A. Neville, “Surface inorganic scale formation in oil and gas industry: As adhesion and deposition processes,” *Journal of Petroleum Science and Engineering*, vol. 137, pp. 22–32, Jan. 2016, doi: 10.1016/j.petrol.2015.11.005.
- [161] K. Kendall, “The adhesion and surface energy of elastic solids,” *J. Phys. D: Appl. Phys.*, vol. 4, no. 8, p. 1186, Aug. 1971, doi: 10.1088/0022-3727/4/8/320.
- [162] A. K. Halvey, B. Macdonald, A. Dhyani, and A. Tuteja, “Design of surfaces for controlling hard and soft fouling,” *Phil. Trans. R. Soc. A*, vol. 377, no. 2138, p. 20180266, Feb. 2019, doi: 10.1098/rsta.2018.0266.
- [163] S. Ebnesajjad, Ed., “Chapter 3 - Material Surface Preparation Techniques,” in *Adhesives Technology Handbook (Second Edition)*, Norwich, NY: William Andrew Publishing, 2009, pp. 37–46. doi: 10.1016/B978-0-8155-1533-3.50006-2.

- [164] D. E. Packham, "Surface energy, surface topography and adhesion," *International Journal of Adhesion and Adhesives*, vol. 23, no. 6, pp. 437–448, Jan. 2003, doi: 10.1016/S0143-7496(03)00068-X.
- [165] S. S. Latthe, C. Terashima, K. Nakata, and A. Fujishima, "Superhydrophobic Surfaces Developed by Mimicking Hierarchical Surface Morphology of Lotus Leaf," *Molecules*, vol. 19, no. 4, pp. 4256–4283, Apr. 2014, doi: 10.3390/molecules19044256.
- [166] A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, and R. E. Cohen, "Robust omniphobic surfaces," *Proceedings of the National Academy of Sciences*, vol. 105, no. 47, pp. 18200–18205, Nov. 2008, doi: 10.1073/pnas.0804872105.
- [167] E. E. Ubuo, I. A. Udoetok, A. T. Tyowua, I. O. Ekwere, and H. S. Al-Shehri, "The Direct Cause of Amplified Wettability: Roughness or Surface Chemistry?," *Journal of Composites Science*, vol. 5, no. 8, Art. no. 8, Aug. 2021, doi: 10.3390/jcs5080213.
- [168] A. Peethan, M. Aravind, and S. D. George, "Chapter 1: Surface Wettability and Superhydrophobicity," in *Advances in Superhydrophobic Coatings*, 2023, pp. 1–25.
- [169] G. Momen and M. Farzaneh, "Facile approach in the development of icephobic hierarchically textured coatings as corrosion barrier," *Applied Surface Science*, vol. 299, pp. 41–46, Apr. 2014, doi: 10.1016/j.apsusc.2014.01.179.
- [170] T. Kim, S. Kwon, J. Lee, J. S. Lee, and S. Kang, "A metallic anti-biofouling surface with a hierarchical topography containing nanostructures on curved micro-riblets," *Microsyst Nanoeng*, vol. 8, no. 1, pp. 1–14, Jan. 2022, doi: 10.1038/s41378-021-00341-3.
- [171] M. H. Abd Aziz *et al.*, "Self-cleaning and anti-fouling superhydrophobic hierarchical ceramic surface synthesized from hydrothermal and fluorination methods," *Applied Surface Science*, vol. 598, p. 153702, Oct. 2022, doi: 10.1016/j.apsusc.2022.153702.
- [172] J. Chen *et al.*, "Superhydrophobic surfaces cannot reduce ice adhesion," *Applied Physics Letters*, vol. 101, no. 11, p. 111603, Sep. 2012, doi: 10.1063/1.4752436.
- [173] E. A. Blekkan and A. Holmen, "Coke formation on metal foils from heavy oils," *Carbon*, vol. 25, no. 6, pp. 827–835, Jan. 1987, doi: 10.1016/0008-6223(87)90158-8.
- [174] Y. Gu *et al.*, "Research progress of biomimetic superhydrophobic surface characteristics, fabrication, and application," *Advances in Mechanical Engineering*, vol. 9, no. 12, p. 1687814017746859, Dec. 2017, doi: 10.1177/1687814017746859.
- [175] D. Kumar, S. Idapalapati, W. Wang, and S. Narasimalu, "Effect of Surface Mechanical Treatments on the Microstructure-Property-Performance of Engineering Alloys," *Materials*, vol. 12, no. 16, Art. no. 16, Jan. 2019, doi: 10.3390/ma12162503.
- [176] G. V. Kuznetsov *et al.*, "Influence of roughness on polar and dispersed components of surface free energy and wettability properties of copper and steel surfaces," *Surface and Coatings Technology*, vol. 422, p. 127518, Sep. 2021, doi: 10.1016/j.surfcoat.2021.127518.
- [177] X. Wang and Q. Zhang, "Role of surface roughness in the wettability, surface energy and flotation kinetics of calcite," *Powder Technology*, vol. 371, pp. 55–63, Jun. 2020, doi: 10.1016/j.powtec.2020.05.081.

- [178] W.-J. Liu *et al.*, “Annealing Effect on the Contact Angle, Surface Energy, Electric Property, and Nanomechanical Characteristics of Co₄₀Fe₄₀W₂₀ Thin Films,” *Coatings*, vol. 11, no. 11, Art. no. 11, Nov. 2021, doi: 10.3390/coatings11111268.
- [179] H. Müller-Steinhagen and Q. Zhao, “Investigation of low fouling surface alloys made by ion implantation technology,” *Chemical Engineering Science*, vol. 52, no. 19, pp. 3321–3332, Oct. 1997, doi: 10.1016/S0009-2509(97)00162-0.
- [180] A. Nejim, C. Jeynes, Q. Zhao, and H. Muller-Steinhagen, “Ion implantation of stainless steel heater alloys for anti-fouling applications,” in *1998 International Conference on Ion Implantation Technology. Proceedings (Cat. No.98EX144)*, Kyoto, Japan, Jun. 1998, pp. 869–872 vol.2. doi: 10.1109/IIT.1998.813806.
- [181] Q. Zhao and B. M. Burnside, “Dropwise condensation of steam on ion implanted condenser surfaces,” *Heat Recovery Systems and CHP*, vol. 14, no. 5, pp. 525–534, Sep. 1994, doi: 10.1016/0890-4332(94)90055-8.
- [182] G. Azimi, Y. Cui, A. Sabanska, and K. K. Varanasi, “Scale-resistant surfaces: Fundamental studies of the effect of surface energy on reducing scale formation,” *Applied Surface Science*, vol. 313, pp. 591–599, Sep. 2014, doi: 10.1016/j.apsusc.2014.06.028.
- [183] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, Sixth. New York: Wiley-Interscience, 1997.
- [184] D. K. Owens and R. C. Wendt, “Estimation of the surface free energy of polymers,” *Journal of Applied Polymer Science*, vol. 13, no. 8, pp. 1741–1747, 1969, doi: 10.1002/app.1969.070130815.
- [185] C. J. Van Oss, M. K. Chaudhury, and R. J. Good, “Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems,” *Chem. Rev.*, vol. 88, no. 6, pp. 927–941, Sep. 1988, doi: 10.1021/cr00088a006.
- [186] S. Wu and K. J. Brzozowski, “Surface free energy and polarity of organic pigments,” *Journal of Colloid and Interface Science*, vol. 37, no. 4, pp. 686–690, Dec. 1971, doi: 10.1016/0021-9797(71)90347-X.
- [187] M. Kalin and M. Polajnar, “The correlation between the surface energy, the contact angle and the spreading parameter, and their relevance for the wetting behaviour of DLC with lubricating oils,” *Tribology International*, vol. 66, pp. 225–233, Oct. 2013, doi: 10.1016/j.triboint.2013.05.007.
- [188] M. Kalin and M. Polajnar, “The Effect of Wetting and Surface Energy on the Friction and Slip in Oil-Lubricated Contacts,” *Tribol Lett*, vol. 52, no. 2, pp. 185–194, Nov. 2013, doi: 10.1007/s11249-013-0194-y.
- [189] T. L. Clare and N. A. Swartz, “Chapter 19 - Characterization of High Performance Protective Coatings for Use on Culturally Significant Works,” in *Intelligent Coatings for Corrosion Control*, A. Tiwari, J. Rawlins, and L. H. Hihara, Eds., Boston: Butterworth-Heinemann, 2015, pp. 641–671. doi: 10.1016/B978-0-12-411467-8.00019-2.
- [190] C. Wei, G. Wang, M. Cridland, D. L. Olson, and S. Liu, “Chapter 25 - Corrosion Protection of Ships,” in *Handbook of Environmental Degradation of Materials (Third Edition)*, M. Kutz,

- Ed., William Andrew Publishing, 2018, pp. 533–557. doi: 10.1016/B978-0-323-52472-8.00026-5.
- [191] R. Asmatulu, “14 - Nanocoatings for corrosion protection of aerospace alloys,” in *Corrosion Protection and Control Using Nanomaterials*, V. S. Saji and R. Cook, Eds., in Woodhead Publishing Series in Metals and Surface Engineering. , Woodhead Publishing, 2012, pp. 357–374. doi: 10.1533/9780857095800.2.357.
- [192] A. Bahadori, *Essentials of coating, painting, and lining for the oil, gas, and petrochemical industries*. Amsterdam: GPP, Gulf Professional Publishing/Elsevier, 2015.
- [193] T. Byrnes, “24 - Pipeline coatings,” in *Trends in Oil and Gas Corrosion Research and Technologies*, A. M. El-Sherik, Ed., in Woodhead Publishing Series in Energy. , Boston: Woodhead Publishing, 2017, pp. 563–591. doi: 10.1016/B978-0-08-101105-8.00024-3.
- [194] Solvay, “Reliable Performance in O&G Extreme Environments - Specialty Polymers.” 2020. [Online]. Available: https://www.solvay.com/sites/g/files/srpend221/files/2018-10/Oil-Gas-Reliable-Performance-in-Extreme-Environments_EN-v2.0_0.pdf
- [195] B. Bhushan, *Principles and applications of tribology*, Second edition. in Tribology series. Chichester, West Sussex, UK: Wiley, 2013.
- [196] C. J. Li, “7 - Thermal spraying of light alloys,” in *Surface Engineering of Light Alloys*, H. Dong, Ed., in Woodhead Publishing Series in Metals and Surface Engineering. , Woodhead Publishing, 2010, pp. 184–241. doi: 10.1533/9781845699451.2.184.
- [197] M. Kandeve, A. Vencl, and D. Karastoyanov, *Advanced Tribological Coatings for Heavy-Duty Applications: Case Studies*. Sofia, BG: Prof. Marin Drinov Publishing House of Bulgarian Academy of Sciences, 2016.
- [198] P. Christoforou, R. Dowding, C. Pinna, and R. Lewis, “Two-layer laser clad coating as a replacement for chrome electroplating on forged steel,” *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, vol. 235, no. 23, pp. 7120–7138, Dec. 2021, doi: 10.1177/09544062211010853.
- [199] A. Vencl, M. Mrdak, and I. Cvijović, “Microstructures and tribological properties of ferrous coatings deposited by APS (atmospheric plasma spraying) on Al-alloy substrate,” *FME Transactions*, vol. 34, pp. 151–157, Sep. 2006.
- [200] X. Yang, C. Zhao-hui, and C. Feng, “High-temperature protective coatings for C/SiC composites,” *Journal of Asian Ceramic Societies*, vol. 2, no. 4, pp. 305–309, Dec. 2014, doi: 10.1016/j.jascer.2014.07.004.
- [201] S. Wu *et al.*, “Structural Design and Fabrication of Multifunctional Nanocarbon Materials for Extreme Environmental Applications,” *Advanced Materials*, vol. 34, no. 52, p. 2201046, 2022, doi: 10.1002/adma.202201046.
- [202] Y. Zhao *et al.*, “Porous architecture and thermal properties of thermal barrier coatings deposited by suspension plasma spray,” *Surface and Coatings Technology*, vol. 386, p. 125462, Mar. 2020, doi: 10.1016/j.surfcoat.2020.125462.
- [203] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, and S.-H. Yu, “A Facile and General Coating Approach to Moisture/Water-Resistant Metal–Organic Frameworks with Intact Porosity,” *J. Am. Chem. Soc.*, vol. 136, no. 49, pp. 16978–16981, Dec. 2014, doi: 10.1021/ja509960n.

- [204] H. Maab and S. Pereira Nunes, "Porous polyoxadiazole membranes for harsh environment," *Journal of Membrane Science*, vol. 445, pp. 127–134, Oct. 2013, doi: 10.1016/j.memsci.2013.05.038.
- [205] R. J. K. Wood and P. Lu, "Coatings and Surface Modification of Alloys for Tribo-Corrosion Applications," *Coatings*, vol. 14, no. 1, Art. no. 1, Jan. 2024, doi: 10.3390/coatings14010099.
- [206] R. Bianco and R. A. Rapp, "Pack cementation diffusion coatings," in *Metallurgical and Ceramic Protective Coatings*, K. H. Stern, Ed., Dordrecht: Springer Netherlands, 1996, pp. 236–260. doi: 10.1007/978-94-009-1501-5_9.
- [207] F. Ropital, P. Broutin, M. F. Reyniers, and G. F. Froment, "Anticoking Coatings for High Temperature Petrochemical Reactors," *Oil & Gas Science and Technology - Rev. IFP*, vol. 54, no. 3, pp. 375–385, May 1999, doi: 10.2516/ogst:1999034.
- [208] B. Bao, J. Liu, H. Xu, Z. Wang, and K. Zhang, "Fabrication of Spinel Coating on Hp40 Alloy and Its Inhibition Effect on Catalytic Coking During Thermal Cracking of Light Naphtha," *Braz. J. Chem. Eng.*, vol. 35, no. 2, pp. 721–730, Jun. 2018, doi: 10.1590/0104-6632.20180352s20160670.
- [209] R. A. Rapp, "The codeposition of elements in diffusion coatings by the pack cementation method," *Materials at High Temperatures*, vol. 11, no. 1–4, pp. 181–184, Jan. 1993, doi: 10.1080/09603409.1993.11689460.
- [210] S. Šteković, *Low cycle fatigue and thermo-mechanical fatigue of uncoated and coated nickel-base superalloys*. Linköping: Department of Managenet and Engineering, Linköping University, 2007.
- [211] C. Bischoff, R. Losada, T. Poulsen, L. Jackowski, and S. Taylor, "Development of Thin Sol-Gel Coatings for Heat Exchanger Fouling Mitigation at Elevated Temperatures," *Heat Exchanger Fouling and Cleaning*, p. 4, 2017.
- [212] E. Mahmoudi, A. Hafizi, M. R. Rahimpour, A. Bolhasani, and A. Shariati, "Inhibition effect of CeO₂ promoted SiO₂ coating on coke growth during steam cracking of ethane," *Chemical Engineering Research and Design*, vol. 136, pp. 271–281, Aug. 2018, doi: 10.1016/j.cherd.2018.05.040.
- [213] H. T. Kwon *et al.*, "Sol-gel derived CeO₂/α-Al₂O₃ bilayer thin film as an anti-coking barrier and its catalytic coke oxidation performance," *AIChE J*, vol. 64, no. 11, pp. 4019–4026, Nov. 2018, doi: 10.1002/aic.16383.
- [214] D. Wang and Gordon. P. Bierwagen, "Sol–gel coatings on metals for corrosion protection," *Progress in Organic Coatings*, vol. 64, no. 4, pp. 327–338, Mar. 2009, doi: 10.1016/j.porgcoat.2008.08.010.
- [215] G. Ruhi, O. P. Modi, A. S. K. Sinha, and I. B. Singh, "Effect of sintering temperatures on corrosion and wear properties of sol–gel alumina coatings on surface pre-treated mild steel," *Corrosion Science*, vol. 50, no. 3, pp. 639–649, Mar. 2008, doi: 10.1016/j.corsci.2007.10.002.
- [216] M. Oksa, E. Turunen, T. Suhonen, T. Varis, and S.-P. Hannula, "Optimization and Characterization of High Velocity Oxy-fuel Sprayed Coatings: Techniques, Materials, and Applications," *Coatings*, vol. 1, no. 1, pp. 17–52, Sep. 2011, doi: 10.3390/coatings1010017.

- [217] Y. Sun, M. Huang, J. Li, Z. Wang, and J. Zhou, "Anti-coking performance of Cr/CeO₂ coating prepared by high velocity oxygen fuel spraying," *Fuel Processing Technology*, vol. 225, p. 107043, Jan. 2022, doi: 10.1016/j.fuproc.2021.107043.
- [218] A. Scrivani, M. Rosso, and L. Salvarani, "Performances and Reliability of Wc Based Thermal Spray Coatings." 15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Relitte (2001), Vol. 2.
- [219] S. Tang *et al.*, "Characterization of CVD TiN coating at different deposition temperatures and its application in hydrocarbon pyrolysis," *Surface and Coatings Technology*, vol. 258, pp. 1060–1067, Nov. 2014, doi: 10.1016/j.surfcoat.2014.07.029.
- [220] S. Tang, N. Shi, J. Wang, and A. Tang, "Comparison of the anti-coking performance of CVD TiN, TiO₂ and TiC coatings for hydrocarbon fuel pyrolysis," *Ceramics International*, vol. 43, no. 4, pp. 3818–3823, Mar. 2017, doi: 10.1016/j.ceramint.2016.12.036.
- [221] S. Tang *et al.*, "Inhibition Effect of APCVD Titanium Nitride Coating on Coke Growth during *n*-Hexane Thermal Cracking under Supercritical Conditions," *Ind. Eng. Chem. Res.*, vol. 53, no. 13, pp. 5432–5442, Apr. 2014, doi: 10.1021/ie401889p.
- [222] S. A. Sarris, S. H. Symoens, N. Olahova, M.-F. Reyniers, G. B. Marin, and K. M. Van Geem, "Alumina-based Coating for Coke Reduction in Steam Crackers," *Materials*, vol. 13, no. 9, Art. no. 9, Jan. 2020, doi: 10.3390/ma13092025.
- [223] C. Yang, G. Liu, X. Wang, R. Jiang, L. Wang, and X. Zhang, "Preparation and Anticoking Performance of MOCVD Alumina Coatings for Thermal Cracking of Hydrocarbon Fuels under Supercritical Conditions," *Ind. Eng. Chem. Res.*, vol. 51, no. 3, pp. 1256–1263, Jan. 2012, doi: 10.1021/ie201978c.
- [224] J. Zhou, Z. Wang, X. Luan, and H. Xu, "Anti-coking property of the SiO₂/S coating during light naphtha steam cracking in a pilot plant setup," *Journal of Analytical and Applied Pyrolysis*, vol. 90, no. 1, pp. 7–12, Jan. 2011, doi: 10.1016/j.jaap.2010.09.011.
- [225] J. Zhang, Q. Xue, and S. Li, "Microstructure and corrosion behavior of TiC/Ti(CN)/TiN multilayer CVD coatings on high strength steels," *Applied Surface Science*, vol. 280, pp. 626–631, Sep. 2013, doi: 10.1016/j.apsusc.2013.05.037.
- [226] H. L. Du, P. K. Datta, D. Griffin, A. Aljarany, and J. S. Burnell-Gray, "Oxidation and Sulfidation Behavior of AlTiN-Coated Ti-46.7Al-1.9W-0.5Si Intermetallic with CrN and NbN Diffusion Barriers at 850°C," *Oxidation of Metals*, vol. 60, no. 1, pp. 29–46, Aug. 2003, doi: 10.1023/A:1024613212818.
- [227] M. J. Kim, S. W. Chung, and D. B. Lee, "High-Temperature Sulfidation of SUS316L, TiN, and CrN Thin Films in (N₂/3.1%H₂O/2.42%H₂S)-Mixed Gas," *Materials Science Forum*, vol. 860, pp. 101–104, 2016, doi: 10.4028/www.scientific.net/MSF.860.101.
- [228] D. Hazelton, "A Surface Science Approach Towards Understanding and Mitigating Fouling and Corrosion in Crude Oil Refinery Units," University of Alberta, 2021.
- [229] P. J. Kelly and R. D. Arnell, "Magnetron sputtering: a review of recent developments and applications," *Vacuum*, vol. 56, no. 3, pp. 159–172, Mar. 2000, doi: 10.1016/S0042-207X(99)00189-X.

- [230] M. Ohring, “Chapter 5 - Plasma and Ion Beam Processing of Thin Films,” in *Materials Science of Thin Films (Second Edition)*, M. Ohring, Ed., San Diego: Academic Press, 2002, pp. 203–275. doi: 10.1016/B978-012524975-1/50008-2.
- [231] J. Musil, P. Baroch, J. Vlček, K. H. Nam, and J. G. Han, “Reactive magnetron sputtering of thin films: present status and trends,” *Thin Solid Films*, vol. 475, no. 1, pp. 208–218, Mar. 2005, doi: 10.1016/j.tsf.2004.07.041.
- [232] S. Berg and T. Nyberg, “Fundamental understanding and modeling of reactive sputtering processes,” *Thin Solid Films*, vol. 476, no. 2, pp. 215–230, Apr. 2005, doi: 10.1016/j.tsf.2004.10.051.
- [233] S. Berg, H.-O. Blom, T. Larsson, and C. Nender, “Modeling of reactive sputtering of compound materials,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 5, no. 2, pp. 202–207, Mar. 1987, doi: 10.1116/1.574104.
- [234] W. D. Sproul, D. J. Christie, and D. C. Carter, “Control of reactive sputtering processes,” *Thin Solid Films*, vol. 491, no. 1, pp. 1–17, Nov. 2005, doi: 10.1016/j.tsf.2005.05.022.
- [235] A. Anders, “Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS),” *Journal of Applied Physics*, vol. 121, no. 17, p. 171101, May 2017, doi: 10.1063/1.4978350.
- [236] R. A. Scholl, “Power systems for reactive sputtering of insulating films,” *Surface and Coatings Technology*, vol. 93, no. 1, pp. 7–13, Aug. 1997, doi: 10.1016/S0257-8972(97)00032-7.
- [237] G. Este and W. D. Westwood, “A quasi-direct-current sputtering technique for the deposition of dielectrics at enhanced rates,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 6, no. 3, pp. 1845–1848, May 1988, doi: 10.1116/1.575266.
- [238] A. Anders, “A structure zone diagram including plasma-based deposition and ion etching,” *Thin Solid Films*, vol. 518, no. 15, pp. 4087–4090, May 2010, doi: 10.1016/j.tsf.2009.10.145.
- [239] J. Ann Gan and C. C. Berndt, “23 - Thermal spray forming of titanium and its alloys,” in *Titanium Powder Metallurgy*, M. Qian and F. H. (Sam) Froes, Eds., Boston: Butterworth-Heinemann, 2015, pp. 425–446. doi: 10.1016/B978-0-12-800054-0.00023-X.
- [240] V. Albaladejo-Fuentes, A. Maria Martos, A. Silvello, S. Dosta, J. Sanchez, and I. G. Cano, “Coatings, Surface Modifications, Spray Techniques (Cold Spray, HVOF/HVAF),” in *Encyclopedia of Materials: Metals and Alloys*, F. G. Caballero, Ed., Oxford: Elsevier, 2022, pp. 451–464. doi: 10.1016/B978-0-12-819726-4.00124-1.
- [241] M. R. Dorfman, “Chapter 22 - Thermal Spray Coatings,” in *Handbook of Environmental Degradation of Materials (Third Edition)*, M. Kutz, Ed., William Andrew Publishing, 2018, pp. 469–488. doi: 10.1016/B978-0-323-52472-8.00023-X.
- [242] M. F. Smith, “3 - Comparing cold spray with thermal spray coating technologies,” in *The Cold Spray Materials Deposition Process*, V. K. Champagne, Ed., in Woodhead Publishing Series in Metals and Surface Engineering, Woodhead Publishing, 2007, pp. 43–61. doi: 10.1533/9781845693787.1.43.

- [243] D. Kumar, “Recent advances in tribology of high entropy alloys: A critical review,” *Progress in Materials Science*, vol. 136, p. 101106, Jul. 2023, doi: 10.1016/j.pmatsci.2023.101106.
- [244] A. R. Govande, A. Chandak, B. R. Sunil, and R. Dumpala, “Carbide-based thermal spray coatings: A review on performance characteristics and post-treatment,” *International Journal of Refractory Metals and Hard Materials*, vol. 103, p. 105772, Feb. 2022, doi: 10.1016/j.ijrmhm.2021.105772.
- [245] M. I. Boulos, P. L. Fauchais, and J. V. R. Heberlein, *Thermal Spray Fundamentals: From Powder to Part*. Cham: Springer International Publishing, 2021. doi: 10.1007/978-3-030-70672-2.
- [246] M. S. El-Eskandarany, “11 - Utilization of mechanically alloyed powders for surface protective coating,” in *Mechanical Alloying (Second Edition)*, M. S. El-Eskandarany, Ed., Oxford: William Andrew Publishing, 2015, pp. 306–321. doi: 10.1016/B978-1-4557-7752-5.00011-5.
- [247] E. Dongmo, M. Wenzelburger, and R. Gadow, “Analysis and optimization of the HVOF process by combined experimental and numerical approaches,” *Surface and Coatings Technology*, vol. 202, no. 18, pp. 4470–4478, Jun. 2008, doi: 10.1016/j.surfcoat.2008.04.029.
- [248] E. Jonda, L. Łatka, and W. Pakieła, “Microstructure and Selected Properties of Cr₃C₂–NiCr Coatings Obtained by HVOF on Magnesium Alloy Substrates,” *Materials*, vol. 13, no. 12, Art. no. 12, Jan. 2020, doi: 10.3390/ma13122775.
- [249] D. M. Mattox, Ed., “Front-matter,” in *Handbook of Physical Vapor Deposition (PVD) Processing (Second Edition)*, Boston: William Andrew Publishing, 2010, pp. i–iii. doi: 10.1016/B978-0-8155-2037-5.00025-3.
- [250] W. D. Bosscher, D. Cnockaert, and H. Lievens, “Advances in Cylindrical Magnetrons”.
- [251] R. De Gryse, J. Haemers, W. P. Leroy, and D. Depla, “Thirty years of rotatable magnetrons,” *Thin Solid Films*, vol. 520, no. 18, pp. 5833–5845, Jul. 2012, doi: 10.1016/j.tsf.2012.04.065.
- [252] H. Rezaei, X. Liu, S. J. Ardakani, K. J. Smith, and M. Bricker, “A study of Cold Lake Vacuum Residue hydroconversion in batch and semi-batch reactors using unsupported MoS₂ catalysts,” *Catalysis Today*, vol. 150, no. 3, pp. 244–254, Mar. 2010, doi: 10.1016/j.cattod.2009.10.005.
- [253] K. Wu, X. Li, C. Wang, W. Yu, and Z. Chen, “Model for Surface Diffusion of Adsorbed Gas in Nanopores of Shale Gas Reservoirs,” *Ind. Eng. Chem. Res.*, vol. 54, no. 12, pp. 3225–3236, Apr. 2015, doi: 10.1021/ie504030v.
- [254] R. C. Reed, T. Tao, and N. Warnken, “Alloys-By-Design: Application to nickel-based single crystal superalloys,” *Acta Materialia*, vol. 57, no. 19, pp. 5898–5913, Nov. 2009, doi: 10.1016/j.actamat.2009.08.018.
- [255] B. Fotovvati, N. Namdari, and A. Dehghanghadikolaei, “On Coating Techniques for Surface Protection: A Review,” *Journal of Manufacturing and Materials Processing*, vol. 3, no. 1, Art. no. 1, Mar. 2019, doi: 10.3390/jmmp3010028.

- [256] K. Simunovic, L. Slokar, and S. Havrlisan, "SEM/EDS investigation of one-step flame sprayed and fused Ni-based self-fluxing alloy coatings on steel substrates," *Philosophical Magazine*, vol. 97, no. 4, pp. 248–268, Feb. 2017, doi: 10.1080/14786435.2016.1257167.
- [257] T. S. Sidhu, S. Prakash, and R. D. Agrawal, "Studies of the metallurgical and mechanical properties of high velocity oxy-fuel sprayed stellite-6 coatings on Ni- and Fe-based superalloys," *Surface and Coatings Technology*, vol. 201, no. 1, pp. 273–281, Sep. 2006, doi: 10.1016/j.surfcoat.2005.11.108.
- [258] D. Nečas and P. Klapetek, "Gwyddion: an open-source software for SPM data analysis," *Open Physics*, vol. 10, no. 1, pp. 181–188, Feb. 2012, doi: 10.2478/s11534-011-0096-2.
- [259] "Alumina Coatings on Ni-based Superalloys: The Impact of Annealing on Heavy Oil Fouling. UNDER REVISION.," 2024.
- [260] "Enhanced Heavy Oil Fouling Resistance of Cobalt-based Spray-Deposited Coatings by Alloy Design and Heat Treatment. UNDER REVISION.," 2024.
- [261] T. Liu, T. Jiang, J. Zhong, K. Guan, Z. Wang, and F. Arjmand, "Failure analysis of sulphidation-oxidation corrosion of Incoloy 800HT superheater tube," *Engineering Failure Analysis*, vol. 142, p. 106798, Dec. 2022, doi: 10.1016/j.engfailanal.2022.106798.
- [262] Kh. A. Al-hatab, M. A. Al-bukhaiti, U. Krupp, and M. Kantehm, "Cyclic Oxidation Behavior of IN 718 Superalloy in Air at High Temperatures," *Oxid Met*, vol. 75, no. 3, pp. 209–228, Apr. 2011, doi: 10.1007/s11085-010-9230-6.
- [263] O. Altin and S. Eser, "Pre-oxidation of Inconel Alloys for Inhibition of Carbon Deposition from Heated Jet Fuel," *Oxid Met*, vol. 65, no. 1, pp. 75–99, Feb. 2006, doi: 10.1007/s11085-006-9002-5.
- [264] D. Coutsouradis, A. Davin, and M. Lamberigts, "Cobalt-based superalloys for applications in gas turbines," *Materials Science and Engineering*, vol. 88, pp. 11–19, Apr. 1987, doi: 10.1016/0025-5416(87)90061-9.
- [265] K. Kanaya and S. Okayama, "Penetration and energy-loss theory of electrons in solid targets," *J. Phys. D: Appl. Phys.*, vol. 5, no. 1, pp. 43–58, Jan. 1972, doi: 10.1088/0022-3727/5/1/308.
- [266] I. Gurrappa, I. V. S. Yashwanth, and J. S. Burnell-Gray, "Sulfidation Characteristics of an Advanced Superalloy and Comparison with Other Superalloys Intended for Gas Turbine Use," *Metall and Mat Trans A*, vol. 44, no. 11, pp. 5270–5280, Nov. 2013, doi: 10.1007/s11661-013-1859-8.
- [267] S. Mrowec, "On the mechanism of high temperature oxidation of metals and alloys," *Corrosion Science*, vol. 7, no. 9, pp. 563–578, Jan. 1967, doi: 10.1016/0010-938X(67)80033-7.
- [268] A. Brückman, "The mechanism of transport of matter through the scales during oxidation of metals and alloys," *Corrosion Science*, vol. 7, no. 1, pp. 51–59, Jan. 1967, doi: 10.1016/S0010-938X(67)80069-6.
- [269] D. Wilson, G. Polley, and S. Pugh, "Ten Years of Ebert, Panchal and the 'Threshold Fouling' Concept," *Heat Exchanger Fouling and Cleaning - Challenges and Opportunities*, p. 25, Jun. 2005.

- [270] D. I. Wilson, E. M. Ishiyama, and G. T. Polley, “Twenty Years of Ebert and Panchal—What Next?,” *Heat Transfer Engineering*, vol. 38, no. 7–8, pp. 669–680, May 2017, doi: 10.1080/01457632.2016.1206407.
- [271] T. O. Dembaremba, S. Majodina, R. S. Walmsley, A. S. Ogunlaja, and Z. R. Tshentu, “Perspectives on strategies for improving ultra-deep desulfurization of liquid fuels through hydrotreatment: Catalyst improvement and feedstock pre-treatment,” *Front. Chem.*, vol. 10, Jul. 2022, doi: 10.3389/fchem.2022.807225.
- [272] B. Grégoire, X. Montero, M. C. Galetz, G. Bonnet, and F. Pedraza, “Mechanisms of hot corrosion of pure nickel at 700°C: Influence of testing conditions,” *Corrosion Science*, vol. 141, pp. 211–220, Aug. 2018, doi: 10.1016/j.corsci.2018.06.009.
- [273] “Synthesis of Ti,Cr,Mn,Fe,Co,Ni,Cu,Zn sulfide by solid-gas reactions, investigation of structural and conducting properties,” Master of Science, Middle East Technical university, 2005.
- [274] F. S. Rocha *et al.*, “Enhanced heavy oil fouling resistance of cobalt-based spray-deposited coatings by alloy design and heat treatment,” *Surface and Coatings Technology*, vol. 495, p. 131528, Jan. 2025, doi: 10.1016/j.surfcoat.2024.131528.
- [275] K. Sotoodeh, “A Review and Analysis of Industrial Valve Material Failures Due to Corrosion and Proposals for Prevention Measures Based on Industrial Experiences in the Offshore Sector of the Oil and Gas Industry,” *J Fail. Anal. and Preven.*, vol. 21, no. 1, pp. 261–267, Feb. 2021, doi: 10.1007/s11668-020-01064-9.
- [276] A. Kundu, K. Nigam, A.-M. Billet, and H. Delmas, “Recent developments on hydroprocessing reactors,” *Reviews in Chemical Engineering*, vol. 19, no. 6, pp. 531–605, 2003, doi: 10.1515/REVCE.2003.19.6.531.
- [277] I. Gurrappa, I. V. S. Yashwanth, and J. S. Burnell-Gray, “Sulfidation Characteristics of an Advanced Superalloy and Comparison with Other Superalloys Intended for Gas Turbine Use,” *Metall Mater Trans A*, vol. 44, no. 11, pp. 5270–5280, Nov. 2013, doi: 10.1007/s11661-013-1859-8.
- [278] K. Natesan, “Oxidation-sulfidation behavior of nickel-base superalloys and M-Cr-Al coatings,” *Materials Science and Engineering*, vol. 87, pp. 99–106, Mar. 1987, doi: 10.1016/0025-5416(87)90365-X.
- [279] S. Kumar, B. Satapathy, D. Pradhan, and G. S. Mahobia, “Effect of surface modification on the hot corrosion resistance of Inconel 718 at 700 °C,” *Mater. Res. Express*, vol. 6, no. 8, p. 086549, May 2019, doi: 10.1088/2053-1591/ab1dc7.
- [280] R. Jafari and E. Sadeghi, “High-temperature corrosion performance of HVOF-sprayed NiCr, NiAl, and NiCrAlY coatings with alkali sulfate/chloride exposed to ambient air,” *Corrosion Science*, vol. 160, p. 108066, Nov. 2019, doi: 10.1016/j.corsci.2019.06.021.
- [281] J. G. Odhiambo, W. Li, Y. Zhao, and C. Li, “Porosity and Its Significance in Plasma-Sprayed Coatings,” *Coatings*, vol. 9, no. 7, Art. no. 7, Jul. 2019, doi: 10.3390/coatings9070460.

- [282] L. N. Moskowitz, "Application of HVOF thermal spraying to solve corrosion problems in the petroleum industry—an industrial note," *JTST*, vol. 2, no. 1, pp. 21–29, Mar. 1993, doi: 10.1007/BF02647419.
- [283] T. S. Sidhu, R. D. Agrawal, and S. Prakash, "Hot corrosion of some superalloys and role of high-velocity oxy-fuel spray coatings—a review," *Surface and Coatings Technology*, vol. 198, no. 1, pp. 441–446, Aug. 2005, doi: 10.1016/j.surfcoat.2004.10.056.
- [284] G. Bolelli, L. Lusvardi, and R. Giovanardi, "A comparison between the corrosion resistances of some HVOF-sprayed metal alloy coatings," *Surface and Coatings Technology*, vol. 202, no. 19, pp. 4793–4809, Jun. 2008, doi: 10.1016/j.surfcoat.2008.04.056.
- [285] P. Fauchais and A. Vardelle, "Thermal Sprayed Coatings Used Against Corrosion and Corrosive Wear," in *Advanced Plasma Spray Applications*, vol. 1, IntechOpen, 2012. doi: 10.5772/34448.
- [286] A. Scrivani, S. Ianelli, A. Rossi, R. Groppetti, F. Casadei, and G. Rizzi, "A contribution to the surface analysis and characterisation of HVOF coatings for petrochemical application," *Wear*, vol. 250, no. 1–12, pp. 107–113, Oct. 2001, doi: 10.1016/S0043-1648(01)00621-4.
- [287] Š. Houdková, E. Smazalová, and Z. Pala, "Effect of Heat Treatment on the Microstructure and Properties of HVOF-Sprayed Co-Cr-W Coating," *J Therm Spray Tech*, vol. 25, no. 3, pp. 546–557, Feb. 2016, doi: 10.1007/s11666-015-0365-5.
- [288] N. Jegadeeswaran, M. R. Ramesh, S. Prakrathi, and K. U. Bhat, "Hot Corrosion Behaviour of HVOF Sprayed Stellite-6 Coatings on Gas Turbine Alloys," *Trans Indian Inst Met*, vol. 67, no. 1, pp. 87–93, Feb. 2014, doi: 10.1007/s12666-013-0317-z.
- [289] H. S. Sidhu, B. S. Sidhu, and S. Prakash, "Hot Corrosion Behavior of HVOF Sprayed Coatings on ASTM SA213-T11 Steel," *J Therm Spray Tech*, vol. 16, no. 3, pp. 349–354, Sep. 2007, doi: 10.1007/s11666-007-9029-4.
- [290] D. Raghu, D. A. Lee, and P. M. Singh, "High-temperature corrosion and wear properties of HVOF coatings of cobalt-based (CoCr) surfacing alloys," NACE International, Houston, TX (US), CONF-990401-, Jul. 1999. Accessed: Feb. 17, 2024. [Online]. Available: <https://www.osti.gov/biblio/20002620>
- [291] G. Oppong Boakye, E. O. Straume, B. G. Gunnarsson, D. Kovalov, and S. N. Karlsdottir, "Corrosion behaviour of HVOF developed Mo-based high entropy alloy coating and selected hard coatings for high temperature geothermal applications," *Materials & Design*, vol. 235, p. 112431, Nov. 2023, doi: 10.1016/j.matdes.2023.112431.
- [292] Q. X. Fan, S. M. Jiang, H. J. Yu, J. Gong, and C. Sun, "Microstructure and hot corrosion behaviors of two Co modified aluminide coatings on a Ni-based superalloy at 700°C," *Applied Surface Science*, vol. 311, pp. 214–223, Aug. 2014, doi: 10.1016/j.apsusc.2014.05.043.
- [293] W. C. Oliver and G. M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," *Journal of Materials Research*, vol. 7, no. 6, pp. 1564–1583, Jun. 1992, doi: 10.1557/JMR.1992.1564.
- [294] J. Kestin, M. Sokolov, and W. A. Wakeham, "Viscosity of liquid water in the range –8 °C to 150 °C," *Journal of Physical and Chemical Reference Data*, vol. 7, no. 3, pp. 941–948, Jul. 1978, doi: 10.1063/1.555581.

- [295] M. A. Farah, R. C. Oliveira, J. N. Caldas, and K. Rajagopal, "Viscosity of water-in-oil emulsions: Variation with temperature and water volume fraction," *Journal of Petroleum Science and Engineering*, vol. 48, no. 3, pp. 169–184, Sep. 2005, doi: 10.1016/j.petrol.2005.06.014.
- [296] G. Prashar, H. Vasudev, and L. Thakur, "Influence of heat treatment on surface properties of HVOF deposited WC and Ni-based powder coatings: a review," *Surf. Topogr.: Metrol. Prop.*, vol. 9, no. 4, p. 043002, Dec. 2021, doi: 10.1088/2051-672X/ac3a52.
- [297] H. Vasudev, L. Thakur, A. Bansal, H. Singh, and S. Zafar, "High temperature oxidation and erosion behaviour of HVOF sprayed bi-layer Alloy-718/NiCrAlY coating," *Surface and Coatings Technology*, vol. 362, pp. 366–380, Mar. 2019, doi: 10.1016/j.surfcoat.2019.02.012.
- [298] G. Bolelli, L. Lusvarghi, and M. Barletta, "HVOF-sprayed WC–CoCr coatings on Al alloy: Effect of the coating thickness on the tribological properties," *Wear*, vol. 267, no. 5, pp. 944–953, Jun. 2009, doi: 10.1016/j.wear.2008.12.066.
- [299] W. Yang, L. Zou, X. Cao, J. Liu, D. Li, and Z. Cai, "Fretting wear properties of HVOF-sprayed CoMoCrSi coatings with different spraying parameters," *Surface and Coatings Technology*, vol. 358, pp. 994–1005, Jan. 2019, doi: 10.1016/j.surfcoat.2018.12.039.
- [300] T. Sahraoui, H. I. Feraoun, N. Fenineche, G. Montavon, H. Aourag, and C. Coddet, "HVOF-sprayed Triballoy®-400: microstructure and first principle calculations," *Materials Letters*, vol. 58, no. 19, pp. 2433–2436, Jul. 2004, doi: 10.1016/j.matlet.2004.02.025.
- [301] P. Sassatelli *et al.*, "Properties of HVOF-sprayed Stellite-6 coatings," *Surface and Coatings Technology*, vol. 338, pp. 45–62, Mar. 2018, doi: 10.1016/j.surfcoat.2018.01.078.
- [302] Z. Zhou *et al.*, "Tribological Properties and Corrosion Resistance of Stellite 20 Alloy Coating Prepared by HVOF and HVOF," *Coatings*, vol. 13, no. 4, Art. no. 4, Apr. 2023, doi: 10.3390/coatings13040806.
- [303] M. A. Zavareh, A. A. D. M. Sarhan, B. B. A. Razak, and W. J. Basirun, "Plasma thermal spray of ceramic oxide coating on carbon steel with enhanced wear and corrosion resistance for oil and gas applications," *Ceramics International*, vol. 40, no. 9, Part A, pp. 14267–14277, Nov. 2014, doi: 10.1016/j.ceramint.2014.06.017.
- [304] V. V. Sobolev and J. M. Guilemany, "Formation of chemical inhomogeneity in the coating structure during high velocity oxy-fuel (HVOF) spraying," *Materials Letters*, vol. 25, no. 5, pp. 285–289, Dec. 1995, doi: 10.1016/0167-577X(95)00174-3.
- [305] J. Wendel, "Thermodynamics and Kinetics of Tungsten Oxidation and Tungsten Oxide Sublimation in the Temperature Interval 200°–1100°C," Master, Lund University, Sweden, 2014.
- [306] G. Bolelli and L. Lusvarghi, "Heat treatment effects on the tribological performance of HVOF sprayed Co-Mo-Cr-Si coatings," *J Therm Spray Tech*, vol. 15, no. 4, pp. 802–810, Dec. 2006, doi: 10.1361/105996306X146721.
- [307] S. Ch, V. T, and A. K, "Materials Solutions to Address High Temperature Fretting Wear in Gas Turbine Combustor Components," Dec. 13, 2018, Rochester, NY: 3397894. doi: 10.2139/ssrn.3397894.

- [308] V. Kuzucu, M. Ceylan, H. Çelik, and İ. Aksoy, “Microstructure and phase analyses of Stellite 6 plus 6 wt.% Mo alloy,” *Journal of Materials Processing Technology*, vol. 69, no. 1, pp. 257–263, Sep. 1997, doi: 10.1016/S0924-0136(97)00027-7.
- [309] A. Farnia, F. Malek Ghaini, J. C. Rao, V. Ocelik, and J. Th. M. De Hosson, “Effect of Ta on the microstructure and hardness of Stellite 6 coating deposited by low power pulse laser treatments,” *Surface and Coatings Technology*, vol. 213, pp. 278–284, Dec. 2012, doi: 10.1016/j.surfcoat.2012.10.065.
- [310] Q. Wang, L. Li, G. Yang, X. Zhao, and Z. Ding, “Influence of heat treatment on the microstructure and performance of high-velocity oxy-fuel sprayed WC–12Co coatings,” *Surface and Coatings Technology*, vol. 206, no. 19, pp. 4000–4010, May 2012, doi: 10.1016/j.surfcoat.2012.03.080.
- [311] L. Tang *et al.*, “Significantly enhanced mechanical and tribological properties of Co-based alloy coatings by annealing treatment,” *Tribology International*, vol. 146, p. 106265, Jun. 2020, doi: 10.1016/j.triboint.2020.106265.
- [312] G. Bolelli, V. Cannillo, L. Lusvarghi, M. Montorsi, F. P. Mantini, and M. Barletta, “Microstructural and tribological comparison of HVOF-sprayed and post-treated M–Mo–Cr–Si (M=Co, Ni) alloy coatings,” *Wear*, vol. 263, no. 7, pp. 1397–1416, Sep. 2007, doi: 10.1016/j.wear.2006.12.002.
- [313] H. Guo, B. Li, P. Yan, and Z. Wu, “Microstructures, mechanical properties and tribological behaviors of HVOF-sprayed CoMoCrSi alloy coatings before and after 800 °C-annealed treatment,” *Journal of Alloys and Compounds*, vol. 909, p. 164662, Jul. 2022, doi: 10.1016/j.jallcom.2022.164662.
- [314] C. D. Prasad, S. Joladarashi, M. R. Ramesh, and M. S. Srinath, “Microstructural and Tribological Resistance of Flame-Sprayed CoMoCrSi/WC–CrC–Ni and CoMoCrSi/WC–12Co Composite Coatings Remelted by Microwave Energy,” *J Bio Tribo Corros*, vol. 6, no. 4, p. 124, Sep. 2020, doi: 10.1007/s40735-020-00421-3.
- [315] K. J. Kubiak, M. C. T. Wilson, T. G. Mathia, and Ph. Carval, “Wettability versus roughness of engineering surfaces,” *Wear*, vol. 271, no. 3, pp. 523–528, Jun. 2011, doi: 10.1016/j.wear.2010.03.029.
- [316] G. McHale, “Cassie and Wenzel: Were They Really So Wrong?,” *Langmuir*, vol. 23, no. 15, pp. 8200–8205, Jul. 2007, doi: 10.1021/la7011167.
- [317] B. J. Ryan and K. M. Poduska, “Roughness effects on contact angle measurements,” *American Journal of Physics*, vol. 76, no. 11, pp. 1074–1077, Nov. 2008, doi: 10.1119/1.2952446.
- [318] Q. Zheng and C. Lü, “Size Effects of Surface Roughness to Superhydrophobicity,” *Procedia IUTAM*, vol. 10, pp. 462–475, Jan. 2014, doi: 10.1016/j.piutam.2014.01.041.
- [319] D. Jin, Z. Di, K. Pan, M. Xiong, F. Yang, and S. Wei, “Hydrophobicity of Cr₃C₂–NiCr coating under mechanical abrasion and thermal annealing,” *Applied Surface Science*, vol. 574, p. 151600, Feb. 2022, doi: 10.1016/j.apsusc.2021.151600.

- [320] M. M. Awad, "Fouling of Heat Transfer Surfaces," in *Heat Transfer - Theoretical Analysis, Experimental Investigations and Industrial Systems*, IntechOpen, 2011, p. 668. doi: 10.5772/13696.
- [321] A. H. Nikoo and M. R. Malayeri, "Incorporation of surface energy properties into general crystallization fouling model for heat transfer surfaces," *Chemical Engineering Science*, vol. 215, p. 115461, Apr. 2020, doi: 10.1016/j.ces.2019.115461.
- [322] S. N. Kazi, G. G. Duffy, and X. D. Chen, "Fouling and Fouling Mitigation on Different Heat Exchanging Surfaces," 2009.
- [323] F. S. Rocha *et al.*, "Alumina coatings on Ni-based superalloys: The impact of annealing on heavy oil fouling," *Surface and Coatings Technology*, vol. 493, p. 131266, Oct. 2024, doi: 10.1016/j.surfcoat.2024.131266.
- [324] S. Patel, J. deBarbadillo, and S. Coryell, "Superalloy 718: Evolution of the Alloy from High to Low Temperature Application," in *Proceedings of the 9th International Symposium on Superalloy 718 & Derivatives: Energy, Aerospace, and Industrial Applications*, E. Ott, X. Liu, J. Andersson, Z. Bi, K. Bockenstedt, I. Dempster, J. Groh, K. Heck, P. Jablonski, M. Kaplan, D. Nagahama, and C. Sudbrack, Eds., in The Minerals, Metals & Materials Series. , Cham: Springer International Publishing, 2018, pp. 23–49. doi: 10.1007/978-3-319-89480-5_2.
- [325] R. G. Munro and S. J. Dapkunas, "Corrosion Characteristics of Silicon Carbide and Silicon Nitride," *J Res Natl Inst Stand Technol*, vol. 98, no. 5, pp. 607–631, 1993, doi: 10.6028/jres.098.040.
- [326] M. J. Madou, *Fundamentals of microfabrication: the science of miniaturization*, 2nd ed. Boca Raton: CRC Press, 2002.
- [327] I. Levin and D. Brandon, "Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences," *Journal of the American Ceramic Society*, vol. 81, no. 8, pp. 1995–2012, 1998, doi: 10.1111/j.1151-2916.1998.tb02581.x.
- [328] I. Neelakanta Reddy, V. Rajagopal Reddy, N. Sridhara, S. Basavaraja, A. K. Sharma, and A. Dey, "Optical and Microstructural Characterisations of Pulsed rf Magnetron Sputtered Alumina Thin Film," *Journal of Materials Science & Technology*, vol. 29, no. 10, pp. 929–936, Oct. 2013, doi: 10.1016/j.jmst.2013.05.002.
- [329] L. Landälv and C. and B. Department of Physics Thin Film Physics. Linköping University, Sweden, "Thin Film and Plasma Characterization of PVD Oxides," Linköping University, Sweden, 2017.
- [330] W. C. Oliver and G. M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," *Journal of Materials Research*, vol. 7, no. 6, pp. 1564–1583, Jun. 1992, doi: 10.1557/JMR.1992.1564.
- [331] K. Strijckmans, R. Schelfhout, and D. Depla, "Tutorial: Hysteresis during the reactive magnetron sputtering process," *Journal of Applied Physics*, vol. 124, no. 24, p. 241101, Dec. 2018, doi: 10.1063/1.5042084.
- [332] F. C. Silva, J. C. Sagás, L. C. Fontana, J. M. C. Miscione, R. C. Cozza, and C. G. Schön, "18 - Growth and properties of Functionally graded ceramic coatings deposited by grid-

- assisted magnetron sputtering,” in *Advanced Ceramic Coatings*, R. K. Gupta, A. Motallebzadeh, S. Kakooei, T. A. Nguyen, and A. Behera, Eds., in Elsevier Series in Advanced Ceramic Materials. , Elsevier, 2023, pp. 401–432. doi: 10.1016/B978-0-323-99659-4.00018-8.
- [333] M. Nofz, I. Dörfel, R. Sojref, and R. Saliwan Neumann, “Microstructure of Bare and Sol–Gel Alumina-Coated Nickel-Base Alloy Inconel 625 After Long-Term Oxidation at 900 °C,” *Oxid Met*, vol. 91, no. 3, pp. 395–416, Apr. 2019, doi: 10.1007/s11085-019-09888-z.
- [334] J. M. Andersson, E. Wallin, U. Helmersson, U. Kreissig, and E. P. Münger, “Phase control of Al₂O₃ thin films grown at low temperatures,” *Thin Solid Films*, vol. 513, no. 1, pp. 57–59, Aug. 2006, doi: 10.1016/j.tsf.2006.01.016.
- [335] Y. Zhao, Y. Qian, W. Yu, and Z. Chen, “Surface roughness of alumina films deposited by reactive r.f. sputtering,” *Thin Solid Films*, vol. 286, no. 1, pp. 45–48, Sep. 1996, doi: 10.1016/S0040-6090(95)08514-9.
- [336] M. Dressler, M. Nofz, I. Dörfel, and R. Saliwan-Neumann, “Influence of sol–gel derived alumina coatings on oxide scale growth of nickel-base superalloy Inconel-718,” *Surface and Coatings Technology*, vol. 202, no. 24, pp. 6095–6102, Aug. 2008, doi: 10.1016/j.surfcoat.2008.07.018.
- [337] M. Dressler, M. Nofz, I. Dörfel, and R. Saliwan-Neumann, “Diffusion of Cr, Fe, and Ti ions from Ni-base alloy Inconel-718 into a transition alumina coating,” *Thin Solid Films*, vol. 520, no. 13, pp. 4344–4349, Apr. 2012, doi: 10.1016/j.tsf.2012.02.006.
- [338] D. M. Gorman, R. L. Higginson, H. Du, G. McColvin, A. T. Fry, and R. C. Thomson, “Microstructural Analysis of IN617 and IN625 Oxidised in the Presence of Steam for use in Ultra-Supercritical Power Plant,” *Oxid Met*, vol. 79, no. 5, pp. 553–566, Jun. 2013, doi: 10.1007/s11085-012-9342-2.
- [339] R. P. Oleksak, C. S. Carney, G. R. Holcomb, and Ö. N. Doğan, “Structural Evolution of a Ni Alloy Surface During High-Temperature Oxidation,” *Oxid Met*, vol. 90, no. 1, pp. 27–42, Aug. 2018, doi: 10.1007/s11085-017-9821-6.
- [340] A. K. Krella, “Chapter 16 - Degradation of protective PVD coatings,” in *Handbook of Materials Failure Analysis with Case Studies from the Chemicals, Concrete and Power Industries*, A. S. H. Makhoul and M. Aliofkhazraei, Eds., Butterworth-Heinemann, 2016, pp. 411–440. doi: 10.1016/B978-0-08-100116-5.00016-8.
- [341] M. Abdoos, B. Bose, S. Rawal, A. F. M. Arif, and S. C. Veldhuis, “The influence of residual stress on the properties and performance of thick TiAlN multilayer coating during dry turning of compacted graphite iron,” *Wear*, vol. 454–455, p. 203342, Aug. 2020, doi: 10.1016/j.wear.2020.203342.
- [342] A. M. de Sousa Malafaia, R. B. de Oliveira, L. Latu-Romain, Y. Wouters, and R. Baldan, “Isothermal oxidation of Inconel 625 superalloy at 800 and 1000 °C: Microstructure and oxide layer characterization,” *Materials Characterization*, vol. 161, p. 110160, Mar. 2020, doi: 10.1016/j.matchar.2020.110160.
- [343] L. Boatemaa, C. Kwakernaak, S. van der Zwaag, and W. G. Sloof, “Selection of healing agents for autonomous healing of alumina at high temperatures,” *Journal of the European*

- Ceramic Society*, vol. 36, no. 16, pp. 4141–4145, Dec. 2016, doi: 10.1016/j.jeurceramsoc.2016.05.038.
- [344] G. R. Holcomb and D. E. Alman, “The effect of manganese additions on the reactive evaporation of chromium in Ni–Cr alloys,” *Scripta Materialia*, vol. 54, no. 10, pp. 1821–1825, May 2006, doi: 10.1016/j.scriptamat.2006.01.026.
- [345] P. Bowen and C. Carry, “From powders to sintered pieces: forming, transformations and sintering of nanostructured ceramic oxides,” *Powder Technology*, vol. 128, no. 2, pp. 248–255, Dec. 2002, doi: 10.1016/S0032-5910(02)00183-3.
- [346] J. Musil, J. Blažek, P. Zeman, Š. Prokšová, M. Šásek, and R. Čerstvý, “Thermal stability of alumina thin films containing γ -Al₂O₃ phase prepared by reactive magnetron sputtering,” *Applied Surface Science*, vol. 257, no. 3, pp. 1058–1062, Nov. 2010, doi: 10.1016/j.apsusc.2010.07.107.
- [347] X. Tang, “Effects of the annealing heating rate on sputtered aluminum oxide films,” *J. Wuhan Univ. Technol.-Mat. Sci. Edit.*, vol. 32, no. 1, pp. 94–99, Feb. 2017, doi: 10.1007/s11595-017-1565-2.
- [348] M. Dressler, M. Nofz, R. Saliwan-Neumann, I. Dörfel, and M. Griepentrog, “Sol–gel derived alumina layers on nickel-base superalloy Inconel-718 (IN-718),” *Thin Solid Films*, vol. 517, no. 2, pp. 786–792, Nov. 2008, doi: 10.1016/j.tsf.2008.08.124.
- [349] T. Connolley, P. A. S. Reed, and M. J. Starink, “Short crack initiation and growth at 600°C in notched specimens of Inconel718,” *Materials Science and Engineering: A*, vol. 340, no. 1, pp. 139–154, Jan. 2003, doi: 10.1016/S0921-5093(02)00169-7.
- [350] N. Birks, G. H. Meier, and F. S. Pettit, “High-Temperature Corrosion Resistance,” *JOM*, vol. 39, no. 12, pp. 28–31, Dec. 1987, doi: 10.1007/BF03257568.
- [351] S. A. Galedari, A. Mahdavi, F. Azarmi, Y. Huang, and A. McDonald, “A Comprehensive Review of Corrosion Resistance of Thermally-Sprayed and Thermally-Diffused Protective Coatings on Steel Structures,” *J Therm Spray Tech*, vol. 28, no. 4, pp. 645–677, Apr. 2019, doi: 10.1007/s11666-019-00855-3.
- [352] X. Gong, B. Wang, Y. He, W. He, and Q. Zhu, “TiN-SiO₂ double layer composite coating with enhanced oxidation resistance and reusability in anti-coking applications,” *Fuel*, vol. 324, p. 124808, Sep. 2022, doi: 10.1016/j.fuel.2022.124808.
- [353] H.-Y. Chen and F.-H. Lu, “Oxidation behavior of titanium nitride films,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 23, no. 4, pp. 1006–1009, Jul. 2005, doi: 10.1116/1.1914815.
- [354] H. Waldl, M. Tkadletz, A. Lechner, C. Czettl, M. Pohler, and N. Schalk, “Evolution of the fracture properties of arc evaporated Ti_{1-x}Al_xN coatings with increasing Al content,” *Surface and Coatings Technology*, vol. 444, p. 128690, Aug. 2022, doi: 10.1016/j.surfcoat.2022.128690.
- [355] H. D. Zhang, B. C. Wang, J. W. Du, and L. Chen, “Mechanical and thermal properties of AlN/Ti_{1-x}Al_xN (x = 0, 0.45 and 0.62) multilayers,” *Surface and Coatings Technology*, vol. 470, p. 129859, Oct. 2023, doi: 10.1016/j.surfcoat.2023.129859.

- [356] A. Joshi and H. S. Hu, "Oxidation behavior of titanium-aluminium nitrides," *Surface and Coatings Technology*, vol. 76–77, pp. 499–507, Dec. 1995, doi: 10.1016/0257-8972(95)02566-9.
- [357] M. Jafari *et al.*, "Thermal degradation of TiN and TiAlN coatings during rapid laser treatment," *Surface and Coatings Technology*, vol. 422, p. 127517, Sep. 2021, doi: 10.1016/j.surfcoat.2021.127517.
- [358] W. Münz, "Titanium aluminum nitride films: A new alternative to TiN coatings," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 4, no. 6, pp. 2717–2725, Nov. 1986, doi: 10.1116/1.573713.
- [359] T. Leyendecker, O. Lemmer, S. Esser, and J. Ebberink, "The development of the PVD coating TiAlN as a commercial coating for cutting tools," *Surface and Coatings Technology*, vol. 48, no. 2, pp. 175–178, Nov. 1991, doi: 10.1016/0257-8972(91)90142-J.
- [360] W. Liu *et al.*, "Preparation and properties of TiAlN coatings on silicon nitride ceramic cutting tools," *Ceramics International*, vol. 44, no. 2, pp. 2209–2215, Feb. 2018, doi: 10.1016/j.ceramint.2017.10.177.
- [361] J. Perez-Mariano *et al.*, "Multilayer coatings for corrosion protection of coal gasifier components," *Materials Chemistry and Physics*, vol. 112, no. 1, pp. 180–185, Nov. 2008, doi: 10.1016/j.matchemphys.2008.05.028.
- [362] L. Volpe, M. G. Burke, and F. Scenini, "Understanding the role of Diffusion Induced Grain Boundary Migration on the preferential intergranular oxidation behaviour of Alloy 600 via advanced microstructural characterization," *Acta Materialia*, vol. 175, pp. 238–249, Aug. 2019, doi: 10.1016/j.actamat.2019.06.021.
- [363] J. Musil, J. Vlček, and P. Zeman, "Hard amorphous nanocomposite coatings with oxidation resistance above 1000°C," *Advances in Applied Ceramics*, vol. 107, no. 3, pp. 148–154, May 2008, doi: 10.1179/174367508X306460.
- [364] V. Simova, S. Knittel, M. Cavarroc, L. Martinu, and J.-E. Klemberg-Sapieha, "Amorphous Si–B–C–N coatings for high-temperature oxidation protection of the γ -TiAl alloy," *Surface and Coatings Technology*, vol. 442, p. 128544, Jul. 2022, doi: 10.1016/j.surfcoat.2022.128544.
- [365] P. S. Souza, A. J. Santos, M. A. P. Cotrim, A. M. Abrão, and M. A. Câmara, "Analysis of the surface energy interactions in the tribological behavior of ALCrN and TiAlN coatings," *Tribology International*, vol. 146, p. 106206, Jun. 2020, doi: 10.1016/j.triboint.2020.106206.
- [366] A. Kozbial *et al.*, "Study on the Surface Energy of Graphene by Contact Angle Measurements," *Langmuir*, vol. 30, no. 28, pp. 8598–8606, Jul. 2014, doi: 10.1021/la5018328.
- [367] A. Leyland and A. Matthews, "On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour," *Wear*, vol. 246, no. 1, pp. 1–11, Nov. 2000, doi: 10.1016/S0043-1648(00)00488-9.
- [368] K.-Y. Law, "Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity: Getting the Basics Right," *J. Phys. Chem. Lett.*, vol. 5, no. 4, pp. 686–688, Feb. 2014, doi: 10.1021/jz402762h.

- [369] M. Annamalai *et al.*, “Surface energy and wettability of van der Waals structures,” *Nanoscale*, vol. 8, no. 10, pp. 5764–5770, 2016, doi: 10.1039/C5NR06705G.
- [370] C. J. Van Oss, R. J. Good, and M. K. Chaudhury, “The role of van der Waals forces and hydrogen bonds in ‘hydrophobic interactions’ between biopolymers and low energy surfaces,” *Journal of Colloid and Interface Science*, vol. 111, no. 2, pp. 378–390, Jun. 1986, doi: 10.1016/0021-9797(86)90041-X.
- [371] J. M. Schuster, C. E. Schvezov, and M. R. Rosenberger, “Analysis of the Results of Surface Free Energy Measurement of Ti6Al4V by Different Methods,” *Procedia Materials Science*, vol. 8, pp. 732–741, Jan. 2015, doi: 10.1016/j.mspro.2015.04.130.
- [372] A. Kondyli and W. Schrader, “Understanding ‘Fouling’ in Extremely Complex Petroleum Mixtures,” *ACS Appl. Energy Mater.*, vol. 3, no. 8, pp. 7251–7256, Aug. 2020, doi: 10.1021/acsaem.0c01326.
- [373] X. Gong *et al.*, “The dominant role of surface chemistry on coking resistance of passivating coating,” *Applied Energy*, vol. 352, p. 121929, Dec. 2023, doi: 10.1016/j.apenergy.2023.121929.
- [374] Y. Miao *et al.*, “Oxidation behavior of SiBCN-Zr composites at 1500 °C prepared by reactive spark plasma sintering,” *Corrosion Science*, vol. 132, pp. 293–299, Mar. 2018, doi: 10.1016/j.corsci.2018.01.003.
- [375] V. Sudarsan, “Chapter 4 - Materials for Hostile Chemical Environments,” in *Materials Under Extreme Conditions*, A. K. Tyagi and S. Banerjee, Eds., Amsterdam: Elsevier, 2017, pp. 129–158. doi: 10.1016/B978-0-12-801300-7.00004-8.
- [376] F. A. Costa Oliveira, R. J. Fordham, and J. H. W. de Wit, “The role of sulphur in the corrosion behaviour of silicon nitride ceramics in reducing environments at high temperatures,” in *Proceedings of the 6th National Meeting of the Portuguese Materials Society*, Porto, 1993, pp. 847–856.
- [377] N. N. Greenwood and A. Earnshaw, Eds., “9 - Silicon,” in *Chemistry of the Elements (Second Edition)*, Oxford: Butterworth-Heinemann, 1997, pp. 328–366. doi: 10.1016/B978-0-7506-3365-9.50015-8.
- [378] R. O. Suzuki *et al.*, “Synthesis of Silicon Sulfide by Using CS₂ Gas,” *Metall Mater Trans B*, vol. 52, no. 3, pp. 1379–1391, Jun. 2021, doi: 10.1007/s11663-021-02103-y.
- [379] W. Grzesik, J. Małecka, and W. Kwaśny, “Identification of oxidation process of TiAlN coatings versus heat resistant aerospace alloys based on diffusion couples and tool wear tests,” *CIRP Annals*, vol. 69, no. 1, pp. 41–44, Jan. 2020, doi: 10.1016/j.cirp.2020.04.024.
- [380] J.-L. Huang and B.-Y. Shew, “Effects of Aluminum Concentration on the Oxidation Behaviors of Reactively Sputtered TiAlN Films,” *Journal of the American Ceramic Society*, vol. 82, no. 3, pp. 696–704, 1999, doi: 10.1111/j.1151-2916.1999.tb01819.x.
- [381] A. Vennemann, H.-R. Stock, J. Kohlscheen, S. Rambadt, and G. Erkens, “Oxidation resistance of titanium–aluminium–silicon nitride coatings,” *Surface and Coatings Technology*, vol. 174–175, pp. 408–415, Sep. 2003, doi: 10.1016/S0257-8972(03)00407-9.

- [382] L. Chavee, E. Serag, M. da Silva Pires, S. Lucas, and E. Haye, "A mechanistic approach of oxidation resistance, structural and mechanical behaviour of TiAlN coatings," *Applied Surface Science*, vol. 586, p. 152851, Jun. 2022, doi: 10.1016/j.apsusc.2022.152851.
- [383] S. Raikar, S. DiGregorio, and O. J. Hildreth, "Sulfidation kinetics of titanium and Ti-6Al-4V with elemental sulfur," *Corrosion Engineering, Science and Technology*, vol. 58, no. 6, pp. 561–566, Sep. 2023, doi: 10.1080/1478422X.2023.2238388.
- [384] S. Das, S. Guha, R. Ghadai, D. Kumar, and B. P. Swain, "Structural and mechanical properties of CVD deposited titanium aluminium nitride (TiAlN) thin films," *Appl. Phys. A*, vol. 123, no. 6, p. 412, May 2017, doi: 10.1007/s00339-017-1032-0.
- [385] H. Zhang, S. Wang, P. Guo, and M. Wang, "Microstructure and Wear Properties Analysis of TiAlN Film Deposited on Cam Profile Using Ion Sputtering," *Tribology Transactions*, vol. 56, no. 6, pp. 968–976, Nov. 2013, doi: 10.1080/10402004.2013.815833.
- [386] J. T. Chen *et al.*, "Characterization and temperature controlling property of TiAlN coatings deposited by reactive magnetron co-sputtering," *Journal of Alloys and Compounds*, vol. 472, no. 1, pp. 91–96, Mar. 2009, doi: 10.1016/j.jallcom.2008.04.083.
- [387] D. M. Devia, E. Restrepo-Parra, P. J. Arango, A. P. Tschiptschin, and J. M. Velez, "TiAlN coatings deposited by triode magnetron sputtering varying the bias voltage," *Applied Surface Science*, vol. 257, no. 14, pp. 6181–6185, May 2011, doi: 10.1016/j.apsusc.2011.02.027.
- [388] A. Raveh, M. Weiss, M. Pinkas, D. Z. Rosen, and G. Kimmel, "Graded Al–AlN, TiN, and TiAlN multilayers deposited by radio-frequency reactive magnetron sputtering," *Surface and Coatings Technology*, vol. 114, no. 2, pp. 269–277, May 1999, doi: 10.1016/S0257-8972(99)00054-7.
- [389] I. Campos-Silva *et al.*, "Effects of scratch tests on the adhesive and cohesive properties of borided Inconel 718 superalloy," *Surface and Coatings Technology*, vol. 349, pp. 917–927, Sep. 2018, doi: 10.1016/j.surfcoat.2018.05.086.
- [390] B. D'Souza, A. Leong, Q. Yang, and J. Zhang, "Corrosion behavior of boronized nickel-based alloys in the molten chloride salt," *Corrosion Science*, vol. 182, p. 109285, Apr. 2021, doi: 10.1016/j.corsci.2021.109285.
- [391] R. C. Morón, A. D. Contla-Pacheco, V. H. Castrejón-Sánchez, L. Melo-Máximo, and I. Campos-Silva, "Estimation of the wear and corrosion synergism of borided Inconel 718 alloy immersed in a neutral aqueous solution," *Ceramics International*, vol. 49, no. 2, pp. 2495–2505, Jan. 2023, doi: 10.1016/j.ceramint.2022.09.225.
- [392] E. Medvedovski, G. L. Mendoza, E. Rząd, M. Solecka, and T. P. Dudziak, "Influence of multi-layered thermal diffusion coatings on high-temperature sulfidation resistance of steels," *Surface and Coatings Technology*, vol. 403, p. 126430, Dec. 2020, doi: 10.1016/j.surfcoat.2020.126430.
- [393] T. P. Dudziak, E. Rząd, E. Medvedovski, and G. L. Mendoza, "Sulfidation-Oxidation Resistance of Thermal Diffusion Multi-Layered Coatings on Steels," *Materials (Basel)*, vol. 14, no. 19, p. 5724, Sep. 2021, doi: 10.3390/ma14195724.
- [394] T. Makogon, *Handbook of multiphase flow assurance*, 1st edition. Cambridge, MA: Elsevier, 2019.

- [395] M. Z. Hasanvand, * Mostafa Montazeri, M. Salehzadeh, M. Amiri, and M. Fathinasab, "A literature review of asphaltene entity, precipitation, and deposition: introducing recent models of deposition in the well column," *JOGPS*, vol. 1, no. 3, pp. 83–89, Sep. 2018, doi: 10.30881/jogps.00016.
- [396] M. I. Suleiman *et al.*, "Thermal dissociation of sulfur species: Analyzing variations in corrosivity of different condensate feedstock," *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, vol. 74, p. 2, 2019, doi: 10.2516/ogst/2018075.
- [397] M. Keunecke, C. Stein, K. Bewilogua, W. Koelker, D. Kassel, and H. van den Berg, "Modified TiAlN coatings prepared by d.c. pulsed magnetron sputtering," *Surface and Coatings Technology*, vol. 205, no. 5, pp. 1273–1278, Nov. 2010, doi: 10.1016/j.surfcoat.2010.09.023.
- [398] Q. Yang, D. Y. Seo, L. R. Zhao, and X. T. Zeng, "Erosion resistance performance of magnetron sputtering deposited TiAlN coatings," *Surface and Coatings Technology*, vol. 188–189, pp. 168–173, Nov. 2004, doi: 10.1016/j.surfcoat.2004.08.012.
- [399] B. Y. Man, L. Guzman, A. Miotello, and M. Adami, "Microstructure, oxidation and H₂-permeation resistance of TiAlN films deposited by DC magnetron sputtering technique," *Surface and Coatings Technology*, vol. 180–181, pp. 9–14, Mar. 2004, doi: 10.1016/j.surfcoat.2003.10.021.
- [400] H. Liu, Y. Huang, X. Wang, and R. Lu, "Effect of CeO₂ on High-Temperature Oxidation Performance of Electron Beam Cladding NiCoCrAlY Coating on Ni-Based Alloy," *Advances in Materials Science and Engineering*, vol. 2020, no. 1, p. 8731315, 2020, doi: 10.1155/2020/8731315.
- [401] H. Wang, Q. Qiu, M. Gee, C. Hou, X. Liu, and X. Song, "Wear resistance enhancement of HVOF-sprayed WC-Co coating by complete densification of starting powder," *Materials & Design*, vol. 191, p. 108586, Jun. 2020, doi: 10.1016/j.matdes.2020.108586.
- [402] J. Wu, J. Wang, Y. Du, H. Li, and X. Jia, "Adsorption mechanism and kinetics of azo dye chemicals on oxide nanotubes: a case study using porous CeO₂ nanotubes," *J Nanopart Res*, vol. 18, no. 7, p. 191, Jul. 2016, doi: 10.1007/s11051-016-3497-8.
- [403] M. Stoian *et al.*, "Total Oxidation of Methane on Oxide and Mixed Oxide Ceria-Containing Catalysts," *Catalysts*, vol. 11, no. 4, Art. no. 4, Apr. 2021, doi: 10.3390/catal11040427.
- [404] R. A. C. Amoresi *et al.*, "CeO₂ Nanoparticle Morphologies and Their Corresponding Crystalline Planes for the Photocatalytic Degradation of Organic Pollutants," *ACS Appl. Nano Mater.*, vol. 2, no. 10, pp. 6513–6526, Oct. 2019, doi: 10.1021/acsanm.9b01452.
- [405] M. Bai, H. Kazi, X. Zhang, J. Liu, and T. Hussain, "Robust Hydrophobic Surfaces from Suspension HVOF Thermal Sprayed Rare-Earth Oxide Ceramics Coatings," *Sci Rep*, vol. 8, no. 1, p. 6973, Dec. 2018, doi: 10.1038/s41598-018-25375-y.
- [406] S. Khan, G. Azimi, B. Yildiz, and K. K. Varanasi, "Role of surface oxygen-to-metal ratio on the wettability of rare-earth oxides," *Appl. Phys. Lett.*, vol. 106, no. 6, p. 061601, Feb. 2015, doi: 10.1063/1.4907756.

- [407] High Temperature Characteristics of Stainless Steel, *A Designer's Handbook n° 9004: High-Temperature Characteristics of Stainless Steel*. Toronto, Ont: Nickel Development Institute (NiDi), 2020.
- [408] D. Bush, “Technical: Sulfide Stress Cracking—NACE MR0175-2002, MR0175/ISO 15156,” *Emerson Process Management Fisher Valves*, p. 9.
- [409] R. G. S. Ritchie, R. S. Roche, and W. Steedman, “Non-isothermal programmed pyrolysis studies of oil sand bitumens and bitumen fractions: 1. Athabasca asphaltene,” *Fuel*, vol. 64, no. 3, pp. 391–399, Mar. 1985, doi: 10.1016/0016-2361(85)90430-2.
- [410] H. Huang, H. Zhang, and D. Han, “Ferrocene addition for suppression of hydrogen sulfide formation during thermal recovery of oil sand bitumen,” *Energy*, vol. 230, p. 120744, Sep. 2021, doi: 10.1016/j.energy.2021.120744.
- [411] V. Lamoureux-Var and F. Lorant, “H₂S artificial formation as a result of steam injection for EOR: a compositional kinetic approach,” presented at the SPE International Thermal Operations and Heavy Oil Symposium, OnePetro, Nov. 2005. doi: 10.2118/97810-MS.
- [412] Q. Wang, “Generation mechanism and control measures for H₂S in oil wells, Liaohe Oilfield,” *Petroleum Exploration and Development*, vol. 35, no. 3, pp. 349–354, Jun. 2008, doi: 10.1016/S1876-3804(08)60082-8.
- [413] “Hydrogen sulfide - IDLH | NIOSH | CDC.” Accessed: Oct. 25, 2024. [Online]. Available: <https://www.cdc.gov/niosh/idlh/7783064.html>
- [414] “Complete specifications for Hydrogen sulfide - CNESST.” Accessed: Oct. 25, 2024. [Online]. Available: https://reptox.cnesst.gouv.qc.ca/en/Pages/fiche-complete.aspx?langue=a&no_produit=4143
- [415] “Carbon, activated, Norit ROW 0.8mm pellets, steam activated, Thermo Scientific Chemicals, Quantity: 100 g | Fisher Scientific.” Accessed: Oct. 25, 2024. [Online]. Available: <https://www.fishersci.com/shop/products/carbon-activated-norit-row-0-8mm-pellets-steam-activated-thermo-scientific/AAL1633436>
- [416] “Zinc oxide based sulfur removal material, HiFUEL r A310, Thermo Scientific Chemicals - Chemicals, Organic compounds.” Accessed: Oct. 25, 2024. [Online]. Available: <https://www.fishersci.se/shop/products/zinc-oxide-based-sulfur-removal-material-hifuel-r-a310-thermo-scientific/15426945>
- [417] S. A. S. Inc, “Activated Carbon Absorption | Index, Capacity | Sentry Air Systems.” Accessed: Oct. 25, 2024. [Online]. Available: <https://www.sentryair.com/activated-carbon-adsorption.htm>

APPENDIX A FAILURE ANALYSIS OF INDUSTRIAL SAMPLES

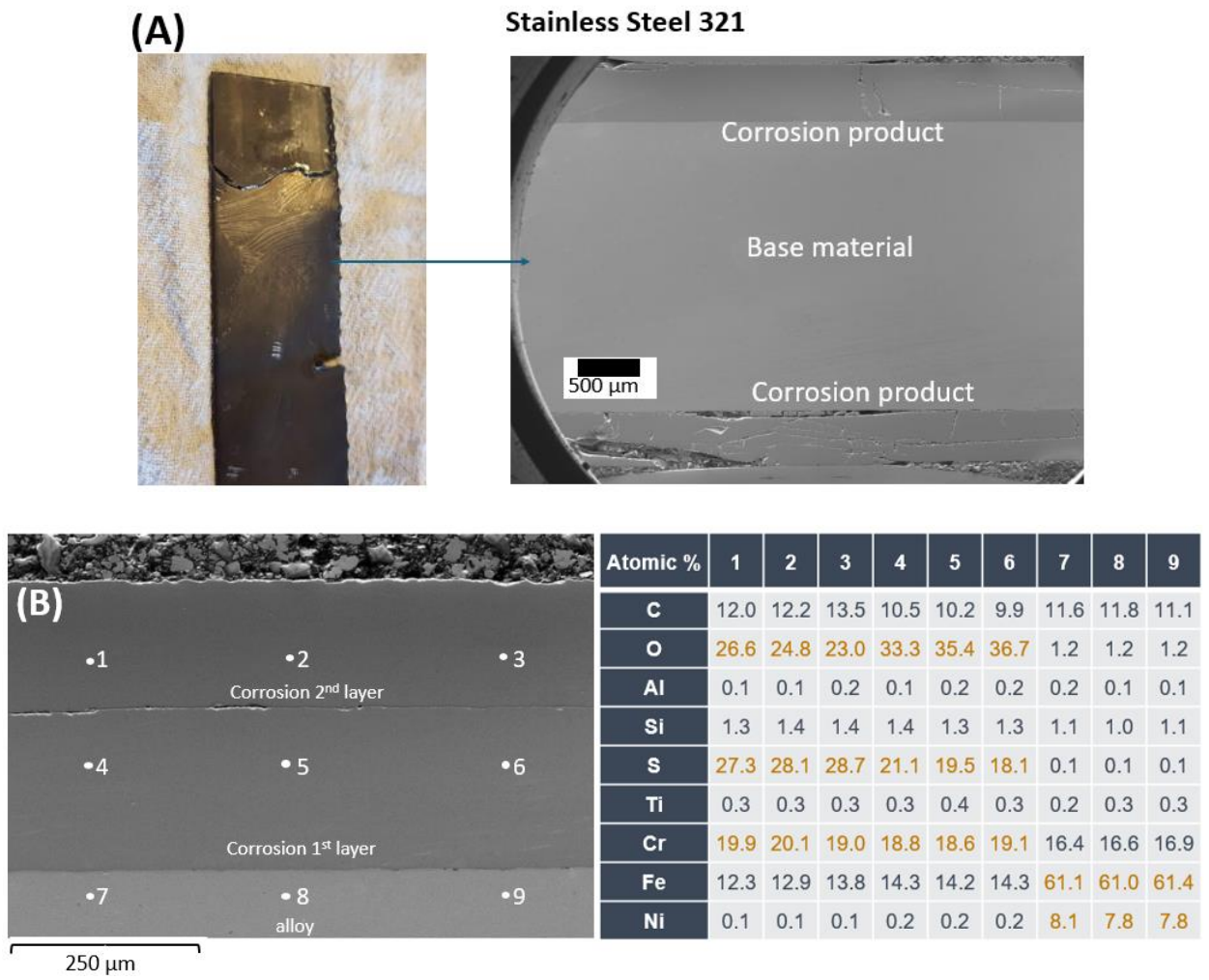
This appendix presents the analysis of industrial samples subjected to a sulfidizing environment. The failure analysis was conducted to gain further insight into the aging process of sulfidation. The stainless steel 321 (Figure A.1) sample was obtained from a catalyst support grid that had been in service, hydrotreating light gas oil, for 11 years at 400 °C and 1600 psi, while the alloy ASTM A638 (Grade 660) (Figure A.2) was sourced from a seal component that had been operational for 3 years at 440 °C and 1580 psi, under environmental conditions containing hydrocarbons, H₂S, and HCl. Both materials are iron alloys containing nickel, and their elemental composition is detailed in Table A.1.

Table A.1 Elemental composition of the nickel-containing alloys.

[wt.%]	Ni	Cr	Fe	Mo	Ti	Al	Si	C	Mn
SS321	7.8	16.8	> 60	-	0.3	-	≤ 1.0	≤ 0.08	≤ 2.0
A638	25.3	14.1	> 52	1.1	2.2	0.2	0.18	≤ 0.08	0.13

The stainless steel 321 metallic sheet has experienced corrosion on both sides (Figure A.1A). The corrosion thickness varies between approximately 400 and 600 μm. This uneven thickness results from the inhomogeneous sulfidation/oxidation processes, and the outer layer became delaminated during the handling of the sample. The corrosion is stratified into layers, with certain areas clearly exhibiting more structural defects. An area with fewer visible defects, divided into two layers, was selected for elemental composition identification using the point ID function from EDS measurements. Nine points were identified across the sample, with three from each layer: the substrate, the first corrosion layer, and the second corrosion layer (Figure A.1B). The atomic distribution of the elements is presented, highlighting areas with a higher concentration of key elements (O, S, Cr, Fe, and Ni). As anticipated, the concentrations of Fe and Ni are greater in the alloy region; however, Cr displays a higher concentration in the corroded areas, indicating preferential Cr diffusion. Oxygen and sulfur are the primary elements associated with corrosion, with S concentrating in the second corrosion layer and oxygen exhibiting a higher concentration in the first corrosion layer. Furthermore, an elemental map was constructed with a total of 27 points,

comprising 9 per region (Figure A.1C), which confirmed the previously described elemental trends. From this mapping, it was observed that the oxygen concentration increases closer to the substrate, while the concentrations of sulfur and chromium rise further away in the second corrosion layer.



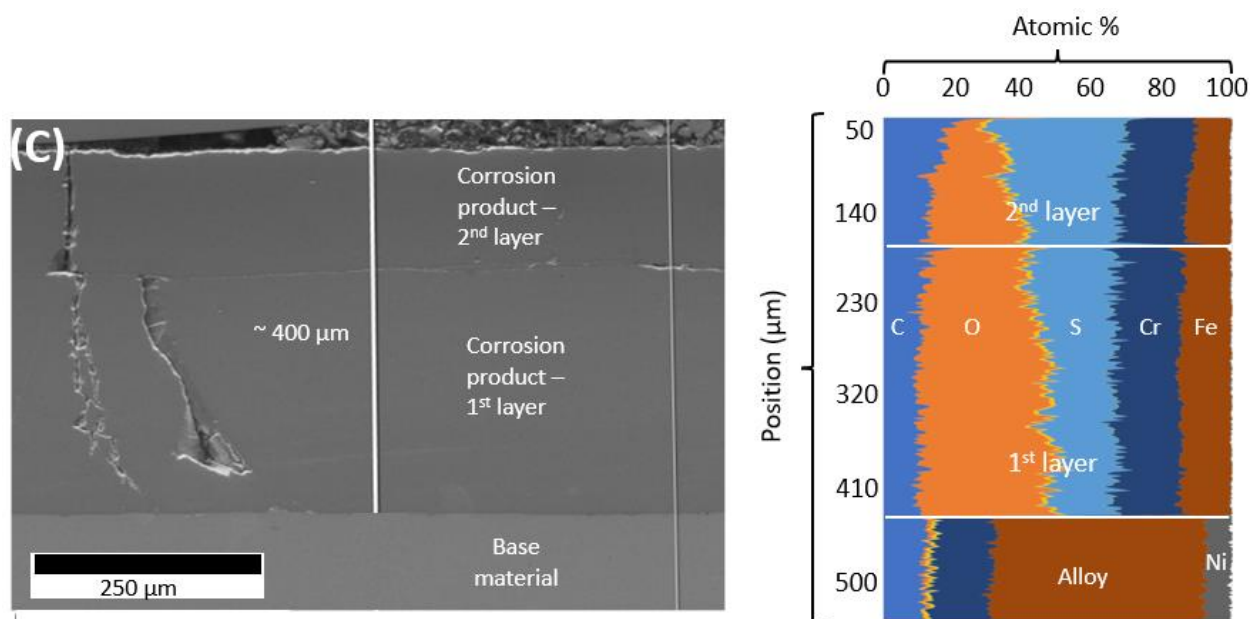


Figure A.1 Stainless Steel 321 catalytic support grid. (A) shows the sample sheet and the corrosion on both sides, (B) shows the elemental identification from point ID EDS, and (C) shows the constructed map from point ID EDS measurements.

The alloy ASTM A638 (Grade 660) sample was obtained from a seal ring (Figure A.2A). A thin black scale formed on the surface exposed to the flowing internal environment, and this area underwent further analysis. The SEM analysis reveals two distinct layers differentiated by elemental density, with a darker layer adjacent to the substrate (Figure A.2B). The EDS map indicates that the first corrosion layer is enriched in oxygen, with aluminum inclusions present at the interface between the first and second corrosion layers. The second corrosion layer is characterized by higher concentrations of Fe and S, displaying numerous Ni-rich clusters and Ni accumulation at the interface of the corrosion layers. The outer edge of the second corrosion layer is also rich in oxygen, suggesting the formation of an additional corrosion layer. The Ni clusters are concentrated near the outer edge of the second corrosion layer, indicating that nickel has leached from the alloy and corrosion layers. The microstructure of the corrosion layers (Figure A.2C) demonstrates that the oxygen-rich layer is nanocrystalline and resembles the corrosion structure observed for SS 321. In contrast, the second corrosion layer, richer in sulfur and nickel, exhibits more defects, including several cracks and pathways that facilitate diffusion and promote continuous corrosion. The observed nickel clusters might have formed by nickel leached through the defects in this layer.

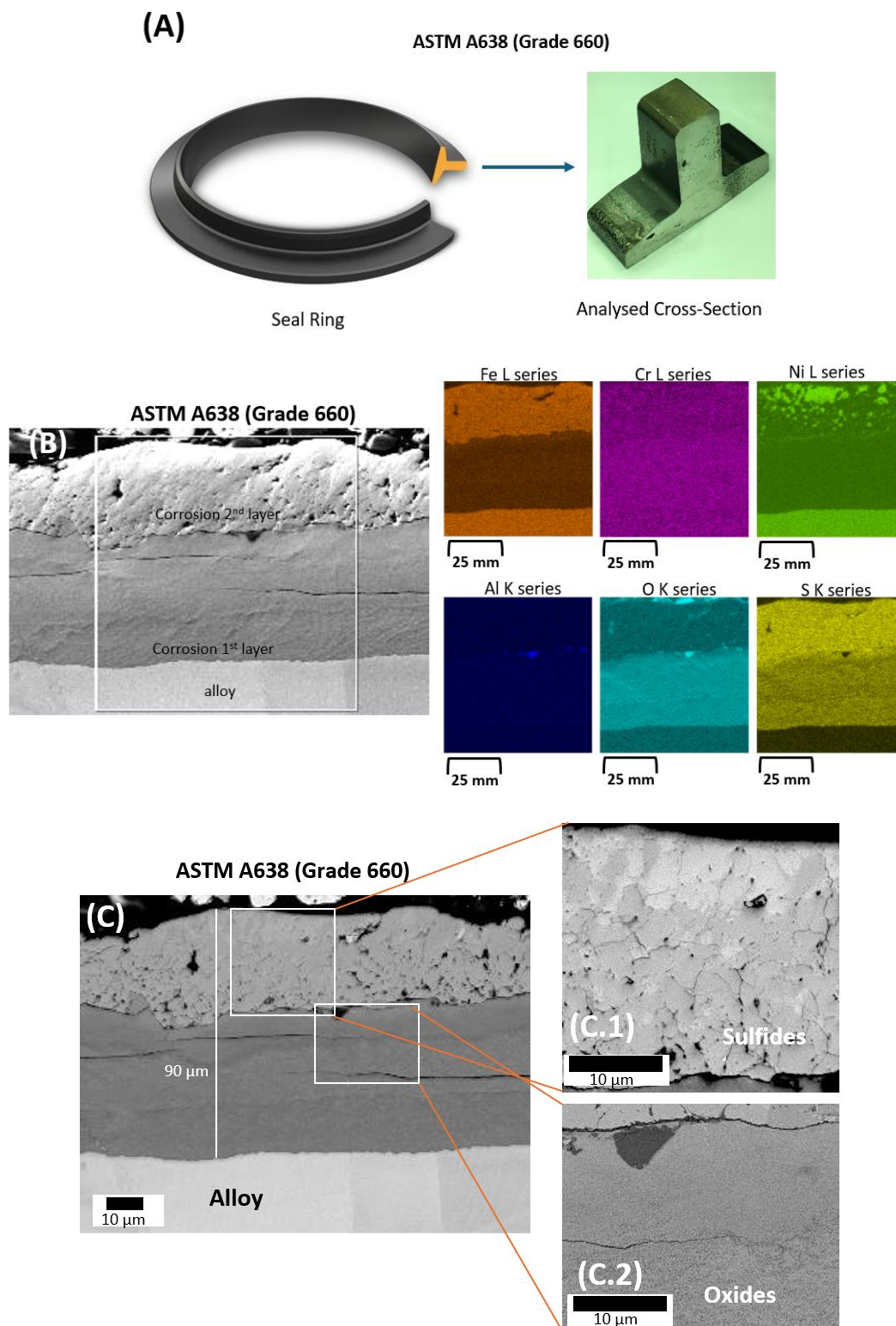


Figure A.2 Alloy ASTM A638 (Grade 660). (A) shows the sample cut from a seal ring, (B) shows the squared area EDS elemental maps, and (C) shows the amplified sulfide- and oxide-rich areas.

APPENDIX B CeO_2 THIN FILM FOULING

This appendix presents the analysis of the CeO_2 thin film before and after the fouling experiments conducted at 1650 psi and 450 °C for 2 hours. The mechanical properties of the CeO_2 thin film were obtained using nanoindentation and micro-scratch tests. The samples coated with CeO_2 were subjected to fouling in the same experimental batch as the alumina coatings.

The CeO_2 thin film was deposited via magnetron sputtering in the same chamber utilized for the alumina coatings, maintaining a pressure of 5 mTorr. The deposition process was conducted in an Ar gas flow, using a Seren RF power supply set to 100 W for 6 hours with a Kurt J. Lesker CeO_2 target. The resulting coating achieved a final thickness of approximately 700 nm. The measured hardness was 10.4 GPa, while the modulus was 174.5 GPa. The coating exhibited poor adhesion (Figure A.3), showing signs of cohesive failure (LC_1) at the very onset of the scratch and an indication of partial removal occurring at 0.6 N, adhesive failure (LC_2) at 2.5 N, and complete coating removal (LC_3) at approximately 9 N.

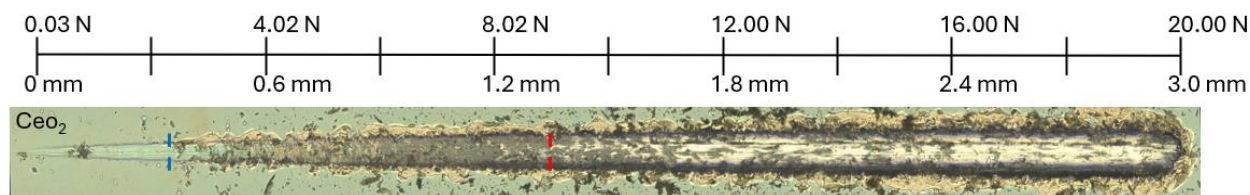


Figure A.3 Scratch tracks of CeO_2 thin film deposited on IN718. The blue mark identifies the cohesive failure LC_2 , and the red mark identifies full coating removal (LC_3).

X-ray diffraction (XRD) measurements were conducted using a Bruker D8 Discover X-ray diffractometer in grazing angle geometry. The 2θ scans were performed over a range of 20 to 90 degrees, with a step size of 0.0103° . The diffractogram confirmed the crystallinity of the CeO_2 (Figure A.4). The observed peaks were matched with the JCPDS card: 34-0394, identifying the planes (111), (220), and (311). The (111) planes are recognized as the most stable among the low-index surfaces of CeO_2 [402], exhibiting subsurface oxygen vacancies in reducing environments [403]. The order of surface stability is as follows: (111) < (110) = (220) < (311) < (100) = (200) [404].

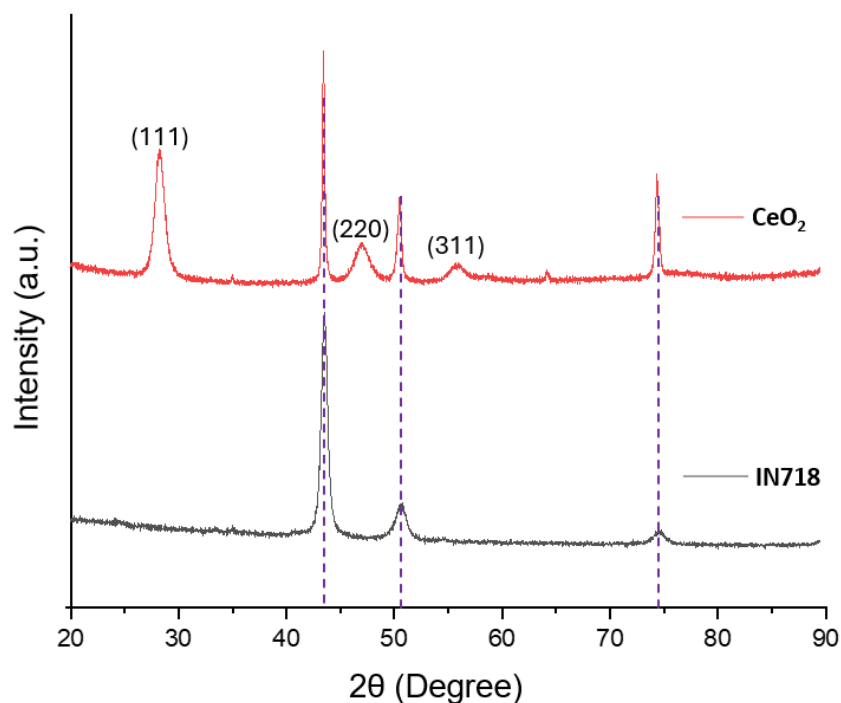


Figure A.4 XRD pattern of the deposited CeO_2 thin film and IN718 substrate. The dashed lines identify the Inconel 718 phases. The crystalline structure orientation of CeO_2 is represented.

To assess the CeO_2 protectiveness against heavy oil fouling, we characterized the samples exposed to the fouling experiment. The samples displayed the formation of a few foulant layer islands on the surface, with the cross-section of an affected area illustrated (Figure A.5). The EDS elemental map reveals that the $7\ \mu\text{m}$ layer of foulant is composed of carbonaceous material, and no sulfur is detected, indicating that CeO_2 effectively protected the surface against sulfidation. Additionally, no diffusion was observed for the coating or the alloying elements.

As previously noted, CeO_2 exhibits catalytic activity that helps to prevent coke formation on the surfaces of materials. However, the results presented here suggest that CeO_2 acted primarily as a passive barrier, protecting against diffusion, and had limited effectiveness in preventing coke deposition. It is well-established that the substrate influences the microstructure, surface morphology, and hydrophobicity of CeO_2 [405]. Additionally, freshly sputter-deposited CeO_2 displays an over-stoichiometric O/Ce ratio, reaching values as high as 3.3. The hydrophobicity of CeO_2 depends on its stoichiometry and surface relaxation in a low-carbon, ultra-high vacuum (UHV) environment. The relaxation period reduces the surface oxygen-to-metal ratio, rendering the surface hydrophobic [406]. Therefore, further investigation of CeO_2 thin films—specifically

exploring the O/Ce ratio and the effects of different substrates—may enhance the coating's anti-coking properties. Furthermore, it has been demonstrated that composites containing CeO_2 improve the overall oxidation resistance and self-repair capabilities of Al_2O_3 and Cr_2O_3 oxide films [400]. This indicates that CeO_2 may function synergistically with other coatings, making it a promising material for further research into the development of composites for sulfidation protection and anti-coking applications.

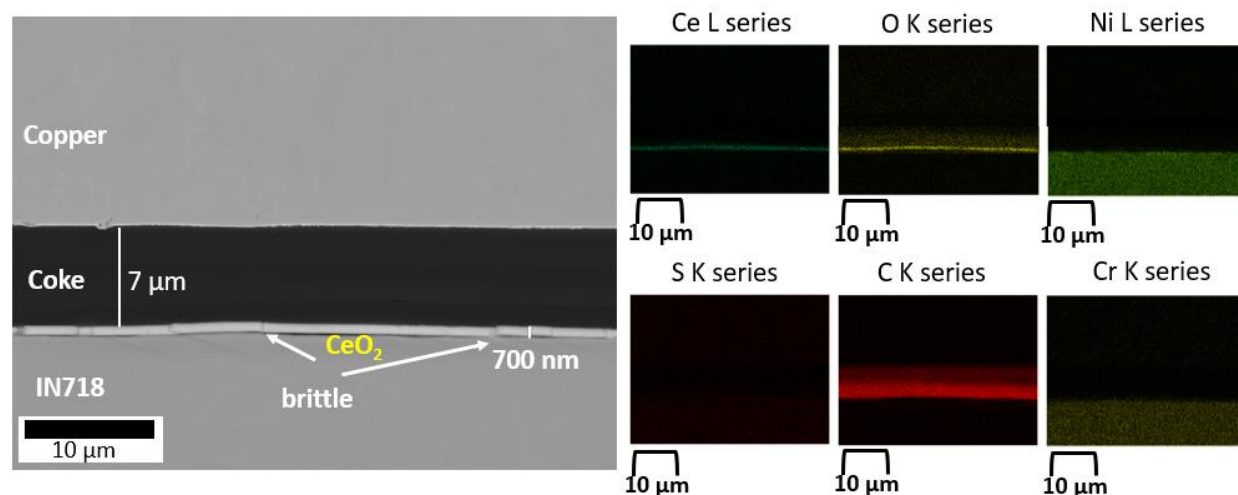


Figure A.5 SEM image and corresponding EDS maps of Inconel 718 coated with CeO_2 thin film after fouling at 450 °C for 2 h.

APPENDIX C PROCESS HAZARD REVIEW

This document was prepared to ensure operational safety during the high-pressure reactor experiments involving sour oil fouling and to clarify some associated risks. The project aimed to replicate the operational conditions (1650 psi and 450 °C) of the LC-FINING ebullating bed reactor used in the hydrocracking process for heavy sand oils, bitumen, or vacuum residuum feedstocks. Contaminants such as sulfur, metal-containing species, and reaction by-products are generated and interact with exposed surfaces, leading to the formation of scales and coke that can damage reactor components.

Pressure and temperature limitations

The main vessel of the reactor is made of SS 316 and is registered with a Maximum Allowable Working Pressure (MAWP) of 5,800 psi at 650 °F (343 °C) and a nominal MAWP of 3,600 psi at 1000 °F (538 °C). The reactor was modified to accommodate the maximum number of coated substrates possible (Figure A.6). These modifications were re-certified and are rated with an MAWP of 2,000 psi at 450 °C for water, oil, and gases, in accordance with the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, and the CSA Standard B-51, Boiler, Pressure Vessel, and Pressure Piping Code. The reactor is connected to a manifold and utilizes Swagelok fittings, all compliant with the specified pressure and temperature requirements.

The tubing used is specified in the Swagelok catalog on page 5, featuring an outer diameter (O.D.) of 1¼” made of SS 316 with a wall thickness of 0.120 inches; the nominal MAWP is 3,600 psi at room temperature. According to Swagelok, the derating factor for SS 316 at 425 °C is 0.79, while at 537 °C, it is 0.76. In the catalog MS-01-107 on page 20, the derating factor for SS 304 at 540 °C is noted as 0.69.

Applying the Swagelok derating factor of 0.76 for 537 °C, the MAWP drops to 2,736 psi. When applying the ANSI B31, Table A-1B derating factor of 0.80 for single welded tubes, the MAWP further reduces to 2,188 psi. Finally, following the guideline of operating only up to 90% of the MAWP for safety purposes, the selected tubes should function at pressures below 1,969 psi.

Continuous use of SS 316 in the temperature range of 800 °F to 1,575 °F (426 °C to 857 °C) is not recommended, as it may compromise the alloy's structure. However, SS 316 typically performs well in operational temperatures that fluctuate above and below this range[407]. According to the

reactor manufacturer, sensitization of the vessel can occur within the temperature range of 850 °F to 1,475 °F (454 °C to 801 °C), creating a detrimental grain boundary condition that may impair the corrosion resistance of austenitic alloys. Therefore, the maximum intended operating temperature is set at 450 °C, with the planned duration of the reaction being approximately only two hours.

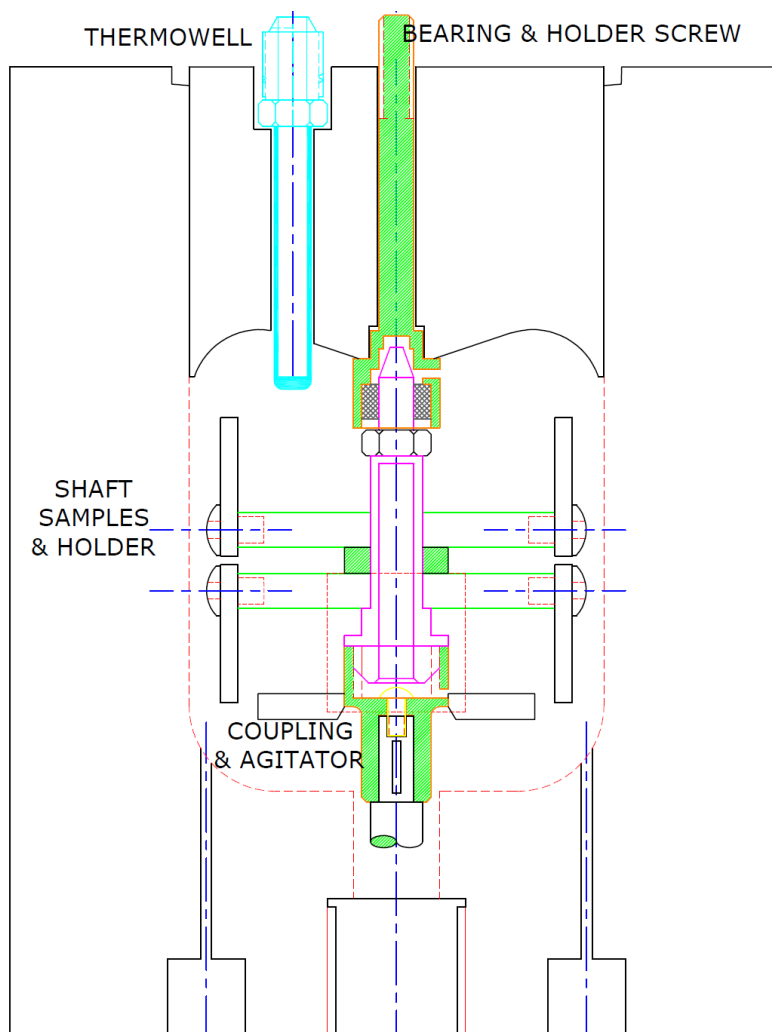


Figure A.6 Internal side view of the reactor modifications. Blue Thermowell, green agitator coupling to magnetic drive and top bearing holder, and purple main shaft body holding the samples represented in black.

Compatibility of materials with corrosive environments

The materials must be corrosion-resistant, particularly with respect to H₂S exposure, and the designations are provided by NACE International. MR0175/ISO 15156 no longer lists individual

alloys of the 300 series; instead, it specifies that alloys with the following elemental ranges are acceptable: C 0.08% maximum, Cr 16% minimum, Ni 8% minimum, P 0.045% maximum, S 0.04% maximum, Mn 2.0% maximum, and Si 2.0% maximum, consistent with SS 316 and 316L.

Austenitic stainless steel materials shall: 1) be in the solution-annealed and quenched or annealed and thermally stabilized heat-treatment condition; 2) be free of cold work intended to enhance their mechanical properties; and 3) have a maximum hardness of 22 HRC for carbon and low-alloy steels. Equivalent cast and wrought alloys are acceptable, including 302, 304 (CF8), S30403 (CF3), 310 (CK20), 316 (CF8M), S31603 (CF3M), 317 (CG8M), S31703 (CG3M), 321, 347 (CF8C), and N08020 (CN7M) [408].

H₂S gas maximum concentration

According to the literature, only a fraction of the sulfur present in the oil is converted to H₂S. The gas formation accounts for only 18% of the total mass loss of the oil. Additionally, H₂S originating from asphaltenes constitutes 2.79% of the total gas volume [409]. The total H₂S yield peaks at 450 °C corresponds to 3% of the total gas volume, equivalent to 4.9 mg/g (H₂S/bitumen) [410]. Thus, about 90 % of the total H₂S released in heavy oils originates from asphaltenes. Additionally, thermally simulated experiments under pyrolytic conditions over a 200-hour reaction period indicate that a maximum of 10% of the total sulfur in bitumen can be converted to H₂S [411].

Considering the thermal cracking of 200 g of heavy oil (~ 6 wt. % sulfur) in the reactor at 450 °C, the total amount of sulfur is calculated to be 12 g. Consequently, the maximum concentration of H₂S for prolonged experiments under pyrolytic conditions would be 1.2 g, corresponding to 6 mg/g (H₂S/bitumen).

In the worst-case scenario, assuming that all H₂S gas leaked out of the reactor at once, and knowing that the hood has internal dimensions of 31.5", 50.5", and 84", resulting in a total volume of 2.19 m³, the concentration of H₂S in the fume hood would be 0.54 g/m³, equivalent to 388 ppm of H₂S. However, it is important to consider two factors: 1) in the absence of water, the experimental conditions proposed in this study, the generation of H₂S is significantly lower than the calculated [412], and 2) H₂S is continuously generated and removed through the airflow of the hood, drastically minimizing the gas concentration in the hood in case of leaks.

The National Institute for Occupational Safety and Health (NIOSH) defines 100 ppm of H₂S as the Immediately Dangerous to Life or Health (IDLH) concentration based on acute inhalation toxicity

data in humans. The Standardized Control Procedure (SCP) establishes that 70 to 300 ppm is the maximum concentration that can be tolerated for 1 hour without serious consequences, while exposure to 400 to 700 ppm can be dangerous after 0.5 to 1 hour. Concentrations in this range may lead to loss of consciousness and potentially death within 0.5 to 1 hour [413].

The safety organization from Quebec, Canada—Commission des Normes, de l'Équité, de la Santé et de la Sécurité du Travail (CNESST)—further states that the Permissible Exposure Limit (PEL) for H₂S in a working environment is set at 8 ppm, with a ceiling limit of 10 ppm. Additionally, due to the potential loss of the sense of smell at concentrations between 100 to 150 ppm, odor cannot be considered a reliable and adequate warning sign of hazardous exposure[414].

To mitigate safety risks and reduce H₂S exposure, the hood is equipped with an H₂S gas sensor and remains completely closed during the experiments. The reactor operator is required to use a chemical gas mask and carry a portable H₂S sensor during reactor manipulations.

H₂S gas removal

According to safety standards, H₂S should be removed from the gas stream before exhaust. Pellets of activated charcoal (0.8 mm) and ZnO (3 mm) are utilized as gas scavengers, primarily targeting H₂S. These pellets are placed in 1" diameter and 4" long tubes arranged in series in the reactor exhaust. This tubing size provides an approximate volume of 66 cm³. The tubes are protected by a mesh material made of SS 304, installed in the fittings to prevent particles from moving downstream or upstream. The mesh size is 0.2 mm, which reduces the flow to 30% in the 1" tube, ensuring that the pressure remains nearly constant, considering that the fittings connected to the reactor system are ¼".

The two filtering materials, sourced from Fischer Scientific, are optimized for gas-phase purification. The activated charcoal is highly efficient for general gas-phase applications [415], while the ZnO particles are specifically tailored for H₂S removal [416]. The activated charcoal has a density of 1.48 g/cm³, and the ZnO has a density of 0.82 g/cm³. Given the 66 cm³ volume of each tube, the filters can accommodate approximately 97 grams of activated charcoal and 54 grams of ZnO. With a maximum sulfur loading capacity of 16% (wt/wt) for activated charcoal [417] and 15% for ZnO [416]; the estimated sulfur removal capacity is 15.5 grams for activated charcoal and 8 grams for ZnO, providing a combined total of 23.5 grams of scavenged sulfur.

As previously calculated, each reactor run processing 200 g of bitumen generates a total of 1.2 g of H_2S . Given that the filters can adsorb a combined total of 23.5 g of H_2S , they can theoretically support up to 20 reaction cycles before requiring replacement. However, since activated charcoal can interact non-selectively with other gases, the filter capacity may diminish over time. To ensure consistent and effective H_2S removal, regular replacement of the filters is recommended.