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Effect of Si and Si-Pt reservoirs on the growth of multilayer coatings for the oxidation protection of γ-TiAl turbine blades

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

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Cette thèse intitulée :

Effect of Si and Si-Pt reservoirs on the growth of multilayer coatings for the oxidation protection of γ-TiAl turbine blades

présentée par Josefina CRESPO VILLEGAS

en vue de l'obtention du diplôme de *Philosophiæ Doctor* a été dûment acceptée par le jury d'examen constitué de :

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DEDICATION

To my beloved parents, Elena and Salome for always be a bridge to possibility

To the creative energy, for the inspiration and guidance through this journey

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RÉSUMÉ

Les performances des moteurs d'avion et leur fonctionnement dans des environnements particulièrement difficiles ont posé un défi constant pour le choix des matériaux appropriés et de leurs caractéristiques. En outre, avec les progrès récents en termes de consommation spécifique de carburant (SFC) et de réduction des émissions de CO₂, la nécessité d'augmenter les températures d'admission (~6°C-9°C/an) pour obtenir des rendements plus élevés des moteurs et réduire le poids des composants rotatifs a considérablement augmenté.

Dans ce contexte, la pertinence de matériaux plus légers avec une performance optimale (haute résistance à l'oxydation et résistance mécanique élevée) au-delà de 700 °C a été élucidée, favorisant le remplacement des superalliages à base de nickel à haute densité actuellement utilisés dans les sections de moteurs à basse température. Dans la turbine à basse pression, des aubes de turbine plus légères en γ -TiAl ont déjà commencé à être utilisées depuis quelques années, en particulier dans les moteurs GEnx et CFM-LEAP.

Des progrès importants dans l'optimisation des propriétés thermo-mécaniques de ces matériaux structurels (c'est-à-dire les alliages à base de Ni, Co et γ -TiAl) ont été réalisés avec l'approche métallurgique via la chimie des alliages. Cependant, l'amélioration de leurs propriétés et l'extension de leurs capacités, en particulier pour la protection des surfaces (spécifiquement la résistance à l'oxydation) nécessitent l'utilisation de revêtements protecteurs.

La variété des revêtements de protection et des approches d'ingénierie de surface disponibles pour de nouveaux développements est très importante. Ils peuvent être distingués selon leur architecture (barrières thermiques de type revêtement multicouche ou de type revêtement à composition graduée), par la méthode de production (techniques chimiques ou physiques en phase vapeur, pression atmosphérique vs basse pression, techniques métallurgiques, etc.), ou la famille des principaux composés constitutifs (siliciures, aluminures, multi-composantes ((MCrAlY; M: métal), à base de Cr, etc.) Au-delà de la diversité des revêtements, tous ces systèmes nécessitent des améliorations continues pour mitiger la dégradation, la délamination ou des effets secondaires indésirables de nature chimique ou mécanique.

En ce qui concerne spécifiquement le développement de revêtements résistants à l'oxydation, la stratégie de convergence pour tous les différents systèmes de revêtement consiste en la formation

de ce que l'on appelle croissance d'oxydes protecteurs (c'est-à-dire Cr₂O₃, SiO₂, Al₂O₃) qui restent thermodynamiquement stables à haute température et présentent une croissance cinétique lente. Celles-ci sont obtenues en utilisant des éléments appropriés dans le revêtement pour interagir avec l'oxygène, tout en limitant l'interaction de l'oxygène avec le matériau ou l'alliage de base.

En termes de technologie et de matériaux, les composés à base de Si- et de Pt- tels que Ti_xSi_y et Pt_xAl_y ont été associés à des applications résistantes à l'oxydation principalement en raison de leurs points de fusion élevés et de leur résistance à l'oxydation forte et intrinsèque, notamment en raison de la nature et de la stabilité de leurs produits d'oxydation (SiO₂ et Al₂O₃, respectivement). Cependant, leur étude n'a été abordée que séparément ; les revêtements Ti_xSi_y ont principalement été produits par des méthodes chimiques (c'est-à-dire, procédé de cémentation en caisse), tandis que les revêtements Pt_xAl_y par dépôt chimique en phase vapeur (CVD) et galvanoplastie.

De plus, à part la structure caractéristique à trois couches des revêtements de barrière thermique (TBC), le développement de revêtements multicouches résistant à l'oxydation - ou barrières de diffusion de l'oxygène - est resté très limité. D'un point de vue fondamental, la compréhension des mécanismes de transport dans les revêtements de protection contre l'oxydation à haute température est cruciale pour une compréhension plus approfondie de ces systèmes, mais ils sont rarement étudiés, en raison de leur complexité.

Ce projet doctoral se concentre donc sur le développement de systèmes de revêtements multicouches plus complexes qui présentent une composition multi-phase de composés à base de Si (Ti_xSi_y) ou de composés mixtes à base de Si et de Pt ($Ti_xSi_y + Pt_xAl_y$), produits à l'aide de méthodes non-traditionnelles dans le domaine de l'aéronautique, spécifiquement la pulvérisation magnétron et le traitement thermique sous vide. Une telle constitution n'a pas été rapportée auparavant, ni dans des revêtements simples, ni dans des architectures multicouches, et les processus de transport à haute température potentiels de ces systèmes ont été fortement soulignés tout au long de cette étude.

Grâce à un suivi efficace des éléments par une analyse chimique combinée de la masse et des surfaces, ainsi que par la microscopie électronique et la spectroscopie de coupes transversales, la compréhension des réservoirs de Si et de Si-Pt (en termes d'épaisseur et de rapport de composition),

et leur rôle dans la croissance microstructurale de chaque zone/couche pour chaque système de revêtements a été détaillée.

De plus, la disponibilité des matériaux dans les réservoirs et leur impact sur le comportement d'oxydation et l'évolution microstructurale de ces multicouches due aux processus de transport pendant l'oxydation à haute température ont été déterminés. La réduction de la cinétique d'oxydation d'un ordre de grandeur a également été atteinte et confirmée sur les systèmes à base de Si (revêtements Ti_xSi_y) avec de faibles réservoirs de Si (3 µm), attribuée aux régimes d'oxydation paraboliques, et confirmée par estimations cinétiques. Pour tous les systèmes de revêtement développés (à base de Si- et de Pt-), un mécanisme d'oxydation protectrice a été clarifié et lié à la formation d'oxydes protecteurs principalement de SiO₂ et d' Al₂O₃ et à la formation très restreinte ou complètement limitée de TiO₂.

Enfin, les éléments du triplet microstructure - processus de transport - comportement d'oxydation ont été corrélés par un modèle phénoménologique pour chacun des systèmes étudiés, soulignant l'auto-organisation des croissances d'oxydes protecteurs dans la structure multicouche spécifique.

Certains des chapitres suivants sont basés sur des références [180,191]. Dans lequel J'ai apporté une contribution majeure à ces travaux en ce qui concerne la conception et la réalisation des expériences, et le développement de revêtements et leur caractérisation, ainsi que dans l'analyse et la discussion des résultats, et la rédaction des manuscrits.

ABSTRACT

The performance of jet engines and their operation in particularly harsh environments has been a constant challenge for choosing suitable materials and their characteristics. Additionally, with the recent advancements in terms of specific fuel consumption (SFC) and reduced CO₂ emissions, the need for increased inlet temperatures (\sim 6°C-9°C/year) for achieving higher engine efficiencies and weight reduction in rotating components has significantly increased.

In this context, the relevance of lighter materials with optimum performance (high oxidation resistance and elevated mechanical strength) beyond the 700 °C has been elucidated, promoting the replacement of the currently used high-density Ni-based superalloys in the lower-temperature jet engine sections. In the low-pressure turbine, lighter γ -TiAl low-pressure turbine blades have already started to be implemented since a few years, specifically in the GEnx and CFM-LEAP engines.

Important progress in optimization of the thermo-mechanical properties of these structural materials (i.e., Ni-based, Co-based, and γ -TiAl based alloys) has been attained with the metallurgical approach via alloy chemistry. However, further improvements in their properties and extended capabilities, specifically for surface protection (i.e., oxidation resistance) demand the use of protective coatings.

The variety of protective coatings and surface engineering approaches available for further development is very significant. They can be distinguished according to their architecture (multilayer or graded composition, thermal barrier coatings), the method of production (chemical or physical vapor techniques, atmospheric pressure vs low pressure, metallurgical techniques etc.), or the family of main constituting compounds (silicides, aluminides, multi-components ((MCrAlY; M: metal), Cr-based, etc.). Beyond the diversity of coatings, all of these systems require continuous improvements to mitigate degradation, delamination, or secondary undesired effects of chemical or mechanical nature.

Specifically for the development of oxidation-resistant coatings, the strategy of convergence for all the different coating systems consists in the formation of the so-called protective oxide scales (i.e., Cr_2O_3 , SiO_2 , Al_2O_3) that remain thermodynamically stable at high temperature and exhibit

slow kinetic growth. This is attained by using appropriate elements in the coating to interact with oxygen, while restricting the oxygen interaction with the base material or alloy.

In terms of technology and materials, Si- and Pt-based compounds such as Ti_xSi_y and Pt_xAl_y have been related to oxidation resistant applications mostly due to their high melting points, and intrinsic high oxidation resistance, particularly due to the nature and stability of their oxidation products (SiO₂ and Al₂O₃, respectively). However, their study has only been addressed separately; Ti_xSi_y coatings have been mostly produced by chemical methods (i.e., pack cementation), while the Pt_xAl_y coatings by chemical vapor deposition (CVD) and electroplating.

Additionally, apart from the three-layered structure characteristic of thermal barrier coatings (TBC), the development of multilayered oxidation-resistant coatings – or oxygen diffusion barriers - has remained very limited. From the fundamental point of view, the understanding of transport mechanism in oxidation protective coatings at high temperature is crucial for a deeper understanding of such systems, but are rarely elucidated, due to their complexity.

The present PhD project focuses on the development of more complex multilayered coating systems that exhibit a multi-phase composition of either Si-based compounds (Ti_xSi_y) or mixed Siand Pt-based compounds $(Ti_xSi_y + Pt_xSi_y + Pt_xAl_y)$, produced with the use of non-traditional methods in the field of aeronautics, namely magnetron sputtering and vacuum thermal treatment. Such particular constitution has not been reported previously neither in single coatings or multilayer architectures, and the potential high-temperature transport processes of these coating systems have been strongly emphasized throughout this study.

By effective tracking of the elements through combined bulk and surface chemical analysis as well as through cross-sectional electron microscopy and spectroscopy, the understanding of either Si and Si-Pt reservoirs (in terms of thickness and compositional ratio), and their role in the microstructural growth of each zone/layer for each coating system has been detailed.

Also, the material availability within the reservoirs and their impact on the oxidation behavior and the microstructural evolution of these multilayers due to the transport processes during high-temperature oxidation have been determined. Additionally, the reduction of the oxidation kinetics by one order of magnitude has been attained and confirmed on the Si-based systems (Ti_xSi_y coatings) with low Si reservoirs (3 µm), attributed to the parabolic oxidation regimes, as confirmed

by kinetic estimations. For all developed coating systems (Si- and Pt- based), a protective oxidation mechanism has been clarified and related to the formation of mostly SiO_2 and Al_2O_3 scales and very restricted or completely limited TiO_2 formation.

Finally, the triplet microstructure - transport processes - oxidation behavior have been correlated through a phenomenological model for each of the studied systems underlining the self-organization of the scales in the specific multilayer structure.

Some of the subsequent chapters are based on references [180,191]. In which I made a major contribution with regard to the design and performance of the experiments, including the development of the coatings and their characterization, as well as in the analysis and discussion of results and writing of manuscripts.

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LIST OF SYMBOLS AND ABBREVIATIONS

ABBREVIATIONS

- APS Atmospheric plasma sprayed
- BLI² Beam ion implantation
- DC Direct current
- 3D Three-Dimensional
- EDS Energy-dispersive X-ray spectroscopy
- FWHM Full width at half maximum
- GIRXD Grazing incidence X-ray diffraction
- HVOF High-velocity oxygen fuel
- MS Magnetron sputtering
- PECVD Plasma Enhanced Chemical Vapor Deposition
- PI³ Plasma immersion ion implantation
- RBS Rutherford backscattering spectroscopy
- RF Radio frequency
- SEM Scanning electron microscopy
- TA Thermal annealing
- TGA Thermal gravimetric analysis
- TGO Thermal growth oxide
- TOF-SIMS Time of flight secondary ion mass spectrometry
- UHV Ultra high vacuum
- TBC Thermal barrier coatings
- W/F Thrust-weight ratio
- XPS X-ray photoelectron spectroscopy

XRD	X-ray	diffraction
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YSZ Yttria-stabilized zirconia

MATERIALS

Pti _x Si _y	Platinum	silicides

- Pt_xAl_y Platinum aluminides
- Ti_xSi_y Titanium silicides

SYMBOLS

α2	Ti ₃ Al
cm	Centimeters
D	Diffusivity rate
eV	Electron volt
E*	Reduced modulus
Er	Reduced modulus
GPa	Gigapascals
ΔG	Gibbs free energy
h	Hour
Н	Hardness
Ι	Intensity
k _p	Parabolic kinetics
k _l	Linear kinetics
k_{log}	Logarithmic kinetics
KeV	Kilo electron volt

kJ/mol Kilo joule per mol

- kV Kilo volts
- MeV Mega electron volt
- mg Milligram
- min Minute
- nm Nanometer
- rpm Revolutions per minute
- µm Micrometers
- μN MicroNewtons
- V Volts
- v/v Volume/volume
- W Watts

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CHAPTER 1 INTRODUCTION

The development of materials for high-temperature applications has been a need for humans since ancient times; it dates back since humans first related to fire and heat, and up to present times considering more complex processes such as the development of sophisticated technologies, devices, and machines. It was mainly at the turn of the 19th to the 20th century that very particular applications related to high temperature were developed, among them the filament lamp, the combustion engine, and later the jet engine. The vital role of materials (i.e., steel, stainless steel, and nickel-chrome alloys) must be highlighted since they appeared as a driving force of such developments. [1]

With time, the knowledge of materials has evolved, which has brought much progress to diverse fields. Diverse families of materials with high-temperature resistance have become available; this currently includes Ti alloys, superalloys (steel, Ni and Ni-Co), and refractory metals (W, Mo, Nb, Ta, Re), ceramic materials, composites, etc. just to mention some. Each type of material is contributing in a very particular way to the feasibility of high-temperature applications in severe environments [1].

For any particular application, the optimum performance of their components is limited by the degradation of the materials that constitute them. With an increase in temperature, the potential for chemical reactions and their kinetics of degradation increases, as well as the possibility for microstructural changes. Therefore, the challenge for materials to maintain long-term stability of their properties (i.e., high strength, resistance to oxidation, etc.), particularly when operating in harsh atmospheres, is closely related to the understanding of the process-structure-properties-performance relationship [1].

Jet engines were originally developed in the 1930s to power aircraft propulsion, and are a precise example of an application in which the performance of materials must rely outstanding upon extreme conditions. Since their introduction, these have been continuously evolving; particularly, with the advancement of structural materials and their processes, which has inherently influenced the progress of jet engine technologies [2].

High temperatures (above 750°C) and stresses are the main parameters to consider when implementing new materials in the jet engine components. The severe conditions at which turbine

blades (e.g., high pressure or low-pressure sections) operate, determine the selection of highperformance materials as a critical step in the design of such complex systems. In this context, the high-temperature oxidation conditions and materials stability above 750°C of the low-pressure turbine blades is the main focus of this study.



Figure 1.1 Schematics of the jet engine turbine, the low-pressure turbine section highlighted in purple is the area of interest in this project, and the operational temperature of γ -TiAl turbines is indicated. Modified from [3,4].

The performance of aircraft engines can be summarized as follows [2]:

- i. The thrust-weight ratio (W/F) which is obtained by compressor blades with a high-aspectratio
- ii. An optimized pressure ratio per unit flow (thermal efficiency of the engine)
- iii. Increase in the firing temperature

Since a higher trust (the force that pulls the aircraft forward) can be obtained with an increased inlet temperature, there has been a constant need to raise the jet engine operating temperatures, while increasing performance. In the low-pressure turbine blades, apart from the temperature increase, there has been a modification of their size, toward higher dimensions, mainly due to the increased fan size (bypass ratio), creating additional requirements for lighter materials with similar

3

thermal properties in comparison to the presently used Ni-based alloys [2]. In addition, low engine weight reduces the structural requirements of the wings and decreases fuel consumption.

According to reports on turbine jet efficiency, new gas turbines have achieved inlet temperatures as high as 1427°C, with related pressure ratios of 40:1 and efficiencies of 45% or higher. With the aim to assure superior performance in the long term operation, the materials used for turbine blades must exhibit certain characteristics, these include low thermal expansion coefficient, high thermal conductivity, resistance to oxidation as well as to corrosion, high rupture strength, and limited creep [2-5]. These characteristics are very often obtained by implementing coating technologies. The use of coatings helps to protect the base material from the severe environment while displaying a certain array of properties that the alloy itself could not exhibit and extending the life of the blades [6-10].

Among the different structural materials for aircraft components, titanium aluminides (γ -TiAl) with a nominal composition of Ti-48Al-2Cr-2Nb (at.%) are intensely investigated because of their potential use in different turbine sections of the jet engine. The lightness of Al and the mechanical characteristics of Ti results in an intermetallic compound with great capabilities, low density (3.8 g/cm³), relatively high melting point (~1447 °C), some room temperature ductility (2-3%), and high specific strength, high yield strength (of up to 1400 MPa depending on alloying), and stiffness (150-175 GPa) make them a very promising material for the aircraft industry, also the Cr and Nb incorporation in this alloy provides improved ductility and oxidation respectively [11-14].

Compared to Ni-based alloys, γ -TiAl materials exhibit lower operational temperatures, but γ -TiAl alloys own half of their weight. However, low ductility and low oxidation resistance are the main challenges to address when considering this alloy [11-15].

In the particular case of the γ -TiAl alloys, which are a cornerstone in the development of lightweight jet engines, there must be a balance of good mechanical properties and oxidation resistance to satisfy the severe requirement of the jet engine components. From the mechanical point of view, a significant limitation of these alloys is the low ductility at ambient temperature and low fracture resistance, and the challenge to exhibit enough oxidation resistance at high temperature while maintaining suitable creep and strength retention [11-15].

The use of γ -TiAl alloys is still restricted due to significant oxidation at high temperatures (>750°C) leading to the formation of mixed oxidation products of Al₂O₃ and TiO₂. The combined growth of these oxides results from the proximity of the metal/oxide equilibrium pressures in the Ti-A1-O system (A1/A1₂O₃ and Ti/TiO₂) at 900°C, as detailed by Rahmel and Spencer [16]. This promotes the growth of either TiO₂, Al₂O₃, or both oxides according to the composition of the regions in the base material. In addition, although Al₂O₃ is a stable and slow-growing protective oxide, the faster growth of TiO₂ with respect to Al₂O₃ (due to a faster diffusivity of Ti in TiO₂ than Al diffusivity in alumina), results in the formation of an unprotective oxide scale, with an outer layer of TiO₂ and a mixed TiO₂/Al₂O₃ interlayer underneath. In such a case, the high internal porosity of TiO₂ acts as a path for oxygen to diffuse into the substrate and cause severe embrittlement of the base material [17-18].

As described above, high-temperature oxidation can result in the growth of unprotective oxide scales which can cause severe chemical degradation of the alloy or component due to the continued oxygen dissolution and diffusion of the elements that constitute the alloy or component. Therefore, the use of coatings that are resistant to high-temperature oxidation is among the most essential methods for the protection of these structural materials. These coatings work by selectively oxidizing elements that will result in the growth of a protective oxide; the coating acts as a reservoir of the elements that will form the protective (thermodynamically stable and slow-growing) oxides, most frequently with Al, Cr, and Si composition [5, 8-11].

The structural stability of these coatings is then related to their thermal stability over time. The durability of the coating is essential; it depends on the composition, thickness, and uniformity. Diverse oxidation-resistant coatings produced by different deposition techniques have been developed and explored over the years. Among these, are the ones containing Pt, as in the Pt diffusion aluminide coatings for Ni-based substrates [19-22], and Si-containing ones, such as the titanium silicides for γ -TiAl substrates, have been considered very promising materials to protect against high-temperature oxidation.

The presence of Pt in the Pt-aluminide coatings can induce an accelerated Al activity and indirectly promote the Al_2O_3 formation; While in the Si-based coatings [23-26], the growth of the protective SiO₂ oxide is attained. Furthermore, titanium silicides (Ti_xSi_y) exhibit a high melting point (2130

°C), low density (i.e., $\rho_{Ti_5Si_3} = \sim 4 g/cm^3$), satisfactory oxidation resistance, and good mechanical behavior (considerable strength at elevated temperature, as well a high hardness and creep resistance) [23-26].

The required properties of the coatings depend on the particular application, and they can be tailored by the deposition conditions and technique used. Among the coating deposition techniques, diffusion coatings are of interest because they can provide high thickness, strong bonding to their substrate, and a continuous grading in composition. These coatings can be obtained by depositing a reservoir of the material of interest either by a chemical or physical deposition process and by subsequent annealing in a suitable atmosphere, promoting in this way the diffusional transport of elements to promote the formation of a graded layer [27].

Development of protective coatings by promoting the growth of slow-growing and thermodynamically stable oxides (i.e., SiO₂, Al₂O₃, Cr₂O₃) is essential for protecting γ -TiAl used in aero-engine components. The available protective coatings (i.e., diffusion coatings, overlay coatings. etc.,) require mitigation of either chemical or mechanical degradation; highlighting the lack of more complex diffusion barriers against oxygen. In addition, there is a missing understanding of the oxidation mechanism in relationship with their microstructural design for a majority of the coating systems.

In response to this scientific challenge and technological gap, the combined effect of Si and Pt which has not been reported in the literature, and their promising behavior as constituents of oxidation-resistant coatings are combined to develop a new multizone oxygen diffusion barrier.

This project proposes to build a surface reservoir of Si and Si-Pt with high precision by combining industrially relevant magnetron sputtering, and subsequent vacuum thermal annealing to form a multi-zone system (multilayered structure) based on the thermally activated diffusion processes, which redistribute the elements in such way that it separates the slow and fast oxidizing constituents, while it builds a protective oxide scale and a barrier against further oxygen diffusion.

1.1 General objective

The **main objective** of this study is to understand the mechanism of oxidation of a protective coating system while considering Si and Si-Pt reservoirs (layers of particular thickness) on γ -TiAl

and tailor its performance in terms of their microstructural evolution. To accomplish the project goal, this study considers several inter-related specific objectives, as described below.

1.2 Specific objectives

- i. Understand the effect of Si reservoir and thermal annealing time, on the microstructural characteristics of the Si-based diffusion coating, and correlate it with their oxidation mechanism.
- Explore the influence of different Si-Pt ratios (i.e Si-rich versus Pt-rich), the thickness of the Si-Pt reservoir, and thermal annealing temperature, on the growth, microstructural evolution, and oxidation behavior of multilayered Si-Pt based diffusion coatings.
- iii. Based on the results obtained, establish/propose an optimum design of Si and/or Si-Pt based diffusion coating system for the γ -TiAl substrate.

1.3 Thesis outline

This thesis is organized into eight main sections (or chapters). The main goal and objectives are described in this *Chapter 1*.

Chapter 2 presents the state of the art and offers the fundamental background to describe the context of this research. It includes the materials aspects of Ti-Al alloys, ranging from the alloy chemistry to their oxidation performance, followed by the fundamentals of oxidation and of solid-state diffusion, as well as an overview of some of the existing oxidation-resistant coating systems prepared by different methods.

In *Chapter 3*, the experimental methods that allow us to conduct this study are detailed. Those are structured in two blocks, first, the overall process for the coating development is described as well as the hybrid steps used for the coating growth, followed by the characterization techniques, with a specific focus on microstructure, composition and oxidation performance.

Chapter 4 is the first part of the presentation of the results, particularly focused on the characterization of the base material before any surface modification, as well as on the surface preparation of the base material using plasma cleaning and its effect on the properties of the base material.

Chapter 5 -Protective Ti_xSi_y coatings for enhanced oxidation resistance of the γ -TiAl alloy at 900°C is devoted to the coating development, particularly the Si-based coatings that were grown at 950°C with different annealing durations. Here the growth of the coating and their oxidation performance at 900°C are studied, as well as the microstructural evolution due to oxidation at high temperature. The related publication is referred as follows: <u>Crespo-Villegas, J., Cavarroc, M., Knittel, S., Martinu, L., & Klemberg-Sapieha, J. E. (2021)</u>. Protective TixSiy coatings for enhanced oxidation resistance of the χ -TiAl alloy at 900° C. Surface and Coatings Technology, 127963.

Chapter 6-Auto-assembly of a multilayer structure in magnetron sputtered Si-Pt reservoirs on γ -TiAl alloy induced by high-temperature annealing and their oxidation behavior presents the results of coating development based on thick Si-Pt reservoirs at 750°C and rich Si compositional ratios. The growth of a Pt-Si-based multilayer coating system and its microstructural evolution due to oxidation at 900°C is also studied. The related publication is referred as follows: Crespo-Villegas, J., Cavarroc, M., Knittel, S., Martinu, L., & Klemberg-Sapieha, J. E. (2022). Selforganization of multilayer structure in magnetron sputtered Si-Pt reservoirs on γ -TiAl alloy induced by high-temperature annealing and their oxidation behavior. *An additional section* with a complementary study of Pt-Si multilayer system growth at 950°C, rich Pt compositional ratios, and thinner Si-Pt reservoirs, as well as their oxidation behavior is discussed in *Appendix A*.

Chapter 7, provides a discussion of the main findings and relevance of this research work, the different Si and Si-Pt coating systems developed in this PhD project, as well as their performing behavior compared with other different approaches built in the framework of this collaborative research FCSEL-SAFRAN.

Chapter 8 summarizes the most important contributions of this PhD work; it also highlights the most important outcomes and provides potential perspectives for future developments.

CHAPTER 2 LITERATURE REVIEW

This chapter provides an overview of the main subjects related to this study: It first introduces the fundamental characteristics of the base material (γ -TiAl alloys), to then continue with the theory of oxidation, including the thermodynamics, kinetics, and diffusion processes; It is at the end complemented by a summary of the different approaches used to develop coating systems for high-temperature applications, from the surface engineering point of view.

2.1 γ-TiAl alloys

2.1.1 Properties of γ-TiAl materials

 γ -TiAl based alloys are an intermetallic compound that has been studied since around the 1950s, and it remains a relevant subject until now. Intermetallic compounds are a type of material whose properties are between those of a metal and a ceramic because of the metallic-covalent bonding that characterizes them. They possess a crystalline order and are denoted "structural" because of their intrinsic mechanical properties [28-32]. In Table 1.1 the inherent attractive characteristics of TiAl are compared with other intermetallics such as the Ni-Al superalloys [32,33].

Property	Ti ₃ Al	TiAl	Nickel-based superalloys
Density, g/cm ³	4.1-4.7	3.7-3.9	8.3
Modulus, GPa	100-145	160-176	206
Yield strength, MPa	700-900	400-650	275-1125
Tensile strength, MPa	800-1140	450-800	1,240
Creep limit, °C	760	1000	1090
Oxidation limit, °C	650	700	1090
Ductility at room temperature,%	2-10	1-4	3-5
Ductility at high temperature, %	10-20	10-60	10-20
Structure	D0 ₁₉	L1 ₀	Fcc/L ₂

Table 2.1: Comparison of titanium aluminides properties and nickel-based superalloys [32,33].

Additionally, intermetallic alloys are of great interest for high-temperature applications due to their beneficial properties such as relatively high melting point, a suitable high-temperature strength, and low density that could decrease the weight of the jet engine components and therefore diminish the concentration of stresses that can be originated during their operational cycles of loading.

However, besides their advantages, they also exhibit certain limitations, such as high brittleness (low ductility) inherent to their ordered nature [33,34].

Their production, particularly for γ -TiAl intermetallics is similar to those used for other metals and alloys, which includes ingot melting, casting, forging, precision casting, and machining [13,35-36].

2.1.2 Ti-Al alloy chemistry and phase equilibria

In the Ti-Al phase diagram of Figure 1.2 (a) [13], three main compounds can be observed, namely Ti₃Al (α 2), TiAl (γ), and TiAl₃; Of these, γ -TiAl alloys are the ones of interest for this study. γ -TiAl alloys are characterized by their composition, with an aluminum content of 46 to 52 atomic percent (at. %). In addition, this alloy contains at least one of the following elements vanadium, manganese, tungsten, tantalum, niobium, or chromium incorporated in a range of 1-10 atomic percent (at. %).

The central part of the Ti-Al phase diagram is shown in Figure 1.2 (b). In this range of concentrations (expressed in at. %), the equilibrium phases are: hcp α -Ti (disordered and liquid), bcc β -Ti (disordered and liquid), as well as the γ -TiAl (ordered, L1₀ structure), and α 2-Ti₃Al (ordered, DO₁₉ structure). The exact extension of each ordered phase is not defined by an absolute composition; instead, it is a range of compositions. These uncertainties are related to the presence of impurities such as oxygen, nitrogen, carbon, and hydrogen [13,35,36-38].

The thermal process for obtaining different TiAl alloys involves several phase transformation reactions. It starts with the solidification of the β phase, a subsequent transformation to the α region, which is followed by a transformation into the $\alpha + \beta$ region and then into the $\alpha 2+ \gamma$ structure. The strong relationship between the desired properties and the microstructure allows one to tailor and tune their characteristics during production. There are two types of Ti alloys, the α -stabilized type,
which is obtained when incorporating a transition metal into the pure Ti lattice. Elements from the VI-A group are well known as the β stabilizers (Cr, Mn, Mo, Si, B, C), while Al, Ga, Sn, Zr can stabilize the α 2 phase [13,35,36-38].



Figure 2.1: (a) Ti-Al phase diagram and (b) central part of the binary Ti-Al phase diagram. Adapted from references [13,14].

Alloying with certain elements has been widely explored, and it has allowed to make significant progress on the limited room temperature ductility and fracture toughness of the α 2 and γ phases mainly because it can (i) produce a relaxation of the restricted slip modes, as well as (ii) delay the kinetics of ordering by changing the long-range order, this is particularly useful on α 2 alloys but still limited on γ alloys. Alloying can also (iii) induce the formation of new constituent phases (i.e., ductile second phases) or (iv) change the transformation behavior during heat treatment and processing [36-40]. In general, for the bi-phasic (duplex microstructure) alloys, the incorporation of additional elements has improved their ductility (i.e., V, Cr, and Mn), and oxidation resistance (Nb and Ta). Specifically, for the obtention of the Ti-48Al-2Cr-2Nb composition, Cr and Nb are incorporated since the presence of Cr induces better ductility, and that of Nb results in beneficial oxidation behavior of the alloy due to the stabilization of the Al₂O₃ scale. However, the further incorporation beyond a critical amount of the additional elements is restricted by the embrittlement that can occur due to the precipitation of the α 2 phase. To develop alloys with the optimum balance of thermo-mechanical properties, the progress in the processing of the alloys continues to evolve,

demonstrating the scientific and technological challenge that arises with the introduction of new materials [36-40].

2.1.3 Crystal structure and microstructure of γ-TiAl alloys

During Ti-Al intermetallic compounds formation, the symmetry at the lattice of the metal element is reduced, which causes an increase in restriction for the available deformation modes. This behavior strongly influences some of their properties shown in Table 1.1; for example, producing higher strength at high temperatures, and a decrease in ductility as well as in fracture toughness. With advances in alloying and processing techniques over the years, significant control over their crystalline structure, microstructural features, grain boundary characteristics, composition, and strength properties has been gained [13,36-40]. The γ -TiAl phase has an ordered face-centered tetragonal L10 type structure, and the α 2 phase is an ordered DO₁₉ structure; both crystal structures are schematically represented in Figure 2.2.



Figure 2.2: Crystal structure of the hexagonal α 2-Ti3Al and tetragonal γ -TiAl. Adapted from reference [13].

The γ -TiAl phase exhibits a broad range of Al content (49 to 66 at.%) and temperature-dependent stability. The γ -TiAl phase seemingly stays ordered up to its melting point. The tetragonality of the γ -TiAl phase is caused by different atomic radios of Ti and Al. For the stoichiometric compound, the tetragonality ratio is 1.02 and can either increase to 1.03 or decrease to 1.01 when increasing or decreasing the aluminum content, respectively [36-40].

The α 2-Ti₃Al phase exhibits an ordered DO19 (hexagonal closed packed) type structure, the compositional stability of the α 2 phase is wide, with Al content in the range of 22-39 at.%, α 2 phase owns low ductility and toughness at room T, that cause their brittleness. Mainly attributed to the scarcity of separate slip systems that can operate simultaneously, the slip along the C axis components requires higher shear stresses [36-40].

There are two types of γ -TiAl alloys: (i) single-phase containing only the gamma (γ) phase, and (ii) bi-phasic, with a mixture of (γ and $\gamma + \alpha 2$). The gamma (γ -TiAl) phase possesses an equiaxed microstructure and the (γ -TiAl+ α 2-Ti₃Al) a lamellar morphology. The lamellar structure contains flat strips of α 2 alternated between thin gamma layers. A duplex microstructure that contains both (equiaxed grains and lamellar colonies) is presented in Figure 2.3. Each of the phases confers to the γ -TiAl alloy specific properties. Then, the volume ratio of gamma to equiaxed (γ)/and ($\gamma + \alpha$ 2) is relevant [13,36-40].



Figure 2.3: Microstructure of a duplex (lamellar and equiaxed) Ti-48Al-2Cr-2Nb.

Ductility is strongly related to the lamellar colonies volume and their morphology. It has been reported that content of 10 vol % of the α 2 phase (with around 35 at.% of Al) is optimal for good ductility. Higher Al content on the α 2 causes brittleness. A content of 30% of the lamellar volume provides an optimal combination of creep resistance at high temperatures while keeping an acceptable tensile strength and ductility. The biphasic region ($\gamma + \alpha$ 2), which exhibits higher ductility, is caused by the reduction of the c/a unit cell parameter when Al is decreased [13,36-40].

The origin of the duplex microstructure ($\gamma/\alpha 2$) originates from the process of fabrication. More specifically, the duplex microstructure is produced by heat treatment in the bi-phasic region. First, the nearly stoichiometric or Ti-rich composition is obtained either by casting or by melting, and a polycrystalline lamellar structure is formed. Such a lamellar structure is heated or hot-worked at high temperature (>1508°C in the bi-phasic region); during the subsequent cooling, the fully lamellar structure is transformed into a duplex structure consisting of equiaxed grains of the single γ -phase and the lamellar structure. The ratio of equiaxed (γ) to lamellar grains ($\alpha 2$) and the grain size of an alloy is governed by the hot working temperature, the duration of hot work will also influence the grain size. The alloy used in the present study exhibited a grain size in the range of ~60 to ~200 µm [13,36-40].

2.2 Oxidation at high temperature

2.2.1 Fundamentals of oxidation and diffusion processes

The oxidation process illustrated in Figure 2.4 occurs when a solid material (metal or alloy) is exposed to an oxidizing atmosphere, most frequently oxygen or air. The oxidation reaction between a metal and reactive gas is expressed by Equations (2.1-2.3) [41].

The main factors affecting oxidation include temperature, time of exposure, gas composition, partial pressure, and material characteristics (i.e., composition, microstructure, surface finish, porosity, etc.). The oxide that forms can grow externally, or internally; For external oxide growth, an oxide scale (the layer of oxide that grows) develops outwardly. For this to occur, the reactive elements must be transported through the metal/alloy-oxygen interface.

The oxide scale that results can be either single oxide (i.e., as in Fe oxidation, which results in Fe₂O₃); or multiple oxides (i.e., as in γ -TiAl oxidation, which results in TiO₂ and Al₂O₃); thin or thick; porous or compact, etc., [17,41-44].



Figure 2.4: External oxidation mechanism at high temperature. Adapted from reference [41].

$M(s) + O_2(g) = 2MO$	(Equation 2.1)
$M(s) + O_2(g) = MO_2(s)$	(Equation 2.2)
$4 \text{ M}(s) + 3 \text{ O}_2(g) = 2\text{M}_2\text{O}_3$	(Equation 2.3)

where M indicates a metal

Internal oxidation can also arise when oxygen dissolves in the system being oxidized and one of the elemental components exhibits high affinity towards oxygen – then both will interact selectively, creating a precipitate internally [41-44].

Oxidation is commonly addressed from the (i) thermodynamic and (ii) kinetics points of view; however, due to the complexity of high-temperature oxidation, particularly of alloys or multi-

component systems, in addition to these approaches (i and ii), the transport of species or diffusion is very important. As an example, the theory of oxidation rates at high temperatures proposed by Wagner considers mass transport processes (particularly diffusion) of the species (ions or electrons) involved in the scale growth [41-42].

According to the Wagner theory,

- (i) During oxidation, mass transport originates due to an activity gradient of the species.
- (ii) Any microstructural defect can influence the mass transport of species.
- (iii) Diffusion processes are caused by gradients of chemical potential within the scale.
- (iv) Electrical potential gradients that occur to separate charges in the participating species are another contribution to the oxidation rate.
- (v) Chemical reactions strongly influence the kinetics of oxidation; however, they are faster than the diffusion processes
- (vi) Since diffusion is the slower transport process (compared to chemical reactions) during oxidation, it is the controlling rate factor in the kinetics of oxidation.

External oxidation occurs first by chemisorption processes of the oxygen (i.e., oxygen dissolution) into the surface of the material, creating a thin monolayer of oxides as a reaction product (i.e., scale formation), while initial growth occurs through solid-state diffusion of the metallic reactive species towards the surface, creating lateral islands (whiskers) normal to the surface that continue to grow by connecting those islands into a continuous film; typically underneath the first layer of oxide scale, there is significant porosity [41-46].

The transport of the reactive species participating in the oxidation process is thermally activated, and their driving force can be either an electric field across the oxide layer with electron transport (for thin films) or can be due to a chemical potential gradient (for thick films). This reaction is fed by the inward diffusional transport of either the oxygen ions towards the oxide/material interface or by outward diffusional transport of material ions towards the oxide/gas interface. The oxidation reaction will only stop if the oxygen partial pressure or the temperature is low. But if high temperature and atmospheric pressure are present, the reaction will continue. The total oxidation rate is determined by the diffusion of the active elements through the oxide scale, the transport of

the diffusing species can be accelerated by microstructural features such as cracks, pores, or grain boundaries, which act as diffusivity paths. [41-46]

Solid-state diffusion in pure materials is mostly controlled by the almost random movement of vacancies. Even in intermetallics which are characterized by their ordered crystalline structures, the presence of crystalline defects occurs while maintaining a local order. Therefore, diffusion in intermetallics is a complex process based on the motion of atoms through the crystalline volume or lattice. There are different diffusion mechanisms (i.e., vacancies, interstitial, impurities) that require high energy and therefore occur at high temperatures [41-46].

There are also microstructural features or defects (i.e., grain boundaries, cracks, or specific grain size) that are as well critical parameters affecting the diffusional transport of species during oxidation; this includes the grain size of the base material. The latter can occur at lower temperatures. A smaller grain size will promote faster diffusion than larger grains; this could be beneficial to accelerate the formation of protective oxides (selective oxidation) in alloys. A higher concentration of defects will benefit the transport of the charged species, and as there are more grain boundaries, the diffusional paths for oxygen are favored due to the weakening Van der Waals forces among the grains. Higher energy is associated with lattice transport, so this type of diffusion is more often related to high-temperature environments. However, both types of diffusion (through the lattice and grain boundaries) can be present during oxidation [41-46].

In the case of Ti and Al, these elements will oxidize preferentially according to their elemental activity and oxygen pressure. Once the surface is completely covered by the oxide scale, the continued oxidation will be dictated by the elemental activity at the oxide-metal interface and will be fed by the diffusion of oxygen through the initial layers of the scale towards the metallic or alloy surface [17,43-46].

In TiAl intermetallics, the diffusivity of Ti in rutile is faster than that of O, while Al in alumina diffuses very slowly. Alumina growth towards the metal-oxide interface and rutile growth towards the gas-oxide interface. When a ternary element is present in the TiAl alloy, the concentration of the active species participating in diffusion can be modified, and the kinetics of oxidation as well. Another effect that ternary elements induce is the influence on the oxide/alloy interface and the oxide characteristics [17,43-46].

2.2.2 Thermodynamics of oxidation

Oxidation can also be seen from a thermodynamic perspective. Thermodynamics is related to the reaction products and their stability, which are controlled by the alloy system, temperature, and the environment, which dictates that the growth of a certain oxide is governed by the standard free energy of formation (ΔG) of the oxide compounds that results in the oxidation reaction [16,42,43]. According to temperature and pressure ΔG° for an oxide formation can be expressed [42] as follows:

$$\Delta G_{M_x O_y} = H_{M_x O_y} - T \Delta S_{M_x O_y}$$
(Equation 2.4)
where,

 $G_{M_x O_y}$ = Standard free energy of formation of an oxide $(M_x O_y)$ $H_{M_x O_y}$ = Enthalpy of formation of an oxide $(M_x O_y)$ $S_{M_x O_y}$ = Entropy of the oxide reaction

When the standard free energy of formation at standard conditions (ΔG°) is known, the standard free energy of formation of a chemical reaction can be related to the equilibrium constant K [42]:

$$\Delta G = \Delta G^{\circ} - RT \ln K$$
 (Equation 2.5)

To express the ΔG as function of the molar components, chemical potential (μ_i) is introduced [42]:

$$\mu_i = \Delta \overline{G} = \left(\frac{\partial G_i}{\partial n_i}\right) \text{ (Equation 2.6)}$$
$$\Delta \overline{G} = \text{Partial molar free energies}$$
$$n_i = \text{number of moles for a respective element}$$

For the oxide to grow, the reactive element must be present at the oxide-metal interface, and the partial pressure of oxygen should exceed the partial pressure equilibrium for the reaction at that

activity of the element. This equilibrium oxygen pressure $p(O_2)$ is established from the ΔG° , with values of unity (1) are considered their relationship can be expressed through Equation 2.7 [42].

$$\Delta G^{\circ} = - \operatorname{RT} \ln \frac{1}{\ln pO_2}$$
 (Equation 2.7)

The Ellingham-Richardson diagram [41] shown in Figure 2.5, presents graphically the thermodynamic stability of a significant set of binary oxides (A+ O₂ = AO₂), over a broad range of temperatures (ΔG° along the Y-axis versus T along the X-axis). The higher the negative value of ΔG° , the more significant the stability of the oxide; most stable oxides appear at the bottom while those with the least stability appear at the top. The ΔG° values in the diagram are indicated by the straight line, and the change in the slope at the melting, boiling, or sublimation points shows the change of entropy for the corresponding reaction. The interception of the free energy line at 0K (absolute zero) indicates the enthalpy change of the reaction [41,42,47].

The partial pressure of oxygen (pO_2) is also provided at the Ellingham-Richardson diagram to allow the determination of oxygen equilibrium pressures, by extending the zero free energy point of the X-axis ($\Delta G=0$) at a temperature of 0K, towards the respective $\Delta G_{Me}/\Delta G_{Mex}O_y$. The dissociation pressure or oxygen equilibrium pressure of the oxide corresponds to the partial pressure at which the metal and oxide are present in equilibrium ($\Delta G=0$). Equilibrium gas mixtures for CO/CO₂ and H₂/H₂O are also supplemented for the scales. [41,42,47].



Figure 2.5: Ellingham-Richardson diagram of the oxides of metals and alloys commonly used in high-temperature applications. Adapted from reference [41].

2.2.3 Kinetics of oxidation

Oxidation kinetics refers to the rate of the oxygen reaction that occurs over time when a material is exposed to an oxygen-containing environment. Kinetics of oxidation is vital to predict or determine the lifetime of the material/component exposed, as well as reaction mechanisms and rate-limiting process during oxidation, particularly when operating at high-temperature conditions. There are three main types of kinetic behavior, as shown in Figure 2.6: logarithmic, parabolic, or linear, each one expresses a particular trend of the reaction velocity between the oxygen atoms and the atoms of the material exposed [41,48].



Figure 2.6: Schematic of the different kinetics of oxidation. Adapted from reference [48]. When the behavior is logarithmic, there is an accelerated start and almost no reaction or very slow oxidation rate after the initial stage (Equation 2.7).

$$X = k_{\log} \log t + C1$$
 (Equation 2.7)
where,

X: mass change over surface or thickness; k_{log} : logarithmic rate constant;

t: time; C1 is a constant.

This is the type of behavior exhibited by metals oxidized at low temperature (and pressure) and noble metals. For this type of oxidation, the rate-limiting mechanism is an ionic and/or electron transport process with an electric field as the driving force [41,48].

The parabolic behavior occurs when the growth rate of the oxide is proportionally inverse to time (Equation 2.8), revealing a decrease in the oxide growth as time progresses. Another way to understand it is from the diffusional transport of the species, in which the diffusional path increased with time, to reach the oxide/gas interface and metal/oxide interface for oxygen and the material, respectively. The kinetic transports are controlled by the thermal diffusion of ionic species (inward

and outward diffusion) strongly influenced by chemical potential gradients. Electron transport across the oxide layer could also be present [41,48].

$$X^2 = k_p t + C2$$
 (Equation 2.8)
where,

X: mass change over surface or thickness; *k*_p: parabolic rate constant;

t: time; C2: constant

The linear behavior is exhibited when there is a proportional growth of the oxide growth with respect to time (Equation 2.9). This kinetic performance shows a very fast interaction between oxygen and the material due to surface and/or phase boundary processes, and undesired effects such as delamination, spallation, and imminent failure of the material [41,48].

$$X = k_1 t + C3$$
 (Equation 2.9)
where,

X: mass change over surface or thickness; k_1 : linear rate constant;

t: time; C3: constant

2.2.4 Oxidation of γ-TiAl alloys

The limited resistance to oxidation at high temperatures of most of the γ -TiAl alloys is due to the preferential growth of TiO₂ over the Al₂O₃ growth. The origin of the oxidation performance of γ -TiAl alloys is connected to their microstructural characteristics (phase composition); more specifically, the oxidation resistance of γ -TiAl alloys is affected by (i) the decrease of the Al content, and (ii) the increase of the fraction volume of the α -2 phase (in which the Ti activity is higher with respect to Al).

As observed in Figure 2.7, the α -2 phase exhibits a preferential growth of TiO₂, over Al₂O₃, while in the TiAl there is an energetic competence between Al₂O₃ and TiO₂. In addition, it has been found that oxygen diffusivity in TiO₂ occurs faster than Al diffusivity in Al₂O₃. Making the growth of TiO₂ more effective from the kinetic point of view [16,17].



Figure 2.7: Variation of the metal oxide equilibrium pressures in the Ti-Al-O system at 900°C. Adapted from reference [16].

Different models have been proposed for the high-temperature oxidation of TiAl alloys, particularly in Taniguchi's model [49] (Figure 2.8) an initial stage in which Ti and Al are oxidized to form, TiO_2 and Al_2O_3 grains respectively; and a subsequent stage with the growth of an inner porous layer of mixed TiO_2 and Al_2O_3 , at which TiO_2 growth overpass the growth rate of Al_2O_3 . The porosity associated with the inner layer, as stated by Taniguchi relates to an initial normal growth of TiO_2 and after a lateral growth of it.



Figure 2.8 Taniguchi's model for the high-temperature oxidation of TiAl alloys. Adapted from reference [49].

The model of Shida and Anada [50] (Figure 2.9) indicated a different oxide scale formation according to the Al content of the alloy; It describes alloys with an Al content below the 65 at.% exhibit a multilayered oxide scale of $TiO_2/Al_2O_3/TiO_2+Al_2O_3/Internal oxide (Al_2O_3 in Ti_3Al)$ (Figure 2.9-a). Meanwhile, alloys with a higher Al content (\geq 75 at.%) do not exhibit the internal oxidation zone (Figure 2.9-b). In their model, it has been shown a correlation on the thickness of the oxide scale as a function of the Al content, in which higher Al content decreased the total thickness of the scale.

The oxidation kinetics of TiAl alloys appear to be a function of oxidation temperature, type of oxidation exposure (isothermal or cyclic), Al content, and time. For isothermal exposure, nearly parabolic behavior has been observed while at cyclic exposure mixed linear and parabolic regimes predominate. The total mass gain has been revealed to decrease as the Al content in the alloy was higher. Shida and Ananda have also reported the influence of ternary addition on the oxide scale that develops on TiAl alloys [50].



Figure 2.9 Shida and Anada's model for the high-temperature oxidation of TiAl alloys. Adapted from reference [50].

2.3 Development of protective coatings through surface engineering

In the area of surface engineering, there is a technological field dedicated to the deposition of coatings with the goal to protect the base material and modify the surfaces by improving their functionality. The surface modification can provide protection against severe environments such as wear, corrosion, oxidation, etc., without compromising the original properties of the base material [10,51-54].

The most promising method to protect γ -TiAl alloys against environmental degradation at temperatures above 750 °C is the use of well adhering protective coatings that act as an oxygen barrier. Since the areas of coating development continue to grow, the existing deposition types of protective coatings are vast and diverse, particularly for oxidation resistant applications, it comprehends diffusion coatings, overlay coatings, thermal barrier coatings (TBC), and halogen effect. The specific properties required for those coatings will depend on the very particular application and can be tailored by the deposition conditions. The selected type of coating must satisfy the desired coating properties and be suitable for the intended application [9, 51-54].

2.3.1 Oxidation resistant coatings

The existing approaches to developing oxidation-resistant coatings are varied, [9,51-54] here is presented an overview of the more highlighted ones through literature according to the type of coatings. Their constitution and their main fabrication methods, as well as their operating oxidation protection mechanism, are addressed.

Diffusion coatings (i.e., Diffusion aluminide coatings, Pt or Cr modified aluminide coatings)

Diffusion coatings [55-65] are obtained by the enrichment of the surface with the specific element(s) and heating in a suitable atmosphere and promoting the diffusional transport of elements to promote the formation of a graded layer. These types of coatings must be strongly adherent to their substrates, and the compositional changes are more gradual through the different zones obtained. These comprehend those coating systems in which an enriched surface, typically with Al, Pt, Si or combinations of those (Al-Cr, Al-Pt, Al-Si) produces an oxidation-resistant thermally grown oxide (or corrosion-resistant oxide).

This type of coating is obtained typically via chemical deposition methods such as pack cementation processes (aluminizing, siliconizing, and chromizing) as well as slurry and liquid siliconizing processes which imply spraying or dipping respectively, with process temperatures in the range of (700-950 °C), with subsequent thermal treatment at higher temperature (1000°C-1100°C). 30-100 μ m is the thickness range for these coating systems [8]. The formation of brittle phases must be optimized in any of the processes related to diffusion coatings [9,55-65].

These types of coatings are usually applied to Ni-based superalloy and cobalt-based materials, their oxidation protection mechanism first arises from the formation of Ni and Al-containing compounds (i.e., NiAl, β -NiAl) or Co and Al compounds, depending on the particular chemistry of the substrate. Additionally, the Al content of the base material will influence the governing diffusional growth transport. Subsequently, the Al-containing compound acts as an Al reservoir for Al₂O₃ formation [9].

Also, aluminide coatings [45] based on TiAl₃ and TiAl₂ phases have exhibited high oxidation resistance, and when a post-deposition heat treatment is applied to these, could evolve into a diffusion-type coating, with increased adhesion while promoting the growth of a continuous and stable Al₂O₃-scale.

The main drawback of this family of coatings involves significant interdiffusion within the substrate which promotes the formation of secondary phases and elemental enrichment from the alloy at the Ni-Al coating. The complete degradation of these coating occurs once the β -NiAl is transformed into γ '-Ni₃Al throughout the thickness of the coating, and aluminum has depleted, causing cracks at the platinum aluminide coating [9]. Diffusion coatings were originally designed for Ni-based substrates, but their use is not limited to it and has already extended to other substrates (i.e., TiAl-based alloys). Si-Al is the most common type of diffusion coating for TiAl substrates [55-65].

Thermal barrier coatings (TBCs)

Consists of a three-layers structure, (1) an inner layer with oxidation and/or corrosion-resistant layer (bond coat,) which prevents the attack of the hot gases while providing improved adhesion between the substrate and the outermost layer; (2) a middle layer denominated as thermally grown oxide (TGO) with Al₂O₃ constitution and (3) an outer insulating layer (top coat) which composition is typically yttria-stabilized zirconia (YSZ) due to their low and stable thermal conductivity overtime at the operating range of the temperatures and is chemically inert at the combustion atmosphere. TBCs [66-69] are produced by atmospheric plasma sprayed (APS) or Electron Beam Physical Vapour Deposition (EB PVD) [9].

A degradation mechanism of these coatings involves delamination of the top-coat due to excessive growth (a cubic growth with respect to time) of about 8-10µm of the TGO by inward diffusion of

the oxygen anions which diffusional transport occurs either by permeation throughout interconnected microstructural defects at the top-coat (i.e., cracks, pores) or lattice transport [10]. Since the TGO exhibits a mismatch of its thermal expansion coefficient ($\sim 8x10^{-6}$ K⁻¹) concerning the one of the bond coat ($\sim 17x10^{-6}$ K⁻¹); and additionally, the associated thermal stresses produced in the TGO during the operational cycles, results in the TGO cracking as their thickness is increased. Other major failure mechanisms of TBCs are related to significant structural changes at the topcoat during the high-temperature exposure, denominated as the sintering effect of the topcoat, which modify the topcoat properties (i.e., elastic modulus and hardness); As well as CMAS (Calcium-Magnesium-Aluminium-Silicate) infiltration from the environment into the topcoat, that decrease the Y₂O₃ content in the YSZ, which leads to their phase transformation, accompanied by a volume increase with subsequent cracking and delamination. [70,71]

Overlay coatings (MCrAlX)

Overlay coatings [72-79] are oxidation-resistant protective coatings with a controlled microstructure and composition that are usually prepared by Physical Vapor Deposition (PVD, such as magnetron sputtering, electron beam evaporation, arc evaporation) as well as Plasma Enhanced Chemical Vapor Deposition (PECVD), Plasma Spraying, High-velocity oxygen fuel (HVOF), atmospheric plasma spray (APS), low-pressure plasma spray (LPPS), composite electroplating and laser plating.

This includes the following systems: (i) MCrAlX coating (where M=metal, X=minor additions) in which M can be Co (highly corrosion-resistant element or Ni (highly oxidation resistant element), and X corresponds to either Y, Hf, Si, or Ta in small incorporation (<1 weight %). MCrAlX coating systems are designed to form Al₂O₃ due to the Al reservoir; particularly Cr reduces the amount of Al needed to grow the protective Al₂O₃ scale. In addition, Cr induces the formation of Cr₂O₃ which is as well protective, while Y and Hf can improve adherence of the formed oxide scale to the substrate by limiting oxide spallation, and specifically Y, inducing anion diffusion oxide growth as well as limiting the Cr₂O₃ oxidation rate; Si and Ta can improve both oxidation and corrosion [68-75]. These systems are typically 125-300 µm thick. A balanced amount of Cr and Al content is required to optimize coating ductility and to limit the formation of γ '-NiAl₃ and Ni-rich phases

which limit their mechanical performance (fatigue life) [72-79]. Overlay protective coatings are strongly developed for Ni and Co-based substrates.

Among these coatings, metal nitride-based composite coatings such as TiAlCrYN, CrAlN, or CrAlYN/CrN have been reported as an effective barrier oxygen diffusion barrier at 900 °C. Among their limitation, coating spallation develops after cyclic oxidation caused by the degradation of the nitride coatings via the Ti-N reaction and the formation of titanium nitrides, which exhibit accelerated oxidation [72-73].

The main element of the overlay coating depends on the main element of the base material, i.e., for Ni-based alloys, the Ni will be present in the overlay coating to reduce diffusion from the Ni present at the substrate. Al₂O₃ is the most protective oxide scale in these coatings (protecting up to \sim 1200°C) while the Cr₂O₃ scale protects up to \sim 900°C [10].

Halogen effect

The halogen effect [80-83] was specifically developed for titanium aluminides. It is based on the addition of halides such as F, Cl, Br, and I into the surface of the TiAl-alloy very often in the form of implantation or microalloying. Particularly, F promotes the oxidation of aluminum, which results in the formation of a slow-growing α -alumina layer originated by the selective transport of gaseous aluminum fluorides (AlF₂ (g)) and their oxidation at a high temperature.

The core reaction is aluminum content-dependent (i.e., demanding for example at least 40 at. % of Al in titanium aluminides), and is also influenced by a defined range of halogen concentration. Since Fluorine is the halogen reported with the major improvements in oxidation resistance, the displayed protecting behavior has been denominated the 'halogen effect''.

Beam ion implantation (BLI²) is reported as the most established technique for the fluorine effect, and plasma immersion ion implantation (PI³) was subsequently developed to counterbalance the geometrical limitations of (BLI²) [45], Plasma immersion ion implantation - is suitable for complex shapes [81]; or Liquid phase application using spraying or painting with fluoro-polymers or immersion in diluted HF [82].

Failure mechanism of oxidation-resistant coatings

The common failure mechanism of oxidation-resistant coatings relates to the structural stability of coatings, which is related to their thermal stability over time. Coatings can degrade either by the interdiffusion process with the substrate or by depleting the elements that form the scale.

Coating degradation can therefore induce other difficulties such as the growth of brittle phases, (i.e., as the close-packed phases) below the coating. The degradation rate of the coating due to diffusion is strongly related to temperature, it may increase massively as the temperature rises [10,84]. Common failure mechanisms reported for oxidation-resistant coatings are summarized in Table 2.2.

Coating family	Working temperature	Type of coating	Failure mechanism
M-Cr-Al-X M: metal, Fe, Ni, Co X: Y, Si, Ta, Hf	800°C-900°C	Overlay	Discontinuous oxide layer Al depletion Cracks inside the coating Interdiffusion Phase modifications Local spallation Degradation
Modified aluminides	900-950°C	Diffusion	Local oxidation Interdiffusion Al depletion Spallation Breakaway oxidation
Surface fluorination	900°C	Halogen effect	Al depletion Fluorine rich layers

Table 2.2: Common failure mechanism reported for oxidation-resistant coatings [10,84].

2.3.2 Oxidation-resistant coatings based on oxides (SiO₂, Cr₂O₂, Al₂O₃)

Slow-growing and thermodynamically stable oxides are fundamental in the development of oxidation-resistant coatings. The parabolic rate constants (represented in the plot as K) of different oxides are compared in Figure 2.10 in the Arrhenius plots (log k_{ν} versus 1/T(K)). The slope corresponds to the activation energy, which is also related to diffusivity [44].



Figure 2.10: Arrhenius plot of growth rates for common oxide scales. Adapted from reference [44].

The thermo-kinetic map in Figure 2.11 organizes the behavior exhibited by different oxide scales as a function of their thermodynamic stability, highlighting Al_2O_3 , SiO_2 , and Cr_2O_3 as the ones with the slower growth rate and superior thermodynamic stability [44].



Figure 2.11: Thermo-kinetic map of various oxide scales showing parabolic rate versus free energy of formation. Optimum performance for stable slow-growing scales in the lower right. Adapted from reference [44].

2.3.3 Materials for oxidation applications

Silicides (Ti-silicides and Pt-silicides)

Silicide materials had raised a lot of interest, particularly those which contain transition metals (i.e., Pt, Ti, among others) because of the displayed properties, like thermal stability and chemical inertness as well as high hardness [85-93].

Ti-Silicides have been related to oxidation, corrosion, and wear-resistant applications [85-89]; While Pt-Si have been mostly related to microelectronic applications (i.e., as a diffusion barrier) in which their chemical inertness is of benefit [90-93].

Pt-silicides and Ti-silicides are some of the compounds which conform to the coating systems developed in this project, their phase diagrams are shown in Figures 2.12 and 2.13, respectively.



Figure 2.12: Ti-Si Phase diagram. Adapted from reference [94].



Figure 2.13: Pt-Si Phase diagram. Adapted from reference [44].

Platinum aluminides

Platinum aluminide materials, more precisely coatings [95,96], were first developed as diffusion barriers to avoid Al inward migration into the Ni-based alloys (NiAl substrates) mainly due to the difference in atomic radii (Al: 1.18 Å; Pt: 1.77 Å) while keeping Al diffusion towards the surface to benefit from the Al₂O₃ formation. Later their use of platinum aluminide was also extended due to the effectiveness of maintaining the Al₂O₃ well adhered to the substrate while avoiding their spallation [15,82-84][•] Platinum aluminide exhibits oxidation resistance at high temperatures and has a high melting temperature that restricts the formation of low melting phases. This intermetallic compound is part of the Pt-based coating system developed for this study; its phase diagram is presented in Figure 2.14.



Figure 2.14: Pt-Al Phase diagram. Adapted from reference [96].

CHAPTER 3 EXPERIMENTAL METHODOLOGY

This chapter presents the methodology applied for the surface engineering performed in this study, including the surface preparation and coating development processes, as well as the applied characterization techniques. First, the surface preparation of the base material is detailed, followed by the description of the hybrid surface modification via magnetron sputtering and subsequent thermal annealing (TA). Characterization of the coating-substrate system is included, with particular focus on assessment of the microstructural evolution and the high-temperature oxidation.

3.1 Surface Engineering Process

The effective surface engineering process that first prepares and subsequently modified the surface of the base material is schematized in Figure 3.1, while some of the experimental procedures are detailed in the subsequent paragraphs.



Figure 3.1: Schematic representation of the surface preparation and coating development strategy.

3.1.1 Surface preparation of the γ -TiAl alloy

 γ -TiAl alloy substrates with a nominal composition of Ti-48Al-2Cr-2Nb (at. %) and a duplex microstructure (equiaxed+lamellar grains) was the base material employed in this study and were provided by Safran Snecma company (France). The specimens were cut by electrical discharge machining, into rectangular shapes of 50 mm x 25 mm x 2 mm (weight: 9.1 g) and 15 mm x 8 mm x 3 mm (weight: 1.4 g). As received substrates possess a machining surface effect, displayed as a rough and oxidized surface appearance, which originates the need for their surface preparation before any characterization or surface modification steps.

The surface preparation is performed using a Struers LaboPol-5 polishing machine. The process is first started by surface grinding each face of the substrate, using SiC grinding papers in the following order: 220, 500, 800, 1200, 2400 up to 4000, using with continuous rotation (~200 rpm). Substrates were subsequently polished using water-based diamond suspension (particle size: 3 μ m) and colloidal silica (particle size: 0.04 μ m) until a mirror surface finish was obtained. Subsequently, the surface of the substrates was ultrasonically cleaned for 20 min in acetone and isopropanol solutions, respectively. From the two different sizes of substrates, the flat ones (50 mm x 25 mm x 2 mm) were used for microstructural and compositional analysis, while for thermogravimetric analysis (TGA), the smaller size substrates (15 mm x 8 mm x 3 mm) were employed. The sample was placed in the vacuum chamber schematically presented in Figure 3.2 for (i) the Ar plasma cleaning of the base material and subsequently, (ii) magnetron sputtering deposition technique was used to perform coating deposition of the Si and Si-Pt reservoirs.

3.1.2 Ar Plasma treatment

The plasma surface treatment was carried out inside of a stainless-steel vacuum chamber with a cylindrical shape and dimension of 20 in diameter and 31 in height (shown in Figure 3.2). The substrate holder was placed inside the chamber using a hook (tungsten wire of either 4 or 7 cm long, that was used according to the dimensions of the substrate). The substrates were mounted with polished sides facing the magnetrons at a distance of about \sim 4 inches apart from the magnetron.

During Ar plasma cleaning, the substrate is connected as a cathode to the RF power supply through a matching unit, and the bombardment of the energetic species present in the plasma is impacted into the substrate surface, removing organic or inorganic contaminants from their surface.



Figure 3.2: Schematic representation of the magnetron sputtering system used in this study for the plasma surface treatment and coating deposition.

Before the Ar plasma cleaning, the chamber was first evacuated to a base pressure of at least 10^{-6} Torr using a pumping station (mechanical and turbomolecular pumps). Later the argon (Ar) atmosphere is generated inside the chamber by introducing a constant Ar flow of 25 sccm while adjusting a working pressure of 60 mTorr, which was maintained by the throttling valve. Subsequently, the RF power supply connected to the substrate sample is turned on by applying a 105 W power and a -800 V self-induced substrate bias voltage to ignite the Ar plasma for the cleaning of the substrate.

The plasma surface cleaning was prolonged for 50 min before coating deposition without heating. Table 3.1 reports the conditions that were used for the plasma surface cleaning of the substrate.

Substrate dimensions	Plasma source	Plasma cleaning time	Chamber conditions		Power (W)	Bias (V)
		(11111)	Pressure (mTorr)	Ar flow (sccm)		
Ti-48Al-2Cr-2Nb 50 mm x 25 mm x 2 15 mm x 8 mm x 3	RF	60	60	25	105	-800

Table 3.1: Conditions for the Ar plasma cleaning of the substrate.

3.1.3 Magnetron sputtering

Sputter deposition technique is essentially based on the generation of a plasma or glow discharge, which requires vacuum conditions to be created and sustained. The plasma is generated within a chamber due to the ionization of noble gas particles (usually Ar) introduced within the chamber using a gas flow in the mTorr range. The ionization of the Ar gas occurs when a sufficiently high electromagnetic field is generated between a cathode (i.e., source material or target) connected to a negative voltage supply and an anode [97-98].

The ionization process consists of the liberation of energetic electrons from the Ar, which leaves the Ar gas ionized (positively charged); Both the ionized gas and electrons conform the plasma. The ionized particles are attracted and impacted into the cathode, which is negatively charged. From this process of bombardment, a momentum transfer (inelastic exchange of energy) arises, that ejects particles (ions, atoms, and secondary electrons) from the cathode. The momentum transfer is the core of the sputtering technique. The secondary electrons generated from the cathode promote a steady-state plasma due to their further collisions with the species within the plasma and by increased electron interactions [97-99].

To improve the level of ionization in the plasma, a magnetron which is a fixed magnet located behind the target also conforms to the sputtering setup. It helps to generate a strong magnetic field around the target, that confines and accumulates the electrons within the plasma close to the target. Which in consequence improves the ionization by increasing the plasma density as well as producing increased sputtering rates from the atomic surface layers of the source material. The ejected species are mostly atoms that in the form of vapor are transported into the substrate. The atomic particles removed from the target material due to the sputtering process will be deposited on the surface of the respective substrate [100,101].

Typical applied voltage is in the range of 300 to 600 DC power. The typical working pressure of the argon plasma is reported in the range of 0.133 to 13.33 Pa (10^{-3} to 10^{-1} Torr). According to the gas pressure inside the chamber, the deposition rates of sputtering can be varied; Still, higher deposition rates can be induced, for example using two magnetrons configuration [97,100,101].

Magnetron sputtering can be used in different modalities, according to the power source used (i.e DC, RF) as well as the type of gases (inert or reactive). If the target is conductive, direct current (DC) can be used to generate the plasma while radio frequency (RF, 13.56 MHz) can be applied in all types of materials, particularly in non-conductive targets. During the RF MS, first, there is a process in which a negative polarization of the atoms in the target and their ejection by the bombardment of the ionized gas occurs. Secondly, the polarization of the target is inversed (positively), causing the ejection and acceleration of the atoms and ionized particles (that were present at the target surface due to the negative polarization) towards the substrate [102,103].

For the growth of the layer, once the atoms or particles reach the surface, they first condense from the plasma and then migrate to nucleate and grow into a film. The obtained microstructure and morphology will strongly depend on the source of atoms and their energy (1-100 eV). Crystallography and microstructure of the coating are mostly determined by the nucleation and growth mechanism of the coating [104-106].

In most PVD (physical vapor deposition techniques) including magnetron sputtering, the microstructure and properties of the coatings are strongly determined by ion bombardment of the coating that develops and by the defects (small microstructural irregularities such as pores, voids, or gaps) that growth during deposition. The reported superior performance of coatings produced by sputtering in comparison to other PVD processes is attained by the densification of the plasma as a result of the improved ionization efficiency and ion bombardment which is achieved with the use of a magnetron [107-110].

High flux of ion current density ($\geq 2 \text{ mA/cm}^2$) at relatively low energy ($\leq 100 \text{eV}$) has been reported to provide an optimum balance between effective densification of the coating while limiting the intrinsic stresses generated, generally, such conditions can be either obtained by the magnetic arrangement in the magnetron sputtering deposition system (i.e., unbalanced magnetron sputtering), or by externally biasing the substrate during deposition [107-110].

Major advantages of magnetron sputtering include; (i) Enhanced uniformity of large-area surfaces; (ii) versatility of compositions; (iii) very particular microstructures as well as structural modifications (iv) superior surface finishing; and (v) improved adhesion [107-110].

The more challenging aspects of PVD techniques such as magnetron sputtering in comparison to other deposition methods (i.e., Chemical vapor deposition, thermal spray, or electroplating) as presented in Table 3.2, implies the moderate to the high operational cost associated with the high vacuum conditions that need to be maintained as well as the target costs, and the lower depositions rates that result in thinner coating thickness [111].

Characteristic	Electro/Electroless plating	Thermal spray	Chemical vapor deposition	Physical vapor deposition
Equipment cost	Low	Low to moderate	Moderate	Moderate to very high
Operating cost	Low	Low to high	Low to moderate	Moderate to high
Process environment	Aqueous solution	atm to low vacuum	atm to medium vacuum	High vacuum
Coating thickness	10 μm-mm range	50µm-mm range	0.1µm-mm range	≤0.1 µm -µm range
Adherence	Moderate mechanical bond to very good chemical bond	Good mechanical bond	Very good chemical bond to excellent diffusion bond	Moderate mechanical bond to good chemical bond
Surface finishing	Moderate coarse to glossy	Coarse to smooth	Smooth to glossy	Smooth to high gloss
Coating materials	Metals	Powders, polymers, metals, ceramics	Metals, ceramic, polymers	Metals, ceramic, polymers

Table 3.2 Comparison of main deposition methods [111].

3.1.4 Deposition of the Si and Si-Pt reservoirs

The same chamber described in the plasma surface treatment (Figure 3.2) was utilized for the deposition of the Si and Si-Pt reservoir. However, a particular configuration was used for the coating deposition, which included either the Si or Si-Pt targets.

Deposition of the Si reservoir

(i) For the deposition of the silicon reservoirs, RF magnetron sputtering was used at room temperature, and in pure Ar plasma at a pressure of 0.6 Pa (5 mTorr), a silicon target of 2 inches of diameter was fixed in front of the magnetron and connected to an RF power supply (13.56 MHz, Advanced Energy generator) at 200 W. The γ -TiAl substrates were RF-biased using a power of ~ 4 W. Three different sets of Si thicknesses (3.0 µm, 6.0 µm, and 9.5 µm) were deposited on flat substrates (50 mm x 25 mm x 2 mm). When small samples (15 mm x 8 mm x 3 mm) were coated for thermogravimetric analysis (TGA), a rotation speed of 10 rpm was applied to achieve complete coating coverage on all the faces (3D - three-dimensional samples) of the γ -TiAl substrates. The rotating sample holder was located 10 cm away from the target, facing the magnetron.

Deposition of the Si-Pt reservoir

Two different sets of conditions were applied for deposition of the Si-Pt reservoirs:

(ii) Deposition of Si-Pt reservoirs was obtained by co-sputtering of Si and Pt. The first set of conditions was established for the deposition of 6.8, 8.4, and 12.2 μ m reservoirs with Si-Pt ratios of 80Si-20Pt, 63Si-37Pt, and 66Si-34Pt (at.%), respectively; It was obtained by co-sputtering of Si and Pt in Ar plasma at a pressure of 0.6 Pa (5 mTorr), using two targets, pure Si target (2 inches of diameter) and Pt target (which consisted of Pt stripes of 2 cm wide and 2 mm thick, mechanically encrusted in a silicon target of 4 inches (10 cm) of diameter for mechanical support), each one connected to an RF-power supply (13.56 MHz) and to a DC power supply respectively.

The Si target connected to an RF-power supply (13.56 MHz) was set to 200 W for the 80Si-20Pt (at.%) composition, while 160 W resulted in approximately 64Si-36Pt (at.%) composition; The power applied to the Pt target was 70 W. Sample was located 10 cm from the magnetron, with continuous rotation (10 rpm).

(iii) Si-Pt reservoirs of 3, 4, and 5 μ m of Si-Pt reservoirs and Si-Pt ratio of 40Si-60Pt (at. %), were deposited by co-sputtering of Si and Pt in Ar plasma at a pressure of 0.5 Pa (4 mTorr). The one connected to the Si target was maintained at 150 W, as well as the one applied on Pt target (150 W). The sample was hooked inside the chamber facing each of the targets from an equal distance (of 10 cm), as in the Si reservoir depositions. Sample was maintained with rotation at 10 rpm during the deposition.

The conditions established for the depositions of the different reservoirs (thicknesses) of Si and Si-Pt by magnetron sputtering are summarized in Table 3.3.

Material	Power (W), Source		Thickness	Compositional ratio	
deposited Si target Pt target		Pt target	Deposited (µm)	(at. %)	
			3		
Si reservoir	200, RF	/	6	100 Si	
			9.5		
			3		
Si-Pt	150, RF	150, DC	4	40 Si - 60 Pt	
reservoir			5		
	200, RF	70, DC	6.8	80 Si - 20 Pt	
	160, RF		8.4	63 Si - 37 Pt	
	160, RF		12.2	66 Si - 34 Pt	

Table 3.3: Selected parameters for the deposition of the Si and Si-Pt reservoirs.

3.1.5 Vacuum thermal annealing

Vacuum thermal annealing was the subsequent step employed after sputter deposition of the films, the two-step process (sputter and vacuum thermal annealing) resulted in a diffusion type coating. For this purpose, it was employed a horizontal loading furnace (VAC AERO furnace) for the thermal annealing of the samples, the system has a maximum temperature capability of 1250 °C and a vacuum in the range of 10⁻⁶ Torr, with Molybdenum heating elements and chamber devoid of contaminating elements. The Argon cooling pressure was in arrange of 637 Torrs -1500 Torrs.

Two different thermal annealing temperatures were studied 950 °C as the upper limit temperature and 750°C as the lower limit temperature and varied treatment times (2 h and up to 24 h) were applied to the different samples. The vacuum atmosphere during the thermal annealing process prevents undesired surface reactions, the vacuum then promotes only the diffusion of the elements in the system or component exposed to the treatment, in which diffusion occurs by thermal activation processes.

3.2 Characterization techniques

3.2.1 Optical Microscopy

Optical microscopy is a technique that allows the observation of microstructural characteristics (i.e., morphology, grain boundaries, phase structures, etc.) using visible light that passes through a series of lenses in a specific array with the purpose to magnify an object of small size, specifically below the human eye. Optical microscopes (Figure 3.3) can magnify up to ~3000X times the original size [102-105]. The image is captured by a light-sensitive camera or photodetector that generates a micrograph. The maximum limit of optical microscopy resolution resides on particle sizes that are near the wavelength of the visible light (400-700 nm or about 0.3 μ m) [112-115].



Figure 3.3: Optical microscopy in phase-contrast mode (lateral view). Adapted from [112].

The different methods of observation in optical microscopy are based on the type of interaction between the visible light and the object, which includes transmitted light (beam light passes through the sample or reflection (surface reflected off the surface), just to mention some. Different methods enhance the image contrast, such as phase contrast, dark field, polarisation, and differential interference, among others. As well as different types of optical microscopes with variations in their setups, for example, the focal or confocal microscopes, the latter are known for improving the visualization resolution and contrast or the inverted wide-field type with improvements in the scanning and observation of samples [116-120]. The Metallurgical observations on the uncoated base material were performed using an optical microscope, Zeiss Axio Scope, equipped with filters and a color camera. Chemical etching of the Ti-48Al-2Cr-2Nb coupons with hydrofluoric acid (HF) solution (10 % v/v) was used to improve the phase contrast of the base material microstructure before any plasma surface modification or thermal annealing treatment.

3.2.2 X-Ray Diffraction (XRD)

XRD is a non-destructive technique used to analyze the phase composition of materials, crystalline structures, as well as orientation (epitaxy), and using their more advanced setups can be useful to determine complex properties such as residual stresses and texture of very diverse materials. The obtained properties are determined by the diffraction pattern that results from a collimated X-Ray (high energy electromagnetic radiation) beam interacting with a powder or a film with a certain angle of incidence, polarization, and wavelength, creating a certain scattering intensity, characteristic of a specific set of lattice planes in the material analyzed. The peaks of those intensities are related to the atomic positions in the lattice planes. The XRD pattern generated can then be seen as evidence of atomic arrangement in a material. While crystalline materials will display well-defined and sharp peaks at very precise angles, amorphous materials will exhibit a maximum that extends over various degrees. Peak broadening can provide information related to the crystallite size of the material [114-116].

The two main components of X-Ray diffraction equipment are the (i) monochromatic radiation, emitted at a specific wavelength (0.2-10 nm, which is comparable to the interatomic spaces of crystalline solid materials), and (ii) a detector, that measures the diffraction intensity pattern. The fundamental of X-ray is based on Bragg's law (Equation 3.1) indicating that the scattered signal of the incident beam is the consequence of the X-ray beam interacting with a crystallographic lattice, creating constructive interferences from the in-phase atomic layers (Figure 3.4) [114-116].

2d
$$(\sin \theta) = \lambda_{\circ}$$
 (Equation 3.1)
where,

d: interplanar spacing of the crystallographic lattice

 θ : X-ray beam angle of incidence

 λ_0 : Wavelength of the X-ray beam



Figure 3.4: (a) Amorphous and (b) crystalline XRD patterns; (c) X-ray beam interacting with a crystallographic lattice, creating constructive interferences from the in-phase atomic layers. Adapted from [117].

The crystalline structure of the substrate before and after any surface modification step is assessed by X-ray diffraction (XRD), using a Bruker, D8-Discover system equipped with a Lynx eye CCD accumulation detector using a 40 kV filtered copper source ($\lambda_{CuK}\alpha$ 0.154 nm) in a theta-two theta (θ -2 θ) configuration from 10° to 90°, and GIRXD at different incidence angles (1°, 2°, 4° and 6°).

To identify effects related to micro-strain on the crystalline structure in the γ -TiAl material's grain size due to the plasma cleaning process powered by an RF-source, the full width at half maximum (FWHM), using a Gaussian fitting of the XRD peaks with the maximum intensity was estimated on the untreated substrate and after the plasma cleaning process.

3.2.3 Scanning Electron Microscopy (SEM)

The main purpose of the technique is to allow the magnification of surfaces with high resolution of their topographic characteristics and to perform micro-chemical composition analysis (when used in electron probe X-Ray microanalyzer mode). SEM can provide imaging of surface features of up to 100000X with a resolution down to 3 to 100 nm, depending on the sample [118].

The SEM configuration is schematized in Figure 3.5 and described below. The SEM system is mainly composed of a (1) electron column, (2) specimen chamber, (3) vacuum pumping system, and (4) electronic control and imaging system. The system works in a vacuum environment to isolate the beam from any scattering (caused by the potential presence of gas atoms) [118-119].

The vacuum environment can be either low $(10^{-6}-1.3 \times 10^{-4} \text{Torr})$ or UHV $(10^{-10} \text{Torr}-1.3 \times 10^{-8} \text{Pa})$ depending on the pumping system and of the system construction. The electron gun, typically produced from tungsten filament (0.25mm) heated up to 2500°C (4530°F), produces a high energy beam of electrons due to the thermionic process; the beam is then oriented through the center of the column and attracted to a positive anode with a power of 5 to 30kV. This voltage is determined by the user accordingly to the type of measurement being performed.



Figure 3.5: Schematic of an SEM system and its main components. Adapted from [118].

SEM technique works by directing a collimated electron beam on a sample, producing an interaction between the electrons of the beam and the sample atoms, from this interaction different signals are produced and collected to provide very particular information about the sample analyzed as summarized in Figure 3.6 (i.e., secondary electrons produce the SEM image and provide topographical information [119];
Auger electrons give surface atomic composition; backscattered electrons provide information related to atomic numbers and phase differences, and X-rays give atomic composition). The size of the electron beam (1-10nm) is the root cause of the images and mappings as well as the nanoscale resolution that can be attained by this technique [118,119].



Figure 3.6: Pear model showing then electron beam interaction with the sample [120].

SEM observations were made on cross-sections of the coated samples using a JEOL JSM7600F system equipped with a field emission gun (a source capable of inducing electrons emission by tunneling process, due to a strong electrostatic field (F), $F>10^7$ V/cm), and with a backscattering electron detector at 5-15 kV for chemical contrast. The cross-sections of the coated samples were obtained with an automatic precision cutting machine (Minitom, Struers).

The specimens were subsequently mounted in epoxy; after 12 h of curing time at 40 °C, the mounting epoxy was completely hardened. Subsequently, we performed mild grinding of the mounted specimens with 800-2000 grade SiC papers, polishing with diamond and silica suspensions, and consecutive cleaning of the surface with acetone and isopropanol. As a final step and for improved SEM observations, the mounted samples were coated with thermally evaporating gold for 45 s.

3.2.4 Energy dispersive X-Ray spectroscopy (EDX/EDS)

EDS is a technique very often incorporated in SEM systems; it consists in focusing a high-energy beam into a material, by impacting the charged particle of the beam (i.e., electrons with energies of about 5-30kV) and producing the emission of electrons from several shells of the analyzed sample. Electrons from the deeper shells will fill those electron vacancies (holes) while emitting X-rays (Figure 3.7), and their energies are collected by an energy dispersive spectrometer, this measurement expresses the energetic difference between two atomic shells in a particular material, which is an indication of their composition [121-122].



Figure 3.7: X-ray emission process. Adapted from [122].

EDS technique offers a fairly fast elemental semiquantitative analysis with broad coverage of elements and exhibits limited sensitivity for detection of those elements with lower atomic mass than Na (i.e H, He, Li, Be, B, C, N, O, F, Ne). Their detection limit is between 1-10 weight % of the element. Lateral spatial resolution is of 1 μ m (with acceleration voltages >5keV) and around 50-100 nm when operating at lower accelerating voltages (<5keV) [121].

It offers the functionalities to analyze single spot or scan areas (elemental maps) that can be converted into compositional profiles with respect to depth, for the last features described it is required to adjust the excitation voltages and additional software processing is needed. EDS X-Max^N detector from Oxford Instruments was used for elemental mapping and composition measurements, both with the Aztec software from Oxford Instruments. The EDS mappings were obtained on cross-sections of the uncoated and coated samples by using the AZtec software to build the compositional profiles by selecting a grid pattern that included 20 EDS line scans to obtain a statistical average as a semiquantitative estimation of their composition.

3.2.5 XPS (X-ray photoelectron spectroscopy)

XPS is a surface-sensitive quantitative technique that provides information about elemental analysis and molecular bonding states at the very surface since their maximum depth capabilities go from 50 to 100 Å, with energy resolution in the range of 1200-5.0 eV in survey mode. It works by applying an X-ray of known energy, very often Al K-alpha at 1486 eV, to produce the ejection of photoelectrons from the material analyzed. The kinetic energy of those electrons collected by the spectrometer will exhibit characteristic energy that is influenced by the electronic transitions of the atomic and molecular orbitals, indicating the binding energy of the element and their bonding state [123-126].

The electronic transitions involved in XPS technique are represented in Figure 3.8. X-ray photoelectron spectroscopy (XPS) has been used for the surface analysis of the uncleaned and Ar plasma cleaned γ -TiAl substrates using a VG ESCALAB 3 MKII system equipped with a Mg K α source, with a power of 300 W. The pressure in the system was $3x10^9$ Torr and the analyzed area was 2x3 mm. The Ar*bombardment conditions used for *in situ* Ar cleaning were very mild to avoid preferential sputtering (2keV for 13 minutes). The energies were corrected to the C1s at 285.0 eV and a Shirley background subtraction was performed. Elemental composition is calculated with Wagner sensitivity factors [123-126].



Figure 3.8: Schematic of electronic transitions involved in an XPS process [126].

3.2.6 Rutherford backscattering spectroscopy (RBS) and Elastic recoil detection (ERD)

Rutherford Backscattering Spectroscopy (RBS) (Figure 3.9) is a non-destructive ion beam technique for quantitative mass analysis of materials (i.e., on thin films, layered structures, or bulk) with respect to depth. It works by directing an ion beam, usually of Helium and Hydrogen ions (\geq 300 keV up to several MeV), into a particular sample. From the interaction between the high energetic ion and the nucleus (i.e., ionization of electrons, collisions with electrons and nucleus), the ion beam loses energy, and can change its trajectory (backscattering) due to the collisions, the deflection depends on the mass of the impacted nucleus and the angle of incidence, which will provide specific information of the material composition. RBS detects backscattered particles as a function of depth by the energy loss occurring during the ion-nucleus interaction.

Due to the kinematic factor, mass analysis can be established, while the quantitative analysis is possible from the different backscattering signals of the cross-section. The best performance of the technique is when detecting heavy elements on lighter substrates; atoms with a lower atomic mass than the incident ion can not be detected by RBS. Gradients of composition and determination of impurities with respect to depth are some of their suitable applications. Their depth resolution goes up to some tens of nanometers over hundreds of nanometers of depth [114,127,128].



Figure 3.9: Schematic representation of the Rutherford backscattering yield from a thick target with surface impurities [128].

The fundamental of ERD is based on the detection of the nucleus energy in a target material, after its collision with an ion beam (i.e. Cu^{9+}), with a higher mass than the one typically used in RBS. ERD also uses higher acceleration (50 MeV), which allows it to be sensitive to atoms with low atomic mass. The energetic beam strikes on the target at a grazing angle of incidence, which causes elastic scattering of the atoms in the target that are then detected by either a solid or gas type detector [123].

For this project, measurements and analyses were performed in the Laboratoire de Faisceaux d'Ions, Université de Montréal. RBS measurements were performed using a 6 MV Tandem accelerator with a 2 MeV beam of helium ions at a scattering angle of 170° to the surface of the targeted sample. The depth profiles were measured by Elastic Recoil Detection in the Time-of-flight mode (ERD-TOF) using the same 6 MV Tandem accelerator with a 40 MeV beam of Co ions at a scattering angle of 30° with respect to the surface of the analyzed sample.

3.2.7 TOF-SIMS

Figure 3.10 shows a schematic representation of the Time-of-flight secondary ion mass spectrometry (TOF- SIMS). This surface analysis technique is based on the bombardment of a surface using high energetic ions that produce the emission of secondary ions. The mass of these secondary ions is analyzed by a detector, by estimating the required time for the ions to arrive at their detection point. It is suitable for the identification of trace elements (organic and inorganic) in low concentrations and can perform compositional depth profiles in a range of few angstroms to some micrometers [129-131].

TOF-SIMS is used for the surface analysis of the uncleaned γ -TiAl and Ar* plasma cleaned substrate. The system is equipped with Bi (25kV) and Cs+ (3 kV) sources. The profiles of the sputtered species were built by sputtering a surface area of 250x250 µm with a Cs+ source, with a depth analysis of around 640 nm.



Figure 3.10: (a) Collision cascade due to ion bombardment, and (b) Time-of-flight mass analyzer schematic. Adapted from [131].

3.2.8 Nanoindentation

Indentation techniques consist in the application of a force on the surface of a material, by using an indenter of known geometry, from indentation measurements Hardness and Elastic properties can be obtained. Before the 1980s, the interest in indentation was mostly related to bulk materials; However, after that time the importance of such properties on thin films became very significant, giving place to sensing indentation or instrumented indentation, a new type of indentation technique where depth and force are simultaneously registered during the whole measurement. Since small forces and small impression areas are associated with this particular type of measurement, this evolved type of indentation provided the possibility to resolve depth changes in the range of nanometers [132-133].

There are diverse types of tips available to perform indentation measurements, according to the specific test and mechanical properties of interest; among those Berkovich and Vickers (pyramidal tips, i.e., for hardness and modulus), Brinell (spherical tip, i.e., for stress-strain) and Rockwell (spherical or conical tip, i.e., for scratch). Hardness and modulus are among the most typical properties obtained from indentation tests. Particularly for hardness (H), their estimation is made from the impression that remains after the plastic deformation caused by indentation, based on the load-displacement curve [132-133].

For determination of the elastic properties in a certain sample volume, indentation module (E*) is used to describe the average of it; While Young's modulus (E) relates to unidirectional elastic properties of larger samples with varied orientations. The latter one is very convenient for the average of single-crystalline elastic constants, and both terms can be used without difference on isotropic materials. The Olivier and Phar method is the standardized approach (since 1992) to effectively relate surface area and penetration depth [132-133].

Nano-indentation was carried out using a TriboIndenter TI950 from Bruker (previously Hysitron) using a Berkovich tip, radius 100 nm, and incremental loads varying from 9500 to 50 μ N. A 5x5 matrix of indentations was measured for each sample. In addition, single grain indentations were also performed.

The experimental indentation load-displacement curves (as observed in Figure 3.11) were analyzed using the Oliver and Pharr method. From the load-displacement curves, loading and unloading sections can be observed; Elastic and plastic deformation is associated with the loading region of the curve due to the contact established between the tip of the indenter and the sample, the unloading section is related to the elastic recovery response of such material. Using the known geometry of the indenter and by fitting the unloading region of the curve, the contact stiffness (slope of the unloading region) at the maximum load can be established.



Figure 3.11 Typical load-displacement curves obtained through nanoindentation.

To obtain hardness, the contact residual depth must be estimated. To obtain the effective contact radius (and the area, A), multiple unloading slopes (S) at various depths and indentations are analyzed.

Equations 3.2 and 3.3 [123] involved in the H and E* determination are summarized below:

$$H = \alpha \frac{L}{D^2}$$
 (Equation 3.2)
$$E^* = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_P}}$$
 (Equation 3.3)

where,

H: Hardness; L: Load; D: Indentation depth

S: Stiffness (slope); A_p: projected contact area

3.2.9 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) schematized in Figure 3.12, is a technique dedicated to the measurement to the detection of any change in the total mass (weight) of a material over time in a controlled atmosphere at a certain temperature as well as the rate of this change. If the total mass gain changed towards an increase, it is an indicator of either gas absorption or chemical reaction (i.e., oxide formation); if the change displayed a decrease in the total weight, it is then a confirmation of volatilization of compounds or decomposition of the analyzed material.

It is often used for testing the oxidation of materials, as well as thermal decomposition and chemical reaction processes. Their main constituents include a thermo-balance and a furnace. During the measurement, the sample is suspended from the balance into the furnace to be heated from room temperature up to the desired temperature. The initial weight is input into the system, and heating and cooling rates, as well as the atmosphere (i.e., oxygen), are as well determined according to the measurement needs. The weight of samples can be varied; it typically goes from 5 to 100 mg and up to 1000 mg [134].

To study the influence of high-temperature exposure on coated systems, two different sets of experiments were prepared. For the assessment of the microstructural and compositional evolution, flat samples were isothermally exposed to laboratory air in a furnace (model OMEGALUX LMF-3550) at 900 °C for 100 h of total exposure time. To investigate the kinetics of oxidation, a set of coated samples with complete coating coverage (three-dimensional (3D) were oxidized in laboratory air at 900 °C for 100 h using a thermo-gravimetric analysis (TGA) system (model Setsys

Setaram). The temperature increase was 20 °C/min during the TGA test (up to 900 °C), and 5 °C/min while cooling the samples. During the test, compressed air was used at 60 mL per minute.



Figure 3.12: Schematic of TGA system and their components [134].

CHAPTER 4 INVESTIGATION OF THE BASE MATERIAL PROPERTIES AND THE EFFECT OF SURFACE PLASMA TREATMENT

This chapter presents the study of the base material: the γ -TiAl alloy, and the assessment of their microstructural, compositional, and mechanical properties as well as their oxidation behavior by different characterization techniques prior to any surface modification. It is as well described the Ar sputter cleaning process, used as a first step of the surface preparation for subsequent coating deposition, and its influence on the substrate properties.

4.1 **Properties of the base material**

4.1.1 Microstructural characterization of the γ-TiAl alloy

The XRD pattern from a γ -TiAl substrate is presented in Figure 4.1. The characteristic phases of the base material are identified, corresponding mostly to the diffraction peaks of the tetragonal γ -TiAl phase, and a minor fraction of hexagonal α_2 -Ti₃Al-phase, without additional phases, detected.



Figure 4.1: XRD pattern of a γ-TiAl substrate.

Observations made by optical microscopy are presented in Figure 4.2 (a-b). Prior to observation, the surface of the substrate was surface grinded and polished as described in the experimental methodology section (Chapter 3) and subjected for ~ 4 minutes to chemical etching with fluoric acid (HF) solution (10% (v/v) to improve the phase contrast. After the etching step, the microstructure of the γ -TiAl substrate is revealed. The microstructure consists of flat equiaxed γ -TiAl grains and mixed γ -TiAl + α_2 -Ti₃Al grains forming lamellar colonies. The contrast of the color of the grains is produced by the selective etching process (due to the different compositions, and orientations of the phases throughout the microstructure). The array of the microstructure displayed is known as "duplex".



Figure 4.2: Optical microscopy images of a flat TiAl48-2-2 sample after polishing and HF etching. (a) Left: 5X, (b) right: 10X.

4.1.2 Compositional assessment of the γ-TiAl alloy

The microstructure of the base material was investigated by SEM and its composition was estimated by semiquantitative EDS measurements.

The surface of a polished γ -TiAl sample at magnifications of 250x and 1000x, and the chemical mapping of the main constituted elements are shown in Figure 4.3 (a-c). The parameters used for EDS analysis and the estimated composition are reported in Table 4.1.



Figure 4.3 SEM image (a) low magnification (250X); (b) high magnification (1000X) and c) EDS mapping of a polished γ-TiAl.

Table 4.1: X-ray emission peaks of Kα and Lα shells [135] for the elements of interest used in EDS.

Element	Kα and Lα shells (keV)	Composition
Ti	K: 4.51 / L:0.45	43.3
Al	K: 1.49	38.8
Cr	K: 5.41 / L:0.57	1.6
Nb	K: 16.58 / L:2.17	2

From the backscattered electron imaging presented in Figure 4.3 (a-b) γ -TiAl phase and the lamellar colonies (α_2 -Ti₃Al) are distinguished. EDS in Figure 4.3 (c) shows the distribution of nominal composition at the bare substrate. It was determined that the elemental contents slightly differ from the substrate stoichiometry (48Ti-48Al-2Cr-2Nb) due to the presence of oxygen and

carbon impurities (Ti: 38.8 at. %, Al: 43.3 at. %, Cr: 1.6 at. %, Nb: 2 at. %, O: 5.3 at. %, C: 9.1 at.%).

The contrast observed through the elemental mapping reveals a more homogeneous distribution observed for Ti, and a lower content of Al signal in the α_2 -Ti₃Al phase in comparison to the γ -TiAl phase. Cr and Nb signals are observed with higher contrast through the α_2 -Ti₃Al phase.

4.1.3 Mechanical properties of the γ-TiAl substrate

Using the nanoindentation technique the evaluation of the mechanical properties on the substrate was performed, as well as on individual grains to see the difference between the mechanical properties of the equiaxed microstructure (γ -TiAl grains) and the lamellar colonies (γ -TiAl + Ti₃Al).

Nano-indentation was carried out using a Berkovich tip and incremental loads varying from 9500 to 50 μ N and, using a 5x5 matrix of indentations, conditions are further detailed through the experimental methodology section (Chapter 3). Hardness and Young's modulus were obtained using the Oliver and Pharr method [136].

The mechanical properties of the bulk material (performed at room temperature) are presented in Figure 4.4 (a-b). The modulus (E*) of γ -TiAl was in the 135–170 GPa range, while the hardness (H) values were 7-9 GPa. The hardness range estimated shows the influence of the duplex microstructure, including the α_2 -Ti₃Al phase fraction present in the lamellar grains.

Grain by grain nano-indentations were also performed for each of the phases (equiaxed and lamellar colonies). The results (H and E*) for the γ -TiAl phase (equiaxed grains) are presented in Figure 4.5 (a-c). Equiaxed grains excibited exhibited hardness values within a distribution of 5-7 GPa, with the higher frequency of values at 7 GPa. While the reduced modulus appear within the 135-170 GPa, being the 150-160 GPa range the one with the higher occurrence.



Figure 4.4: (a) Hardness (H) and (b) reduced modulus (E*) of γ-TiAl sample from nanoindentation.



Figure 4.5: (a) Distribution of Hardness, H and (b) Reduced modulus (E*) estimated from the(c) equiaxed grains in the base material.

Lamellar grains, which are a combination of two different phases, appear are in a close array of alternating γ -TiAl lamellae and subsequent α_2 -Ti₃Al. The combined contribution of both phases to the mechanical properties (H and E*) of the lamellar phase is reported in Figure 4.6 (a-c).

One can observe that the lamellar colonies present a broad distribution of reduced modulus, from 120 to 200 GPa, and hardness in the 4-10 GPa range. This is mainly due to the tetragonal (γ -TiAl) and hexagonal (α_2 -Ti₃Al) alternating lamellae inducing a crystalline constraint at the interface, which generates an anisotropic mechanical behavior for each lamella that adds additional complexity to the analysis of the individual phases within the lamellar colonies.



Figure 4.6 (a) Hardness (H) and (b) reduced modulus (E*) distribution estimated from the (c) lamellar colonies.

4.1.4 Oxidation resistance of the uncoated γ -TiAl alloy

 γ -TiAl samples were exposed to isothermal oxidation in ambient laboratory air at 700, 800, and 900 °C, using a conventional oven. Their microstructure was studied by XRD after 100 h of exposure. The XRD pattern obtained for the different temperatures are presented in Figure 4.7. Changes in microstructure of the base material are only identified when the temperature of exposure was at least 800 °C or higher. In those cases (800 °C and 900 °C), XRD analysis of the oxidized samples confirmed the presence of a mixed oxide scale formation of TiO₂ and Al₂O₃, (predominantly rutile-TiO₂ phase and most probably mixed γ -Al₂O₃ and α -Al₂O₃ phases, as indicated by the overlapping signals of α - Al₂O γ -Al₂O phases). Although very thin TiO₂ and Al₂O₃ scales could have develop for the sample exposed to 700 °C, only the diffracted peaks of the substrate were noticed.



Figure 4.7: XRD of γ -TiAl substrates exposed to different temperatures 700, 800, and 900°C for 100 h at in a conventional oven, with lab air atmosphere.

A micrograph of the oxidized cross-section of the substrate after 100 h at the highest temperature (900 °C) is shown in Figure 4.8. A mixed oxide scale with a total thickness of around 12 μ m is confirmed at the substrate surface.

The oxide scale of the 48Ti-48Al-2Cr-2Nb alloy that growth after oxidation at 900°C, exhibits an oxide scale with a layered structure [136,137], similar to the one excibited exhibited by other TiAl alloys with Al content in the range of 30-55 at.% of Al. Consisting of an outer layer of TiO₂, which growths towards the oxide-gas interface, and a subsequent Al_2O_3 layer that develops beneath the outer TiO₂, towards the oxide-base material interface; while the innermost layer is Al_2O_3 dispersed with TiO₂ or mixed $Al_2O_3+TiO_2$ [137,138].

The growth of the outermost layers is sustained by outward diffusion of metals cations of Ti and Al, via interstitial mechanism. Meanwhile for the growth of the inner layer, inward diffusion of oxygen anions is required through the vacancy mechanism [137].

This type of growth is originated by the oxygen partial pressure required for the growth of the respective oxides according to the regions of composition at the base material, single single-phase region (γ -TiAl), or bi-phasic region (γ -TiAl+ α 2-Ti3Al), as has been described for the Ti-Al-O system [16].

With more accelerated kinetics of the TiO_2 with respect to the one of the Al_2O_3 , the mixed oxide scale composed of titanium oxide (TiO_2) and aluminum oxide (Al_2O_3) results in a non-protective behavior due to the porous nature of the TiO_2 oxide [17]. Elemental enrichments of either chromium and/or niobium seem to accumulate at the oxide/substrate interface due to their out-diffusion during oxidation.



Figure 4.8: SEM cross-section image of the uncoated γ -TiAl after 100h of oxidation at 900°C.

For a more detailed examination of the mass increase as a function of time, and the related kinetic behavior, another substrate sample was exposed to 900°C, for 100 h using TGA, as presented in Figure 4.9.

The total mass gain-for the uncoated substrate was 4.6 mg/cm² after 88.5 h of exposure, above this time the oxide scale formed at their surface started to delaminate. The mass gain over time shows mixed regimes, with a linear behavior (k_1 of 3.5×10^{-11} g \bullet cm⁻² \bullet s⁻¹) during the first 14 h and a parabolic regime above this elapsed time (k_p of 6.38×10^{-11} g² \bullet cm⁻⁴ \bullet s⁻¹).



Figure 4.9: Total mass gain measured by TGA as a function of time during oxidation at 900°C of the uncoated γ -TiAl.

4.1.5 Conclusions on the base material properties

Optical and SEM imaging revealed a duplex microstructure with large γ -TiAl equiaxed grains and lamellar colonies, composed of α_2 -Ti₃Al + γ -TiAl phases. XRD diffraction results show a dominant signal attributed to the γ -TiAl, a component of both types of phases (equiaxed and lamellar), while the minor fraction of the hexagonal α_2 -Ti₃Al exhibited a low diffraction response. The impact of the duplex microstructure on the mechanical properties was investigated by indentation tests, and showed the reduced elastic modulus E*, in the 150–170 GPa range, while the broader distribution of the hardness values observed depended more on the fraction of the α_2/γ phases. It confirmed the unprotective nature of the oxide scale that grew on the uncoated base material when exposed to temperatures over 800°C. The kinetic nature, with mixed linear and parabolic regimes, was established for uncoated substrate as well as a significant mass gain.

4.2 Ar-plasma sputter clean treatment

4.2.1 Effect of the plasma surface treatment on the structural properties at the surface.

The effect of Ar-plasma sputter clean treatment on the crystal structure of polished γ -TiAl substrates using an RF source (105W, 800 DC power, for one hour) is shown in Figure 4.10.



Figure 4.10: X-ray diffraction pattern of the untreated γ-TiAl sample and a sample sputter clean by Ar plasma using an RF-power source. Cleaning conditions: 105 W (~800 V DC power) for 1 h, at 50 mTorr.

The X-ray diffraction patterns of the γ -TiAl substrate before and after the Ar-plasma treatment were obtained using a θ -2 θ configuration mode and confirmed the presence of the same phases and diffraction planes for both samples (untreated γ -TiAl - and sputter clean γ -TiAl), suggesting the preservation of the random crystallographic orientation of the substrate after plasma treatment.

Given the large penetration of the X-rays in θ -2 θ configuration (~ 6.6 µm), it is expected that the X-ray diffraction data in the Figure 4.10 comes mainly from the deeper surface of the γ -TiAl substrate with a strong effect of the bulk.

Since the Ar-plasma treatment occurs on the substrate surface it was necessary to analyse the structural properties of the plasma-treated substrate with X-ray diffraction in grazing incidence mode (Figure 4.11). This operation mode allows the analysis of the substrate in a closer approach to its surface since it has a lower penetration depth [139] (from 0.7 to $3.5 \mu m$). Then, the effect of the plasma cleaning at different surface penetration depths was studied by orienting the X-ray beam at different angles with respect to the surface.

The XRD patterns of an untreated (but polished) γ -TiAl and of a sputter clean γ -TiAl sample are presented in Figure 4.11 (a-b). It was not observed the presence of new diffraction planes or changes in the peak positions. This means that the effect of the plasma treatment does not cause the formation of new phases. According to observations on the peak intensity ratios (**I**_{sputter clean γ -TiAl /**I**_{untreated γ -TiAl}) for the different X-ray penetration depths, it is not observed any preferential crystallographic orientation.}}

From the estimation of the Full width at half maximum (FWHM), using a Gaussian fitting of the peak with the maximum intensity (111), a value of 0.482 (ϵ = 0.008) for the untreated substrate and one of 0.431 for the plasma cleaned sample (ϵ = 0.009), was calculated, this confirmed the absence of any broadening effect of the XRD peaks and therefore no micro-strain on the crystalline structure, neither change on the γ -TiAl base material's grain size due to the plasma cleaning process.



Figure 4.11: Comparison of a GIXRD pattern at different depths (θ=1°, 2°, 4°, 6°) of a γ-TiAl sample (a) untreated (b) Ar-plasma treated using an RF-power source. Plasma cleaning conditions: 105 W (~800 V DC power) for 1 h, at 50 mTorr.

4.2.2 Effect of the plasma surface treatment on the chemical composition

With RBS-ERD techniques the original substrate composition and the thickness of the oxide layer on the surface of the γ -TiAl before any surface treatment was investigated. RBS-ERD measurements are presented in Figure 4.12 (a-b).



Figure 4.12: Depth profile of a polished TGA γ-TiAl sample, extracted from RBS measurements.a): full scale with Ti, Al, Nb, and O. b): enlarged scale to observe the oxygen penetration into the substrate.

The RBS-ERD volume analysis confirms a composition of 47Ti-49Al-2Nb-2Cr. In addition, it can be seen that the nominal thickness of the native oxide is approximately 25 nm with an oxygen content of about 30 at. % at the very surface. Also, this native oxide formed on the substrate is most probably a mixture of TiO₂ and Al₂O₃. It can be noticed that Cr is not reported in ERD due to a low mass selectivity between Cr and Ti by this method and the large Ti/Cr ratio in the alloy. The effect of the plasma surface treatment on the chemical composition of the γ -TiAl samples was studied by X-ray photoelectron spectroscopy.

The general survey scans (Figure 4.13) of the γ -TiAl sample before the sputter clean treatment revealed the presence of titanium (Ti), aluminum (Al), niobium (Nb), chromium (Cr), and oxygen (O) as well as some common impurities such as carbon (C), nitrogen (N) and calcium (Ca). Please note that XPS is analyzing the signal provided from 10 nm depth. On the sample subjected to sputter clean treatment inside of the sputtering chamber, the removal of the impurity elements from the surface of the substrate was confirmed, as appears in Figure 4.13, where the signals of N and Ca do not appear on the general survey obtained after the plasma treatment.



Figure 4.13: Chemical surface characterization: (a) XPS general survey of an untreated sample and an Ar-plasma sputter clean of γ -TiAl samples 105 W (~800 V DC power) for 1 h, at 50

In addition to the general surveys, high-resolution scans were performed in the selected binding energy ranges for Al2p, Ti2p, Cr2p, Nb3d, and O1s to determine the elemental composition. The chemical composition estimated from those surveys is summarized in Table 4.2. From those values, it is observed a decrease in the atomic concentration of the common impurities (N, Ca, Na and C) on the sample that received the Ar-plasma surface treatment.

	Bonding energy (BE)	Relative atomic percent (At.%)	
Line of atomic orbital		Untreated y-TiAl	Sputter clean γ-TiAl
Al2p	74.1	6.4	9.6
Nb3d	207.4	0.3	0.3
C1s	285.1	42.8	36.3
Ca2p	347.3	1	-
N1s	399.7	1.6	_
Ti2p	458.6	4.9	7.5
O1s	530.8	41.7	45.5
Cr2p3	577.3	0.5	0.8
Na1s	1071	0.8	-

 Table 4.2: Identification and quantification of the chemical elements obtained from the general

 XPS survey scans.

Also, it was found an increase in the atomic concentration of the metallic elements (Ti, Nb, Cr, and Al) as well as in other elements such as oxygen (O). This result revealed that the use of an Arplasma treatment leads to the removal of the adsorbates at the substrate surface. While the increase in the composition of the metallic elements indicates their exposure to the substrate surface once the impurities are removed.

The increase in oxygen content after the surface plasma treatment suggests that after the break of the sputtering chamber vacuum, the substrate in ambient conditions tends to be coated by oxygen

molecules. To study a closer effect of the sputter clean on the γ -TiAl samples, it was necessary to perform the surface cleaning in-situ of the XPS chamber. In Figure 4.14 it is presented the general survey of the sample before and after the in situ sputter clean procedure.



Figure 4.14: XPS general survey of untreated γ-TiAl and sputter clean γ-TiAl inside the XPS chamber (Ar cleaning conditions in XPS chamber: 2 KeV for 13 minutes).

As previously, by the observed decrease in peak intensity of the binding energy of carbon and nitrogen it is confirmed that the Ar-ion etching had removed some adsorbates from the substrate surface. It is as well observed an increase in the peak intensity of the binding energy of some metallic elements suggesting that the in situ sputter clean treatment has led to the exposure of some metallic elements (Ti, Al, Cr, and Nb). The Ar-ion sputter clean conditions were very mild to avoid preferential sputtering of elements.

To obtain further information about the atomic concentration before and after the in situ sputter clean process, high-resolution scans were obtained in the respective selected binding energy of the chemical elements. As shown in Figure 4.15 (a) and (b), Al 2p consists of two wide peaks of Al oxidized (~74.0 eV) and metallic Al (~71.0 eV) while three peaks are observed at ~464.0, ~459.0 and ~454.0 eV representing Ti transition oxidation states, Ti oxidized and Ti metallic, respectively, observed in Figure 4.15 (c) and (d).



Figure 4.15: XPS high-resolution core-level spectra (Al2p and Ti2p) obtained from untreated [(a) and (c)] and treated γ-TiAl sample [(b) and (d)].

The quantitative observation from high-resolution XPS is summarized in Table 4.3. According to the signals from the oxidized species in the Al2p and Ti2p, a slightly lower atomic concentration of oxidized titanium (8.8 at. %) in comparison to oxidized Aluminium (10 at. %) was detected for the as-polished sample (untreated γ -TiAl). After the in situ sputter clean process, the amount of oxidized titanium (1.3 at. %) is much lower than the oxidized aluminium (8.2 at. %). This behavior could be explained by considering the sputtering yield of these materials. According to their sputtering yields values, metallic aluminum is sputtered two times faster than metallic titanium (Al ~ 2.1 atoms/ion and Ti ~ 1 atoms-ion, data obtained from Ar+ plasma at 2 KeV) [140-141] suggesting that after sputter clean process aluminum concentration should be lower than titanium

concentration. However, the resulting XPS data does not confirm this statement. To understand the lower concentration of oxidized titanium signal (titanium associated with oxygen) in comparison to oxidized Aluminium signal, their binding energy must be considered, in addition to the sputtering yield. Even though the sputtering yield of metallic aluminum is much faster than metallic titanium, it is more difficult to sputter aluminum oxide than titanium oxide. This is caused by the higher energy threshold needed to sputter Al₂O₃ molecules.

The effective atomic sputtering threshold is ~ 3.45 eV/atom for Al₂O₃ while for TiO₂ it is around ~3.20 eV/atom. It is closely related to the higher binding energy between the aluminum-oxygen bond (Al-O, 1675 kJ/mol), compared to the binding energy of the titanium-oxygen bond (Ti-O, 938 kJ/mol). This is in agreement with the tendency shown in Table 4.3 where there is more oxidized Al with respect to oxidized Ti.

Table 4.3: High-resolution XPS	analysis of untreated and in-situ treated	ated γ -TiAl samples. Cleaned

Orbital	Identification	Uncleaned γ-TiAl (at. % of elements)	γ-TiAl after in situ sputter clean treatment at 2 keV. (at. % of elements)
Al2p	Metallic Al	1.6	13.6
	Oxidized Al	10	8.2
Ti2p3	Metallic Ti	2.3	29.1
	Oxidized Ti	8.8	1.3
O1s	Al-O and Ti-O	35	27.1
	Al-OH and Ti-OH	32.9	10.9
	С-О	9.4	3

at 2 keV for 13 minutes.

TOF-SIMS analysis (Figure 4.16) revealed that the oxygen molecules coated the γ -TiAl sample. From the combined study among XPS and TOF-SIM it was found that right after the γ -TiAl samples leave the cleaning chamber, they tend to form an oxide layer which has a thickness of ~ 6 nm. It can be observed from Figure 4.17 that the oxygen molecules are mainly associated with aluminum and titanium ions.



Figure 4.16: Profile composition of the main species of a γ -TiAl sample after cleaning at 3 keV by cesium ions (Cs+, 640 nm, 250x250 μ m) inside of the TOF SIMS chamber.

4.2.3 Effect of the plasma surface treatment on the mechanical properties

The mechanical properties (hardness, H and reduced modulus, E_r) of the untreated and sputter clean γ -TiAl substrate using an RF power source are presented in Figure 4.17. In the case of the untreated substrate, its hardness values are around 7-10 GPa and modulus in the range of 150-175 GPa, presented in Figure 4.18 (a) and (b).

It indicates that the surface plasma treatment using an RF power source does not modify the hardness (H) neither the reduced modulus, (E_r) of the base material.



Figure 4.17: Mechanical characterization: Hardness (a) and reduced modulus (b) for a RF plasma-treated γ-TiAl sample. Ar cleaning conditions: 105 W (~800 V DC power) for 1 h, at 50 mTorr.

4.2.4 Conclusions on the effect of the plasma surface treatment

This research work has reported the effect of the Ar-plasma treatment on the structural (crystalline structure) and mechanical (H, Er) properties of γ -TiAl based alloys. According to the X-ray diffraction studies the Ar-plasma cleaning does not induce changes in the structural properties of

the substrate, or the crystallinity of the γ -TiAl substrate. A combination study between XPS and TOF-SIMS determined that the plasma-treated γ -TiAl substrate is naturally covered by an ultrathin oxygen layer (thickness around 6 nm) in ambient conditions. In-situ XPS measurements revealed that the Ar-plasma treatment removes common adsorbates from the γ -TiAl substrate surface as well as revealed that metallic aluminum (Al) is sputtered faster than metallic titanium (Ti) while aluminum oxide (Al₂O₃) is more difficult to sputter than titanium oxide (TiO₂). In terms of mechanical properties, nanoindentation measurements showed that after the plasma cleaning, the hardness and modulus of the γ -TiAl sample remained unmodified.

CHAPTER 5 ARTICLE 1: PROTECTIVE TI_xSI_y COATINGS FOR ENHANCED OXIDATION RESISTANCE OF THE γ -TIALALLOY AT 900 °C

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This chapter present the development of titanium silicide protective coatings using different Si reservoirs (3.0 μ m, 6.0 μ m, and 9.5 μ m of initial Si thickness) deposited by magnetron sputtering, followed by different periods (2 h to 24 h) of vacuum thermal annealing at 950 °C. The microstructural growth of titanium silicides influenced by the initial Si reservoir and their evolution following oxidation was investigated.

5.1 Effect of annealing time at 950 °C on the growth of Ti_xSi_y

In the first part of this work, the effect of TA on the 3 μ m Si coatings is evaluated. Si was deposited on the surface of the γ -TiAl substrates and vacuum annealed at 950 °C for 2 h, 8 h, 16 h, and 24 h. Cross-sectional images of the as-deposited coating and the corresponding XRD patterns before and after TA annealing are presented in Figure 5.1.

For the as-deposited coating, shown in Figure 5.1 (a), the diffraction peaks primarily correspond to amorphous Si, represented by a characteristic broad hump with low intensity and a contribution of a small amount of crystalline Si, as well as SiO₂. The latter one must have been formed during the exposure of ambient conditions of the as-deposited Si, when removed from the vacuum atmosphere of the deposition chamber. The corresponding tetragonal γ -TiAl signals, which are characteristic of the Ti-48Al-2Cr-2Nb substrate, are still visible.

The cross-sectional SEM image is shown in Figure 5.1 (b) of the as-deposited 3 μ m Si layer reveals a compact and dense microstructure. After TA (Figure 5.1 (c)), the new peaks in the XRD patterns

mainly correspond to the hexagonal Ti_5Si_3 phase, and some of them to the tetragonal Ti_5Si_4 phase, orthorhombic $TiSi_2$ phase, and the cubic Ti_2Si , the former one is observed only with the shorter annealing time (2 h). For all the coated and annealed samples, the $TiAl_2$ phase is noticeable.



Figure 5.1 (a) XRD patterns and (b) cross-sectional SEM of the as-deposited 3 μ m thick Si coating on γ -TiAl, and (c) XRD after their vacuum thermal annealing at 950 °C during 2 h, 8 h, 16 h, and 24 h, respectively.

Different durations of TA gave rise to a redistribution of the elements as revealed by SEM on crosssections of the Ti_xSi_y/γ -TiAl systems presented in Figure 5.2 (a-d).



Figure 5.2: SEM cross-sections of the Ti_xSi_y/γ -TiAl systems after different annealing times at 950 °C: (a) 2 h, (b) 8 h, (c) 16 h, and (d) 24 h.

The SEM images in Figure 5.3 indicate the presence of three different zones: (I) The outer zone is located further from the substrate, and it corresponds to a Ti_xSi_y coating with dense morphology. The defects (i.e., porosity, fracture) observed at the very edge of the coating are an artifact due to sample preparation [142] (cutting and polishing) for microstructural observations. During annealing, the diffusional growth of the titanium silicide coating is produced by the inward diffusion of Si towards the substrate and the outward diffusion of Ti towards the Si top layer.

Once the first titanium silicide phases are formed, the depth distribution of Si continues throughout the titanium silicide compounds. (II) The second (interdiffusion) zone represents an intermediate

layer between the inner Al enriched zone and the Ti_xSi_y coating. The interdiffusion zone can be described as traces of localized Ti_xSi_y that did not coalesce to form a continuous layer. The diffused traces on the Ti-Al matrix are a microstructural feature related to a temperature effect [143]. Since the diffusional transport of elements is temperature-dependent, a very high temperature (>950 °C) is required to accelerate and balance the diffusional flux of the elements involved.

(III) The third region next to the substrate corresponds to the TiAl₂ intermetallic zone, which is reported to be mechanically brittle [1]. The latter one is formed due to an enrichment in aluminum compared to the initially balanced ratio between Ti and Al in the original composition of the substrate (Ti-48Al-2Cr-2Nb). Different rates of diffusion (i.e., $D_{Si} \neq D_{Ti} \neq D_{Al}$) promote this gradient in composition. In addition, the Al enrichment is also due to the Ti consumed by its reaction with Si, which is associated with a more negative Gibbs energy of formation for the titanium silicides ($\Delta G_{950 \ C}$ TiSi₂: -172.16 kJ/mol; $\Delta G_{950 \ C}$ TiSi: -153. 23 kJ/mol; $\Delta G_{950 \ C}$ Ti₅Si₄: -718.27 kJ/mol; $\Delta G_{950 \ C}$ Ti₅Si₃: -578.62 kJ/mol) [142] with respect to that of the titanium aluminide phases ($\Delta G_{950 \ C}$ TiAl: -21.49 kJ/mol; $\Delta G_{950 \ C}$ TiAl₂: -33.39 kJ/mol), for which the values were estimated according to reference [145].

The thicknesses of zones I, II, and III for samples with the 3 μ m thick Si layers and annealed for different periods were determined from the Ti_xSi_y/ γ -TiAl SEM cross-sections (see Figure 4). One can observe an increase in thickness for all the different zones as the annealing time progressed from 2 h to 8 h. Specifically, for Ti_xSi_y (zone I), the average thickness ranges from 1.9 μ m to 3 μ m. For 2 h and 8 h of annealing, the thickness increased from 1.9 μ m to 2.6 μ m, and it reached 3 μ m after 16 h and 24 h of TA. The thickness estimated for the interdiffusion zone (zone II) is 1.3 μ m after 2 h of annealing, reaching a stabilized range of values of about 2.1-2.3 μ m after 8 h, 16 h, and 24 h of TA, respectively. The silicide-forming reaction consumed the Ti atoms that outward diffused from the substrate, leaving an Al enriched zone III (TiAl₂) of up to 3.4-3.7 μ m thick. Also, an increase in the total thickness of the multi-zones in the range of 5.3 μ m up to 8.9 μ m is observed in Figure 5.3, as the annealing time progressed.



Figure 5.3: Effect of vacuum annealing time at 950 °C on the thickness of the different zones: TixSiy-zone I; Interdiffusion-zone II; and TiAl2-zone III; and the total thickness of the multizone structures at the Ti_xSi_y/γ -TiAl interface, for an initial 3 µm thick.

Cross-sectional EDS measurements were used to investigate the distribution of elements (Ti, Al, Nb, Cr, Si, and O) in the Ti_xSi_y/ γ -TiAl system after annealing at different times. The compositional profiles obtained are related to the atomic transport through the γ -TiAl polycrystalline structure and the thermally activated motion of the elements over time, leading to a concentration gradient at a certain depth. Such behavior can be generally linked to a non steady-state diffusion [146]. To better describe the distribution of the titanium silicide phases, a compositional profile from the surface up to the TiAl₂ zone, and a total depth in the range of 5-7 μ m range, which provided improved resolution of the elemental distribution. is presented in Figure 5.4. The different regions are identified throughout the compositional mappings, starting at the top layer (Zone I - Ti_xSi_y coating), interdiffusion layer (Zone II - Ti, Al, Si) and subsequent Al – enrichment layer (Zone III).


Figure 5.4: Elemental distribution at and around the Ti_xSi_y/γ -TiAl interface following different annealing times: (a) 2 h, (b) 8 h, (c) 16 h, and (d) 24 h.

Compositional profiles were obtained to determine of the atomic content of the different elements at the Ti_xSi_y/ γ -TiAl system; and according to the stoichiometry of the Ti_xSi_y compounds, the most probable Ti_xSi_y phases have been assigned. Similar methodologies have been reported previously [142-147]. The compositional mappings reveal the influence of the thermal annealing time on the formation of different Ti_xSi_y phases. For a short annealing time (2 h – Figure 5 (a)) in Zone I, Ti₂Si and Ti₅Si₃ are the predominant phases detected within the first 1 µm, followed by a minor Al content (Ti₂Si+Al) up to a depth of 1.9 µm. Deeper (>1.9 µm), the interdiffusion Zone II exhibits higher Ti (55-50 at. %) and Al (25-55 at. %) contents to Si (≤25 at. %), while 62 at. % of Al is found in the Al enriched Zone III. As the annealing time was prolonged >2 h, we observe progressive inward diffusion of Si.

For the 8 h annealed sample, similar phases to the 2 h annealed sample are observed within the first 1 μ m. In both phases, around ≤ 10 at% of Al is found. Subsequently, there is a Ti₅Si₄ phase, not observed with the short annealing (2 h), as well as Ti₅Si₃ with Al content.

The interdiffusion zone shows a slightly lower Ti content (50-45 at. %), while the Al enriched zone remains very similar (65 at. %) to the previous sample. The growth and distribution of the titanium silicide phases reveal that short TA (2 h and 8 h) promotes the growth of titanium silicide compounds with either lower energy of formation [62,148] or lower Si content (i.e., Ti₂Si and Ti₅Si₃).

With an annealing time of 8 h or beyond (16 h and 24 h TA), the higher concentration of Si appears deeper within the Ti_xSi_y coating ($\geq 0.5 \mu m$ depth) and reveals the formation of titanium silicides with a more balanced ratio of Ti and Si such as Ti_5Si_4 and TiSi. With longer TA (16 h and 24 h), the elemental composition within the Al enriched zone indicates an increase in Al up to 67 at.%. For both samples, interdiffusion exhibits similar elemental concentrations as those estimated for the 8 h TA sample.

Overall, the strong coupling between Ti and Si is indicated by their elemental contents, and the confirmation of titanium silicide formation phases after 2 h of annealing and above, suggests uphill diffusion of Ti towards the surface, as the one indicated in the formation of NiPtAl [149]. The driving force of uphill diffusion relates to the chemical potential gradients established between Ti and Si [150].

Longer annealing times have induced a more restricted Ti outward diffusion, as documented by a lower Ti content at the outer edge of the coating. This underlines the role of Si, which reacts with Ti, while the titanium silicide formation inhibits its further outward diffusion [151].

5.2 Effect of 6 µm and 9.5 µm thick Si reservoirs on the growth of Ti_xSi_y

5.2.1 Microstructure of thick Ti_xSi_y coatings

To evaluate the effect of Si reservoir on the evolution of the Ti_xSi_y/γ -TiAl system, thick silicon coatings (6.0 µm and 9.5 µm) were deposited on γ -TiAl. Based in the study on the 3 µm Si reservoir

samples, we chose comparable TA times. Specifically, the thick Si-coated samples were thermally annealed at 950 °C for 8 h and 16 h, and Figure 5.5 shows the corresponding XRD patterns.

The diffraction peaks are similar to those observed in the 3 μ m Si coatings after TA (Figure 5.1), with the characteristic phases of the substrate, the tetragonal γ -TiAl and hexagonal α 2-Ti₃Al, as well as the phases corresponding to the hexagonal Ti₅Si₃, tetragonal Ti₅Si₄, and orthorhombic titanium silicides (TiSi and TiSi₂). However, there are more peaks related to TiSi phases in comparison to the annealed 3 μ m Si samples.



Figure 5.5: XRD patterns of 6.0 μ m and 9.5 μ m thick Si deposited on γ -TiAl and thermally annealed at 950 °C for 8 h and 16 h.

The thicker Si reservoirs promote the growth of more varied Ti_xSi_y compounds, including the silicon-rich (TiSi: 50Ti-50Si and TiSi₂: 33.3Ti-66.6Si) and titanium-rich silicides (Ti₅Si₄ + Ti₅Si₃). As the Si reservoir increase to 9.5 µm, the higher availability of Si promotes the formation of the TiSi phase, as observed by comparing the diffraction peaks. The microstructure of the coatings was investigated by SEM is presented in Figure 5.6 (a-f).

The as-deposited coatings appear to be compact (Figure 5.6 (a-b)), while some particles observed at the outer edge of the 6 μ m Si reservoir (Figure 5.6 (a)) are due to the specimen preparation (cutting and polishing). After TA, three zones (I: Ti_xSi_y, II: Interdiffusion, III: Al enrichment), previously described for samples with 3 μ m of Si are also detected (Figures 5.6 c-f).

Figure 5.6 (c) reveals the modified Ti_xSi_y/γ -TiAl region for the 6.0 µm thick Si sample after 8 h of annealing, which yields a total depth of 21.2 µm (zone I: 7.2 µm, zone II: 7.4 µm and zone III: 6.6 µm).

When annealed for 16 h (Figure 5.6 (e)), the zones become larger (zone I: 10.6 μ m; zone II: 9.1 μ m and zone III: 10 μ m) with a total depth of 29.7 μ m. In comparison, the 9.5 μ m thick Si sample yields larger zone thicknesses after 8 h of TA (zones I: 11.8 μ m, zone II: 15.8 μ m and zone III: 8.7 μ m, total depth of 36.3 μ m) (Figure 5.6 (d)), that further grow after the 16 h annealing time (zone I: 14.3 μ m, zone II: 10.2 μ m, zone III: 11.9 μ m, total depth of 36.4 μ m) (Figure 5.6 (f)).

For samples with the 6.0 μ m + 16 h TA and 9.5 μ m + 8 h TA, we observe defects caused by the Kirkendall effect (see Figures 7 (d) and (e)) due to which the voids appear either close to the surface of the Ti_xSi_y layer or at the interface between the coating and the interdiffusion zone.

The origin of the Kirkendall effect relates to the differences in diffusivity rates [152] of the participating elements through the coating-substrate interface during the high-temperature interdiffusion processes (i.e., thermal annealing).

Formation of the Kirkendall voids is favored in boundary regions at adjacent interfaces [10], as particularly observed in the $6.0 \,\mu\text{m} + 16 \,\text{h}$ TA sample, namely in locations with the most significant gradients of concentration, indicating higher diffusional flux and higher potential for dissimilar diffusivities of the elements (specifically, Si and Ti in our case).



Figure 5.6: Cross-sectional SEM images of the (a) 6.0 μ m and (b) 9.5 μ m thick Si reservoirs on γ -TiAl substrates, and (c-f) the multi zones at the Ti_xSi_y/ γ -TiAl interface after thermal annealing.

5.2.2 Comparison of the Ti_xSi_y microstructural evolution of the Si reservoirs

Figure 5.7 (a-b) summarizes the effect of the Si thickness (3.0 μ m, 6.0 μ m and 9.5 μ m) and the TA time (8 h and 16 h) on the growth of the different zones at the Ti_xSi_y/ γ -TiAl interface.

Si reservoirs of 3 μ m produce thinner zones, with the narrowest interdiffusion zone (II), and the thickest TiAl₂ zone (III). This is due to the limited inward diffusion of Si (smaller thickness of the Si reservoir). For thick Si reservoirs (6.0 μ m and 9.5 μ m) and shorter annealing time (8 h), the interdiffusion zone (II) is thicker since there is more Si inward diffusion (high Si reservoir). Still, there is limited time for the titanium silicide reaction, which produces an increase in the localized traces of the Ti_xSi_y concentration without the formation of a continuous layer. Due to the thick initial Si reservoir (which increases the Si activity to inward diffuse), the Ti outward diffusion is more limited, as confirmed by the lowest thickness observed for the TiAl₂ zone (III).

For the larger Si reservoirs (6.0 μ m and 9.5 μ m) and longer annealing (16 h), there is both enough time for the reaction and sufficient Si availability to produce a Ti_xSi_y layer as the thickest zone (I). Under these conditions, the growth of the interdiffusion layer is restricted since there is more time to promote the titanium silicide reaction.

Overall, the Ti_xSi_y coating yields a large thickness with the thicker Si reservoirs and longer times of annealing. Similarly, the interdiffusion zone (II) gets thicker with higher initial Si thickness but thinner when annealing is longer. On the contrary, the Ti depleted zone (III: TiAl₂) becomes less thick when the Si reservoir is larger. Additionally, for shorter annealing time, the thickness growth of the zones exhibited an almost linear dependence [25], while for longer times, it approaches a parabolic type; such kinetics tendencies have been observed in the growth of layers The total depth of the Ti_xSi_y/γ -TiAl system (zones I+II+III: Ti_xSi_y + interdiffusion + TiAl₂) increases with higher Si reservoirs and longer annealing time.



Figure 5.7: Effect of the initial Si coating thickness (3.0 μ m, 6.0 μ m and 9.5 μ m) on the thickness of the different zones at the Ti_xSi_y/ɣ-TiAl interface upon annealing at 950 °C for (a) 8 h and (b)

5.3 Oxidation resistance of the Ti_xSi_y/γ -TiAl systems

5.3.1 Oxidation performance of the Ti_xSi_y/γ -TiAl system with a 3µm thick Si layer

3 μ m thick Si-coated samples thermally annealed in vacuum for 2 h, 8 h, 16 h and 24 h, respectively, have been exposed to extended oxidation in a conventional oven in lab air at 900 °C for 100 h. The resulting XRD patterns are shown in Figure 5.8.



Figure 5.8: XRD patterns for a system formed by an initial 3 μm thick Si on γ-TiAl annealed at 950 °C for 2 h, 8 h, 16 h and 24 h, and exposed to oxidation at 900 °C in air for 100 h.

The XRD patterns reveal diffraction peaks from the γ -TiAl substrate for all samples, as described in section 5.1. The coatings remain rich in titanium silicide compounds such as Ti₅Si₃ and Ti₅Si₄ with a presence of some TiSi₂, whose peak intensity appears more pronounced than prior to oxidation (Figure 5.1).

In addition, new phases related to SiO_2 and TiO_2 , with a minor proportion of Al_2O_3 , are detected. Diffraction peaks due to TiO_2 have a very low intensity, suggesting small quantities. SiO_2 appears to be amorphous (metastable) on the sample after 2 h of TA, and minor diffraction peaks indicate the presence of crystalline (stable) SiO₂ on all samples. Cross-section SEM images of the Ti_xSi_y/γ -TiAl samples after 100 h of oxidation in air at 900 °C are shown in Figure 5.9.



Figure 5.9: SEM cross-section images of the Ti_xSi_y/γ -TiAl system for the initially 3 µm thick Si on γ -TiAl thermally annealed for (a) 2 h; (b) 8 h; (c) 16 h; (d) 24 h and oxidized in air at 900 °C for 100 h.

For all coated samples with a thin Si reservoir (3 μ m), one can observe the growth of an outer surface oxide layer with a thickness between 1.6 μ m and 2.4 μ m. The oxide scale is noticed either as a single layer or a bi-layer structure. The more external layer is constituted of brittle particles, while the inner layer appears continuous and more compact. The bi-layer structure is well defined on the sample with 8 h of thermal annealing. The outermost oxide layer is brittle and did not remain continuous after the specimen preparation for microstructural observations on all samples.

A localized EDS analysis on the bi-layer oxide scale of the 8 h TA sample (indicated by green and blue squares, respectively) shows the presence of a higher Ti content with respect to Si in the outer oxide layer (L₂: 70.6 at. % O, 13.5 at. % Ti, 8.7 at. % Si, 6.7 at. % Al, 0.5 at. % Cr), a similar ratio

of Si to Ti at the inner oxide layer (L₁: 65.4 at. % O, 16.5 at. % Ti, 14.9 at. % Si, 2.5 at. % Al, 0.7 at. % Cr), as well as low content of Al and traces of Cr in both of them.

After oxidation, the Ti_xSi_y coating decrease in thickness for all samples due to the consumption of Ti and Si atoms to grow their respective oxides. The interdiffusion zone (II) appears significantly depleted for samples with short times of annealing (2 h and 8 h), and their Al-enriched zone (III) seems non-continuous (i.e., 2 h TA sample) or disappearing (i.e., 8 h annealed sample). Particularly for the longer thermal treated samples (16 h and 24 h), the interdiffusion zone does not exhibit substantial degradation, while the Al enrichment zone shows a lower thickness than prior to oxidation.

The overall changes in the elemental distribution of the Ti_xSi_y/γ -TiAl system due to oxidation were obtained by using EDS compositional profiles shown in Figure 5.10 (a-d). The analysis was performed on the total cross-sections (up to 20 µm of depth) of the coated samples. Although the interdiffusion zone is indicated, it is not discussed here since it almost overlapped with the Ti_xSi_y layer and the Al enrichment zone.

After oxidation, for the 2 h annealed sample (Figure 5.10 (a)), within the first 2 μ m of depth, the atomic concentration profile reveals the presence of Ti, Si, and O (related to TiO₂ and SiO₂) with an oxygen content of about 50 at. %. By comparing the Ti-Si ratio after oxidation with the one obtained after annealing (Figure 5.4), the most probable phase transformations within the Ti_xSi_y region can be identified. The Ti_xSi_y region is marked by a decrease in the Ti concentration (from 60 at. % to 35 at. %) and of Si (from 35 at. % to 25 at. %), suggesting phase transformation of the titanium silicide compounds (most probably from Ti₂Si to Ti₅Si₃, and from Ti₅Si₄).

For the sample thermally annealed for 8 h and subsequently oxidized (Figure 5.10 (b)), the maximum oxygen concentration at the surface is about 65 at.%. Oxygen is detected within the first 3 μ m of depth. The Ti_xSi_y has lower Si and Ti concentrations than before oxidation (before oxidation 55-60Ti:30-40Si; after oxidation 35Ti:25Si), indicating phase transformation within the titanium silicide coating, similar to the ones observed in the 2 h TA sample. At depths higher than 4 μ m, less significant Al enrichment is observed than before oxidation, with a Ti/Al ratio of approximately 45 at. % / 55 at. %, closer to the original substrate composition.

The sample annealed for 16 h (Figure 5.10(c)) exhibits about 30 at. % of oxygen. This value is lower compared to the samples with shorter annealing time and with 24 h of annealing. The Ti/Si content ratios are not as significantly different as in the previous samples when compared to those observed after annealing. The sample annealed for 24 h (Figure 5.10 (d)) exhibits an oxygen content of about 70 at. % within the first 1 μ m, with a tail spanning well to a depth of 2 μ m. The compositional ratio of Si and Ti remained similar to those estimated prior to oxidation.



Figure 5.10: Compositional depth profiles of the Ti_xSi_y/γ -TiAl system oxidized in air at 900 °C for 100 h for the initially 3 µm thick Si on γ -TiAl annealed at different temperatures for different times: (a) 2 h, (b) 8 h, (c) 16 h, and (d) 24 h.

5.3.2 Thermo-gravimetric measurements and oxidation kinetics of the 3 μm Si reservoir

To assess the oxidation performance of the coating, thermogravimetric analysis (TGA) in the isothermal mode was performed for 100 h in lab air at 900 °C for selected Ti_xSi_y/ γ -TiAl 3D coated samples. Figure 5.11 presents the mass gain ($\Delta m/S$) as a function of time (*t*) for the 3 µm Si coated samples, annealed for 2 h, 8 h, and 16 h, in comparison with the uncoated substrate.

The bare substrate exhibits a rapid increase of weight, up to a point when the delamination of the oxide scales (TiO₂ and Al₂O₃) occurred after 88.5 h, corresponding to a mass gain value of 4.6 mg/cm². For the coated samples, $\Delta m/S$ was in the range of 1.3-2.2 mg/cm² for 100 h, while it was 1.6-2.1 mg/cm² for a total time of 88.5 h. None of the coated samples exhibited any delamination up to the end of the experiment. One can observe that the application of the Si coatings and subsequent formation of the Ti_xSi_y protective layer lead to a decrease in mass gain by 52-72 % compared to the $\Delta m/S$ value of the uncoated γ -TiAl.



Figure 5.11: TGA total mass gain as a function of time during oxidation at 900 °C of 3 μm Si coated samples preliminarily and vacuum thermally annealed for different times.

To assess the oxidation mechanism associated with the samples, we applied Equations 2.8 and 2.9 to describe the oxidation kinetics by fitting the experimental curves in Figure 5.11. The linear and parabolic oxidation parameters, k_l , and k_p , were obtained from the mass change/surface ($\Delta m/S$) versus time (t) or versus square root of time ($t^{1/2}$), respectively. A constant, C_i , was added to the oxidation rate when a steady state was not reached at the very beginning of the oxidation. The results are summarized in Table 5.1. Of particular interest are any deviations from the parabolic behavior since they can indicate additional contributions to the oxidation mechanism occurring in the protective Ti_xSi_y layers apart from diffusion.

Table 5.1: Comparison of the oxidation parameters for uncoated and coated γ -TiAl substrates after oxidation at 900 °C. R2 represents the quality of the fitting.

Samples	Total mass gain (W, mg/cm ²) after 88.5 h		R ²	Oxidation regime
Uncoated y-TiAl	4.6	k_1 : 3.5 x10 ⁻¹¹ k_p : 6.4 x10 ⁻¹¹	0.992	Linear Parabolic
γ-TiAl + 3 μm Si + 2 h TA	1.6	k _p : 8.4 x10 ⁻¹²	0.990	Parabolic
γ-TiAl + 3 μm Si + 8 h TA	1.3	$k_{\rm p}$: 3.5 x10 ⁻¹² + $C_{\rm i}$ $C_{\rm i}$: 2.8 x10 ⁻⁴	0.987	Parabolic
γ-TiAl + 3 μm Si + 16 h TA	2.1	$\mathbf{k}_{\mathbf{p}}$: 8.9 x10 ⁻¹² + $C_{\mathbf{i}}$ $C_{\mathbf{i}}$: 3.6 x10 ⁻⁴	0.988	Parabolic

The uncoated γ -TiAl presents a combination of linear and parabolic regimes; in the linear regime (within the first 14 h of oxidation), the oxidation kinetics relates to interfacial reactions at the surface and/or phase boundaries, while in the parabolic regime (above 14 h of exposure) oxidation is governed by the diffusion processes, with $k_1 = 3.5 \times 10^{-11} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and $k_p = 6.4 \times 10^{-11} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$, respectively.

For all coated samples, the mass gains are of the same order of magnitude, and they follow a parabolic oxidation rate behavior for the whole time of exposure. The k_p value obtained for the 2 h TA sample was $8.4 \times 10^{-12} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$, while for the 8 h TA and 16 h TA, it yielded $3.5 \times 10^{-12} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$, respectively. Indeed, the k_p values for the coated samples are one order of magnitude lower than for the bare substrate confirming the effectiveness of oxidation protection.

In Table 5.2, the oxidation kinetics of different types of coatings fabricated by similar or complementary methods are compared with the results obtained in this work. Since each system and measurement methodology exhibit their particularities, the parabolic constants cannot be compared directly, but one should rather compare the improvement of the oxidation kinetics by considering k_p of the uncoated vs the coated substrate.

Specifically, a coating system produced by pack siliconizing [153] exhibited one order of magnitude improvement (uncoated $k_p = 3.8 \times 10^{-10} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$; coated $k_p = 4.9 \times 10^{-11} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$). However, these coatings were relatively thick (~7-24 µm) compared to ours, and the oxidation conditions were less severe (800°C). Gray *et al.*[154] have shown that coatings produced by the CVD process improve oxidation kinetics by one order of magnitude (uncoated $k_p = 7.5 \times 10^{-15} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$; coated $k_p = 9.4 \times 10^{-16} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$) but after a longer exposure time of 500 h.

Although the thickness range (1-2 μ m) of their coatings and the ones of the present study are close, the higher process temperature and longer deposition time employed for the coatings in ref. [154] could lead to differences in the thermodynamic stability of the phases present in the Ti_xSi_y coatings. Similarly, a reduced oxidation rate by about two orders of magnitude compared to the substrate (uncoated $k_p = 1.8 \times 10^{-8} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$; coated $k_p = 1.3 \times 10^{-10} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$) has been observed for coatings produced by pack aluminizing [155] and subsequent electrodeposition of silica, while the coating thickness was very large (>50 µm).

The comparison of the oxidation performance of the coated γ -TiAl substrates presented in this work can be completed by referring to Hindam and Whittle [156] who studied the oxide scale formation (Cr₂O₃ and Al₂O₃) at a high temperature of 900-1300 °C using non-Si-containing systems. Specifically, these authors analyzed "chromium oxide-former" alloys (i.e., Co-Cr, Fe-Cr and Ni-Cr) and "alumina-former" alloys (i.e., Co-Cr-Al, Fe-Cr-Al, Ni-Cr-Al, Ni-Al, and Pt-Al) for which they reported the following range of the kinetic growth rate, $k_{p \text{ at } 900 \text{ °C}} = 10^{-10} \cdot 10^{-12} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ and $k_{p \text{ at } 900 \text{ °C}} = 10^{-13} \cdot 10^{-14} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$, respectively.

In the coating system developed in our study, the kinetics of oxidation of the base material is improved by one order of magnitude. The sputtering process of Si followed by annealing at a moderate temperature (950 $^{\circ}$ C) used for the coating growth is beneficial due to the industrial compatibility. In addition, the relatively small thickness of the Ti-Si coatings has the advantage of no adhesion issues compared to very thick coating systems.

Table 5.2: Comparison of the oxidation performance at 800 °C-1000 °C of Si based coatings (TixSiy and Si-Al) for TiAl alloys produced by different methods.

Substrate	Coating (including thickness)	Method (including temperature and time)	Oxidation time lapsed for the k_p estimation and oxidation temperature	$k_{\rm p} ({\rm g}^2 \bullet {\rm cm}^{-4} \bullet {\rm s}^{-1})$	
				Uncoated substrate	Coated
Ti-6Al-1Mn	Ti _x Si _y (~7-24 μm)	Pack siliconizing [153] (800-900 °C, 6-20 h)	340 h at 800 °C	3.8x10 ⁻¹⁰	4.9x10 ⁻¹¹
Ti-45Al-2Mn-2Nb- 1B	Ti _x Si _y (~1-2 μm)	CVD [154] (1010 °C, 50 h)	500 h at 900 °C	7.5x10 ⁻¹⁵	9.4 x10 ⁻¹⁶
Ti-50Al	Si-Al (>50 μm)	$\begin{array}{ll} Pack & aluminizing \\ [155] (1000 \ ^{\circ}C, 2 \ h) + \\ electrodeposition & of \\ SiO_2 \end{array}$	60 h at 1000 °C	1.8x10 ⁻⁸	1.3 x10 ⁻¹⁰
Ti-48Al-2Cr-2Nb	Ti _x Si _y (~2-3 μm)	Sputter-deposition [this work] (Ambient temp.) + vacuum TA (950 °C, 2-16 h)	100 h at 900 °C	6.4x10 ⁻¹¹	3.5-8.9x10 ⁻¹²

5.3.3 Microstructural evolution of oxidized Ti_xSi_y/γ -TiAl systems with 6 μ m and 9.5 μ m thick Si reservoirs

Microstructural and compositional characteristics of samples with initial silicon thicknesses of 6.0 μ m and 9.5 μ m, vacuum thermally annealed for 8 h and 16 h and oxidized in a conventional oven for 100 h in lab air at 900 °C are presented in Figures 5.12 and 5.13.

As shown by the SEM cross-sectional images (Figures 5.12 (a,d) and 5.12 (a,d)), all samples exhibit an oxide scale on top of the coating with thicknesses in the range from ~1.4 to ~9.5 μ m. However, non-continuous oxide scale formation is observed on the sample with 8 h of thermal annealing, compared to 16 h TA sample. After oxidation, the Ti_xSi_y coating does not exhibit significant degradation, and neither interdiffusion zone shows depletion. Al enrichment zone appears thicker than prior to oxidation for all thick samples.

As observed from the EDS mappings (Figures 5.12 (b,e) and 5.13 (b,e)), the main oxide scale exhibits either a single layer or a bi-layer structure for all samples. The thicker and more common oxide layer possesses a coarse morphology and is composed of mixed oxides of Si and Al with Cr enrichment. Particularly, a pronounced Al and Cr enrichment was revealed throughout the Ti_xSi_y coating for all samples with thick Si reservoirs.

A bi-layer oxide scale is well defined in the case of the sample with 6 μ m of initial Si reservoir and 16 h of TA (Figure 5.13 (a)). The composition of the outer oxide scale appears similar to the other 9.5 μ m thick samples (Si and Al oxides with Cr enrichment), but with a minor presence of TiO₂ underneath the thickest oxide layer, followed by a SiO₂ layer.

For these thicker titanium silicide layers, outward migration of Al and Cr from the underneath layers (interdiffusion zone and substrate) appears to be intensified, particularly for a longer annealing time (16 h) (Figure 5.13 (b,e)). This is probably caused by a higher Si content leading to more Ti bonded to Si, which in turn increase the activity [157] of Al and Cr. For samples with 3 μ m of Si (although not shown), this effect is weaker.

Compositional profiles were constructed from the EDS mappings, as shown for the oxidized samples in Figures 5.12 (c,f) and 5.13 (c,f). Their elemental composition is detailed from the outer surface to the deeper layers. Mixed Si and Ti oxides are detected in the outer layer (Z1), for samples with 6 μ m + 8 h TA (Figure 5.12(c)), and 9 μ m + 8 h TA (Figure 5.12(f)). The oxygen and Ti contents appear higher for the samples with larger Si reservoirs (6 μ m + 8 h TA: 36 at. % O, 27-32 at. % Si, and 18-36 at. % Ti; 9 μ m + 8 h TA: 54-27 at. % O, 27 at. % Si, and 18-54 at. % Ti), as also documented by a thicker outer scale formation observed for the 9 μ m + 8 h TA sample.

In the Ti_xSi_y coating (Z2), the elemental Ti-Si ratio indicated TiSi, Al, and Ti-Si-Al compounds for the 6 μ m + 8 h TA sample (36-45 at. % Ti, 36-27 at. % Si, and 9-36 at. % Al), and the Ti₅Si₃ compound for the 9 μ m + 8 h TA sample (54 at.% Ti, and 36 at. % Si).

The elemental ratios observed for samples with 6 μ m + 16 h TA (27-45 at. % O, 9 at. % Al, 15 at. % Si and 45 at. % Ti, in Figure 5.13 (c) and 9.5 μ m + 16 h TA (22-54 at. % O, 9 at. % Al, 18 at. % of Si, and 45 at. % Ti, in Figure 5.13 (f), suggests in addition to Si and Ti oxides, Al oxide within the outer layer (Z1). The Ti-Si ratio in the Ti_xSi_y coating (Z2) indicates Ti₅Si₃ compound formation for both samples (54 at. % Ti, and 36 at. % Si).

For all thick samples described in this section, the interdiffusion zone (Z3) exhibits a slightly higher Al content to Ti, and a lower Si concentration. The Al enrichment zone (Z4) shows twice the Al content with respect to Ti, which corresponds to the TiAl₂ compound.



Figure 5.12: Cross-sectional SEM, and EDS mapping and compositional depth profiles of Ti_xSi_y/γ -TiAl systems with initial Si thicknesses of 6.0 µm (a-c) and 9.5 µm (d-f) after 8 h of TA, and after 100 h of oxidation at 900 °C.



Figure 5.13: Cross-section SEM, and EDS mapping and compositional profiles of Ti_xSi_y/γ -TiAl systems with initial Si thicknesses of 6.0 µm (a-c) and 9.5 µm (d-f) after 16 h of TA, and 100 h of oxidation at 900 °C.

5.3.4 Phenomenological model of the microstructural evolution and oxidation of the Ti_xSi_y/γ -TiAl system and discussion

In the following, we describe a phenomenological model that explores two different aspects of the produced coatings: (i) the influence of the Si reservoir and thermal annealing on the oxide scale formation, and (ii) the microstructural evolution of the Ti_xSi_y/γ -TiAl system due to high-temperature oxidation.

First, solid state diffusion processes govern the oxidation rate of the Ti_xSi_y/ γ -TiAl system, as observed from the estimated oxidation growth rates (see Table 5.1) and the related parabolic behavior. The kinetics of the oxide scale formation reaction expresses the rate of diffusional transport of the species at the oxygen-coating interface and implies a linear relationship between the growth rate of the oxide scale and the driving force for their growth (including concentration and chemical potential gradients) [158-159]. The second aspect, which explores the microstructural evolution of the deeper layers, suggests interfacial reactions [160] in the adjacent zones (inner zones) as responsible for the observed microstructural changes via SEM micrographs, EDS mappings, and compositional profiles, (i.e., depletion of the interdiffusion zone in the 3 μ m Si reservoir samples, or deeper Al enrichment zone in the 6.0-9.5 μ m Si reservoir samples).

Both types of contributions, namely diffusion and potential interface reactions, which occur simultaneously during the oxidation of the samples, are described by the phenomenological model proposed and schematically illustrated in Figure 5.14 that combines the theoretical aspects [158-165] and our experimental results.

The reaction steps described in the experimental part of this work are illustrated by panels presented in the following order: Si deposition (Panel A); Vacuum thermal annealing (Panel B); Simultaneous processes occurring during high-temperature oxidation (Panel C); And the formation of the final microstructure obtained after annealing and subsequent oxidation (Panel D).



Figure 5.14: Phenomenological model of the high-temperature oxidation of the Ti_xSi_y/γ -TiAl system.

Fabrication of the oxidation protection system starts with the deposition of a specific Si reservoir on top of the γ -TiAl substrate – in the context of this work, three different Si thicknesses are studied (**Panel A**). Upon vacuum annealing, the surface region undergoes microstructural and chemical transformations (**Panel B**), leading to the formation of Ti_xSi_y coating, Ti-Al-Si (interdiffusion zone), and TiAl₂ (Al enrichment zone). The thickness and composition of the individual zones depend on the annealing time and initial Si thickness.

During subsequent oxidation (**Panel C1**), molecular oxygen from the environment at 900 °C dissociates ($O_2 => O^{-2}$) and the reaction between the oxygen anions and the cations diffuses to the top surface (either Si, Ti, Al, and Cr) leads to the nucleation of the first oxide scale layer. Its discontinuity and porosity allow for an inward transport of oxygen and an outward migration of the reactive species [142-144] at the oxide scale/Ti_xSi_y interface. Although the diffusivity of the species involved is different ($D_{Si} \neq D_{Ti} \neq D_{Al} \neq D_{Cr}$), they all depend on the chemical potential gradient (the driving force for the diffusion), which increases with a higher concentration of the species and their flux toward the oxygen-coating interface.

For the 3 μ m thick Si reservoir, the presence of the Ti₂Si, Ti₅Si₃, and Ti₅Si₄ phases with a higher Ti to Si ratio, induces a significant Ti gradient, that feeds the Ti+O reaction with enough outward diffusion of Ti to produce an outer scale with significant Ti oxide content. Since titanium oxide is porous, it allows for an inward diffusion path for oxygen and an outward path for Si. Although Al and Cr also outward diffuse towards the oxide scale, their flux is less significant since their initial content in the coating is much lower. The inner formation of Si oxide and outward formation of Ti oxide (as particularly seen in Figure 5.9 (b)) is also supported by the reported variations of the metal oxide equilibrium pressures in the Ti-Si-O system [16] in which the Si oxide is more stable due to a decreased activity of Ti since it is fixed in the Ti-Si bonds.

For the samples with larger Si reservoirs (6.0 μ m and 9.5 μ m), richer content in Si (due to the TiSi₂, TiSi phases), and a lower content of Ti₅Si₃ and Ti₅Si₄ compounds, provided a more restricted environment for the Ti oxide formation. In addition, the higher Si reservoir feeds the Si-oxygen reaction with enough Si to grow a thick oxide scale without significant depletion of the coating (as seen in Figures 5.12 (a,d) and 5.13 (a,d). Also due to the significant outward migration of Ti, to form the thick titanium silicide layer, a more significant outward migration of Al and Cr toward

the oxide scale is noticed (as seen in Figures 5.12 (b,e) and 5.13 (b,e), leading to Al oxide formation as well as Cr enrichment. The inner growth of a thin Ti oxide layer is explained by the more efficient restriction of Ti activity, and the inner growth caused by the Si oxide formation underneath it, which improves the Ti oxide stability [16].

Panel C2 indicates three distinct interface regions. Specifically, at the **Interface region 1** (**Interdiffusion zone - Ti_xSi_y layer**), the concentration gradient of the Ti, Si and Al cations leads to interface reactions that feed the Ti-Si formation, supporting the growth of the Ti_xSi_y layer while balancing the outward migration of the elements to the top surface (mostly Si and Ti).

The reactions within the Interface region 1 can be significant. These can give rise to a depletion of the elements (Ti, Si, and Al) within the interdiffusion zone (as observed in samples with a $3\mu m$ Si reservoir - Figure 5.9 (a, b) due to their continued consumption within the boundary regions.

Recombination of the Ti and Al cations (via solid-state boundary reactions) present within the **Interface region 2 (Interdiffusion zone - TiAl2 layer**) can balance Ti depletion in some areas of the TiAl2 layer (as observed in samples with a 3 μ m Si reservoir in Figure 5.9 (a,b).

Within the **Interface region 3 (TiAl₂ layer- Substrate)**, the sustained Ti migration from the TiAl₂ layer across the Interface region 2 leads to a deeper Al enrichment (as identified in samples with the 6.0 μ m and 9.5 μ m thick Si reservoirs – see Figures 5.12 (a,d) and 5.13 (a,d).

Panel D illustrates the two different types of microstructure that are characterized by the oxide scales of the Ti_xSi_y/γ -TiAl system after 100 h of oxidation at 900 °C, as identified from the SEM observations (Figures 5.9, 5.12, and 5.13). The oxide scale of the samples with a smaller initial Si reservoir (3 µm) is composed of a bi-layer structure in which mixed Si and Ti oxides are detected; Si oxide appears more abundant in the inner layer, while more Ti oxide prevails in the outer layer.

For samples with a larger Si reservoir (6.0 μ m and 9.5 μ m), the oxide scales exhibit a more protective nature. In such a case, the thick outer layer is mostly composed of Al and Si oxides with a significant Cr enrichment, with a very thin inner layer of Ti oxide, and SiO₂ also observed at the bottom (as confirmed from compositional mappings).

5.4 Conclusions

In the present work, we demonstrated a feasibility to fabricate effective coatings that provide oxidation protection of γ -TiAl substrates, while using a hybrid process consisting of magnetron sputtering of a Si reservoir layer, followed by vacuum thermal annealing at 950 °C. Specifically, we studied the influence of the initial growth conditions (Si reservoir thickness and annealing time) on the formation of a Ti_xSi_y/ γ -TiAl multi-zone structure. After subsequent 100 h of oxidation at 900 °C in laboratory air, the thermogravimetry study on the 3µm Si reservoir showed that the oxidation process is primarily controlled by diffusion, best described by the parabolic oxidation coefficient, k_p. The values of k_p = 3.5-8.9 x10⁻¹² g² • cm⁻⁴ • s⁻¹ for the coated surfaces were found one order of magnitude lower than for the bare substrate (k_p = 6.4 x10⁻¹¹ g² • cm⁻⁴ • s⁻¹).

In the coated samples with a larger Si reservoir (6 μ m and 9.5 μ m), it was possible to restrict the growth of TiO₂ scale by forming a multilayer oxide scale of mixed SiO₂ and Al₂O₃ at the surface, and inner SiO₂. Based on the experimental evidence, we proposed a phenomenological model that describes the relationship between the oxide scale formation and the microstructural evolution of the multiple zones, and that underlines the correlation between the oxidation process to the different Si reservoirs and compositions.

The methodology and insights explored in this study contribute to the understanding of the formation of multi-zone oxidation-resistant structures and their use in practical applications such as the protection of jet engine components, manufacturing tools, and others.

CHAPTER 6 ARTICLE 2: SELF-ORGANIZED MULTILAYER STRUCTURE IN MAGNETRON SPUTTERED Si-Pt RESERVOIRS ON γ-TiAl ALLOY INDUCED BY HIGH-TEMPERATURE ANNEALING AND OXIDATION

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This chapter presents the work about the influence of Si-Pt-based coatings on a Ti-48Al-2Cr-2Nb alloy when exposed to a high-temperature oxidation environment (900 °C). The coatings were deposited by magnetron sputtering, using different Si (63-80 at.%) and Pt (20-37 at.%) concentrations as well as varied thicknesses (6.8-12.2 μ m). The evolution of the microstructure of the as-deposited Si-Pt layers has been tuned by thermal annealing (TA) in high vacuum (10⁻⁶ Torr) at 750 °C for 16 h, and is evaluated by XRD, SEM, and EDS analyses.

6.1 Microstructural and compositional characteristics

Si-Pt coatings with different thicknesses between 6.8 and 12.2 μ m and with different Si-Pt ratios, thermally annealed for 16 h at 750 °C, were analyzed by XRD and the results are presented in Figure 6.1 (a-b). The XRD patterns of the as-deposited sample with 6 μ m Si-Pt are shown.

The peaks correspond to the tetragonal Pt_2Si , orthorhombic PtSi, and tetragonal γ -TiAl. This latter arises from the Ti-48Al-2Cr-2Nb substrate (Figure 6.1 (a)). As observed, the presence of platinum silicide compounds before annealing is confirmed.

This indicates that Si and Pt reaction takes place during the sputtering process, either through sequential growth of Pt_2Si (activation energy: 1.0 eV [166]; energy of formation: -28 kJ/mol [167]), followed by PtSi (activation energy: 1.5 eV [166]; energy of formation: -33 kJ/mol [167]), or

simultaneously [168]. It is highly probable that sublattice-diffusion and Pt occupation of the interstitial space within the Si lattice [167] take place (Si lattice parameter: 0.543 nm; Pt lattice parameter: 0.392 nm) [169].

After annealing, the composition of the phases revealed by XRD suggests the transport and redistribution (diffusion) of the substrate and coating elements (see Figure 1(b)). The features include the tetragonal γ -TiAl substrate, the orthorhombic PtSi, and tetragonal Pt₂Si compounds, with the addition of a mixture of Ti_xSi_y phases (tetragonal Ti₅Si₄, hexagonal Ti₅Si₃, as well as the orthorhombic TiSi and TiSi₂) and the Pt_xAl_y compounds (hexagonal Pt₂Al₃ and rhombohedral Pt₅Al₃). The Pt₂Si and TiSi signals became more intense for annealed samples with a higher Si-Pt reservoir, while the brittle TiAl₂ and Ti₅Si₃ phases were detected with higher intensity on the lower Si-Pt reservoir annealed samples.



Figure 6.1: XRD patterns of the (a) as-deposited ($6\mu m$) Si-Pt coating, and (b) the thermally annealed samples at 750 °C for 16 h.

Morphology and composition of the as-deposited and thermally annealed coatings were analyzed by SEM, as shown in Figure 6.2 (a-f). A dense structure was confirmed for the as-deposited Si-Pt films (Figure 6.2(a-c)), which appear to exhibit certain brittleness, as indicated by the fracture observed at the cross-sectional sample (Figure 6.2 (a)) after sample preparation (cutting, grinding and polishing) for microstructural observations. The SEM observations have also shown coarse features (most probably agglomerated particles of Si-Pt composition) on the thicker samples (8.4 μ m and 12.2 μ m), contrary to a smoother surface observed on the thinner coating (6.8 μ m). The smoother morphology of the as-deposited sample with a lower Pt content (Figure 6.2(a)) can be related to the composition, in which mostly PtSi was confirmed by XRD (Figure 6.1) before annealing. As the Pt content increased on the thicker samples (as estimated from EDS) a more mixed composition can rise (PtSi and Pt₂Si) and produce a coarser microstructure [167].

Vacuum thermal annealing treatment (16 h at 750 °C) resulted in the formation of sub-layers of different thicknesses as shown in Figure 6.2 (d-f). On the micrographs the areas are identified as follows: **zone 1**, **zone 2**, and **zone 3**, all of them defined as compact regions; in addition, there are two types of interdiffusion zones denoted as **interdiffusion A** and **B**, respectively, as well as **Al enrichment**.

As deposited After annealing d) 80 at.% Si a) 6.8 μm Si-Pt 20 at.% Pt Zone 1 Zone 2 Interdifussion A Zone 3 Interdiffusion B Al enrichment Substrate **b)** 8.4 μm Si-Pt 63 at.% Si **e**) 37 at.% Pt Zone 1 Zone 2 Interdifussion A Zone 3 Interdiffusion B Al enrichment Substrate 10µm 10µm 66 at.% Si c) 12.2 µm Si-Pt **f**) 34 at.% Pt Zone 1 Zone 2 Interdifussion A Zone 3 Interdiffusion **B** Al enrichment Substrate 10µm

Figure 6.2: SEM images of as deposited samples acquired in the LEI observation mode (a-c) and thermally annealed (d-f) acquired in the LABE mode; Si-Pt samples: (a-d) 6.8µm (80Si-20Pt, at.%); (b-e) 8.4µm (63Si-37Pt, at.%), and (c-f) 12.2µm (66Si-34Pt, at.%). After annealing, for all samples, the thickest layer is observed at the top (**zone 1**) and is constituted of Pt_xAl_y and Pt_xSi_y compounds. In the case of the sample with a higher initial Si content (80 at.%) **zone 1** (Figure 6.2 (d)) exhibits a microstructure constituted of smaller features (dendritic type). Samples with a lower Si content (64-66 at.%) and a higher thickness (Figure 6.2 (e-f)), possess a columnar microstructure in their **zone 1**. Such columns are often related to the distinct growth rates of the phases (*i.e.*, Pt_xAl_y and Pt_xSi_y). The strain generated during the change of volume occurs during the formation of platinum silicides, while Pt atoms are introduced into the Si lattice [166,170]. This volume change is greater with a higher Pt reservoir (higher Pt content and thickness).

The thicker coated sample (Figure 6.2 (f)), exhibits tilted mesopores between the coalescences columns, an observation that has not been made on the samples with a lower thickness and a higher Si content (80 at.%) (Figure 6.2(e)) in which a more compact microstructure and a lower density of micropores has been seen. The two different types of microstructure can be related to the difference in the Si/Pt ratio and the growth process, especially to the surface mobility of the Si and Pt atoms during sputtering and thermal annealing.

In all cases (Figure 6.2 (d), (e), (f)) a thinner layer (**zone 2**) was identified just below zone 1, which appeared denser and thicker on samples with a higher Pt content. Underneath it, the first interdiffusion region (**Interdiffusion A**) appeared in which elemental traces of zone 2 (Al, Ti, Si, and Pt) did not form a continuous layer, but formed segregated intermetallic phases which are not easily distinguishable.

Zone 3 is a thin, compact, and continuous layer composed of Ti, Si, and Al, and it also presents a thick interdiffusion region (**Interdiffusion B**). In addition, **Al enrichment** develops at the bottom of the sublayers for all of the thermally annealed samples.

The different zones identified by EDS analysis for all annealed samples are described by the compositional profiles presented in Figure 6.3 (a-c). The three main zones can be clearly distinguished, while the interdiffusion and Al enrichment regions are partially overlapping between zones 2 to 3, as well as between zone 3 and the substrate, respectively.



Figure 6.3: EDS Elemental distribution of the different Si-Pt coatings after annealing: (a) 6.8 μm (80Si-20Pt, at.%); (b) 8.4 μm (63Si-37Pt, at.%), and (c) 12.2μm (66Si-34Pt, at.%).

Pt appears homogeneously distributed and mainly located in the top zones 1 and 2. Si diffuses inward and deeper than Pt, and it is also seen within the top layer (zone 1) as well as underneath (zone 2) and deeper throughout zone 3. The outward diffusion of Ti up to zones 2 and 3 leads to the formation of titanium silicides. Al distribution is broader than Ti; it is identified at a low concentration at the very top layer or significantly enriched in the deepest zone. Additionally, Al outward diffusion can be limited by the low solubility of Al in silicides [171]; therefore, the silicides can be considered an Al diffusion barrier. Cr and Nb remained mostly restrained within the substrate, and the presence of oxygen was not significant neither in the coating or in the substrate. The occurrence of oxygen during the growth of this type of coating is undesired because it would promote oxygen transport inwards to the substrate and cause either the growth of unprotective oxides or oxygen embrittlement of the base material.

Although similar elemental distributions prevail for the different samples, the total depth of their distributions varied due to the different initial Si-Pt reservoirs. In **zone 1**, the elemental contents (36 at.% Pt, 36 at.% Si, 27 at.% Al) suggest the presence of PtSi and Pt_5Al_3 in all samples.

Particularly for thick samples (Figures 6.3 (b) and 6.3(c)), the Pt_xAl_y compound is observed localized at the bottom of zone 1.

For the different samples, the range of the elemental contents within **zone 2** (27-45 at.% Ti, 36-0 at.% Pt, 36-63 at.% Si) suggests the formation of either TiSi or TiSi₂, or interdiffusion of Ti, Pt, and Si. Particularly for the sample with a medium Si-Pt reservoir (8.4 μ m), a PtSi compound formation is detected in zone 2, as indicated by a more significant Pt content. The elemental distribution in **zone 3** (36 at.% Ti, 27-0 at.% Si, 36-63 at.% Al) indicates the presence of TiSi compound, interdiffusion of Al, Si, and Ti, as well as Al enrichment.

6.2 Microstructural evolution after oxidation

Following oxidation at 900°C for 100h of the thermally annealed samples, the microstructural modifications were explored using XRD (Figure 6.4) and SEM (Figure 6.5 (a-c)). Most of the phases already identified before oxidation (see Figure 6.1) remained. However, some new ones appear, suggesting structural transformations during the oxidation process (see Figure 6.4).



Figure 6.4: XRD patterns of the Si-Pt-based coatings after annealing and oxidation.

The XRD peaks related to the γ -TiAl substrate, and the titanium silicide signals due to Ti₅Si₄ and Ti₅Si₃ as well as Pt₂Al₃, Pt₅Al₃, and PtSi phases can be identified, while TiSi, TiSi₂, and Pt₂Si are no longer detected, and PtAl appears as a new phase. The high-temperature exposure in the air has led to the development of aluminum and silicon oxides (Al₂O₃ and SiO₂).

The microstructural evolution of the self-organized multilayer coating after oxidation is well illustrated by the SEM micrographs in Figure 6.5 (a-c). Particularly, the appearance of the inner layers changed in comparison to the micrographs observed after TA (Figure 6.2 (d-f)). The origin of these changes is linked to the elemental availability (effective concentration) and their diffusional redistribution through the layers.

The changes observed among the samples included a different morphology at the **interdiffusion zone A**, now combined into **zone 3**, and a more compact **interdiffusion zone B**, with a less scattered distribution of the diffused features and a deeper **Al enrichment** (due to depletion of Ti that outward diffuses) compared to the state before oxidation.

Among the main particularities, for the sample with a medium Si-Pt reservoir (8.4 μ m) (Figure 6.5(b)), a thin but well-defined sublayer under **zone 1** can be observed. This layer was not present prior to oxidation. On the same sample (Figure 6.5 (b)), **interdiffusion zone B** seems reduced, and it now appears merged into a dense and mostly continuous layer. For the sample with a higher initial Si-Pt reservoir (12.2 μ m) (Figure 6.5 (c)) the total number of layers is now decreased, with the region identified as **zone 2** significantly thicker, and no **zone 3** more observed.

The elemental partition into the layers after oxidation is illustrated by the EDS maps presented in Figure 6.6 (a-c). Oxygen enrichment is well restricted through the top layer, or zone 1. For all samples, the oxidized layer (zone 1) consists of a mixture of Al_2O_3 and SiO_2 , with metallic Pt precipitation. This effect is more significantly observed for the thicker coated sample (Figure 6.6(c)) Outward diffusion of Al towards the top layers and deeper Pt distribution are noticed after oxidation for all samples. Outward transport of Cr is observed for all oxidized samples without particular differences among the different coatings; Nb (although not shown) does not exhibit any significant change in its distribution after annealing or oxidation.



Figure 6.5: SEM micrographs of the microstructural evolution of the Si-Pt based coatings after oxidation: (a) 6.8 μm reservoir, (b) 8.4 μm reservoir, and (c) 12.2 μm reservoir.



Figure 6.6: EDS maps of Si-Pt based coatings after annealing and oxidation; (a) 6.8 μ m (80 at% Si, 20 at.% Pt); (b) 8.4 μ m (63 at% Si, 37 at.% Pt), and (c) 12.2 μ m (66 at% Si, 34 at. % Pt).

The chemical changes are further documented by compositional profiles (Figure 6.7 (a-c)).



Figure 6.7: Compositional profiles of Si-Pt based coatings after annealing and oxidation: (a) 6.8 μ m (80Si-20Pt, at.%); (b) 8.4 μ m (63Si-37Pt, at.%), and (c) 12.2 μ m (66Si-34Pt, at.%).
For the 6.8 µm thick Si-Pt sample (80 at.% 20 at.% Pt) in Figure 6.7 (a), the presence of oxygen (~48 at.%) was confirmed within the top layer, accompanied by Si (~16 at. %) and Al (~10 at. %). Oxygen is well restricted to the top surface (**zone 1**), and it is only associated with Si and Al (i.e, Al₂O₃, SiO₂), and surrounded by localized Pt. The elemental content within the inner layers is as follows: **zone 2** - Pt~10at. %, Ti ~45 at. %, Si ~45 at. %; this suggests the presence of the TiSi compound with some Pt, probably related to the Pt_x(Si,Al)_y phases, which do not oxidize; **zone 3** – The values of Ti ~50 at. %, Si ~50 at. %; and interdiffusion (Al~ 40at. %, Ti ~35 at. %, Si ~25 at. %) indicate significant interdiffusion of Si, Ti, and Al (probably (Al,Ti)_xSi_y). The deeper layer is Ti depleted/Al enriched, with a TiAl₂ composition.

Analysis of the 8.4 μ m thick Si-Pt sample is shown in Figure 6.7 (b). A similar composition within **zone 1** was detected as in the previous sample, but a higher Pt content is found (O~43 at.%, Pt~35 at.%, Si~18-13 at.%, and Al ~5-10 at.%). In **zone 2**, (Pt,Ti)_xSi_y, is characterized by its Pt content (~20 at.%) and by a slightly lower Ti (~40 at.%) and Si (~40 at.%) concentrations compared to the previous sample. **Zone 3** possesses similar ratios for Ti and Si, and Al is present as well (Ti ~45 at.%, Si ~45 at.%, Al~10 at.%).

The thicker (12.2 µm) Si-Pt sample is shown in Figure 6.7 (c). In **zone 1**, a higher concentration of oxygen (O ~ 42-48 at. %,) is accompanied by Pt, Si, and Al (Pt ~32 at. %, Si ~ 17 at. %, Al ~5-10 at. %). In **zone 2**, (Pt,Ti)_xSi_y, which is not oxidized in any of the presented samples, possesses a significantly higher Pt content (~35 at.%) in comparison with the previous observations; one can also observe Ti (~30 at.%) and Si (~30 at.%), probably as a Pt-Ti-Si compound (Pt_x(Si,Al)_y). Interdiffusion of Ti, Si, and Al contributes to **zone 3** (Ti ~40 at.%, Si ~15 at.%, Al ~40 at.%), with TiAl₂ at the very bottom as in the previous samples.

6.3 Thickness of the sublayers after annealing and oxidation

The growth of each zone after annealing and their evolution due to oxidation is schematically illustrated for each sample in Figure 6.8 (a-f). Below, the common tendencies are first described, followed by the particularities of each sample.



Figure 6.8: Thickness evolution of the individual zones due to thermal annealing and oxidation.

After annealing, the multilayer obtained indicates that the top layer (**zone 1**) (Pt_xSi_y and Pt_xAl_y) and the **interdiffusion zone B** (Ti-Al-Si) grow with a higher initial Si-Pt reservoir.

The growth of **zone 2** (Pt_xSi_y and Ti_xSi_y) and the **interdiffusion zone A** (Ti-Pt-Si) appears more influenced by the initial Pt content than by the Pt-Si thickness.

As observed on the sample with a higher Pt content (37 at. %), a higher thickness of **zone 2** is accompanied by a thinner **interdiffusion zone A**.

The thicknesses of **Zone 3** (Ti_xSi_y) and of the **Al enrichment zone** remained very similar with no apparent dependence on the initial Si-Pt reservoir.

After oxidation, the most significant redistribution of elements in different layers is observed on the sample with the highest initial Si-Pt reservoir (12.2 μ m) in which fewer sublayers are formed (Figure 6.5 (c)) and no interdiffusion zone A (Figure 6.8(c)) neither zone 3 (Figure 6.8 (d)) are present.

For all samples after oxidation, **zone 1** continued to grow with a higher thickness than before oxidation, related to the formation of the oxides (SiO₂ and Al₂O₃).

A particular tendency is observed after oxidation for **zone 2** and the **interdiffusion A** layers. The thickness of **zone 2** significantly decreases for samples with a smaller initial reservoir, showing depletion of elements that out diffuse to the top layer. However, the thickness of this zone considerably increases for the sample with the highest initial reservoir (12.2 μ m).

This evolution is likely due to a more pronounced outward element migration at the inner layers (Interdiffusion A and zone 3). **Interdiffusion A** behaves differently for each sample; its thickness decreases for the lowest Si-Pt reservoir (6.8 μ m), it slightly increases for the 8.4 μ m sample, and it completely disappears for the highest Si-Pt thickness (12.2 μ m), suggesting different solid-state boundary reactions at this layer.

Thickness of the **Interdiffusion B** decreases indicating a depletion of elements due to their outdiffusion to zones 2 or zone 3. Meanwhile, an increased thickness is noticed for **zone 3**, supporting a significant outward diffusion from the deepest layers. **Zone 3** remained only in samples with lower initial Si-Pt reservoirs (6.8 and 8.4 μ m). The **Al enrichment zone** grows in thickness due to the continued Ti outward diffusion from the base material. This process is faster for the sample with the lowest initial Si-Pt reservoir, suggesting that the driving force for diffusion is influenced by the specific initial Si-Pt reservoir.

6.4 Discussion

6.4.1 Hierarchical composition of the layered system after annealing

The majority of the phases that have been identified after the initial annealing are thermodynamically stable [14,-172,173] and they display comparable energies of formation [174]. The complexity of the hierarchical composition and phase formation observed in the multilayer system resides in the non-equilibrium processes that occur at the interfaces, in which different thermodynamic, diffusional (kinetic), and even crystallographic aspects must be taken into consideration.

If only the energetic aspect is considered, then the phases displaying the most negative enthalpy of formation (H^0) values would be energetically favored to grow first due to the largest change of free energy involved [43]. Some Pt_xAl_y compounds exhibit the most negative free enthalpy of formation (*i.e.*, PtAl: -100.2 kJ/mol, Pt₂Al₃: -96.5 kJ/mol, Pt₃Al: -63.6 kJ/mol, reported for a temperature of 1200°C) [157]. However, as expressed in the effective enthalpy of formation rule [175], the growth of the phases and particularly their growth sequence is also influenced (i) by the thermodynamic activity (effective elemental concentration available) at a certain interface or zone, particularly that in which the limiting element is the one required in a higher concentration for a specific compound formation, as well as (ii) by the nucleation barriers.

In this context, silicide compounds are the ones that satisfy the highest availability in the outer layer (64-80 at.% Si), demanding minimum diffusion transport for their growth. Among the two different types of silicide compounds seen in the multilayer presented here, namely Pt_xSi_y (*i.e.*, $Pt_2Si: -59.4$ kJ/mol and PtSi: -61.7 kJ/mol reported for a temperature of 1200°C) [174] and Ti_xSi_y phases (*i.e.*, $TiSi_2: -57$ kJ/mol, TiSi: -72.6 kJ/mol, $Ti_5Si_3: -73.8$ kJ/mol, $Ti_5Si_4: -78.5$ kJ/mol, reported for a temperature of 1200°C) [174], the growth of Pt_xSi_y is preferred due to the significant concentration (elemental content) of both elements in the top layer, as well as due to the more negative energy of formation of Ti_xSi_y .

For the growth of the inner layers, either Pt_xAl_y or Ti_xSi_y could potentially grow since their energies of formation are comparable. In addition, the growth at the inner layers is also strongly linked to mobility or diffusional transport. Specifically, out-diffusion of Al and Ti as well as inward transport of Pt and Si to feed the respective aluminide and silicide compounds.

With the Si/Pt ratio and initial thickness of the Si-Pt reservoir, several effects are induced: (i) The differences in the Si/Pt ratio influence the concentration of the diffusing species; ii) As the initial thickness of the coating increases, the consequently higher diffusional length increases the diffusional path of the species (since diffusion is a function of distance and the square root of time for the kinetic transport); iii) Since the diffusion of Si and Pt is mainly related to their thermodynamic activity (*a*) and their effective concentration [175], deeper Si and Pt inward diffusion is promoted in the case of larger Si-Pt initial reservoirs.

Due to the fact that initial Pt content is lower in comparison to Si for all samples, Pt compounds appear closer to the surface (inducing limited Pt availability with respect to Si). Also, since mobility strongly depends on atomic size [176], and since the atomic radius of Pt is higher than that of Si, a deeper Si inward diffusion compared to Pt has been noticed. This result is confirmed by the deeper growth of titanium silicide compounds (Ti_xSi_y) in comparison with any Pt-containing compound.

Ti outward diffusion is more pronounced than that of Al due to a higher chemical potential gradient between Ti and Si. As a consequence, a more significant inward transport of Si compared to Pt can be observed. Additionally, Al outward diffusion is probably limited due to low solubility of Al in silicides [171]. This supports faster outward diffusion of Ti with respect to Al, thus inducing TiAl₂ (Al enrichment) formation at the deepest level of the layers for all samples. On the contrary, Ti_xSi_y behaves as a barrier to the outward diffusion of Al.

6.4.2 Effect of oxidation on the compositional evolution

The oxidation mechanism observed in the coating system exposed to air (oxygen) at 900°C for 100 h is first attributed to superficial oxidation and the growth of oxides at the oxide-zone 1 interface. Such oxidation behavior is strongly related to the composition of the top layer (zone 1), particularly enhanced by the presence of a noble element (Pt) as well as more reactive elements (Si, Al). Oxygen atoms dissolve into the external surface of the top layer (zone 1) to react with the less noble elements (*i.e.*, Si, Al) that outward diffuse from the Pt_xSi_y-Pt_xAl_y compounds already present at

zone 1. This leads to the formation of oxide compounds (SiO₂ and Al₂O₃), while causing subsequent consumption of the Si and Al and leaving localized Pt surrounding the oxide. Once the first layer of oxide develops, the oxygen anions continue to diffuse inward through the oxide scale, and the reactive elements (Si and Al cations) continue to outward diffuse.

From this behavior, one can deduce that the total depth of oxidation is a function of the constant supply of reactive species (Si and Al cations) according to a diffusion-controlled process (parabolic contribution) and their reaction with oxygen at the oxide-zone 1 interface. In addition, solid-state interface reactions (linear contribution) lead to the formation of mixed kinetic contributions, with parabolic and linear regimes, suggesting that the continuous supply of the active diffusing elements (Si and Al cations) at the oxide-zone 1 interface is the limiting oxidation step.

As estimated from the SEM images (Figure 6.5) and the thicknesses increase of zone 1 after oxidation (Figure 6.8(a)), the samples exhibiting a higher Pt content display a higher thickness increase of the top layer to about ~5.1 μ m (37 at.% Pt) and 2.9 μ m (34 at.% Pt), respectively, associated with a more pronounced Pt precipitation produced during the oxide formation, and probably due to a higher concentration of defects (caused by the microstructural characteristic of these samples, as observed and described after thermal annealing) that accelerated the transport mechanism of the diffusing elements. On the contrary, the Si-rich samples exhibit a more compact microstructure, confirmed by a lower increase (of about ~2.2 μ m) in thickness.

The behavior described above underlines the role of the sublayers in the multilayer structure in which the $Pt_xSi_y-Pt_xAl_y$ top layer acts as a continuous reservoir of Al and Si which supplies and maintains the exclusive growth of protective oxides (Al₂O₃ and SiO₂) not allowing TiO₂ to form. The protective nature of such oxide scale is particularly indicated by the restriction of the TiO₂ growth, which difference in their growth rate with respect to the one of Al₂O₃ appears significant (Al₂O₃ - $k_{p at 900 \circ C} \sim 10^{-10}$ -10⁻¹⁴ · cm⁻⁴ · h⁻¹; TiO₂ - $k_{p at 900 \circ C} \sim 10^{-4} g^2$ · cm⁻⁴ · h⁻¹) [177, 156].

The composition of zone 2 by itself offers efficient oxidation protection since it provides a secondary Si reservoir for the SiO₂ growth (by outward displacement of zone 2). In addition, the Ti_xSi_y layer effectively captures the Ti ions (limiting Ti activity) that outward diffuse from the substrate and hinders their interaction with oxygen to avoid TiO₂ formation.

6.4.3 Oxidation mechanism and microstructural changes

To describe the oxidation mechanism and the microstructural changes due to oxidation of the multilayer Si-Pt reservoirs, a phenomenological model schematically presented in Figure 6.9 is proposed.

Panel A shows the multilayer arrangement obtained after the vacuum thermal treatment with a dendritic type of structure within the top layer and a higher Si content (80 at.% Si vs 20 at.% Pt) and a lower thickness ($6.8 \mu m$ Si-Pt).

Panel B shows a multilayer system for the sample with a columnar microstructure, which contained a different Si-Pt ratio (66 at.% Si - 34 at.% Pt) and a higher Si-Pt reservoir (12.2 μm).

Panels C and D present the different diffusion processes and reactions occurring during oxidation for both types of multilayered systems after thermal annealing; they can be described as follows:

At **Interface 1**, located at the top surface of zone 1 in contact with the atmosphere, the oxidation reaction occurs through outward diffusion of Si and Al cations and their subsequent reaction with the oxygen anions at the oxygen-zone 1 interface. The mixed oxide scale growth is followed by inward diffusion of oxygen anions throughout the oxide scale, and the inward displacement of the elements (Si, Al) in zone 1 (towards interface 1), and zone 2 (towards interface 2).

At **Interface 2**, there is mostly Si outward diffusion, that continues to feed the Si-O reaction, while depleting the thickness of zone 2 (Pt_xSi_y) due to their continuous consumption. This is particularly observed with a lower initial Si-Pt thickness (Panel C).In the region located between the interdiffusion A and zone 2 (**Interface 3**), the interface reactions involving Si, Ti, and Pt induced a decrease of thickness at the interdiffusion zone A, illustrated in Panel E for the sample containing 80 at.% Si and 20 at.% Pt, or their complete depletion, as illustrated in Panel F for the sample containing 66 at.% Si and 34 at.% Pt, in which a significant thickness increase of zone 2 has been observed.

At **interface 4**, for the sample shown in Panel D, accelerated interface reactions are suggested between zone 3 and the interdiffusion zone A, which leads to recombination of both layers towards the outer layers (into zone 2). The reactions between the interdiffusion zone B and zone 3 (**interface 5**) involve feeding of the Ti_xSi_y reaction for both types of multilayers, which gives rise to an increase in the thickness of zone 3 (Panel E) or zone 2 (Panel F).

Interface 6 involves the outward migration of Ti from the base material towards interdiffusion zone B (with Ti-Si-Al composition), which creates deeper Al enrichment while depleting the previous composition and decreasing the thickness of the interdiffusion zone B. The main diffusional transport at **interface 7**, between the substrate and the Al enriched zone, is Ti outward diffusion which contributes to deeper Al enrichment.

Interface 3, **interface 4**, and **interface 5**, which comprise the two interdiffusion zones, respectively, are the ones with a high energetic disorder, and which more significantly promote the microstructural re-organization of the multilayers.



Figure 6.9: Schematic illustration of the formation of self-organized multilayers based on Si-Pt reservoir due to oxidation at 900°C.

6.5 Conclusions

In the present study, we investigated the protection of γ -TiAl substrates by applying novel Si-Ptbased magnetron sputtered coatings. Following vacuum thermal annealing (750 °C) and subsequent oxidation in ambient air at 900 °C, the coatings exhibit a self-organized multilayer architecture with varied thicknesses of the individual layers corresponding to different phases and compositions including Pt_xAl_y, Ti_xSi_y, and Pt_xSi_y compounds. Specifically, the surface oxidation mechanism and interface reactions were shown to depend on the initial Si-Pt reservoir, namely its thickness and Si/Pt ratio. The hierarchical phase formation, graded composition, and microstructural evolution were described by taking into consideration the thermodynamic and diffusional characteristics of the elements and compounds involved in shaping the multilayered systems.

In particular, we demonstrated that the presence of Pt_xSi_y , Pt_xAl_y , and Ti_xSi_y layers acts as a diffusion barrier against Ti outward diffusion to the outer-most layer. As a result, no TiO₂ layer was found at the surface, rendering the self-organized Si-Pt-based structure a promising candidate for the protection against oxidation for different applications including aerospace, manufacturing, energy, and other sectors.

As a future perspective for this work, a detailed evaluation of the mechanical properties (such as tensile strength, creep, fatigue, etc.) of the Si-Pt based multilayer coating systems is necessary to provide a holistic understanding of the microstructure-mechanical property relationship, that is a cornerstone for their practical implementation for use in high-temperature and other harsh environments.

CHAPTER 7 GENERAL DISCUSSION

This chapter offers a discussion of the elements of the present Ph.D. project: (a) The main achievements and findings attained in this work. (b) The relevance of the methodology proposed and results in the field of oxygen diffusion barriers and related subjects are reviewed by comparing them with available literature. (c) Limitations are acknowledged, and (d) recommendations for future developments are indicated. (e) Further insights are established through new questions linked to this research. Additionally, (f) the different coatings generated in the framework of this collaborative research between SAFRAN and FCSEL are compared in terms of their oxidation behavior.

7.1 (a) Main achievements and findings attained in this Ph.D. project

Three main objectives were established for this Ph.D. project; the 1st and 2nd objectives comprised understanding of the influence of Si and Si-Pt reservoirs (thickness, compositional ratio) and thermal annealing conditions (temperature and treatment duration) on the microstructural characteristics (growth and evolution) of Si- and Si-Pt based coatings respectively, and their correlation to high-temperature oxidation.

In this context, a summary of the different multilayered coating systems developed in this work is presented in Figure 7.1. Three main coatings architectures were effectively fabricated by magnetron sputtering and thermal annealing processes. A multi-zone structure, Ti_xSi_y/γ -TiAl, has been obtained based on Si reservoir, and multi-layered structures, Pt_xSi_y , Pt_xAl_y / Ti_xSi_y/γ -TiAl, based on Si-Pt reservoirs.

For each system, it was possible to determine the very particular effect of initial growth conditions by tracking the thickness progression for each zone/or/layer though describing their microstructural characteristics, and by linking those to the most probable thermo-chemical factors influencing the growth behavior of the layers; from this, more precise tuning of the growth of the layers can be implemented when designing such types of coating systems.

Through determining the microstructural characteristics before and after oxidation, a comparative phenomenological description for each system was established, elucidating the differences in the oxide scale mechanism and their specific oxide scale structure, as well as the evolution of the layers in terms of composition and thickness.

Particularly for the Ti_xSi_y/γ -TiAl multi-zone structure, the coated systems with low Si reservoirs (3µm) and diffusion-controlled oxidation process with a parabolic behavior were confirmed according to kinetic estimations (presented in Chapter 5). Still, in such systems, Ti activity was not decreased as effectively to completely limit the TiO₂ growth.

A more protective oxide formation, with a mixed Si and Al oxide composition (SiO₂+Al₂O₃), has been attained when increasing the Si reservoirs to $\geq 6\mu$ m Si thick or higher (i.e., 9.5 µm Si), in which their interdiffusion zone (Ti_x(Al,Si)_y) acts as a Ti trap via the Ti-Si reaction, that restricts outward diffusion of Ti from the base material. It was demonstrated that phase transformation or chemical reactions between the top layer and the inner zones (i.e., Interdiffusion/Ti_xSi_y layer) were strongly influenced by the initial Si reservoir. The degradation mechanism of the Ti_xSi_y/ γ -TiAl is based on the depletion of the protective elements (Si) in the Ti_xSi_y layer and in the Interdiffusion zone. A more complex system was developed with the Si-Pt-based multilayer coatings, in which an oxide scale with a fully protective oxide nature (SiO₂/Al₂O₃ + Pt) has been observed. In this coating architecture, each layer can serve either as a Si-Al reservoir or as a Ti trap via the Ti_xSi_y reaction. Specifically, the role of each layer has been elucidated, the particular composition of the top layer provided Si and Al reservoir for the SiO₂/Al₂O₃ formation, while the second layer (Pt_xSi_y) acts as a secondary reservoir for Si, and the deeper inner layers [(Pt,Ti)_xSi_y, Ti_xSi_y, Ti_x(Al,Si)_y (Pt,Ti)_xAl_y], each one, respectively, providing an effective Ti diffusion barrier.

The 3rd objective consisted of the establishment/proposition of an optimum design of Si- and/or Si-Pt-based diffusion coating systems for the γ -TiAl substrate. A limited coating degradation was confirmed for each coating system developed, and the protective oxide scale formation was revealed (by mostly SiO₂ and Al₂O₃ oxide formation). In addition, complete restriction of inward oxygen transport towards the substrate or the inner layers has been shown, while each coating system could be potentially used as a protective oxygen diffusion barrier for the γ -TiAl base material. It can be stated that the Si-Pt-based multilayered coating system with high Si content (63-80 Si/20-37 Pt, at.%) would offer the most effective oxidation behavior in terms of full restriction of the TiO₂ formation while providing additional reservoirs of the protective elements due to the inner layer compositions that remained rich in Si and Pt. Microstructurally, the dendritic type of microstructure, attained with the highest Si content (80 at.%) would offer the most restricted diffusional paths for oxygen, as elucidated by the lower thickness of oxide scale formation of their more compact microstructure.



Figure 7.1: Summary of the different coating systems developed in this Ph.D. project and their multilayer structure. Si coatings labeled as (i) are presented in Chapter 5; Si-Pt coatings with high Si content and labeled as (ii) are presented in Chapter 6; Si-Pt coatings with high Pt content and labeled as (iii) are presented in Appendix A

7.2 (b) The relevance of the proposed methodology in the field of oxygen diffusion barriers

The relevance of this work resides in the contribution of new developments in terms of novel compositions and multi-component coating architectures in the field of oxidation-resistant coatings for high-temperature applications, oxygen diffusion barriers, and related areas.

As has been stated in the literature review, the already explored multilayer coating systems or smart coating systems are relatively less often reported, in comparison to more simple coating designs (one layer- or bi-layer structures) [10,178], due to the use of multiple processes which imply added complexity. In this sense, the multizone Si-based/multilayer Si-Pt-based coatings fabricated in this project demonstrate the feasibility and bring the possibility for the advancement of such coating developments on TiAl-based alloys. This counterweighted the majority of the complex coating systems that have been mostly optimized for Ni-based substrates [10,178].

Among the protective oxide scales, Al_2O_3 exhibits the highest oxidation resistance temperature (>900°C, up to the melting point of the blade). Additionally, the Cr enrichment observed in some of the coatings, supports the beneficial Al_2O_3 formation, since Cr decreases the critical Al content needed for Al_2O_3 growth [179]. Particularly, the Si-Pt multilayer system is very unique in terms of the chemical constitution (multi-component nature), for which there are no comparable coating systems (Si-Pt based compounds in multilayered architecture) reported in the literature. The resulting multi oxide scale formation (SiO₂, Al_2O_3 , Cr) when oxidized offers a broad temperature range of oxidation protection for high-temperature applications.

The performance attained by Si-based multizone coatings (with 3µm of initial Si thickness), is comparable (one order of magnitude lower for the coated system)[180] to the reports for coatings of a similar constitution (tested at similar oxidation conditions) [155,181,182]. Since the oxidation product confirmed in the Si-based coating systems developed and exhibit mostly SiO₂, they could provide a good cyclic oxidation resistance response [179] due to significant SiO₂ formation.

In the context of the diffusion transport mechanism, this work contributes by approaching the diffusional process via the microstructure control which has not been explored before in coating systems, but mostly in bulk materials [183]. Regarding the applicability of the coating systems in

turbine blade components, the present coating systems could potentially be suitable as a bond coat technology [184,185].

7.3 (c-d) Limitations and recommendations for future developments

In terms of characterization methods, combined chemical surface analysis techniques (i.e., EDS) and bulk structural analysis (XRD) were applied to obtain a complete overview of the phases within the multizone/multilayered coating systems. However, for future developments, it could be of great benefit to include additional techniques such as Field Emission Scanning Electron Microscopy-Electron Backscatter Diffraction (FSEM-EBSD) and Ion Mass Spectroscopy (SIMS) to determine the compositional distributions with an increased resolution that would help to describe the diffusion transport process with improved accuracy. For compositional analysis, higher sensitivity and improved spatial resolution could be achieved by SIMS measurements, and particularly for oxide scales characterization, detailed crystallographic information could be acquired with inversed pole figures (IPF) in EBSD. The implementation of RBS-ERD could also be relevant to measuring elemental diffusivities and hence increasing understanding of the transport process in the multilayered systems.

Further quantitative insights into the kinetics of oxidation of the Si-Pt-based coatings could be reached by additional TGA analyses. Particularly, these sets of samples were already produced, but not analyzed due to the unavailability of the scheduled TGA system; those kinetics results will allow one to further study the oxidation kinetic of Si-Pt-based coatings characteristics in the future.

7.4 (e) Further work: New questions linked to this research

New questions linked to this work, are related to the evaluation of the mechanical properties such as tensile strength, creep properties of the multilayer coating systems to clarify the microstructuremechanical properties relationship.

The main question to address is if the mechanical testing results (such as Young's modulus (~185 MPa or above), high-temperature yield strength (~400 MPa or above), and high creep strain rate (>10⁻⁴ s⁻¹)) [186-188] of the coating systems considered in this study would accelerate practical implementation in structural applications in high-temperature environments.

7.5 (f) Summary of coatings generated during the collaborative research between SAFRAN and FCSEL

The coating architectures prepared by other complementary approaches in the framework of this collaborative research project are summarized in Table 7.1. The table includes coating architecture, oxide scale nature, and kinetic oxidation parameters of the base material γ -TiAl and of the coating/substrate systems. It can be observed that each methodology results in a unique coating architecture with a very particular oxide scale formation.

In the coating system produced by the halogen effect [188], the Al_2O_3 was attained, as confirmed by the specific oxide scale constitution. On the other hand, for the Si-B-C-N coatings [189], the oxide scale consisted exclusively of SiO₂. It is important to mention that the Si-B-C-N coatings consist of a Ti_xSi_y interlayer, that has been developed based on the deposition of Si reservoir and simultaneous vacuum thermal annealing process inspired by the work of this Ph.D. project.

All coated systems exhibited a protective nature, with slow growth and thermodynamically stable oxides (SiO₂, Al₂O₃). A protective performance for the coating systems fabricated in this framework of research [180,189-191] is confirmed by comparing their oxidation kinetic regimes with those reported at similar oxidation conditions [192-197]. In all cases, the oxidation kinetics of at least one order of magnitude slower than the uncoated substrate have been reached.

Table 7.1: Summary of coating systems developed during the collaboration of FCSEL with

As deposited	Coating architecture	Oxidation	Kinetic regime
coating system	and main constituents	conditions	Linear: k_{i} (g cm ⁻² s ⁻¹)
/Reference		and oxide	Parabolic: k_p (g ² cm ⁻⁴ s ⁻¹)
		scale	
		composition	
<u>Si-based coatings</u> J. Crespo [180]	Graded composition, Multizones Ti _x Si _y	900°C, 100 h SiO ₂ , Al ₂ O ₃ , Cr, TiO ₂	Uncoated: k _i : 3.5 x 10 ⁻¹¹ k _p : 6.4 x 10 ⁻¹¹ <u>Coated:</u> k _p : 3.5-8.9 x 10 ⁻¹²
<u>Si-Pt based coatings</u> Pt rich content Si-rich content	Graded composition, Multilayer Pt _x Al _y , Pt _x Si _y , Ti _x Si _y , Pt _x Si _y , Pt _x Al _y , Ti _x Si _y	900°C, 100 h Al ₂ O ₃ , SiO ₂ , TiO ₂ SiO ₂ , Al ₂ O ₃ , Pt	Not tested Not tested
J. Crespo [191]			
Amorphous Si-B-C- N coatings with a-Si interlayer V. Simova [190]	Graded composition, Bi-layer Ti _x Si _y /Si-B-C-N	800°C, 100 h SiO ₂	Uncoated: k _p : 3.1 x 10 ⁻¹² <u>Coated:</u> k _p : 6.5 x 10 ⁻¹⁴
AlOF coatings	Graded composition, Bi-layer	875°C, 100 h TiO2, Al2O3	Uncoated: kp:1.0 x 10 ⁻⁸
F. Bergeron [189]		2, 2-5	k _p :1.0 x 10 ⁻⁹

SAFRAN.

CHAPTER 8 CONCLUSIONS AND PERSPECTIVES

This chapter summarizes the main contributions of this Ph.D. work, with particular emphasis on the main findings, gained insights, and future perspectives for the development of oxidation-resistant coatings for γ -TiAl materials.

8.1 Conclusions

This research work has reported a novel surface engineering methodology for the development of a multilayered oxygen diffusion barrier for the γ -TiAl alloy, based on Si and Si/Pt surface enrichment and induced diffusional transport.

Through the plasma sputter cleaning process, the surface of the base material was effectively prepared for the deposition by removing the naturally formed oxide layer and external adsorbates, without modifying the composition, microstructure, and mechanical properties of the γ -TiAl alloy.

The proposed and investigated approaches have demonstrated a possibility to change the oxidation mechanism of γ -TiAl by effectively decreasing the formation of the titanium oxide scale; This has been replaced by depositing Si reservoirs leading to the formation of a Ti_xSi_y/ γ -TiAl multi-zone structure that prevents diffusion of oxygen from the surface toward the substrate bulk as well as out-diffusion of Ti from the bulk while protecting against high-temperature oxidation at 900°C.

In addition, this study described the fabrication of a novel Si-Pt-based multilayer coating system with a complex oxygen diffusion barrier architecture, in which varied initial Si-Pt reservoirs (thickness and the Si/Pt ratio) influence their oxidation behavior. The hierarchical phase formation, graded composition, and microstructure evolution were described taking into consideration thermodynamic and diffusion aspects of the elements and compounds involved in the multi-layered coating systems. The influence of each layer on the oxidation behavior was elucidated. It particularly provided an understanding about the impact of the reservoir of the protective elements and their interaction with the substrate materials, the mechanism of the interaction for the multilayered growth, and their further microstructural evolution due to oxidation.

Among the Si-Pt systems, in those with Si rich compositions, the TiO_2 layer was fully restricted during the total exposure time (100 h), making this structure a potential candidate for the protection

against oxygen inward diffusion into the γ -TiAl when exposed to high-temperature environments, such as in the low-pressure turbine of the jet engine.

This study contributes to the design of effective Si-containing oxidation-resistant coating systems and proposes the development of new and more robust films based on Si/Pt compounds that provide a continuous reservoir for the protective oxides to grow while restricting the undesired outward diffusion of substrate elements, in particular Ti.

This project benefited from a holistic approach applied to the development of such systems, by combining film fabrication methods, self-organization of the microstructure, and specifically controlling and understanding of the oxidation process.

8.2 Perspectives

The development of new multilayered coating systems based on Si and Si-Pt reservoirs has effectively been attained and demonstrated, and their oxidation protection mechanism has been elucidated. Future acceptance and implementation of the demonstrated approaches will further be enhanced by optimizing the coatings' mechanical performance. Suitable film architectures can thus be employed as complex oxygen diffusion barrier systems or as effective bond coats in the existing or new thermal barrier coatings (TBCs).

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APPENDIX A SI-PT BASED COATINGS GROWTH BY THERMAL ANNEALING AT 950°C ON γ-TIAI AND THEIR MICROSTRUCTURAL EVOLUTION DUE TO HIGH-TEMPERATURE OXIDATION

This chapter presents the growth of a Si-Pt multilayer system, under the influence of an annealing temperature of 950°C. The effect of (i) a Si-Pt reservoir in the range of 3-5 μ m as well as (ii) a richer Pt content with respect to Si (40Si-60Pt, at.%) and their effect in the growth of the multilayer system are addressed, subsequently, their microstructural evolution and oxidation behavior are discussed.

A.1 Growth of the multilayer Si-Pt/γ-TiAl system at 950 °C, influenced by Si-Pt reservoir (thickness) and thermal annealing time

Microstructure of the coatings

Si-Pt reservoirs of 3, 4, and 5 μ m thick were deposited by magnetron co-sputtering and thermally annealed in a vacuum for 8 h or 16 h respectively at 950°C. By EDS mappings (Figure A.1(a)) and compositional profiles (Figure A.1(b)), the chemical nature of the layers before thermal annealing was investigated.

Both elements (Si and Pt) appear homogeneously distributed throughout the as-deposited Si-Pt coating, and their composition was estimated at around 60 at.% of Pt and 40 at.% of Si prior to thermal annealing for all the samples.

Subsequently, all samples were thermally treated at a temperature of 950 °C, sample with 3 μ m of Si-Pt reservoir was annealed for 16 h, while those deposited with 4 μ m and 5 μ m of Si-Pt were annealed for 8 h.

By XRD measurements (Figure A.2) the crystallinity of the as-deposited Si-Pt reservoir and thermally annealed samples was investigated. On the as-deposited coatings, it is observed in addition to the characteristic peaks of the base material (tetragonal γ -TiAl), mostly PtSi (orthorhombic) and some Pt₂Si (tetragonal) phases.

After thermal annealing, a rich composition was confirmed by the diffracted signals. From which the crystallographic peaks the related to γ -TiAl substrate, as well as diverse platinum aluminides


Figure A.1: (a) EDS mapping and (b) compositional profile of a 3µm thick Si-Pt as-deposited coating before thermal annealing.



Figure A.2: (a) XRD pattern of the as-deposited Si-Pt layer, (b) XRD phases of the coating after thermal annealing at 950°C.

EDS mappings obtained after thermal annealing are presented in Figure A.3. For all samples, the hierarchical composition observed through the multilayers was established by the elemental transport – diffusion – that occurs during annealing.

Additionally, the elemental distribution depth which determines the thickness of the different layers was particularly influenced by the initial Si-Pt reservoir (thickness).

The top layer appeared brittle and less compact, while the deeper layers appeared very dense. The outward diffusion of the elements from the substrate is confirmed with the presence of either Ti or Al in some of the layers. Nb and Cr although not included in the EDS mappings below (Figure A.3), are not observed in the multilayer after annealing, and neither is oxygen.

	3 μm SiPt + 16h T	A			
a)					
	y−TiAl Substrate 10 μm	<u>10 μm</u>	10 μm	10 μm	10 μm
	4 μm SiPt + 8h TA	Pt	Si	Ti	Al
b)	Constitution of the second	AND SUPERARY	n a fair a fa		
	y−TiAl Substrate				
	10 µm	10 µm	10 µm	10 µm	10 µm
	5 μm SiPt + 8h TA				
c)		Mener Manager	ACALAR ET BOAL		A Share and the second second
	γ−TiAl Substrate				
		10 µm	10 µm	10 µm	10 um

Figure A.3: SEM image-EDS mapping of (a) 3 µm thick Si-Pt+16h TA; (b) 4 µm thick Si-Pt+8h TA and (c) 5 µm thick Pt-Si/+8h TA.

After annealing, different regions are distinguished throughout the EDS mappings, each one is designated according to their constitution (L1) $Pt_xAl_y-Pt_xSi_y - top$ layer, (L2) $Pt_xSi_y-Ti_xSi_y$ or $(Pt,Ti)_xSi_y$, (L3) Pt-Ti-Al or $(Pt,Ti)_xAl_y$. The compositional profile for the sample with 3µm of Si-Pt and 16 h of thermal annealing, is shown in Figure A.4.

7.5 μ m of thickness is the total growth for this multilayer system, distributed as follows. On the first layer (**L1**) of 2.4 μ m, higher Al content to Pt is identified, most probably related to PtAl₃ and PtAl₂ compounds; the second layer (**L2**) of 3.9 μ m thick, is composed of mostly PtSi (1.5 μ m thick)

and some Pt_5Al_3 ; while beneath there is TiSi, Ti₅Si₃ (2.4 µm thick). The deeper layer (L3) of 1.2 µm thick is related to Pt-Ti-Al.



Figure A.4: EDS compositional profiles of 3 μ m thick Si-Pt +16 h TA.

The semiquantitative compositional profile for a sample with 4 μ m of Pt-Si layer with 8 h of TA is presented in Figure A.5. From it, the formation of a 12 μ m thick coating system is observed. The top layer located further from the substrate, and which exhibits porosity is composed of 3.7 μ m of mixed Pt_xAl_y and Pt_xSi_y compounds (most probably: PtAl₂, PtAl, and PtSi). The second layer of 6.1 μ m thick, is distributed in two different regions of compositions, the thickest one is related to PtSi compound (5.1 μ m) and Pt₅Al₃, with a thin layer of TiSi (1 μ m). The third layer of 2.2 μ m thick is associated with Pt-Ti-AL.



Figure A.5: EDS compositional profiles of 4 µm thick Si-Pt+8 h TA.

The compositional profile of the sample with 5 μ m of PtSi and 8 h of TA is shown in Figure A.6. It shows the formation of 14.4 μ m of the coating system, the layers that grow were distributed similarly to the previous, with their particular thickness. First 4.4 μ m of PtAl and PtAl₂, as well as some PtSi. Subsequently, 5.6 μ m of PtSi and Pt₅Al₃, followed by a 1 μ m thick of TiSi. Pt-Ti-Al appears as the deepest layer at 3.4 μ m thick.



Figure A.6: EDS compositional profiles of 5 µm thick Si-Pt +8 h TA.

Table A.1 Summarizes the thickness and main phases of the different layers identified by EDS for each sample. From the observations performed by SEM and the semiquantitative estimation obtained by EDS compositional profiles, it is confirmed that the higher the initial thickness of Si-Pt reservoir, the thicker the layers that grow, as was observed for all the layers containing Pt-based compounds, a particular growth tendency is observed on the layer constituted of exclusively Ti_xSi_y compound (TiSi, Ti_5Si_3) at the inner layer (L2), which thickness decreased as the initial Si-Pt reservoir becomes higher. Platinum aluminides with richer Al content are observed at the top layer (L1) with a lower Si-Pt reservoir (3 µm).

	Thickness and composition of the layers						
Sample	3 μm SiPt +16h TA at		4 μm SiPt+8h TA at 950°C		5 µm SiPt+8h TA at 950°C		
	950°C						
	Thickness	Stoichiometry	Thickness	Stoichiometry	Thickness	Stoichiometry	
Layer 1	2.4 µm	PtAl ₃ and PtAl ₂	3.7 µm	PtAl, PtAl ₂ and	4.4 μm	PtAl, PtAl ₂ and	
(L1)				PtSi		PtSi	
Layer 2	2.4 µm	PtSi, Pt5Al3	5.1 µm	PtSi, Pt5Al3	5.6 µm	PtSi, Pt ₅ Al ₃	
(L2)	1.5 µm	TiSi, Ti ₅ Si ₃	1.0 μm	TiSi	1.0 μm	TiSi	
		(33-6)Pt-(33)Si-		(33-22)Pt-(33)Si-		(33)Pt-(22-33)Si-	
		(22-11)Al-(22-		(22-11)Al-(22-		(22-6)Al-(33)Ti	
		55)Ti		33)Ti		at.%	
		at.%		at.%			
Layer 3	1.2 μm	Pt-Ti-AL	2.2 µm	Pt-Ti-AL	3.4 µm	Pt-Ti-AL	
(L3)		(20)Pt-(40)Ti-		(20)Pt-(40)Ti-		(20)Pt-(40)Ti-	
		(40)Al at.%		(40)Al at.%		(40)Al at.%	

Table A.1: Thickness and composition of the growth of the Pt-Si based coating on γ -TiAl by semiquantitative surface analysis (EDS).

A.2 Oxidation of the Si-Pt based coatings at 900 °C and their microstructural evolution

The thermally annealed samples (Si-Pt based coatings deposited on γ -TiAl) were oxidized in the air for 100 h in a conventional oven, at 900°C. The evolution of the samples after thermal exposure was assessed by XRD and is presented in Figure A.7.

All the XRD signal characteristics of the substrate and related to the Pt_xAl_y compounds (Pt_2Al_3 , Pt_5Al_3 , $PtAl_3$



Figure A.7: Comparison of the XRD diffraction pattern of the 4 μ m thick+8 h TA (purple), 5 μ m+8 h TA (green) and (violet) 3 μ m+16 h TA Pt-Si

SEM cross-sectional images obtained after oxidation and their EDS elemental mapping of the oxygen at the multilayer system is shown in Figure A.8, while the other constituting elements it is shown in Figure A.9.

In Figure A.8, it can be observed that the main multilayer arrangement is maintained after oxidation, with the most significant morphological and compositional changes are observed at the top layer, i.e., as revealed by the darker contrast in the top layer, in comparison to the one seen before oxidation.

For all oxidized samples, oxygen distribution appears restricted into the top layers, and particularly more effectively contained in the top layer for a sample with 5 μ m of Si-Pt.



Figure A.8: (a-c) Cross-sectional SEM images and (d-f) EDS mapping of the oxygen signal for the Si-Pt-based multilayer on γ -TiAl after 100 h oxidation in air at 900 °C.



Figure A.9: SEM image and EDS mapping of Si-Pt multilayer coating system on γ -TiAl after 100 h of oxidation in air at 900°C; (a) 3 μ m thick Si-Pt+16 h TA, (b) 4 μ m thick Si-Pt+8 h TA and (c) 5 μ m thick Si-Pt+8 h TA.

Compositional distribution of the layers after oxidation is described in Figure A.10, Figure A.11, and Figure A.12. For a sample with 3μ m of Si-Pt +16h of TA sample (Figure A.10) oxygen within the first 5.5 µm of depth (top layer), in which composition is related to mixed oxides of mostly SiO₂ and Al₂O₃ and of TiO₂, as well as remanent platinum-based compounds (PtAl and PtSi). The second layer (L2) of 3.3 µm thick, exhibits a rich constitution related to PtSi, PtAl₃, and TiSi, Ti₅Si₃. The bottom layer (L3) shows to be composed of Al, Ti, and Pt. The oxygen content estimated for all samples is in a range of 55 to 63 at.%.

From Figure A.11 (a) and (b), it can be observed the EDS elemental mapping and compositional profile of the 4 μ m of Si-Pt with 8 h of TA sample respectively. The first layer of 6.0 μ m thick exhibits similar composition to the previous sample (Al₂O₃, SiO₂, and TiO₂, as well as PtSi and PtAl). A similar thickness (5.5 μ m) is estimated for the second layer (L2), where it is as well noticed

the presence of mixed composition (mostly PtSi with minor PtAl content, as well as TiSi, Ti₅Si₃ beneath). At the bottom of the multilayer (L3) an Pt-Ti-Al layer of 2 μ m of thickness is confirmed.



Figure A.10: (a) SEM and (b) EDS compositional profiles of 3 μ m thick Si-Pt+16 h TA based coating growth on γ -TiAl after 100 h of oxidation in air at 900 °C.



Figure A.11: (a) SEM image and b) EDS compositional profiles of 4 μ m+8 h TA, Pt-Si based coating growth on γ -TiAl after 100 h of oxidation in air at 900 °C.

In comparison to previous samples, a slightly different distribution of the elemental composition is observed for the 5 μ m of Pt-Si with 8h of TA sample (Figure A-12), their composition at the top layer of 7 μ m thick suggest (Al₂O₃, SiO₂, and PtAl), as well as a lower Si content than before oxidation, suggesting none PtSi compound at the first layer. From their cross-sectional image, it can be seen a well-defined thin layer of TiO₂ is located at the bottom of the first layer (L1). The inner layer (L2) of 5 μ m thick exhibited a much higher Pt content, or Pt₅Al₃ compound, as well as PtSi and TiSi. A higher thickness (4 μ m) is estimated for the third layer (L3), which exhibited as well higher Pt content but was also associated with Al and Ti (Al-Ti-Pt).



Figure A12: (a) SEM and (b) EDS compositional profiles of a 5 μ m thick Pt-Si +8 h TA-based coating growth on γ -TiAl after 100 h of oxidation in air at 900 °C.

61.	Thickness of the layers and semiquantitative composition						
Sample	3μm SiPt 8h TA		4µm SiPt 8h TA		5µm SiPt 16h TA		
	Thickn	Stoichiometry	Thickness	Stoichiometry	Thicknes	Stoichiometry	
	ess				S		
Layer 1	5.5 µm	Al ₂ O ₃ , SiO ₂ ,	6.0 µm	Al ₂ O ₃ , SiO ₂ ,	7 µm	Al ₂ O ₃ , SiO ₂ ,	
(L1)		TiO ₂ , PtAl, PtSi		TiO ₂ , PtAl, PtSi		TiO ₂ , PtAl, PtSi,	
						Pt ₂ Si	
Layer 2	2.5 µm	PtSi,PtAl ₃ ,	5.0 µm	PtSi, PtAl,	4.5 µm	PtSi, Pt ₂ Si, PtAl	
(L2)	0.8 µm	TiSi,Ti ₅ Si ₃	0.5 μm	TiSi, Ti ₅ Si ₃	0.5 µm	TiSi	
		(26-13)Pt-(26-0)Si-		(21-28)Pt-(21-7)Si-		(14-35)Pt-(21-	
		(6-39)Al-(26-		(6-21)Al-(25-42)Ti-		28)Si-	
		45)Ti-(16-0)O		(22-0)O		(21-7)Al-(17-	
		at.%		at.%		34)Ti-(21-0)O	
						at.%	
Layer 3	1.3 µm	Pt-Ti-Al	2.0 µm	Pt-Ti-Al	4 µm	Al-Ti-Pt	
(L3)		(10Pt-45Ti-45)		(10Pt-45Ti-45)		(25Pt-35Ti-40Pt)	
		at.		at.%		at.%	

Table A.2: Thickness and composition of the layers after 100 h of oxidation at 900 °C.

A.3 Discussion about the growth of the multilayer and their evolution after oxidation

From the microstructural observations on the multilayer system, the growth of the layers suggests that as the Si-Pt initial reservoir increased, the total thickness of the multilayer structure increased, as well as the Si and Pt inward diffusion. Particularly the inward diffusion of Pt appeared deeper than Si, most probably due to the higher initial Pt content with respect to Si (60 at. % Pt - 40 at.% Si), which could have increased the Pt flux that diffused towards the inner layers, as confirmed by the deepest layer of Pt-based composition (Pt-Ti-Al), while the thermal annealing time influence mostly the stoichiometry of the compounds that are formed.

For all coated systems, the layer containing platinum silicide was the thickest, promoted by their lower energy of formation (Pt₂Si: 28.8 kJ/mol, PtSi: 33 kJ/mol; Pt₃Al: 70 kJ/mol, Pt₂Al:88 kJ/mol, Pt₂Al₃: 95 kJ/mol, PtAl₂: 84 kJ/mol; TiSi₂: 45 kJ/mol, TiSi: 65 kJ/mol, Ti₅Si₃: 72.5 kJ/mol, Ti₅Si₄: 81 kJ/mol) [21-23]. The growth of Pt_xSi_y at the top layer did not require diffusion paths for their formation, since the Si-Pt reservoir is already at the surface before annealing. The lowest thickness observed corresponds to Ti_xSi_y layer, their limited growth was primarily due to the low availability of Si with respect to Pt, and the higher energy of formation of the Ti_xSi_y in comparison to the other Si-containing compound (i.e., PtSi or Pt₂Si).

A schematic of the microstructural evolution of the Pt rich-Si-Pt based multilayers is presented in Figure A.13.

After oxidation, the microstructural evolution of the top layer (L1) involves a thickness increase in the range of 2.3-2.9 μ m (3 μ m +16h TA: 2.9 μ m higher; 4 μ m +8h TA: 2.3 μ m higher; 5 μ m +8h TA: 2.6 μ m higher), originated by the oxygen incorporation into the Pt_xAl_y- Pt_xSi_y layer and the oxide formation between O-Al as well O-Si atoms. Particularly those reactions between Al from the Pt_xAl_y and O from the ambient, promote significant phase transformations at the top layer (I), (i.e., PtAl₃→PtAl; PtAl₂→PtAl, as well as Pt enrichment as in the Pt₂Si observed after oxidation), those type of reactions are detailed below (Equation A.1-Equation A.6). In addition, the PtSi compound at the top layer, feeds the Si-O reaction (Equation A.7-A.8), while promoting as well further Pt availability.

$$\begin{array}{ll} \operatorname{PtAl_{3}} \rightarrow [\operatorname{Pt}]_{(s)} + [\operatorname{Al_{3}}]_{(s)} & (\text{Equation A.1}) \\ [\operatorname{Pt}]_{(s)} + 2[\operatorname{Al_{3}}]_{(s)} + 3[\operatorname{O_{2}}]_{(s)} \rightarrow \operatorname{PtAl} + 3\operatorname{Al_{2}O_{3}} & (\text{Equation A.2}) \\ [\operatorname{Pt}]_{(s)} + 4[\operatorname{Al_{3}}]_{(s)} + 9[\operatorname{O_{2}}]_{(s)} \rightarrow \operatorname{Pt} + 6\operatorname{Al_{2}O_{3}} & (\text{Equation A.3}) \\ \\ \operatorname{PtAl_{2}} \rightarrow [\operatorname{Pt}]_{(s)} + [\operatorname{Al_{2}}]_{(s)} & (\text{Equation A.4}) \\ 2[\operatorname{Pt}]_{(s)} + 3[\operatorname{Al_{2}}]_{(s)} + 3[\operatorname{O_{2}}]_{(s)} \rightarrow 2\operatorname{PtAl} + 2\operatorname{Al_{2}O_{3}} & (\text{Equation A.5}) \\ \\ [\operatorname{Pt}]_{(s)} + 2[\operatorname{Al_{2}}]_{(s)} + 3[\operatorname{O_{2}}]_{(s)} \rightarrow \operatorname{Pt} + 2\operatorname{Al_{2}O_{3}} & (\text{Equation A.6}) \\ \\ \\ \operatorname{PtSi} \rightarrow [\operatorname{Pt}]_{(s)} + [\operatorname{Si}]_{(s)} & (\text{Equation A.7}) \\ \\ [\operatorname{Pt}]_{(s)} + [\operatorname{Si}]_{(s)} + [\operatorname{O_{2}}]_{(s)} \rightarrow \operatorname{Pt} + \operatorname{SiO_{2}} & (\text{Equation A.8}) \end{array}$$

The behavior observed at the inner layer (II) involves two regions of composition, the upper Pt_xAl_y - Pt_xSi_y composition and beneath the Ti_xSi_y composition.

The total thickness of layer II decreased (by 0.6-1.6 μ m range) in comparison to the one estimated before oxidation, particularly influenced by the thickness decrease of the layer with Ti_xSi_y composition; additionally, a different elemental composition (stoichiometry) was noticed after oxidation, caused by redistributions in the mass and of the diffusional flux - solid-state boundary reactions - between adjacent layers. Such as TiSi \rightarrow TiSi+Ti₅Si₃ (Equation A.9-A.10), related to deeper Ti and outward diffusion from the deeper layers (interface 2) and Si out-diffusion towards the Pt_xAl_y- Pt_xSi_y region; On the contrary the upper Pt_xAl_y- Pt_xSi_y layer remained very similar in thickness. But with compositional changes in the Pt_xAl_y, Pt₅Al₃ \rightarrow PtAl (Equation A.11-A.12), due to Al diffusing from deeper layers. The described changes were observed for samples with 3 μ m, 4 μ m, and 5 μ m of initial Si-Pt reservoir respectively.

$$TiSi \rightarrow [Ti]_{(s)} + [Si]_{(s)} \qquad (Equation A.9)$$

$$4[Ti]_{(s)} + 4[Si]_{(s)} + 2[Ti]_{(s)} \rightarrow Ti_5Si_3 + TiSi \qquad (Equation A.10)$$

$$Pt_5Al_3 \rightarrow [Pt_5]_{(s)} + [Al_3]_{(s)} \qquad (Equation A.11)$$

$$[Pt_5]_{(s)} + [Al_3]_{(s)} + 2[Al]_{(s)} \rightarrow 5PtAl \qquad (Equation A.12)$$

For the bottom layer Al-Ti-Pt (III) two different trends were noticed:

The thickness of the Al-Ti-Pt remained very similar to prior oxidation ($\pm 0.2 \ \mu$ m), with minor changes in the elemental distribution (prior oxidation: 40Al-40Ti-20Pt; after oxidation: 45Al-45Ti-10Pt). These were observed for samples with 3 μ m and 4 μ m of initial Si-Pt reservoir. Indicating, the outward diffusion of Ti and Al from the substrate (at interface 3), Pt consumption is due to interface chemical reaction between layers III and II (interface 2).

The thickness of the Al-Ti-Pt increased in comparison to the one estimated prior oxidation (0.6 μ m higher), with noticeable changes in the elemental content (prior oxidation: 40Al-40Ti-20Pt; after oxidation: 40Al-35Ti-25Pt). These were observed for the 5 μ m of the initial Si-Pt reservoir sample. Elucidating, a more significant outward diffusion of Ti and Al from the substrate (at interface 3), and interface chemical reactions between layers III and II (interface 2) that cause Ti consumption from layer II and deeper inward diffusion of Pt from layer III.



Figure A.13: Schematic representation of the microstructural evolution at the interface coating substrate zones after oxidation for a sample with 3 µm thick of Si-Pt and 16 h TA. (Thickness are represented in an aspect ratio 1cm:1µm).

A.4 Conclusions

The oxygen remained restricted mostly at the top layer for the three different systems, with higher Si-Pt reservoirs (4-5 μ m), the oxygen depth was less significant (in which the thickness of the top layer increased by 62% and 59 % respectively) in comparison with lower Si-Pt- reservoir (3 μ m) (with a top layer thickness increasing by 120%). Indicating a more effective oxygen restriction with increased Si-Pt reservoir.

The multilayer obtained with Si-Pt reservoir of 3-5 μ m thickness and vacuum thermal annealing at 950°C lead to a complex hierarchical compositional arrangement that provides (i) oxygen dissolution in a Pt-Si-Al containing matrix, while forming Si and Al oxides (Top layer-layer I), with a continuous reservoir of the reactive elements (Si, Al, Ti) (layer II) and additionally an (III) Pt diffusional barrier layer with enough Pt content to restrict the outward migration of Ti and Al from the substrate

APPENDIX B LIST OF PUBLICATIONS AND CONTRIBUTIONS TO CONFERENCES

Peer reviewed publications related to this work

Crespo-Villegas, J., Cavarroc, M., Knittel, S., Martinu, L., & Klemberg-Sapieha, J. E. (2021). Protective TixSiy coatings for enhanced oxidation resistance of the γ -TiAl alloy at 900° C. Surface and Coatings Technology, 127963.

Crespo-Villegas, J., Cavarroc, M., Knittel, S., Martinu, L., & Klemberg-Sapieha, J. E. (2022). Self-organization of multilayer structure in magnetron sputtered Si-Pt reservoirs on γ -TiAl alloy induced by high-temperature annealing and oxidation. Status: Submitted to Applied Surface Science.

Contributions to conferences

"Protective Ti_xSi_y coatings for enhanced oxidation resistance of the γ -TiAl alloy at 900° C". ICMCTF, oral presentation, San Diego California, 2019.