



Full length article

Synthesis and characterization of $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}/\text{D0}_{23}$ intermetallics: Understanding the stability of silicon substitution

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ABSTRACT

$(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}/\text{D0}_{23}$ are phases that may form in aerospace and automotive aluminium alloys. The substitution of Zr/Ti in these solid solutions is widely reported in the literature; however, it remains relatively unexplored for Si. In this work, *in situ* precipitation of $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}/\text{D0}_{23}$ intermetallics was performed using Al-Si-Zr-Ti alloys. The precipitation, sedimentation and concentration of numerous intermetallic particles were accomplished by filtrating the residual molten aluminium using a temperature/pressure-controlled vessel adapted with a PoDFA filter. A combination of SEM, TEM, XRD and EMP analysis allowed the identification of $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}/\text{D0}_{23}$ intermetallics concentrated within α -FCC matrices of non-Si-doped (sample S2) and Si-doped (samples S4 and S6) alloys. EDS analysis confirmed that Zr and Ti substitute each other in the D0_{22} and D0_{23} phases, whereas Si substitutes in Al sites. Acceptance of Si inside the D0_{23} phase was not expected according to FTlite (FactSage) and TCAL7 (Thermo-Calc) databases. Additionally, Si was found to enhance the formation of $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}$ intermetallics with high Zr-content, contrary to FactSage 7.3 predictions. TEM results showed intermetallic/FCC crystal coherency for samples S2 and S6, implying that these intermetallics acted as nucleation sites for the Al-phase due to their small lattice mismatch. Furthermore, Si site occupancy was calculated for both $(\text{Al},\text{Si})_3\text{Ti-D0}_{22}$ and $(\text{Al},\text{Si})_3\text{Zr-D0}_{23}$ phases via DFT, showing that sites 2b and 4e are the most favorable for Si occupation, respectively. Finally, a thermodynamic model is derived to describe Si substitution upon solidification. Experimental and numerical examinations indicate that Si substitution preferentially occurs in the D0_{22} intermetallics compared to the D0_{23} phase.

1. Introduction

Primary $\text{Al}_3\text{Ti-D0}_{22}$ and $\text{Al}_3\text{Zr-D0}_{23}$ intermetallics are frequently encountered in aluminium alloys and master alloys [1]. Depending on the type of aluminium alloys being produced, their formation/precipitation can either be promoted (such as for grain refinement purposes [2]) or avoided (when these primary phases form coarse particles within the aluminium matrix). As an example, Chen & Fortier [3] have recommended using less than 0.10 wt% of Ti in the 356/357 aluminium alloys, which is the solubility limit within these Al-Si-Mg-Ti-Fe systems. Their experimental work shows that, above this value, several blocky and flake-like Ti-Al-Si-based intermetallics precipitate as primary phases during casting. Such intermetallics are problematical as they cause feeding blockage in the tubes of horizontal continuous

casting units and wormhole defects in T-ingots. Besides, they are detrimental for cast parts because they compromise the ductility of the materials and can cause surface defects [3]. Grain refinement for ingots of aluminium alloys is employed to promote the formation of equiaxed grains [4]. Formation of large/elongated grains is undesired as they deteriorate the mechanical properties of cast alloys [5]. For instance, large twinned columnar grains compromise the yield strength, tensile elongation to fracture and fabricability of alloys. Also, coarse-grained structures induce surface defects. By contrast, hot cracking in cast ingots is satisfactorily managed with an equiaxed structure [6]. For wrought aluminium alloys, grain refinement is required to obtain uniform microstructures and refined microporosity [7].

Grain refinement methods are divided into (i) chemical refining methods (by adding inoculants to the alloy) and (ii) physical refining

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techniques (by applying external forces to the melt) [8]. Guan & Tie [9] proposed a classification for current processing techniques in aluminium alloys including four categories: the addition of grain refiners, rapid solidification, severe plastic deformation and grain refining by vibration and stirring during solidification. Grain refinement by inoculant particles has been widely studied for aluminium alloys [10–12]. The potency of Al_3Ti particles as grain refiners was first described by Crossley & Mondolfo and explained through the peritectic nucleation theory [13]. This theory correlates the nucleation mechanisms with the peritectic reaction of the Al-rich side of the Al-Ti phase diagram. Al_3Ti intermetallics also play an important role in the nucleation mechanisms established by the duplex nucleation theory in Al-Ti-B-based grain refiners. This theory states that an Al_3Ti layer is formed around the TiB_2 grain refiners and remains stable when the grain refiner is added to a hypo-peritectic alloy, acting as a nucleation site for the α -Al phase [9]. For the case of grain refinement using Al-Ti-C master alloys, Al_3Ti is also found at the TiC_x/Al interface when $x < 0.7$ [14]. Apart from that, it is known that high silicon levels in cast Al-Si alloys compromise the effectiveness of Al-Ti-B/Al-Ti-C grain refiners compared to diluted wrought Al-alloys [15]. Therefore, the investigation of silicon's affinity for $\text{Al}_3(\text{Zr,Ti})$ -derived phases is relevant as it may provide insights into the adverse impact of silicon on the grain-refining efficiency of traditional Al-Ti-B/Al-Ti-C inoculants. Al_3Zr were also reported to act as heterogeneous nucleation sites for the α -Al phase [16]. Chen and Kang [17] studied the solidification of Al-Ti and Al-Zr alloys. They reported that both Al_3Ti and Al_3Zr particles act as heterogeneous nucleation sites for the α -Al phase. This is due to the small interplanar and interatomic mismatch between these phases [17]. Recently, Salloum-Abou-Jaoude et al. [18] reported that Si can be found inside Al_3Zr intermetallics. Based on Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis, they also suggested that an $\text{Al}_3(\text{Zr}_{1-x-y}\text{Ti}_x\text{Si}_y)$ primary intermetallic acted as a nucleation site for Al α -grains of AA6082 Direct Chill (DC)-cast billets. In their study, a thorough crystallographic analysis to explain the presence of Si within the crystal structure of this solid solution was not performed. The presence of Si in this intermetallic phase was associated with atomic substitution on Zr and Ti sites [18].

For the elaboration processes of wrought aluminium alloys, primary-intermetallic nucleation during solidification is not preferred because the primary particle size is difficult to control. Large faceted $\text{Al}_3\text{Ti-DO}_{22}$ and/or $\text{Al}_3\text{Zr-DO}_{23}$ intermetallics can act as stress concentration zones initiating cracking during downstream processing [19, 20]. Because of the critical importance of the $\text{Al}_3\text{Ti-DO}_{22}$ and $\text{Al}_3\text{Zr-DO}_{23}$ intermetallics in the elaboration of aluminium alloys, a precise understanding of their thermodynamic behavior and the effect of minor solution elements on their energetic stability, crystallography and dynamics of nucleation/growth is crucial for alloy design of next-generation advanced aluminium alloys.

From a recycling point of view, it is advantageous to properly describe Si partitioning within the phase assemblage for scrap recycling processes. Apart from the effective and well-implemented recycling procedures for beverage cans [21], recycling strategies usually involve the mixing of wrought and cast scrap/parts from different sources. Such items comprise castings with considerable amounts of Si [22]. Si can participate in the formation of secondary or subsequent phases of interest for aluminium alloys, such as the α -AlMnSi [23], α -AlFeMnSi [23], α -AlFeSi [24], β -AlFeSi [25], δ - Al_3FeSi_2 [26], π -AlFeMgSi [27] and Mg_2Si [28]. However, $\alpha(\text{Al})$ precipitation as the primary phase can be altered if $(\text{Al,Si})_3(\text{Zr,Ti})$ -based intermetallics ($\text{DO}_{22}/\text{DO}_{23}$) are formed. These intermetallics have great thermal stability [29,30]. Control of other impurities in the scrap should also be monitored to avoid primary-intermetallic precipitation. That is the case of V, which is more frequently found in primary aluminium due to the decline in coke quality for anode production [31]. Although substitution of V within $(\text{Al,Si})_3(\text{Zr,Ti})$ -based phases is out of the scope of this study, it has been experimentally proven that V can substitute Zr and

Ti sites of both DO_{22} and DO_{23} trialuminide intermetallics [32]. First-principles calculations have shown that the $\text{Al}_3(\text{Ti,V})\text{-DO}_{22}$ phase has a close-to-ideal solution behavior [33], which guarantees the stability of phases at high temperature by configurational entropic effects [34,35].

The thermodynamic stability of an intermetallic can be greatly modified by the potential addition of alloying elements or impurities within its crystal structure. Silicon is one of such important elements. It is present in various amounts in the majority of aluminium alloys in the form of either an impurity or as an alloying element for both wrought and cast alloys (e.g. 4xxx alloys [36], 6xxx alloys [37], A356 alloy [38], etc.). Therefore, understanding the effect of Si on the formation of Al_3Ti and Al_3Zr primary phases becomes a focal point in alloy design. Engineers and scientists could fine-tune its presence to either promote or suppress the formation of key primary intermetallics in aluminium alloys. A reliable thermodynamic description of Si within the crystal structure of $\text{Al}_3\text{Zr-DO}_{23}$ and $\text{Al}_3\text{Ti-DO}_{22}$ solid solutions is therefore required for designing and fine-tuning the chemistry of the next-generation of aluminium alloys.

CALPHAD-like thermodynamic databases such as the FTLite light alloy database available in the FactSage [39], currently account for Si substitution on Al sublattice sites for the thermodynamic description of the $\text{Al}_3\text{Ti-DO}_{22}$ solid solution via the Compound Energy Formalism (CEF) [40]. However, the potential substitution of Si on Al sublattices in the $\text{Al}_3\text{Zr-DO}_{23}$ structure is not accounted for. Aside from this energetic description limitation, the existing thermodynamic description of the partially ordered DO_{23} phase is able to describe and predict the substitution of elements such as Ti and V in Zr sublattices. Remarkably, thermodynamic calculations performed with FTLite show that Ti can occupy Zr sites at atomic ratios greater than 0.5 Ti/(Ti+Zr) under certain equilibrium conditions, i.e. when the amount of Zr in aluminium alloys is significantly smaller than Ti, but it is enough to stabilize the $\text{Al}_3\text{Zr-DO}_{23}$ over the $\text{Al}_3\text{Ti-DO}_{22}$ phase. The significant solubility of Ti inside the $\text{Al}_3\text{Zr}_{1-x-y}\text{Ti}_x\text{Si}_y$ intermetallics has already been reported by Salloum-Abou-Jaoude et al. [18] in their work on the processing of commercial AA6082 DC-cast billets. In that study, the crystallographic structure of this phase was not determined. Then, it remained unclear whether these intermetallics had a DO_{22} or DO_{23} crystallographic structure. Jo et al. (2020) [41] have recently suggested that Si can substitute Al sites in the $(\text{Al,Si})_3(\text{Zr,Ni,Fe})\text{DO}_{23}$ -like intermetallic of the Al-14Si-3Cu-4.5Ni casting alloy. Similarly, prior DFT simulations have demonstrated that Si substitution within Al sites of the $\text{Al}_3\text{Zr-DO}_{23}$ is energetically favorable [42]; nevertheless, the evaluation of Si substitution within the $\text{Al}_3\text{Ti-DO}_{23}$, $\text{Al}_3\text{Zr-DO}_{22}$ and $\text{Al}_3\text{Ti-DO}_{22}$ are required to fairly compare the ground state of the $(\text{Al,Si})_3(\text{Ti,Zr})\text{-DO}_{22}/\text{DO}_{23}$ solid solutions.

Schob et al. [43] fabricated a 33.3at.%Zr-45at.%Al-21.7at.%Si alloy at 1200 °C, the resulting metal was then powdered and cold-pressed. This alloy followed a homogenization process of 4–12 h at 1200 °C. Following their analysis, they reported that an $(\text{Al}_{1-x}\text{Si}_x)_3\text{Zr}$ phase was present in the alloy. Surprisingly, this intermetallic phase displayed a DO_{22} structure after X-ray Diffraction (XRD) analysis, even though no Ti was present in the nominal composition. Although a chemical analysis of this phase was not performed, they suggested an approximate composition of $(\text{Al}_{\sim 0.9}\text{Si}_{\sim 0.1})_3\text{Zr}$ based on the lattice parameters. They suggested that small acceptance of Si promoted the formation of the DO_{22} structure over the known $\text{Al}_3\text{Zr-DO}_{23}$ stable phase. Nakamura et al. [44] explored the precipitation of Al_3Zr through age-hardening in Al-Zr-Si and Al-Zr-Ge chill-cast alloys. They observed DO_{22} crystal structures instead of DO_{23} , attributing this to Si and Ge substituting for Al sites in Al_3Zr precipitates. The $(\text{Al}_{1-x}\text{Si}_x)_3\text{Zr-DO}_{22}$ phase is also referred to as the τ_1 phase in the literature [45,46]. Jain and Gupta [45] have shown that both DO_{23} and $\text{DO}_{22}(\tau_1)$ can coexist in the Al-rich region of the isothermal Si-Al-Zr sections at 900 °C, 1000 °C and 1100 °C.

Analysis of important intermetallics for aluminium alloy manufacturing can be difficult to perform because of their relatively low proportions compared to α -grains or other secondary phases in commercial

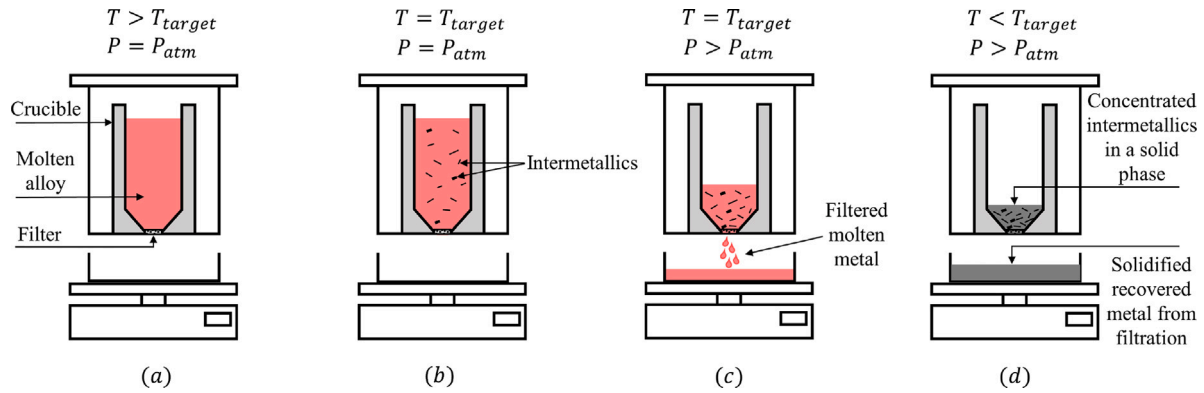


Fig. 1. Graphical representation of the different steps during the synthesis of intermetallics in a PoDFA setup. (a) The molten alloy is introduced in the crucible adapted with a filter at the bottom. (b) Formation of intermetallics at the target temperature (T_{target}). (c) Increase of pressure inside the chamber to promote filtration of the molten metal. (d) By the end of the test, intermetallics are concentrated in an FCC-matrix at the bottom of the crucible.

alloys. Moreover, the direct chill casting of commercial aluminium alloys is performed at relatively high cooling rates, which in the majority of cases prevents the formation of intermetallics, alloying elements (such as Ti and Zr) rather supersaturate the α -Al phase for those conditions. In order to create an environment close to thermodynamic equilibrium, a methodology for the synthesis of massive intermetallics is presented in this work. A Porous Disk Filtration Analyzer (PoDFA) method, adapted with a heating system, is proposed for the synthesis of $(Al, Si)_3(Zr, Ti)-D_{022}/D_{023}$ intermetallics. Control of temperature along with filtration and low cooling rates allowed to obtain large intermetallics concentrated inside Al-matrices. Samples were later thoroughly analyzed to understand Si site occupancy within the D_{022} and D_{023} phases. Density-functional theory (DFT) calculations were also performed to describe Si occupancy inside these crystal structures. Finally, a thermodynamic model based on DFT calculations is derived for the diluted Al-Si-Ti-Zr system.

2. Experimental methods

Sample preparation – 1.8 kg of molten alloys were prepared in an electric resistance furnace at 800 °C using aluminium 4N, silicon (99.4% purity) and Al-10wt%Ti/Al-5wt%Zr master alloys. A crucible containing a PoDFA filter (ABB Group) was preheated inside a chamber adapted with a thermocouple. The crucible (Fig. 1a) is made up of an inner layer of stainless steel, an outer shell of carbon steel and it is insulated with a blanket of synthetic vitreous fiber (SVF). It has an outside diameter of 13.3 cm (5 1/4 in), a height of 20.3 cm (8 in) and a weight of 1.36 kg. The molten metal (at 800 °C) was transferred into the crucible as shown in Fig. 1a. Subsequently, the temperature of the liquid was gradually decreased until reaching the target temperature (± 5 °C) for the precipitation of intermetallics (Fig. 1b). The system was equilibrated around the target temperature for 15 min. Then, the gauge pressure was increased up to 0.65 bar to start filtration (Fig. 1c). Finally, the heating source for the chamber was turned off and an Al-matrix containing a high concentration of intermetallics was obtained at the bottom of the crucible (Fig. 1d).

Three model alloy compositions were selected for PoDFA experiments (Table 1). Specimens of molten alloys were collected during alloy preparation at 800 °C and were solidified in small molds. The composition of those specimens was inspected by Spark Optical Emission Spectroscopy (Table 1). Sample S2 was prepared by adding Zr and Ti into molten aluminium; however, a small contamination of Si accounting for 0.04 wt% was detected (Table 1). Samples S4 and S6 were fabricated with higher amounts of Zr compared to S2. Sample S4 has the lowest content of Ti; conversely, sample S6 has the largest concentration of Ti. Moreover, samples S4 and S6 were intentionally doped with ~ 1 wt% of Si (Table 1).

Table 1

Nominal composition of S2, S4 and S6 molten alloys and their corresponding equilibration temperature in the PoDFA setup.

Sample	Composition (wt%)								Equilibration temperature
	Zr	Ti	Si	Fe	Ni	Ga	V	Al	
S2	0.11	0.18	0.04	0.04	0.01	0.01	0.02	Balance	703 °C
S4	0.22	0.10	0.98	0.04	0.02	0.01	0.01	Balance	699 °C
S6	0.23	0.30	0.92	0.05	0.02	0.01	0.01	Balance	716 °C

Fig. 2 shows the equilibrium phase diagrams for samples S2 (a), S4 (b) and S6 (c), computed with the FTLite database of FactSage 7.3 [39] and by neglecting Fe, Ni, Ga and V impurities due to their relatively small amount within the alloys. Al_3Zr-D_{023} is the primary precipitate for all compositions according to thermodynamic calculations. Al_3Zr-D_{023} is the equilibrium phase in the molten metal for the imposed equilibration temperature in samples S2 and S4 (dark square in Figs. 2a and 2b, respectively). For sample S6, an equilibrium with both Al_3Zr-D_{023} and Al_3Ti-D_{022} phases is predicted (dark square in Fig. 2c). It is essential to acknowledge that Fig. 2 was exclusively employed for experimental design purposes. Note that intermetallic phases acquired through the current processing technique (Fig. 1) might exhibit non-equilibrium compositions. In that case, the non-iso-compositional behavior of phases can be effectively approximated using Scheil-cooling calculations.

Sample characterization – The obtained samples from the PoDFA setup were sectioned (Fig. 3a and Fig. 3b). Subsequently, they were cold mounted and polished (Fig. 3c). Polishing was carried out with water and sandpapers with granulation of P180, P600, P1200, respectively, for 30 s each. Afterward, Struers DiaPro diamond solutions and polishing pads were utilized as follows: 6 min of polishing with a 6 μ m diamond solution, 6 min with a 3 μ m diamond solution and 3 min with a 1 μ m diamond solution. Microstructure and elemental analysis was carried out by means of light microscopy, Electron Microprobe (EMP) and EDS analysis.

Crystallography was evaluated through X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) analysis. XRD patterns were collected using $K_\alpha(Mo)$ as a radiation source for local analysis near the filter side of the collected sample (Fig. 4a). A global scan using $K_\alpha(Cu)$ was also performed as illustrated in Fig. 4b. For TEM analysis, Focused Ion Beam (FIB) lamellas were extracted through the lift-out technique. Subsequently, three noncolinear zone axes were identified in all phases by controlled tilting and Selected Area Electron Diffraction (SAED) pattern acquisitions.

3. Numerical methods

DFT simulations were carried out by means of the VASP software [47,48] based on the generalized gradient approximation (GGA)

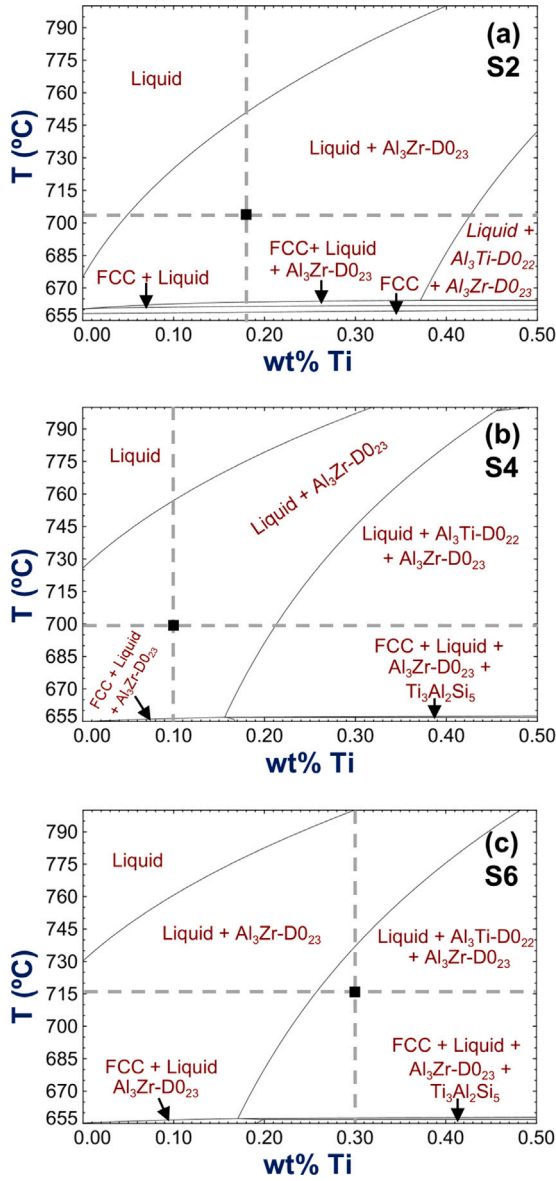


Fig. 2. Equilibrium phase diagram for samples S2(a), S4(b) and S6(c) obtained with FTLite database of FactSage 7.3 [39]. Black diamonds correspond to the experimental equilibration temperature in the PoDFA setup before filtration.

with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function [49]. Pseudopotentials with the projector augmented wave (PAW) method were employed with a 600 eV cut-off energy. Lattice parameter relaxation was performed for both D0₂₂ and D0₂₃ structures. The atomic positions were also relaxed in the case of the D0₂₃ structure. The relaxation continues until the Hellman–Feynman forces are lower than 1 meV/Å. For k-point sampling of the Brillouin zone, a dense grid of 11 × 11 × 5 and 13 × 13 × 3 was used for the D0₂₂ and D0₂₃ structures, respectively. The total energy of different ordered configurations simulating the substitution of Al by Si was calculated. For this purpose, Si atoms were distributed on sites 2b and 4d of the D0₂₂ structure and on sites 4c, 4d and 4e of the D0₂₃ structure. The schematic of crystal sites within the D0₂₂ and D0₂₃ structures are provided in Figure E1 of the Electronic Supplementary Material (ESM). This substitution scheme yielded a total of 8 and 16 ordered configurations called *end-members* for the D0₂₂ and D0₂₃ structures, respectively. Note that our calculations were performed in spin polarization and showed that all the generated *end-members* are non-magnetic.

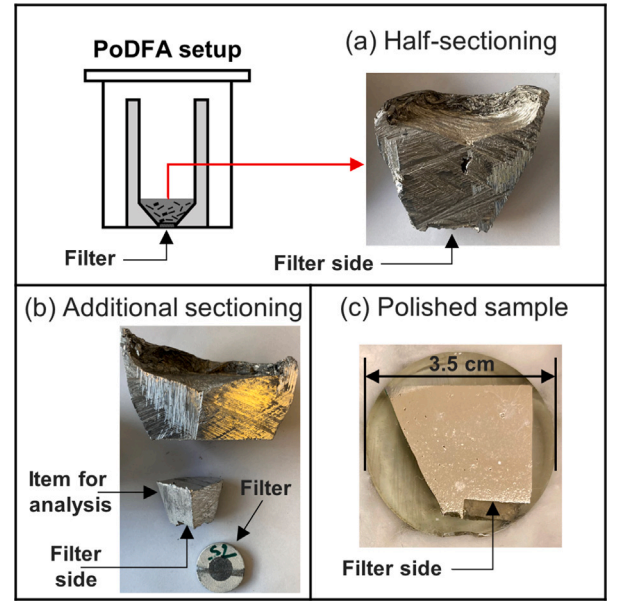


Fig. 3. (a) Half-sectioned recovered metal at the bottom of the crucible in the PoDFA setup. (b) Additional sectioning to obtain the item for chemical and crystallographic analysis. (c) Polished sample.

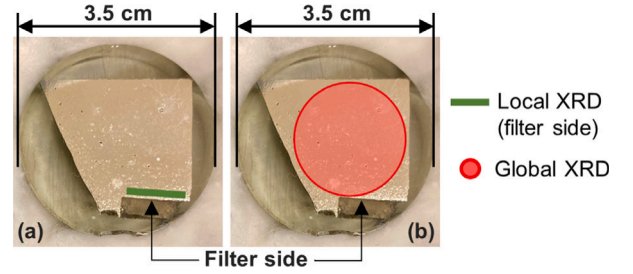


Fig. 4. Regions for local (a) and global (b) XRD analysis.

The formation enthalpy of a given *end-member* is the difference between the total energy of the *end-member* and the sum of the pure element energies which compose the *end-member*, in their reference states. The mixing enthalpy of the solid solution is then calculated by subtracting the formation enthalpy of the solid solution *end-member* $\text{Al}_{3-x}\text{Si}_x\text{M}$ (with $x \neq 0, 3$ and $M = \text{Ti, Zr}$) to the mole fraction weighted sum of the formation enthalpy of the reference compounds (*i.e.* Al_3M and Si_3M with $M = \text{Ti, Zr}$ for both D0₂₂/D0₂₃ structures).

Silicon site fraction occupancy was computed using the CEF (Bragg–Williams approximation) [40] without considering the non-ideal contribution to the configurational entropy of mixing. For instance, the Gibbs free energy of the D0₂₂ solid solution resulting from Si substitution on sites 2b and 4d is given by:

$$G^{\text{D0}_{22}}(T) = \sum_{i,j=\text{Al,Si}} \left[y_i^{2b} y_j^{4d} \right] \cdot H_{ij}^{\text{for,D0}_{22}} + RT \sum_w a^{(w)} \cdot \sum_{i=\text{Al,Si}} y_i^{(w)} \ln y_i^{(w)} \quad (1)$$

y_i^{2b} is the site fraction of the element i on site 2b, $H_{ij}^{\text{for,D0}_{22}}$ is the formation enthalpy of the *end-member* exhibiting element i on site 2b and element j on site 4d, R is the gas constant, $a^{(w)}$ is the multiplicity of the site w . In addition, we consider that the heat capacity of an intermetallic compound is given by the weighted sum of the heat capacities of the pure elements: this is the Neumann–Kopp rule [50]. This approximation implies that the enthalpy of formation does not change with temperature and therefore allows the use of the 0 K DFT calculated

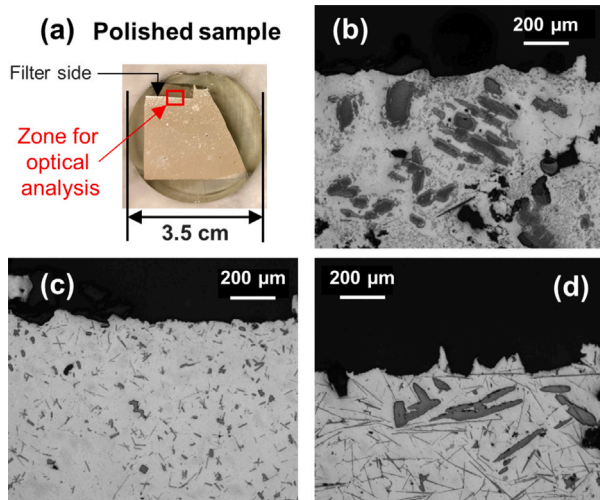


Fig. 5. Light microscopy micrographs at x100 magnification for solidified samples: S2 (b), S4 (c) and S6 (d). An example of the zone of analysis for the polished samples is presented in (a).

enthalpies of formation at any temperature. This methodology has been extensively described in former works [51,52].

4. Results and discussion

4.1. Intermetallics morphology and crystallographic analysis via XRD

Solidified samples were examined near the filter side (Fig. 5a) under light microscope at x100 magnification. All samples (S2 in Fig. 5b, S4 in Fig. 5c and S6 in Fig. 5d) present faceted intermetallics (dark particles) concentrated within the α -FCC matrix (bright area). Samples also exhibited platelet intermetallics around the faceted intermetallic phases, especially sample S6. Although the samples were expected to be fully liquid during alloy preparation at 800 °C, the phase diagram of sample S6 (Fig. 2c) suggests minor incomplete melting, potentially correlated with the formation of coarse intermetallics. However, sample S2 was fully melted at 800 °C (Fig. 2a) and also exhibited coarse intermetallics, complicating the direct association between incomplete melting and coarse intermetallic formation. EDS analysis is presented in further sections to identify the chemistry of the phases. Thermochemical calculations, performed with the FTLite database of FactSage [39], show that the amounts of intermetallics to be obtained are: 2.66 g of $\text{Al}_3\text{Zr-D0}_{23}$ /kg of alloy-S2; 3.11 g of $\text{Al}_3\text{Zr-D0}_{23}$ /kg of alloy-S4 and (5.86 g of $\text{Al}_3\text{Zr-D0}_{23}$ + 1.19 g of $\text{Al}_3\text{Ti-D0}_{22}$)/kg of alloy-S6. Therefore, the methodology employed in this work is useful to precipitate and develop big intermetallic particles whose mass fraction is low compared to the α -Al phase (Al-Si-Ti-Zr diluted alloys). *i.e.*, considering reasonable amounts of alloying elements comparable to industrial alloys. In this way, the formation of undesired phases can be investigated. This is an issue frequently observed in the industry when the produced batch's chemistry differs from the specification due to differences in the raw materials. Hence, the PoDFA-based technology helps to study the effect of traces of alloying elements (such as Ti, Zr, V, among others) to stabilize intermetallic phases (Fig. 5).

XRD patterns for local and global analysis are reported in Figs. 6 and 7, respectively. The quantitative analysis reported in those figures was obtained by Rietveld refinement [53]. A summary of crystallographic identification and refined lattice constants for all samples is presented in Table 2. Contrary to predictions from the FactSage 7.3 phase diagram (Fig. 2), formation of the D0_{22} phase was not expected for samples S2 and S4. Additionally, both D0_{22} and D0_{23} were foreseen in sample S6 (Fig. 2). However, only the D0_{22} was detected in both local and global

XRD analysis for this sample (Table 2). Overall, a higher concentration of intermetallics was detected at the bottom of the samples near the PoDFA filter side (local XRD), except for sample S6 exhibiting an equivalent high intermetallic content within the Al-matrix in both local and global (overall specimen area) XRD analysis.

4.2. Evidence of intermetallic-enhanced nucleation of the α -Al phase

TEM measurements were performed to confirm the crystallographic structure of the subgrains appearing in intermetallics of samples S2 and S6 (Figs. 8b and 9b). These phases were also chemically characterized by EDS in further sections. A representation of the extracted FIB lamellas for TEM analysis is reported in Fig. 8c for sample S2. SAED patterns were acquired for three different zone axes of the α -Al and D0_{22} phases in a specific region of sample S2 (Fig. 8). Zone axes for α -Al phase correspond to the [011], [112] and [013] families of directions. SAED patterns were obtained for almost identical tilts of the goniometer for all phases in the FIB lamella (Fig. 8c), demonstrating coherency between crystals. This allowed the characterization of the $\text{Al}_3\text{Ti-D0}_{22}^{(1)}/\text{D0}_{22}^{(2)}$ subgrains by following analogous [011], $[\bar{1}21]$ and [031] zone axes of the α -Al phase. As a comparison basis, the simulated electron diffraction patterns of non-Si/Zr-doped $\text{Al}_3\text{Ti-D0}_{22}$ and non-Si/Ti-doped $\text{Al}_3\text{Zr-D0}_{23}$ single DFT-crystals is presented in Table E1 (ESM). Experimental observations for a beam direction of [0 6 1] (Fig. 8i and Fig. 8l) are consistent with the simulated diffraction pattern for the $\text{Al}_3\text{Ti-D0}_{22}$ crystal (Figure b in Table E1 of the ESM). The simulated diffraction pattern $\text{Al}_3\text{Zr-D0}_{23}$ for a comparable beam direction (*i.e.*, [0 12 1]) is displayed in Figure (c) of Table E1 (ESM). The D0_{23} would have exhibited a more complex pattern than the D0_{22} . *e.g.*, the characteristic (1 0 $\bar{1}$) signal in the D0_{23} structure appears for a beam direction of [0 12 1] (Figure c in Table E1 of the ESM), but it does not display for an equivalent beam direction of [0 6 1] in the D0_{22} crystal. Thus, the crystal structure of the subgrains captured in the FIB lamella corresponds to the D0_{22} .

Fig. 8n, Fig. 8o, and Fig. 8p display the SAED patterns for three noncolinear zone axes collected at the $\text{D0}_{22}^{(2)}/\text{FCC}$ interface captured in the FIB lamella of sample S2 (Fig. 8m), indicating common diffraction spots between phases. As shown in Fig. 8n, planes corresponding to the $\{111\}_{\text{Al}}$ and $\{112\}_{\text{D0}_{22}}$ families are parallel. Furthermore, Fig. 8n indicates that the beam direction for aluminium, denoted as B(FCC) = [011], is congruent with the beam direction of the intermetallic phase, represented as B(D0_{22}) = [021]. Therefore $\langle 011 \rangle_{\text{Al}} \parallel \langle 021 \rangle_{\text{D0}_{22}}$, establishing the orientation relationship (OR) between the intermetallic and the Al phase as $\{111\}_{\text{Al}} \parallel \{112\}_{\text{D0}_{22}}$, $\langle 011 \rangle_{\text{Al}} \parallel \langle 021 \rangle_{\text{D0}_{22}}$. Since $\langle 011 \rangle_{\text{Al}}$ is equivalent to $\langle 110 \rangle_{\text{Al}}$, this is consistent with the experimental OR documented by Chen and Yang [17]. Nucleation of coherent phases appeared to follow the sequence: $\text{D0}_{22} \rightarrow \alpha$ -Al phase. The nucleation of the FCC phase assisted by intermetallics has been reported by Salloum et al. [18], which was inferred from micrographs showing intermetallics at the core of the FCC-grains. Lattice parameters for three phases are presented in Fig. 8. Wang et al. [54] reported an experimental value of $a = 3.857 \text{ \AA}$ and $c = 8.584 \text{ \AA}$ for $\text{Al}_3\text{Ti-D0}_{22}$, Karpets et al. [55] reported $a = 3.853 \text{ \AA}$ and $c = 8.587 \text{ \AA}$. Also, Norby & Christensen [56] indicated $a = 3.8537 \text{ \AA}$ and $c = 8.5839 \text{ \AA}$. Lattice parameters of the $\text{Al}_{2.98}\text{Si}_{0.02}\text{Ti-D0}_{22}$ intermetallics of this work were $a = 3.90 \pm 0.08 \text{ \AA}$ and $c = 8.65 \pm 0.17 \text{ \AA}$ for $\text{Al}_{2.98}\text{Si}_{0.02}\text{Ti-D0}_{22}$ and $a = 3.92 \pm 0.08 \text{ \AA}$ for and $c = 8.65 \pm 0.17 \text{ \AA}$ $\text{Al}_{2.99}\text{Si}_{0.01}\text{Ti}_{0.93}\text{Zr}_{0.07}\text{-D0}_{22}$. Hence, estimations of the lattice parameters are compatible with the data reported in the literature.

For sample S6, SAED patterns were obtained for three different mono-crystalline zones; *i.e.*, the Zr-absent $\text{D0}_{22}^{(1)}$ region and for the $\text{D0}_{22}^{(2A)}$ and $\text{D0}_{22}^{(2B)}$ subgrain zones captured in the FIB lamella (Fig. 9c). Lattice parameters of $\text{D0}_{22}^{(1)}$ intermetallics of sample S6 are comparable to those of $\text{D0}_{22}^{(1)}$ in sample S2 as they have equivalent chemistry. For the subgrains accepting Zr ($\text{D0}_{22}^{(2A)}$ and $\text{D0}_{22}^{(2B)}$), the c lattice parameter is

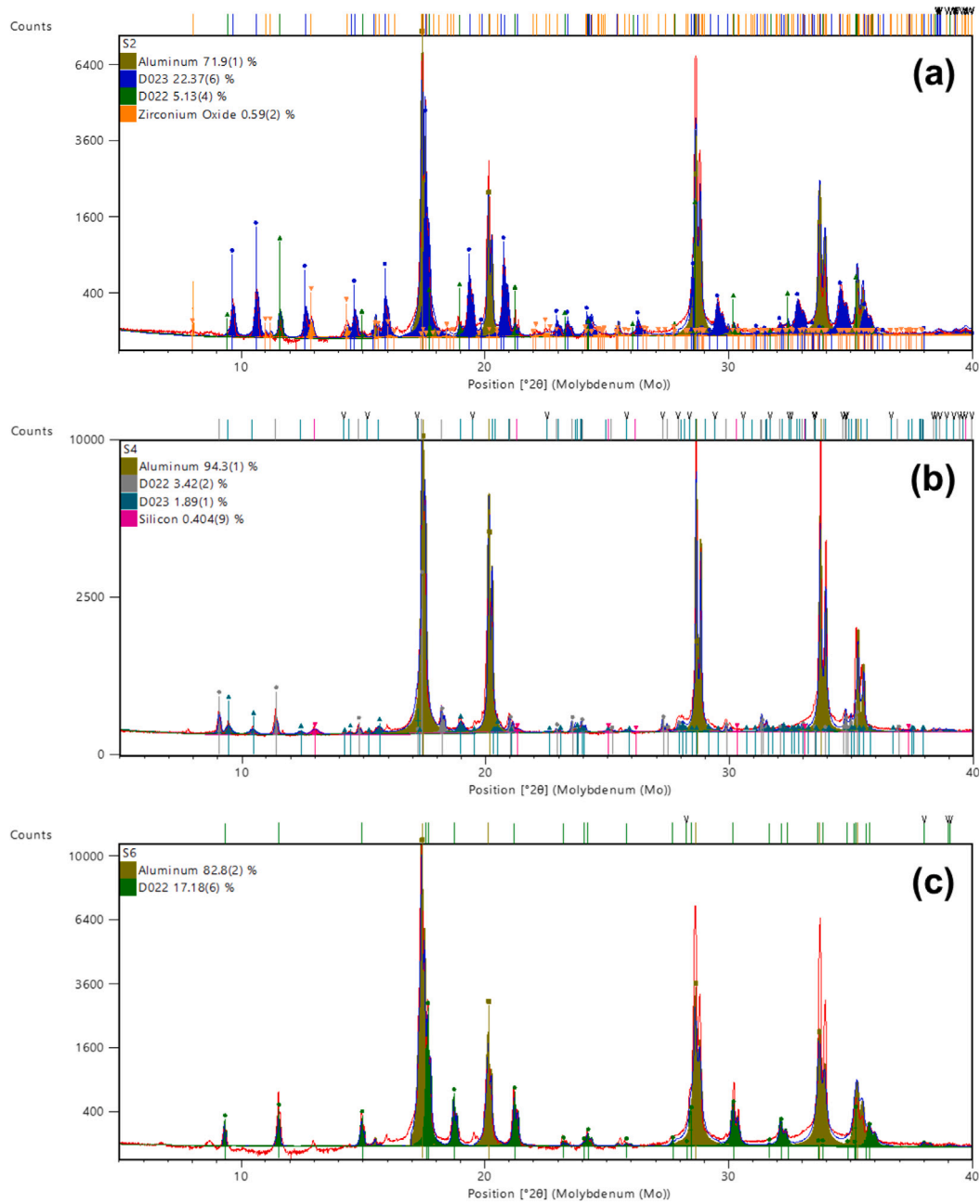


Fig. 6. Local XRD patterns and quantitative analysis determined by Rietveld refinement for samples S2(a), S4(b) and S6(c).

Table 2

Summary of phase identification and associated lattice constants obtained through X-ray diffraction (XRD) analysis for samples S2, S4 and S6. Local and global regions for XRD analysis within the filtrate specimens are illustrated in Fig. 4. XRD patterns can be found in Figs. 6 and 7.

Sample	Local XRD				Global XRD			
	Phases	Lattice parameters (Å)			Phases	Lattice parameters (Å)		
		a	b	c		a	c	
S2	71.9(1)% Aluminium	4.05492(2)	...	...	93(1)% Aluminium	4.05074(4)	...	
	22.37(6)% D0 ₂₃	3.93562(4)	...	16.8780(2)	6.6(1)% D0 ₂₃	3.9304(4)	16.844(1)	
	5.13(4)% D0 ₂₂	3.8524(1)	...	8.6173(3)	...	...	...	
	0.59(2)% ZrO ₂	5.150(2)	5.214(3)	5.325(2)	...	...	...	
S4	94.3(1)% Aluminium	4.05188(1)	...	...	96.2(1)% Aluminium	4.050762(9)	...	
	1.89(1)% D0 ₂₃	4.0030(4)	...	17.217(1)	1.20(1)% D0 ₂₃	3.9885(3)	17.2012(7)	
	3.42(2)% D0 ₂₂	3.89226(4)	...	8.9654(2)	2.36(2)% D0 ₂₂	3.8922(1)	8.9645(3)	
	0.404(9)% Silicon	5.428(1)	...	...	0.235(8)% Silicon	5.4333(3)	...	
S6	82.8(2)% Aluminium	4.05287(7)	...	...	81.8(2)% Aluminium	4.04971(2)	...	
	17.18(6)% D0 ₂₂	3.8501(2)	...	8.7075(2)	16.90(5)% D0 ₂₂	3.8534(3)	8.6958(1)	
	...	...	...	...	1.35(5)% Corundum	4.758(2)	12.980(4)	

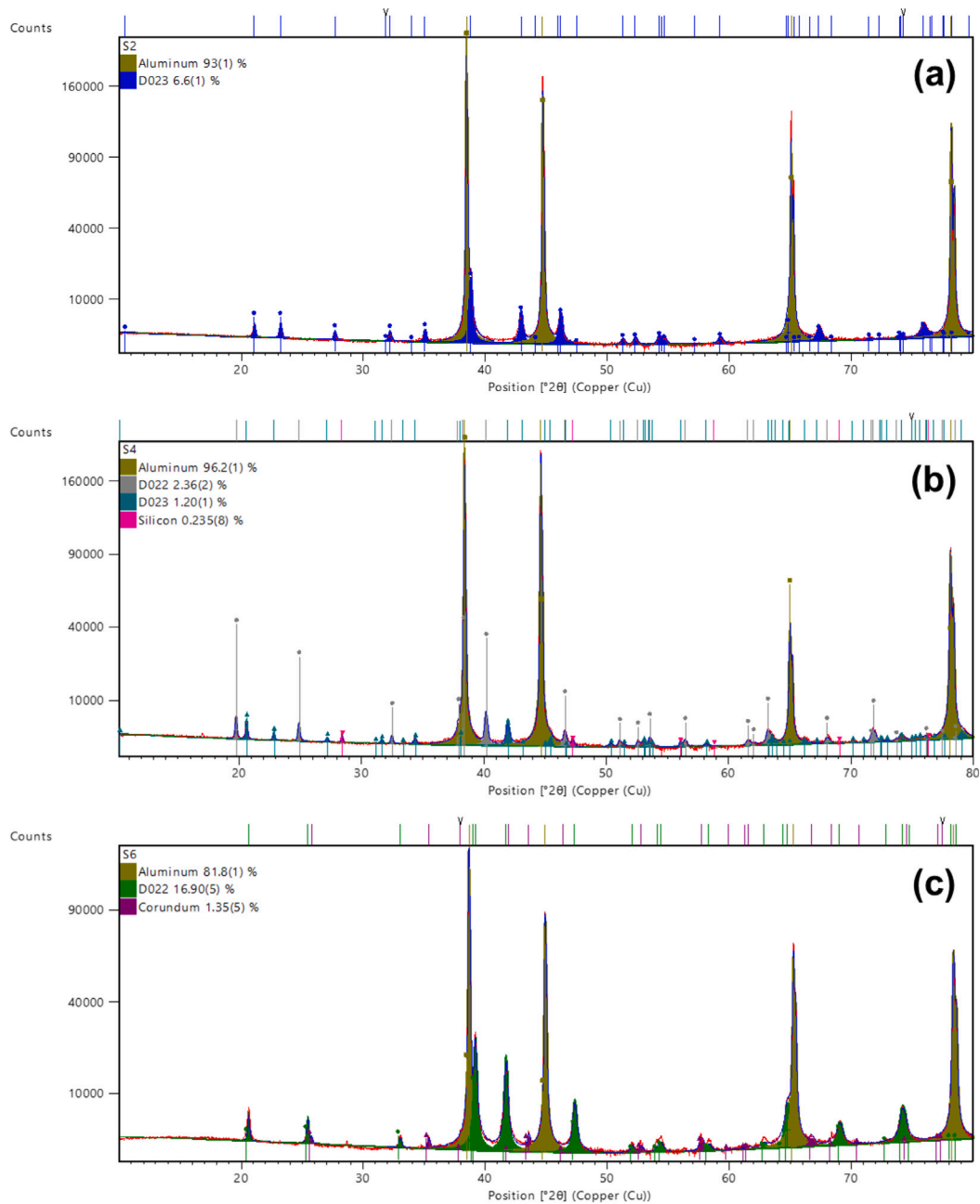


Fig. 7. Global XRD patterns and quantitative analysis determined by Rietveld refinement for samples S2(a), S4(b) and S6(c).

larger than the one reported for $\text{D0}_{22}^{(1)}$. The increase in the c parameter induced by Zr acceptance in the pseudo-binary $\text{Al}_3(\text{Ti},\text{Zr})\text{-D0}_{22}$ solid solution has already been documented in the literature by Molecular Dynamics (MD) and DFT calculations [57]. Diffraction patterns for the D0_{22} phase of sample S6 (Fig. 9) are consistent with the simulated TEM patterns of the non-Si/Zr-doped $\text{Al}_3\text{Ti-D0}_{22}$ crystal for a beam direction $B = [0 \ 1 \ 0]$ (Figure [e] in Table E1 of the ESM).

Additional SAED patterns were collected at the interface of $\text{D0}_{22}^{(1)}/\alpha\text{-FCC}$ phases (Fig. 9m) and at the interface of the $\text{D0}_{22}^{(2A)}/\alpha\text{-FCC}$ (Fig. 9n). SAED patterns revealed crystallographic coherence between all phases. Similarly to sample S2 (Fig. 8), the D0_{22} intermetallic in sample S6 appears to have acted as a nucleation site for the FCC phase.

The lattice mismatch between the “ a ” parameter of the $\alpha\text{-Al}$ phase and the “ a ” and “ c ” constants of the D0_{22} intermetallics is presented in Table 3. For the three directions of the fundamental unitary cells,

the lattice difference of intermetallics with respect to the $\alpha\text{-Al}$ phase is small. The aforesaid suggests that $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})\text{-D0}_{22}$ intermetallics acted as nucleation sites for the $\alpha\text{-Al}$ phase and resulted in crystallographic coherency of these phases as shown in the SAED patterns (Figs. 8 and 9). According to Wang et al. [16], the interplanar spacing misfit (f_d) between compatible pairs of planes should be smaller than 10% for favorable orientation relationships (OR). Chen and Yang [17] experimentally showed that $\{111\}_{\text{Al}} // \{112\}_{\text{D0}_{22}}$ is a favorable alignment for aluminium and the non-Si/Zr-doped Al_3Ti intermetallic. Considering the cube-on-cube OR ($\{111\}_{\text{Al}} // \{112\}_{\text{D0}_{22}}$) and the TEM measurements of this work, the interplanar spacing misfit is smaller than 10% (Table 3) for all cases (i.e., for all intermetallic regions and the α -phase captured in the FIB lamellas as shown in Figs. 8c and 9c). Hence, acceptance of Si impurities in the D0_{22} phase does not compromise its capability to nucleate the FCC-phase.

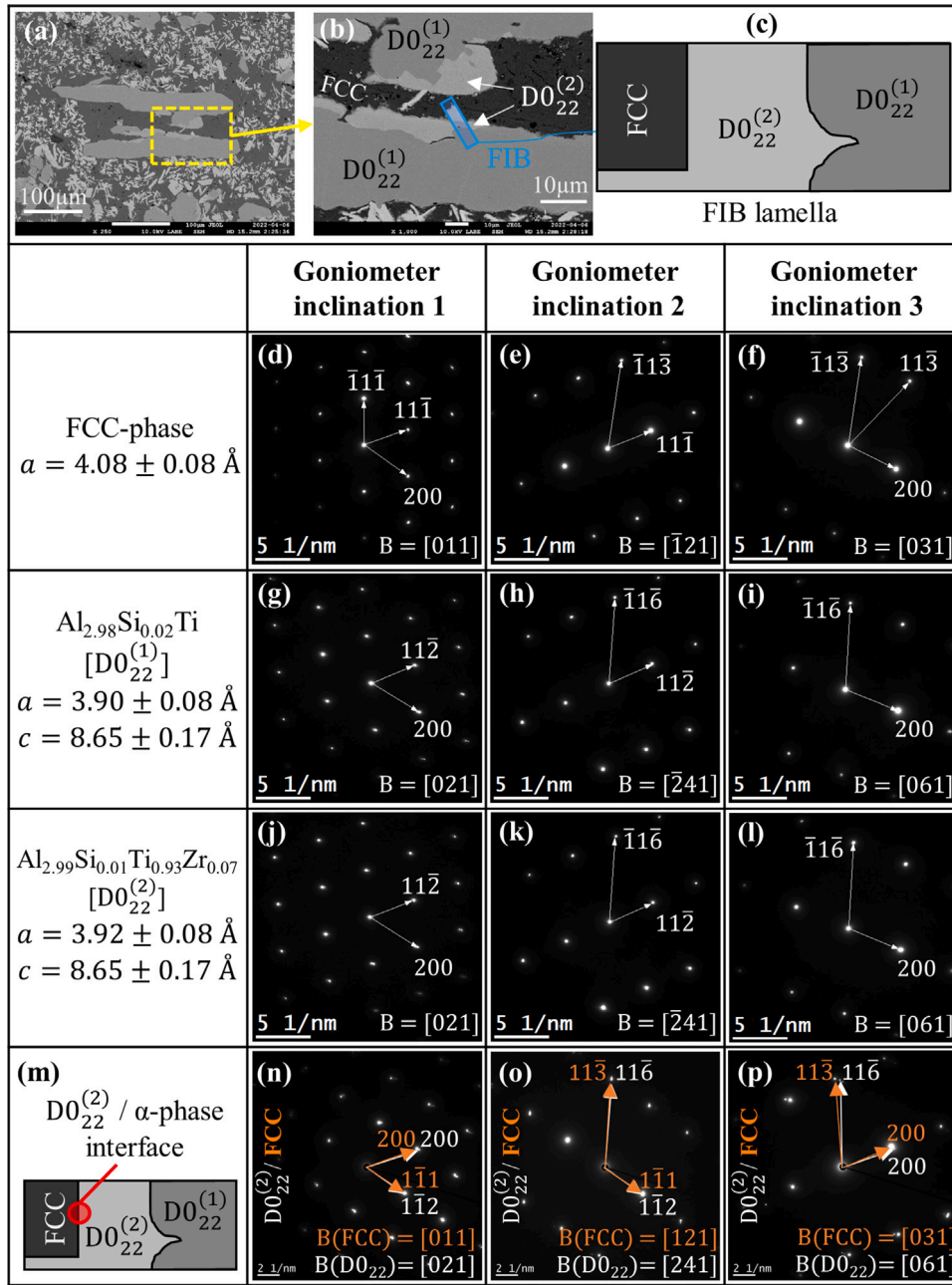


Fig. 8. Summary of the TEM analysis performed for sample S2. (a) and (b) are micrographs showing the target zone for FIB sectioning (blue rectangle) to obtain a FIB lamella (c). Selected area electron diffraction patterns are presented in (d), (e) and (f) for the α -phase; (g), (h) and (i) for the Al_{2.98}Si_{0.02}Ti-D0₂₂⁽¹⁾ sub-grain; and (j), (k) and (l) for the Al_{2.99}Si_{0.01}Ti_{0.93}Zr_{0.07}-D0₂₂⁽²⁾ sub-grain. (m), (n), (o) and (p) show the diffraction patterns at the D0₂₂⁽²⁾/α-phase interface (m).

Table 3

Lattice misfit between the aluminium matrix (M) and the inoculant intermetallic particle (P) in samples S2 and S6. The interplanar spacing misfit (f_d) is also presented.

Sample	Intermetallic zone in FIB lamella	Lattice misfit $\frac{ a_M - a_P }{a_P} \times 100\%$	$\frac{ 2a_M - c_P }{c_P} \times 100\%$	Interplanar spacing misfit $f_d = \frac{ d_M - d_P }{d_P} \times 100\%$
S2	D0 ₂₂ ⁽¹⁾	5 ± 3%	6 ± 3%	1 ± 3% ^a
	D0 ₂₂ ⁽²⁾	4 ± 3%	6 ± 3%	1 ± 3% ^a
S6	D0 ₂₂ ⁽¹⁾	4 ± 3%	6 ± 3%	1 ± 3% ^a
	D0 ₂₂ ^(2A)	5 ± 3%	7 ± 3%	1 ± 3% ^a
	D0 ₂₂ ^(2B)	5 ± 3%	7 ± 3%	1 ± 3% ^a

^a $\{111\}_{Al} // \{112\}_{D0_{22}}$.

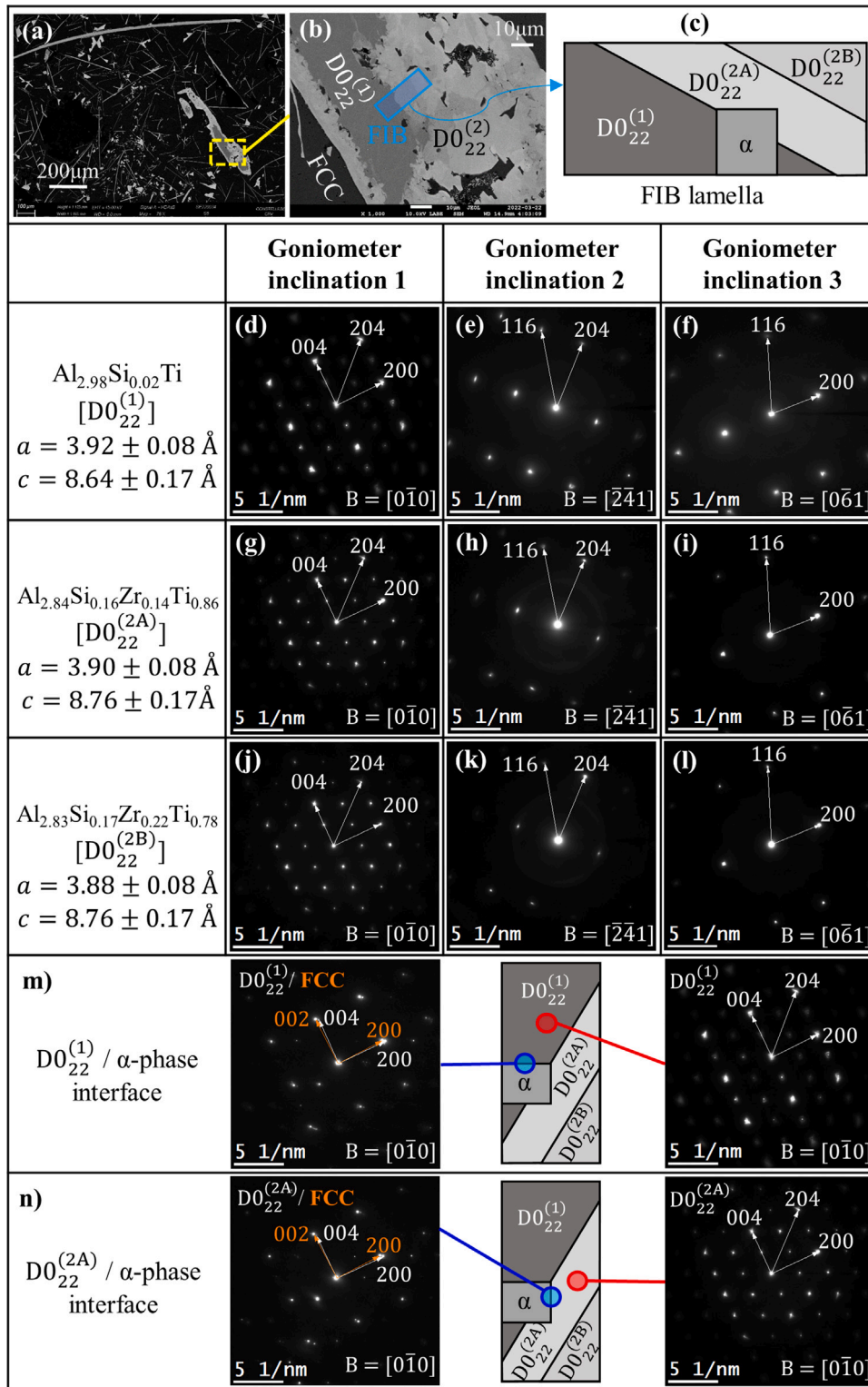


Fig. 9. Summary of the TEM analysis performed for sample S6. (a) and (b) are micrographs showing the target zone for FIB sectioning (blue rectangle) to obtain a FIB lamella (c). Selected area electron diffraction patterns are presented in (d), (e) and (f) for the $\text{D}0_{22}^{(1)}$ phase; (g), (h) and (i) for the $\text{D}0_{22}^{(2A)}$ subgrain; (j), (k) and (l) for the $\text{D}0_{22}^{(2B)}$ subgrain. (m) and (n) show the diffraction patterns at the $\text{D}0_{22}^{(1)}/\alpha$ -phase and α -phase/ $\text{D}0_{22}^{(2A)}$ interfaces.

4.3. Solidification sequence scenario

Electron microprobe elemental mappings for samples S2, S4 and S6 near the filter side of recovered samples are presented in Fig. 10. From this mapping, it can be inferred that: (i) the $\text{D}0_{22}$ intermetallics (red-brown particles in Fig. 10b) were probably the first precipitates

in sample S2 because of their large size ($> 50 \mu\text{m}$). Additionally, this intermetallic accepted the minor traces of Si in the initial non-intentionally-Si-doped melt S2 (0.04 wt% of Si [Table 1]). Note that, after precipitation of intermetallics, the remaining molten metal solidified as Si-absent FCC (dark area in Fig. 10b). This is consistent with the TEM observations (Figs. 8 and 9), i.e., the $\text{D}0_{22}$ being the primary phase

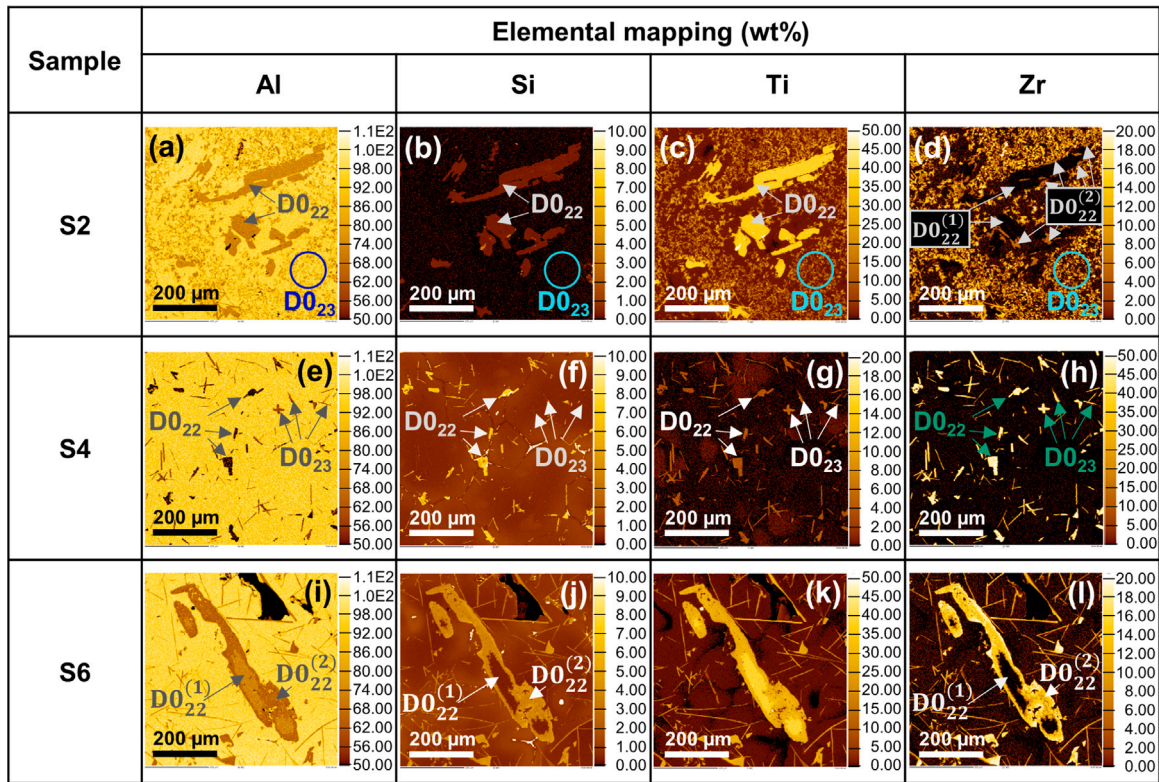


Fig. 10. Electron microprobe elemental maps for samples S2, S4 and S6 near the filter side of recovered samples.

and potentially acting as a nucleant particle for the FCC phase. (ii) small $D0_{23}$ intermetallics also appeared in sample S2. Since the initial melt only contained traces of Si, the $D0_{23}$ phases are mainly formed of Al, Ti and Zr. *i.e.*, $Al_3(Ti,Zr)$ intermetallics. (iii) The core of the big particles in sample S2 did not accept Zr ($D0_{22}^{(1)}$ in Fig. 10d); however, it can be observed that some of its edges ($D0_{22}^{(2)}$ orange sections in Fig. 10d) accepted Zr. Given the abrupt compositional contrast at the $D0_{22}^{(1)}/D0_{22}^{(2)}$ interface, it is likely that $D0_{22}^{(2)}$ underwent epitaxial growth atop the pre-existing $D0_{22}^{(1)}$ intermetallic. This complex partitioning kinetics highlights a challenge posed by the current processing conditions. From one side, equilibrium conditions cannot be claimed because of the compositional differences observed in the $D0_{22}$ phase. On the other hand, the absence of Zr within the $D0_{22}^{(1)}$ zone restricts its modeling *via* Scheil cooling calculation. Further investigations are required to uncover the precise solidification mechanisms. According to the XRD analysis (Table 2), the $D0_{22}$ was only detected near the filter-side of the solidified specimen (Fig. 4a). In contrast, the $D0_{23}$ was detected in both local and global XRD patterns as the foremost intermetallic concentrated in the Al-matrix. (iv) The core of the massive intermetallic in sample S6 ($D0_{22}^{(1)}$ in Fig. 10j and Fig. 10l) displayed an equivalent behavior as the core of the red-brown particles of sample S2 (Fig. 10b); *i.e.*, it did not accept Zr and accepted a limited amount of Si. Equivalently to S2, it is presumed that $D0_{22}^{(2)}$ grew on top of the existing $D0_{22}^{(1)}$ intermetallic structure. (v) For sample S4, the particle size is significantly smaller than those encountered in samples S2 and S6. Note that melt S4 had the lowest content of Ti (0.10 wt% of Ti [Table 1]), which probably avoided the formation of Zr-absent Al_3Ti-D0_{22} intermetallics. Note that the Al/Si content allows for distinguishing the crystallography of those phases in sample S4. As reported by Schob et al. [43] a small acceptance of only 10% in the Al sublattice is enough to stabilize the $(Al_{0.9}Si_{0.1})_3Zr-D0_{22}$ phase over the Al_3Zr-D0_{23} . $D0_{22}$ intermetallics are therefore colored in black in Fig. 10e, while the $D0_{23}$ are represented by orange. Analogously in the Si mapping (Fig. 10f), $D0_{22}$ intermetallics are colored in yellow and $D0_{23}$ particles are almost

indistinguishable from the Al-matrix because of their low content on Si. (vi) For samples intentionally doped with ~ 1 wt% of Si, *i.e.* S4 and S6, Si segregated along the FCC-grains and ultimately formed eutectic Si at the grain boundaries by the end of solidification (Fig. 10f and Fig. 10j).

4.4. Quantification of Al/Si substitutability in $D0_{22}$ and $D0_{23}$ phases

SEM micrographs were obtained at specific zones of sample S2 (Fig. 11a, Fig. 11b and Fig. 11c), sample S4 (Fig. 11d, Fig. 11e and Fig. 11f) and sample S6 (Fig. 11g, Fig. 11h and Fig. 11i). The observed phases were analyzed by EDS to determine their elemental composition (reported in Table 4). Although the Spark Optical Emission Spectroscopy analysis (Table 1) indicated minor contamination by Fe, Ni, Ga, and V these impurities were not discernible through EDS. This limitation in detection arises from the threshold constraints of the EDS technique.

Large particles ($> 50 \mu m$) were identified for samples S2/S6; and smaller particles ($\sim 40 \mu m$) for sample S4 (Fig. 11). Zr-absent Al_3Ti-D0_{22} subgrains have essentially the same elemental composition in samples S2 (region 2 in Fig. 11c) and S6 (region 10 in Fig. 11i). For sample S2, zone 3 corresponds to the $D0_{22}$ composition used for the thermodynamic modeling of this work. The independent and smaller ($< 30 \mu m$) $D0_{23}$ intermetallics (phases 4, 5 and 6 in Table 4) were also taken into account for the model. Since the molten metal of sample S2 was non-intentionally doped with Si, it is possible to infer the intermetallics structure based on the Zr/(Zr+Ti) sublattice substitution ratio. Karpets et al. [55] evaluated the stability of the $Al_3(Ti_{1-x}Zr_x)$ -based solid solutions at different Zr/(Zr+Ti) ratios between 0 and 1 in 75at.%Al-Zr-Ti alloys. When only Ti was present in the system, the Al_3Ti-D0_{22} was the stable structure while Al_3Zr-D0_{23} was the stable phase when Ti was not included. For the range [0.04:0.32] of Zr/(Zr+Ti) during alloy preparation, they found an equilibrium between the $D0_{22}$ and $D0_{23}$ phases. Peculiarly, the $D0_{22}$ phase accepted a Zr sublattice substitution of only [0.035:0.08] (Zr atoms)/(Ti sites), which compares well with the $D0_{22}$ phase of sample S2 of this work

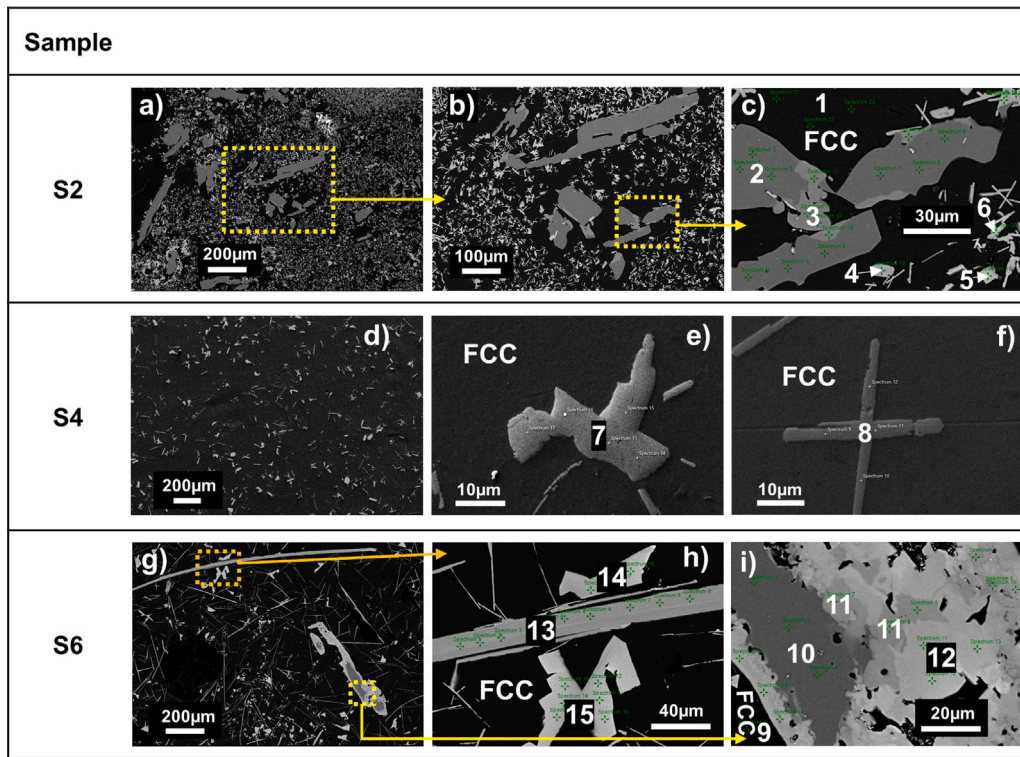


Fig. 11. Scanning electron microscope (SEM) micrographs. (a), (b) and (c) correspond to sample S2; (d), (e) and (f) for sample S4; (g), (h) and (i) stand for sample S6. Numbers in white highlight the different phases within each sample. The chemical composition of the phases is reported in Table 4.

Table 4

Chemical composition of phases reported in Fig. 11. Gray highlighted data correspond to Scheil-cooling data used for the thermodynamic model of this work.

Sample	Label	Phase	at. %				Substitution ratio	
			Al	Si	Ti	Zr	Zr/(Zr+Ti)	Si/(Al+Si)
S2	1	FCC	99.3	0.4	0.2	0.1	...	...
	2	D0 ₂₂	74.7	0.4	24.9	0.0	0.000	0.006
	3	D0 ₂₂	75.1	0.2	23.0	1.7	0.069	0.002
	4	D0 ₂₃	74.5	0.2	20.2	5.1	0.202	0.002
	5	D0 ₂₃	74.6	0.2	17.9	7.3	0.289	0.002
	6	D0 ₂₃	76.2	0.2	16.7	6.9	0.292	0.003
S4	7	D0 ₂₂	64.8	9.1	3.9	22.2	0.851	0.123
	8	D0 ₂₃	73.7	0.7	4.7	20.9	0.817	0.009
S6	9	FCC	98.4	1.4	0.1	0.1	...	...
	10	D0 ₂₂	73.9	0.4	25.6	0.0	0.00	0.006
	11	D0 ₂₂	70.6	3.9	22.0	3.5	0.137	0.053
	12	D0 ₂₂	70.1	4.2	20.0	5.7	0.221	0.057
	13	D0 ₂₂	71.1	3.4	21.2	4.3	0.170	0.045
	14	D0 ₂₂	69.7	4.6	18.9	6.9	0.267	0.062
	15	D0 ₂₂	69.6	4.7	18.8	6.9	0.270	0.063

(i.e., $Zr/(Zr+Ti) = 0.069$ as shown in Table 4). Equivalently, Karpets et al. [55] reported that Ti was able to substitute at [0.59:0.88] (Ti atoms)/(Zr sites), analogous to [0.12:0.41] $Zr/(Zr+Ti)$ in the D0₂₃ phase. Corresponding satisfactorily with the D0₂₃ phase in sample S2 is this work (i.e., $Zr/(Zr+Ti)$ ranging from 0.202 to 0.292 as shown in Table 4).

For the intentionally Si-doped sample S4, two main morphologies are observed in the intermetallic phases (Fig. 11d); that is, D0₂₂ faceted particles (Fig. 11e) and D0₂₃ platelet intermetallics (Fig. 11f). The

chemical composition of the D0₂₂ and D0₂₃ phases of sample S4 are respectively reported in Table 4. The D0₂₂ phase of sample S4 accepts a higher Si/(Al+Si) substitution ratio when compared to the D0₂₃ phase (0.123 Si/(Al+Si) in D0₂₂ vs. 0.009 in D0₂₃). This implies that Si has a preferential affinity for the D0₂₂ under the specific operational conditions of this work. Zhu et al. [58] performed first-principles calculations to investigate Si sublattice substitution in Al₃Ti-D0₂₂. They found that Si has a highly energetically favorable preference for Al sublattice sites in this structure. The same conclusion was obtained by Yang et al. [59] by both EDS analysis and first-principles calculations of the (Al,Si)₃Ti-D0₂₂ phase.

In sample S4, D0₂₂ and D0₂₃ phases have comparable ratios of Zr and Ti. Thus, the strategy for crystallographic identification comparing the $Zr/(Zr+Ti)$ ratios in D0₂₂/D0₂₃ from Karpets et al. [55] (in Al-Zr-Ti alloys) does not apply anymore. Si plays an important role in the phase equilibria in the quaternary Al-Si-Zr-Ti system because of the different partitioning of Si in the tetragonal phases. As observed by Schob et al. [43] in a Al-Si-Zr alloy, a sublattice substitution as small as (Al_{0.9}Si_{0.1})₃Zr is enough to stabilize the D0₂₂ over the D0₂₃ phase. In this work, the D0₂₂ intermetallic of sample S4 accepted a sublattice substitution larger than 0.1 Si/(Al sites) (Table 4), while Si substitution in the D0₂₃ phase only accounted for 0.009 Si/(Al sites) (Table 4). Hence, results are consistent with the findings of Schob et al. [43]. i.e., Si induces a stabilization effect on the D0₂₂ phase, allowing it to incorporate high contents of Zr.

As previously described, only the D0₂₂ intermetallic was detected with XRD analysis (Table 2) and TEM analysis (Fig. 9) in sample S6. Scheil-cooling data for this phase is reported in Table 4. This includes the chemical composition at the shell of the big particles on sample S6 (zones 11 and 12 in Fig. 11i), as well as additional D0₂₂ intermetallics captured in the Al-matrix (phases 13, 14 and 15 in Fig. 11h).

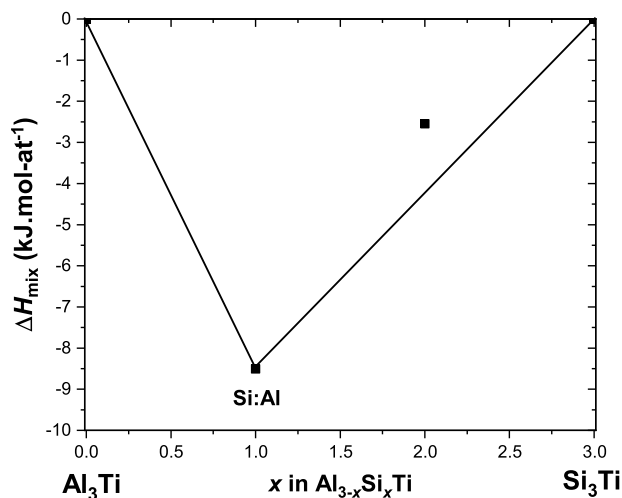


Fig. 12. Mixing enthalpy of $(\text{Al},\text{Si})_3\text{Ti-D0}_{22}$ solid solution calculated by DFT at 0 K. The ground-state *end-member* is labeled with the first element occupying the site 2b, the second element occupying the site 4d. The ground-state is represented by the solid black line.

4.5. Thermodynamic interpretation of Si site occupancy in $\text{D0}_{22}/\text{D0}_{23}$ solid solutions

The formation enthalpy of the *end-members* generated for the D0_{22} structure we computed with DFT are reported in Table E2 (ESM). The obtained value for the $\text{Al}_3\text{Ti-D0}_{22}$ composition (-38.771 kJ/mol-at) is in good agreement with all the DFT-GGA calculations available in the literature [60–66], ranging from -38.11 kJ/mol-at [61] to -38.90 kJ/mol-at [60]. The formation enthalpy of the $\text{Al}_3\text{Ti-D0}_{23}$ *end-member* was estimated as -39.230 kJ/mol-at (Table E3), which is lower than the calculated value of the $\text{Al}_3\text{Ti-D0}_{22}$. Hence, D0_{23} is the ground state for the Al_3Ti stoichiometry. This is consistent with other DFT calculations reported in the literature [67]. Let us note that, to our knowledge, no other *end-members* simulating the specific substitution of Al by Si on sites 2b and 4d of the D0_{22} structure have been investigated to determine their thermodynamic stability. Zhu et al. [58] reported an appealing investigation of Si substitution in both Al in Ti sites of $\text{Al}_3\text{Ti-D0}_{22}$ supercells. Their findings indicated Si has a preferential affinity for Al sites. In another work, Si substitution was investigated via DFT calculations by Yang et al. [59], they reported that the formation enthalpy of $(\text{Al},\text{Si})_3\text{Ti-D0}_{22}$ crystals is lower than that of the stoichiometric $\text{Al}_3\text{Ti-D0}_{22}$. Nevertheless, their simulation supercells were built targeting only a 9.375 at. % Si/(Si+Al+Ti) substitution in random Al sublattice sites.

DFT calculations allowed us to determine the enthalpy of mixing of the D0_{22} solid solution as shown in Fig. 12. The ground-state plotted in Fig. 12 reveals that site 2b is the most favorable for Si occupation. Moreover, the substitution of Al by Si on this site significantly increases the thermodynamic stability of the solution. Indeed, the mixing enthalpy of the D0_{22} solid solution is minimal and relatively negative (-8.5 kJ/mol-at) when site 2b is occupied by Si, which also indicates a relatively strong level of chemical ordering.

The Si site fractions were computed at 300 K and 1650 K and are presented in Fig. 13. These calculations indicate that site 2b is more favorably occupied by Si than site 4d, at any temperature. These calculations were also used to quantify the chemical ordering of the solid solution via the calculation of its configurational entropy of mixing, plotted in Fig. 14. This figure shows that the solid solution is highly ordered at 300 K as we had qualitatively suspected by analyzing the enthalpy of mixing calculated at 0 K. Moreover, the solid solution remains partially ordered at any temperature since even at 1650 K (temperature close to the decomposition temperature), the configurational entropy

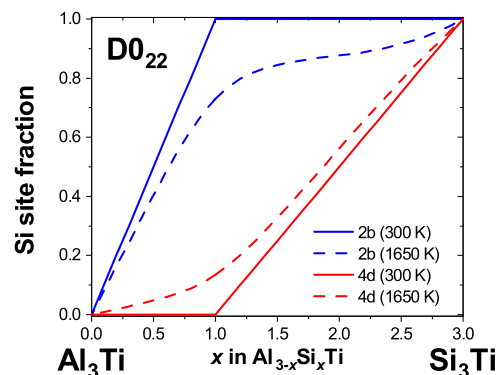


Fig. 13. Site fraction of Si on sites 2b and 4d of the D0_{22} structure calculated at 300 K (solid line) and 1650 K (dashed line).

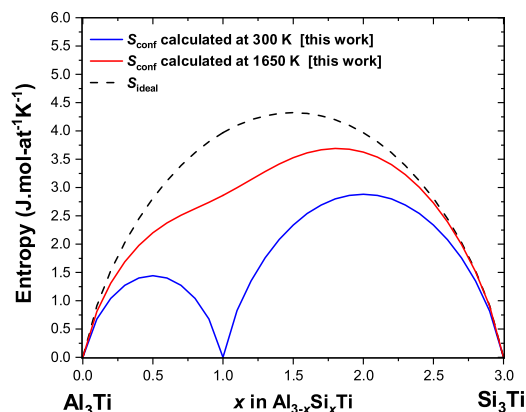


Fig. 14. Configurational entropy of mixing of the D0_{22} solid solution calculated at 300 K and 1650 K compared to the configurational entropy of an ideal solid solution.

of the solid solution shows a significant deviation from that of an ideal solution. Interestingly, the $(\text{Al},\text{Si})_3\text{Zr-D0}_{22}$ *end-members* exhibited an equivalent Si substitution behavior as the stable $(\text{Al},\text{Si})_3\text{Ti-D0}_{22}$ *end-members*. *i.e.*, relatively exothermic enthalpy of mixing minimized by the 2b-Si-substituted *end-member* (Figure E2) and equivalent site fraction of Si at 300 and 1650 K in 2b and 4d sites (Figure E3). This explains the relatively high amounts of Zr encountered in the D0_{22} phases of this work (Table 4).

The formation enthalpy of the D0_{23} solid solution *end-members* is reported in Table E3. One should note the good agreement between our calculation of the formation enthalpy of the $\text{D0}_{23}\text{-Al}_3\text{Zr}$ compound (-47.033 kJ/mol-at) with the DFT-GGA calculations available in the literature (-46.77 kJ/mol-at [62], -46.78 kJ/mol-at [68], -47.28 kJ/mol-at [69]). Similarly to the literature review concerning the D0_{22} solid solution, to our knowledge, the substitution of Al by Si on sites 4c, 4d and 4e of the D0_{23} structure has not been characterized in any other study. The DFT calculations we performed were used to determine the D0_{23} solid solution mixing enthalpy as presented in Fig. 15. The calculated ground-state indicates that site 4e is the most favorable for Si occupation, followed by site 4d. Moreover, this figure clearly shows that the thermodynamic stability of the solution is improved by Si substitution since the mixing enthalpy of the solid solution is quite exothermic, with a minimum value of -5.5 kJ/mol-at.

Fig. 16 reports the calculations of the site fraction of the D0_{23} solid solution at 300 K and 1900 K, respectively. From these figures, it is clear that site 4e is the most favorable one for Si substitution at any temperature. From the site factors we have calculated, the configurational entropy of the solution has been determined and plotted in Fig. 17. Even though the D0_{23} solid solution appears to be chemically ordered

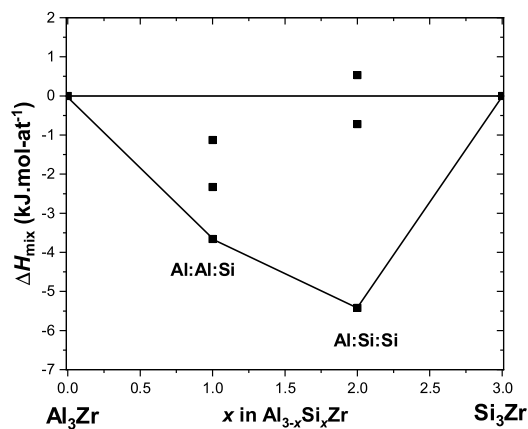


Fig. 15. Mixing enthalpy of $(\text{Al,Si})_3\text{Zr-D}_{023}$ solid solution calculated by DFT at 0 K. The ground-state *end-member* is labeled with the first, second and third elements occupying sites 4c, 4d and 4e, respectively. The ground-state is represented by the solid black line.

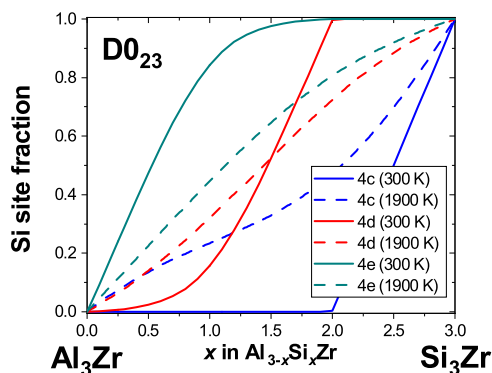


Fig. 16. Site fraction of Si on sites 4c, 4d and 4e of the D_{023} structure calculated at 300 K (solid line) and 900 K (dashed line).

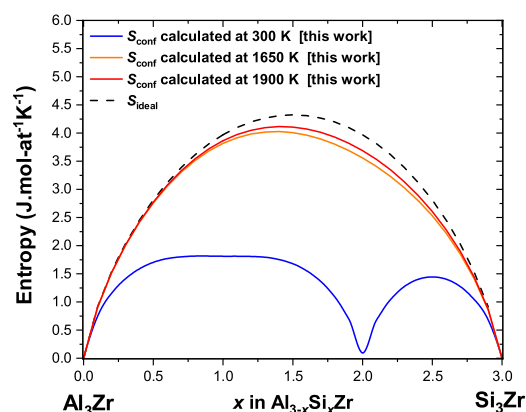


Fig. 17. Configurational entropy of mixing of the D_{023} solid solution calculated at 300 K, 1650 K and 1900 K compared to the configurational entropy of an ideal solid solution.

at 300 K, the ideal nature of the solution is highlighted at higher temperatures since its configurational entropy of mixing calculated at 1650 K and 1900 K are closer to the one of an ideal solution.

The crystalline arrangement of an ordered intermetallic compound is influenced by the optimized electronic structure, primarily shaped by the valence electrons. In trialuminides, the electronic structure is specifically associated with the formation of cubic and tetragonally distorted fcc-based supercells. In particular, Leineweber et al. [71]

made a comprehensive observation indicating a consistent pattern in the predominant Al_3TM structures, where TM represents a transition metal belonging to the iii, iv, and v groups. This sequence of group numbers directly corresponds to L_{12} , D_{023} , and D_{022} superstructures, respectively [71]. Yannello & Fredrickson [70] reported the ground-state structures based on the number of valence electrons per Al_3TM trialuminide. As illustrated at the bottom of Fig. 18, they showed that the L_{12} structure (associated with group-iii) is stabilized by 12 electrons/TM, the D_{023} structure (related to group-iv) is stabilized by 13 electrons/TM, and the D_{022} structure (corresponding to group-v) is stabilized by 14 electrons/TM. In this work, the Al_3Zr and Al_3Ti stoichiometries comprise 13 valence electrons/TM and thus correspond to the D_{023} structure. This scheme analysis is consistent with the enthalpy of formation surface projection considering the ground state *end-members* of this work and assuming ideal behavior for Ti/Zr substitution (Fig. 18a, which derives from the $\text{D}_{022}/\text{D}_{023}$ formation enthalpies bottom view in Fig. 18b). Additionally, it can be observed that the number of electrons per trialuminide increases to 14 for the $\text{Al}_2\text{Si}(\text{Ti,Zr})$ stoichiometry; therefore, Si substitution shifts the ground state to the D_{022} structure as it occurs in the group-v Al_3TM trialuminides. Also, this is consistent with the ground state projection at the $\text{Al}_2\text{Si}(\text{Ti,Zr})$ stoichiometry presented in Fig. 18a, i.e. D_{022} being the preferred configuration at 0 K when Al is partially substituted by Si. Conversely, the number of valence electrons per AlSi_2TM and Si_3TM *end-members* is higher than 14; thus exceeding the maximum of electrons allowed in ground state crystals (bottom of Fig. 18). This behavior explains the small acceptance of Si in $\text{D}_{022}/\text{D}_{023}$ structures quantified experimentally in this work (Table 4).

Crystallographic structure permutation has also been observed when substituting late transition metals within Al sites, e.g., the substitution of Cu or Zn within $(\text{Al,Cu})_3\text{Ti}$ and $(\text{Al,Zn})_3\text{Ti}$, respectively, leads to the formation of the L_{12} structures [72,73] rather than adopting tetragonal configurations. Contrary to the effect of Si, structure rearrangement induced by Zn and Cu is associated with a decrease in the electron-per-atom ratio.

4.6. Implications on the solidification process via *sheil* -cooling simulations of aluminium-rich Al-Si-Ti-Zr alloys

As presented in the experimental part of this work, Si can be found in both $\text{D}_{022}/\text{D}_{023}$ intermetallics. Therefore, a proper modulation of Si partitioning is required to correctly predict the phase assemblage in the Al-Si-Zr-Ti system. In this matter, a thermodynamic model was constructed using the *end-members* from Tables E2 (D_{022} phase) and E3 (D_{023} phase) employing the CALPHAD approach. The DFT models for the D_{022} and D_{023} solid solutions were coupled with the stoichiometric compounds available in the FTLite database of FactSage [39]. The FCC, liquid and all available solutions from this dataset were also considered. Due to the non-equilibrium compositions observed in the intermetallic phases of this study, the *Scheil*-cooling approach was applied to tailor the new $\text{D}_{022}/\text{D}_{023}$ thermodynamic models. This method provides a means to approximate the non-iso-compositional behavior of phases upon cooling. *Scheil* cooling calculations were conducted according to the nominal composition of the three molten alloys previous to the PoDFA tests (Table 1) considering only Al, Si, Zr and Ti. Gray-highlighted data in Table 4 (EDS analysis) corresponds to the compositions considered as *Scheil*-cooling data, which were used for the DFT-based thermodynamic modeling.

The phase assemblage evolution upon cooling of samples S2, S4 and S6 are respectively reported in Fig. 19a, Fig. 19d and Fig. 19g of. The elemental composition of the simulated $\text{D}_{022}/\text{D}_{023}$ phases at the equilibration temperature during the PoDFA tests (Table 1) are represented by red bars in sub-figures (b)/(c) for sample S2, (e)/(f) for sample S4 and (h)/(i) for sample S6 in Fig. 19. Cooling calculations are compared to the mean compositions of intermetallics from EDS measurements (blue bar) and to the predictions from FactSage 7.3 (green bar). At

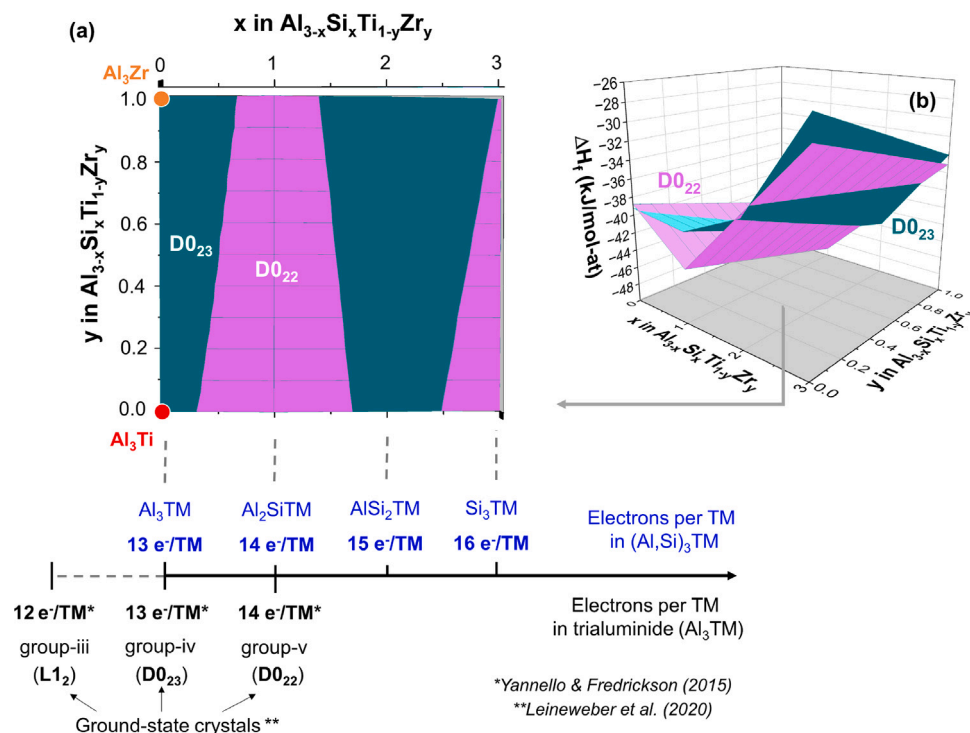


Fig. 18. (a) Ground-state projection derived from the (b) formation enthalpies of the D0₂₂ (purple) and D0₂₃ (teal) structures. The bottom of the figure compares the electrons per (Al,Si)₃TM end-members of this work with those in Al₃TM trialuminides reported by Yannello & Fredrickson [70] and Leineweber et al. [71].

first glance, it is shown that the thermodynamic model of this work is capable of reproducing the phase assemblage of the three alloys. FactSage 7.3 fails in predicting the D0₂₂ intermetallics for samples S2 and S4. As shown in the equilibrium phase diagrams of section 2 (Fig. 2), alloys S2 and S4 were designed targeting the single formation of D0₂₃ intermetallics. However, experimental results show the D0₂₂ also precipitate for those alloy compositions. Additionally, only the D0₂₂ phase was experimentally observed in sample S6 (Fig. 19h); however, FactSage 7.3 predicted a non Si-doped Al₃(Zr,Ti)-D0₂₃ phase (Fig. 19i) along with the D0₂₂ intermetallic.

Acceptance of Si in the D0₂₂/D0₂₃ phases is negligible for sample S2. This is because the S2 alloy was not purposely doped with Si. On the other hand, D0₂₂ phase in samples S4 and S6 accept a non-negligible amount of Si. The DFT-based solution model of this work adequately describes Si substitution for the D0₂₂ phase. For the D0₂₃ phase appearing in sample S4, Si substitution was not even expected with FactSage 7.3. An examination of the D0₂₃ solution model in FactSage 7.3 indicates that Si substitution was not accounted for. The new thermodynamic model provides a more accurate phase assemblage for the Al-Si-Zr-Ti alloys compared to FactSage 7.3. This is particularly valuable for Si-doped alloys promoting the precipitation of both D0₂₃/D0₂₂ phases. In this case, the model allows inferring the crystallographic structure based on the Si content. e.g., in sample S4, the Zr/Ti ratios are comparable in both D0₂₃/D0₂₂ phases. It is noteworthy that the DFT-based model already indicates that Si content is the main distinguishing factor in those intermetallics. This is especially valuable for industrial applications. e.g., by performing a chemical analysis the (Al,Si)₃(Ti,Zr) intermetallics, their crystallography can be easily deduced based on the Si content. Karpets et al. [55] studied the phase assemblage of 75at%Al-Zr-Ti alloys and concluded that the D0₂₂ has a limited acceptance of Zr in Ti sites, with a maximum of 0.08 Zr/(Zr+Ti). For the extended Al-Si-Zr-Ti system, the above solubility rule from Karpets et al. [55] does not apply anymore. For example, in the D0₂₂ intermetallic found in alloy S4 (Fig. 19e), a Zr substitution ratio higher than 0.8 Zr/(Zr+Ti) in Ti sites was estimated, which is 10 times larger

than the maximum value observed by Karpets et al. in the ternary Al-Zr-Ti alloys [55], i.e., 0.08 Zr/(Zr+Ti). The D0₂₂ intermetallics found in sample S6 (Fig. 19h) also displayed a Zr substitution higher than 0.08 Zr/(Zr+Ti) of Ti sites. Hence, Si in the D0₂₂ phase enhances the acceptance of Zr compared to non-Si doped Al₃(Ti,Zr)-D0₂₂ intermetallics. Si and Zr then yield a coupled stabilization effect on the D0₂₂ phase. As observed in sample S4, Si substitution preferentially occurs in the D0₂₂ phase compared to the D0₂₃. Karpets et al. synthesized a ternary 52.4%Al-35.4%Zr-12.2%Ti alloy [55] and obtained the Al₃Zr_{0.6}Ti_{0.4}-D0₂₃ intermetallic. The 52.4%Al-35.4%Zr-12.2%Ti alloy from Karpets et al. [55] was prepared with 0.26 Ti/(Ti+Zr) g/g content, which is comparable to the 0.31 Ti/(Ti+Zr) g/g used for preparation of alloy S4 of this work. Conversely, an equilibrium of both (Al,Si)₃(Ti,Zr)-D0₂₂/D0₂₃ phases with high contents of Zr were obtained herein (Fig. 19e and 19f). Similarly, this indicates that Si plays an important role on the stabilization of the Zr-rich (Al,Si)₃(Ti,Zr)-D0₂₂ intermetallic. Note that the D0₂₃ intermetallic naturally accepts high percentages of Zr substitution even in the Al-Zr-Ti framework. e.g., Karpets et al. [55] reported that the D0₂₃ phases can accept large amounts of Ti in Zr sites, ranging from 0.20 to 0.88 Ti/(Ti+Zr) in 75at%Al-Zr-Ti alloys. This explains the high acceptance of Zr in the D0₂₃ phase (Fig. 19f) even without Si-doping in the alloy (Fig. 19c).

As a side note, it is worth mentioning that Si precipitated at the end of the Scheil solidification for the Si-doped samples (Fig. 19d and Fig. 19g). This is compatible with the electron microprobe elemental maps reported in Fig. 10, where Si is found at the grain boundaries of samples S4 and S6. However, further experiments are necessary to assess the precipitation of the Ti-rich (Al,Si)₃(Ti,Zr) intermetallic fractions presented in Sections 4.3 and 4.4 (samples S2 and S6). These phases are not compatible with Scheil-cooling nor with equilibrium calculations, necessitating additional investigation.

While the thermodynamic model of this work was developed using Scheil-cooling calculations, it successfully approximated equilibrium data for the ternary Al-Si-Zr system found in the literature, which relies on annealing techniques [45]. This is evident in Fig. 20b, Fig. 20d, and Fig. 20f, where the black symbols represent the compositions reported

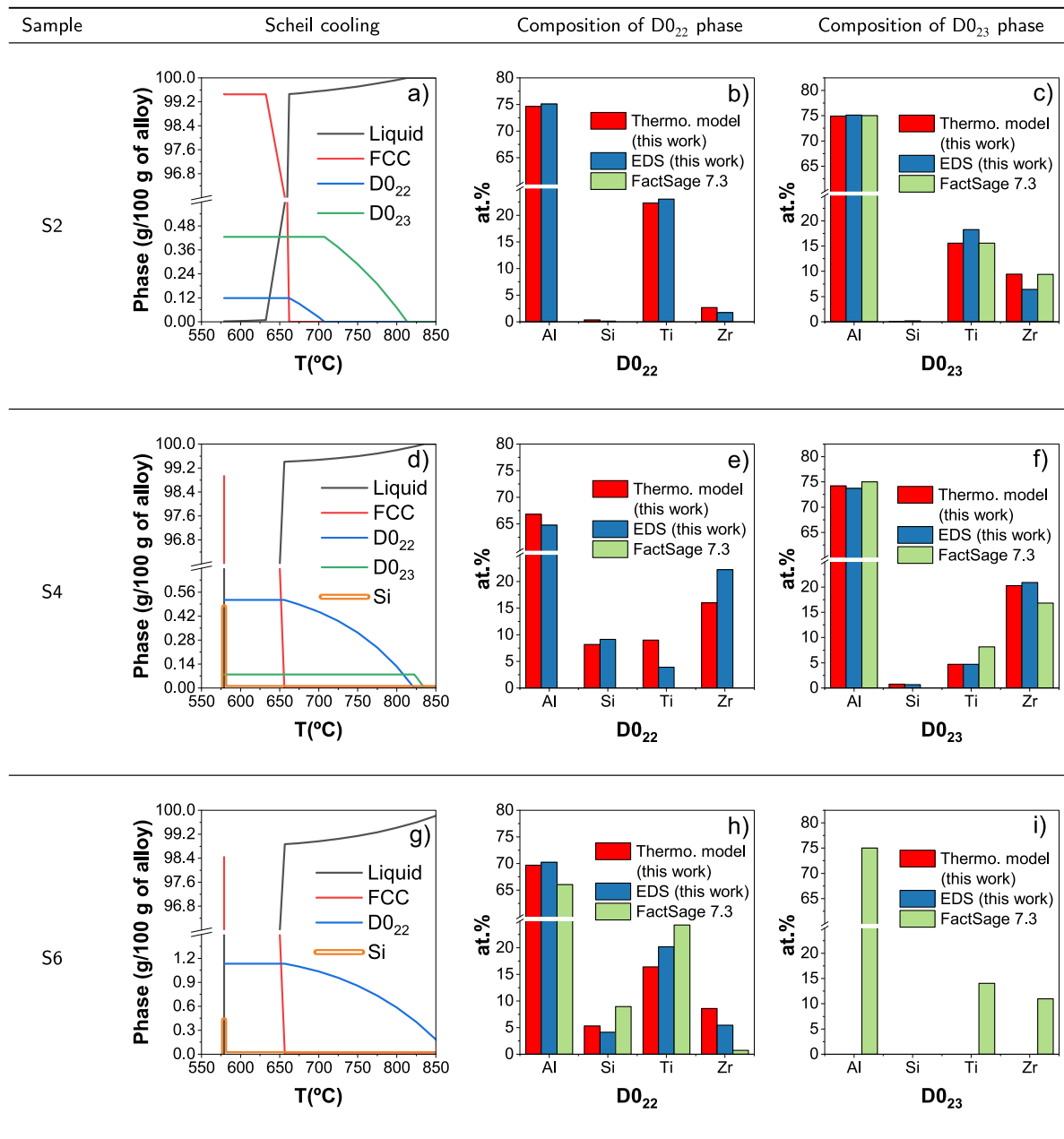


Fig. 19. Scheil cooling diagrams (second column) for each sample using the DFT-based thermodynamic model. The mean elemental composition of the $D0_{22}/D0_{23}$ phases from the PoDFA setup (EDS analysis of Table 4) is represented by the blue bars. EDS data is compared to the predictions of the DFT-based model (red) and FactSage 7.3 (green) at the equilibration temperatures reported for the PoDFA experiments (Table 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

by Jain & Gupta [45]. Despite a slight overestimation of silicon content within the $D0_{22}$ phase in these figures, the new model provides a more accurate phase assemblage compared to FactSage 7.3. Notably, the previous FactSage 7.3 diagram did not display the $D0_{22}$ phase in the Al-Si-Zr domain and the $D0_{23}$ structure was solely present as an Al_3Zr stoichiometric compound (Fig. 20). It is suggested to perform further experiments in the Al-Si-Zr-Ti framework to obtain additional training data for the CALPHAD assessment. Emerging techniques, such as the heating PoDFA setup of this work, could be helpful for data generation. A quick and supplementary arising approach for data collection is the use of laser-induced breakdown spectroscopy (LIBS) [74,75], which has demonstrated effective results for the evaluation of the liquidus line in the Al-Ti diluted system using automated robots [75].

5. Conclusions

The present work reports for the first time the process to precipitate and concentrate $(Al,Si)_3(Zr,Ti)$ -based intermetallics in an FCC-matrix using a heating PoDFA apparatus. SEM, EDS, EMP, XRD and TEM investigations of the samples, combined with DFT and cooling calculations, result in the following main conclusions:

1. Synthesis of low mass fraction ($<10g/kg$ of alloy) $(Al,Si)_3(Zr,Ti)$ $D0_{22}/D0_{23}$ intermetallics within Al-Si-Zr-Ti alloys was accomplished.
2. Sublattice substitution of Si within Al sites of the Al_3Zr-D0_{23} and Al_3Ti-D0_{22} phases was confirmed.
3. Crystallographic analysis corroborated the effective nucleation of the alpha-FCC phase with $(Al,Si)_3(Zr,Ti)$ intermetallics due to

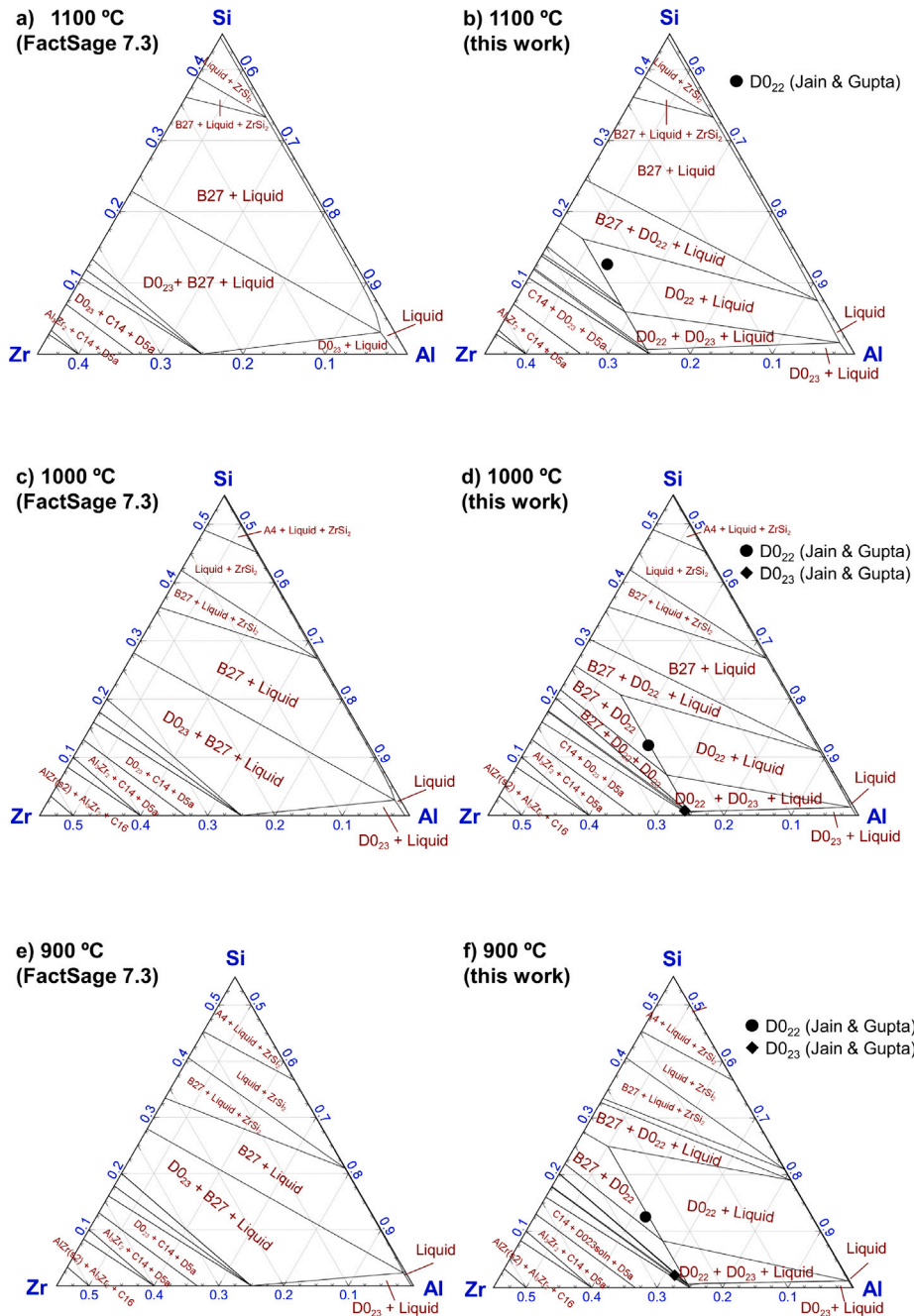


Fig. 20. Al-Si-Zr isothermal sections computed with FactSage 7.3 at (a) 1100 °C, (c) 1000 °C and (e) 900 °C, compared to those obtained with the new thermodynamic model (b, d and f, respectively) and data from Jain & Gupta [45].

their small lattice mismatch. Additionally, it is shown that acceptance of Si in the $D0_{22}$ phase does not significantly modify the aluminium/intermetallic interplanar spacing misfit ($f_d < 10\%$), thus preserving the potency of these intermetallics to nucleate the Al-phase.

- For the Si-doped sample S4 (quaternary Al-Si-Zr-Ti alloy), it has been found that Si promotes the formation of Zr-rich $(Al, Si)_3$ (Zr,Ti)- $D0_{22}$ intermetallics. This does not occur in the Al-Zr-Ti framework reported in the literature, where the $D0_{22}$ phase has a limited acceptance of Zr in Ti sites, and exclusively the $D0_{23}$ phase naturally forms Zr-rich Al_3 (Zr,Ti)- $D0_{23}$ intermetallics. To some extent, acceptance of Zr in the $D0_{22}$ phase of sample S6 was also higher than FactSage 7.3 predictions. This study

shows that a Si impurity can promote the stability of the $D0_{22}$ intermetallics enhancing the Zr acceptance.

- DFT calculations showed that site 2b of the $(Al, Si)_3$ Ti- $D0_{22}$ and site 4e of the $(Al, Si)_3$ Zr- $D0_{23}$ solid solutions are the most energetically favorable sites for Al substitution by Si atoms.
- A DFT-based thermodynamic model to describe the Al_3 Zr- $D0_{23}$ and Al_3 Ti- $D0_{22}$ phases was proposed to model Si substitution upon cooling. Scheil cooling calculations with this thermodynamic model provided a qualitatively good phase assemblage description for the tested Al-Si-Zr-Ti alloys.
- Numerical and experimental tests indicate that Si has a preferential affinity for the $D0_{22}$ compared to the $D0_{23}$ phase.

Then Si content helps enlivening the crystallographic structure of $(\text{Al},\text{Si})_3(\text{Zr},\text{Ti})$ intermetallics.

CRedit authorship contribution statement

Juan-Ricardo Castillo-Sánchez: Conceptualization, Methodology, Investigation, Formal Analysis, Writing – Original Draft. **Georges Salloum-Abou-Jaoude:** Conceptualization, Methodology, Formal Analysis, Supervision, Resources, Funding acquisition, Writing – Original Draft. **Aïmen E. Gheribi:** Formal Analysis, Writing – Review & Editing. **Paul Lafaye:** Methodology, Investigation, Validation, Formal Analysis, Writing – Original draft. **Kentaro Oishi:** Formal Analysis, Writing – Review & Editing. **Jean-Philippe Masse:** Methodology, Investigation, Validation, Formal Analysis, Writing – Original draft. **Etienne Bousser:** Formal Analysis, Writing – Review & Editing. **Gilles L'Espérance:** Resources. **Jean-Philippe Harvey:** Conceptualization, Methodology, Formal Analysis, Supervision, Resources, Funding acquisition, Writing – Original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.actamat.2023.119455>.

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