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Article

Microstructures and Isothermal Oxidation of the Alumina Scale Forming $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ Alloys

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Abstract: Nb–silicide based alloy will require some kind of coating system. Alumina forming alloys that are chemically compatible with the Nb–silicide based alloy substrate could be components of such systems. The intermetallic alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ were studied in the cast, heat treated and isothermally oxidised conditions at 800 and 1200 °C to find out if they are alumina scale formers. The alloys were designed using the alloy design methodology NICE and were required (i) not to have stable solid solution phase in their microstructures; (ii) not to pest and (iii) to form alumina scale. Their microstructures consisted of silicides and aluminides. Both alloys satisfied (i) and (ii) and formed thin scales at 800 °C. At 1200 °C the former alloy suffered from internal oxidation and formed alumina intermixed with Ti rich oxide beneath a thick “layered” scale of mixed oxides that contained Ti and/or Al and/or Si. There was no internal oxidation in the latter alloy that formed a thin continuous well adhering $\alpha\text{-Al}_2\text{O}_3$ scale that was able to repair itself during oxidation at 1200 °C. In both alloys there was severe macrosegregation of Si, which in $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was almost double that in $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. The severe macrosegregation of Si contributed to the formation of a “layered” structure in the former alloy that was retained at 800 and 1200 °C. Both alloys met the “standard definition” of High Entropy Alloys (HEAs). Compared with the range of values of the parameters valence band (VEC), δ and $\Delta\chi$ of bcc solid solution plus intermetallic(s) HEAs, only the $\Delta\chi$ of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ was within the range and the parameters VEC and δ of both alloys respectively were outside and within the corresponding ranges. The alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ exhibited strong correlations between the parameters $\Delta\chi$, δ and VEC, and the range of values of each parameter was wider compared with the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. There was a strong correlation only between the parameters $\Delta\chi$ and δ of the latter alloy that was similar to that of the former alloy.

Keywords: high entropy alloys; intermetallics; pest oxidation; high temperature oxidation; Nb–silicide based alloys; coatings; complex concentrated alloys; multi-principle element alloys

1. Introduction

Nb–silicide based alloys could replace Ni-based superalloys in advanced gas turbines to enable the latter to operate at higher turbine entry temperatures so that engine performance targets with new and stringent environmental targets can be met. These alloys have microstructures that contain bcc Nb solid solution (Nb_{ss}), tetragonal and/or hexagonal Nb_5Si_3 silicides and other intermetallic compounds, such as tetragonal Nb_3Si silicide, C14- NbCr_2 Laves phase and $\text{Al}_5\text{-Nb}_3\text{X}$ ($\text{X} = \text{Al}, \text{Ge}, \text{Si}, \text{Sn}$) compounds. The Nb_{ss} and the intermetallic compounds are alloyed [1–3]. For example, the Nb_5Si_3 can be very rich in Ti and Hf. The volume fractions of Nb_{ss} and Nb_5Si_3 are important for achieving

a balance of creep, oxidation and toughness properties. A high vol.% of Nb_{ss} is disadvantageous to creep and oxidation.

A strategic objective of the development of Nb–silicide based alloys is the improvement of their oxidation. The approach used to achieve the latter has been to find out which alloying additions affect oxidation. Research has demonstrated that the alloying elements Al, B, Cr, Fe, Ge, Hf, Sn and Ti improve the oxidation of Nb–Si based alloys. Alloy development has shown that Nb–silicide based alloys can offer a balance of properties.

Oxidation resistance often controls the life of high temperature alloys in structural engineering applications. Dense, continuous and adherent Al₂O₃ or SiO₂ oxides protect alloys from oxidation at high temperatures ($T > 1000$ °C). These oxides are the most protective, because of their high thermodynamic stability and the low diffusivities for anions and cations. Unfortunately, Nb–silicide based alloys are not alumina formers, because in these alloys the concentration of Al must be kept low owing to the adverse effect of this element on mechanical properties (ductile to brittle transition temperature-DBTT of the Nb_{ss}, toughness, high temperature strength and creep of the alloy). Furthermore, the concentration of Si in these alloys, which can be as high as 20 at.%, cannot assure the formation of silica scale. In other words, the Nb–silicide based alloys are not alumina or silica formers. Instead, their scales consist of Ti niobates, AlNbO₄, CrNbO₄ and oxides of Nb and Ti [4,5].

In the operating environment of an aero-engine, the Nb–silicide based alloys will require protection via some kind of coating system. A requirement of the coating system is chemical compatibility with the substrate. One approach to the design of a coating system for Nb–silicide based alloys is to consider thermal barrier type coating systems consisting of a bond coat and top coat, where the bond coat could be a layered multi-material system or a functionally graded material forming in situ α -Al₂O₃ between the bond coat and the top coat. A layered multi-material coating system has been suggested by Jackson et al. [6].

Is there α -Al₂O₃ forming alloy(s) that could be used in coating system(s) compatible with Nb–silicide based alloys? The need to answer this question has motivated investigations in our research group that resulted in the research presented in this paper. The latter focusses on two Nb–Ti–Si–Al–Hf alloys that were studied as part of an ongoing research programme that aims to discover which (if any) alloys of Al–Hf–Nb–Si–Ti–X systems are alumina formers. The two alloys were not studied as coatings applied on a Nb–silicide based substrate in order to eliminate the effects of substrate and coating process on microstructure and oxidation.

The structure of the paper is as follows. First the approach used to design and select the two alloys is explained. Then the experimental techniques used for the characterisation of the alloys are described. The results for the cast and heat treated alloys are presented before their isothermal oxidation at 800 and 1200 °C is presented. The discussion considers first the macrosegregation and microstructures of the alloys, which are also compared with High Entropy Alloys, and then their oxidation behaviour is considered.

2. Design and Selection of the Alloys of This Research

Our goal was to design and develop α -Al₂O₃ scale forming Nb–Ti–Si–Al–Hf alloys. The design of the alloys studied in the research reported in this paper was guided by the alloy design methodology NICE, which was recently described in Reference [4], and current knowledge about the oxidation of Nb–Si based alloys. Briefly, in NICE there are three key parameters that guide the design (selection) of Nb–Si based alloys. These are based on electronegativity ($\Delta\chi$), atomic size (δ) and number of valence electrons per atom filled into the valence band (VEC). There are relationships between these parameters and the concentrations of elements in alloys and the weight gains of the latter in isothermal oxidation. These relationships were discussed in Reference [4].

The Nb_{ss} is known to be the Achilles' heel in the oxidation of Nb–Si based alloys. We decided to design alloys (i) with zero volume fraction of Nb_{ss} and (ii) with microstructures that should contain Al rich, Si rich and/or Al and Si rich intermetallic phases, in particular transition metal aluminides and

silicides. The choice of intermetallics was guided by the literature [7–24]. Below we discuss why we preferred certain intermetallic compounds to be stable in the microstructures of our alloys.

2.1. Which Intermetallic Compounds?

We did not want the alloys to exhibit catastrophic pest oxidation. Taking into consideration the alloying elements that are known to improve the oxidation of Nb–silicide based alloys (see Section 1) a good starting point was to consider the Ti–Al system. The intermetallic compounds of the Ti–Al system are known not to pest [7]. Aluminium rich TiAl, and the TiAl₂ and TiAl₃ aluminides can form alumina scales but Al poor TiAl and Ti₃Al form titania rich scales and oxidise at much higher rates [8]. For example, when TiAl with 50 at.% Al was oxidised in air at 950, 1100 and 1200 °C, at the two higher temperatures TiO₂ scale formed and there was internal oxidation. Parabolic oxidation kinetics were followed at the low temperature where the oxidation was independent of specimen preparation and fabrication method [9]. Furthermore, the alloying of TiAl with Nb promoted the formation of continuous alumina scale on TiAl (50 at.% Al) at 950 °C independent of surface preparation or exposure environment (air or O₂) but the alloying with Hf had a minimal effect [9]. The alloying of TiAl with Si improved oxidation resistance [10]. For Al poor TiAl it is known that the addition of 4 to 12 at.% Nb in Ti–48Al increased oxidation resistance at 850 °C and that the alloys developed continuous bands of dense alumina beneath titania rich surface layer that formed during the early stages of oxidation [11]. When TiAl₂, which was sputter deposited on TiAl, was oxidised in air at 800 and 900 °C, only external well adhering almost micro-crack free θ -Al₂O₃ scale was formed on the TiAl₂ [12]. In the isothermal oxidation of arc melted TiAl₃ parabolic oxidation kinetics were followed above 1000 °C for 100 h in flowing oxygen and α -Al₂O₃ scale formed. Cyclic oxidation tests at 982 °C also confirmed that α -Al₂O₃ formed after 20 cycles [13].

With Nb and Al as constituent elements of the alloys to be designed the oxidation of intermetallic compounds in the Nb–Al binary system also was considered. NbAl₃, which is isomorphous with TiAl₃, is the only compound in the Nb–Al system that can form continuous α -Al₂O₃ scale at high temperatures [14] but it is known to pest, with the worst behaviour exhibited between 650 and 850 °C [15]. Unlike TiAl₃, the NbAl₃ aluminide has a narrow solubility range. Like the TiAl₃, the depletion of Al by the initial formation of the oxide layer results in the formation of a lower compound, namely Nb₂Al, beneath the scale. The latter compound influences the structure, stability and adherence of the oxide layer. Nb₂Al cannot form continuous alumina. Rupture of the initial alumina layer is followed by the rapid growth of AlNbO₄ and Nb₂O₅ and the consumption of Nb₂Al, which is then followed by the growth of alumina again on the NbAl₃. Repetition of this process results in a layered scale and nearly linear oxidation kinetics. Excess Al prevents the formation of the layered structure but degrades the long term oxidation resistance, because of Al evaporation and alumina growth in grain boundaries. However, alloying the NbAl₃ with Ti promotes external α -Al₂O₃ scale formation at lower Al concentrations than those required for the binary alloys [7].

Taking into account that Ti and Si are key alloying elements that are known to improve the oxidation of Nb–silicide based alloys (see Section 1) we also considered the Ti–Si system. The intermetallic compounds of the Ti–Si system do not suffer from pest oxidation [15]. We were not interested in the Ti₃Si compound, because it is isomorphous with Nb₃Si and the latter is known to pest. However, we were interested in the Ti₅Si₃, because it is isomorphous with the hexagonal Nb₅Si₃ and for the following reasons. The Ti₅Si₃ has excellent oxidation resistance in oxygen at $T > 1000$ °C but insufficient oxidation resistance in air [16]. Also, it has excellent oxidation resistance in air at 1200 °C when it contains small vol.% of Ti₅Si₄ or TiSi₂ [17,18]. For example, arc melted Ti₅Si₃ gained weight 31 mg/cm² after cyclic oxidation at 1149 °C for 50 h and its scale consisted of TiO₂ (about 80 vol.%) and SiO₂ (α -cristobalite) [19] but for Si-depleted Ti₅Si_{2.8} the initial formation of SiO₂ was not favoured and TiO₂ grew on the surface, while for the Si-rich Ti₅Si_{3.2} the SiO₂ was more favourable than TiO₂ [18].

With Nb and Si in the alloys to be designed we also considered the oxidation of intermetallic phases in the Nb–Si system. The Nb₃Si, Nb₅Si₃ and NbSi₂ compounds exist in the temperature range 700 to 850 °C forming Nb₂O₅. In Nb–silicide based alloys, Nb₅Si₃ silicide grains can be contaminated by oxygen [20]. Interstitials can stabilise the hexagonal γ Nb₅Si₃ (hP16, D8₈, prototype Mn₅Si₃) [21]. The hexagonal Ti₅Si₃, owing to its Mn₅Si₃-type structure (isomorphous with γ Nb₅Si₃), can incorporate interstitial ternary additions (has one interstitial site per formula unit corresponding to about 10 at.% at 1000 °C [22]) that modify its oxidation resistance without changing the crystal structure [19]. The concentration of interstitial oxygen in Ti₅Si₃ is about 6 at.% [18]. Interstitial ternary oxygen additions increased the oxidation resistance of binary Ti₅Si₃, for example the weight gain of Ti₅Si₃O_{0.25} at 1000 °C was 0.45 mg/cm² after 240 h, and the weight gain of Ti₅Si₃O_{0.75} at 1079 °C was 0.82 mg/cm² after 130 h while at 1306 °C the weight gain was 1.1 mg/cm² after 240 h [19]. The scale formed on Ti₅Si₃ doped with interstitial oxygen consisted of crystalline silica matrix forming a continuous layer that contained titania particles. The alloying with oxygen promoted the formation of thin silica layer in the early stages of oxidation [18].

The microstructure of Ti₅Si₃-8 wt.% Al contained a dispersion of TiAl₃ (Ti_{0.25}(Al_{0.67}Si_{0.08})) of about 15 vol.% and Al₂O₃ and a small volume fraction of Ti₅Si₄ in which the concentration of Al was very low [17]. The scale formed on the Ti₅Si₃-8 wt.% Al alloy after 80 h at 1200 °C in air was about 30 μ m thick and contained α Al₂O₃ and TiO₂ and no SiO₂ [17]. The scale was made of two layers; an outer overlapping layer of Al₂O₃ and TiO₂ and an inner layer of Al₂O₃ [17]. There was a depletion of the TiAl₃ compound and an increase of the vol.% of Al₂O₃ in the substrate after the oxidation [17]. It is also known that the alloying of Ti₅Si₃ with Nb within the solubility limit (about 15.6 at.%) improved the oxidation resistance in flowing dry air at 900 °C of single crystal alloys that were produced using the Czochralski method [23]. Finally, it has been reported that a Ti(Al_xSi_{1-x})₂ (0.15 < x < 0.3) coating on Ti–6Al–4V substrate decomposed to a layered structure that consisted of the Ti₅Si₄ and TiSi silicides at 850 and 950 °C and that the latter significantly improved the oxidation resistance [24].

In summary, (a) Al rich TiAl, TiAl₂ and TiAl₃ can form α Al₂O₃; (b) Nb and Si benefit the oxidation of TiAl; (c) Ti improves the oxidation of NbAl₃ that can form α Al₂O₃; (d) Ti₅Si₃ has oxidation resistance at 1200 °C when in synergy with (in the presence of) small vol.% of Ti₅Si₄ and TiAl₃; (e) interstitial oxygen in Ti₅Si₃ improves its oxidation resistance; and (f) alloying Ti₅Si₃ with Al suppresses SiO₂ formation, and promotes formation of α Al₂O₃ beneath alumina and titania scale in air at 1200 °C.

Therefore, the literature guided us to aim to have in the microstructures of the alloys to be designed (a) Al rich TiAl, TiAl₂ and TiAl₃ aluminides where Ti would be substituted by Nb and Hf, and Al by Si and (b) Me₅Si₃ and Me₅Si₄ silicides, where Me is transition metal; and (c) to avoid the formation of Nb rich tri-aluminide. In particular, Me₅Si₃ silicide of hexagonal structure was desirable. We had good reasons to believe that the latter was possible in alloys of our chosen system (see Section 1), because our previous research had indicated that hexagonal Nb₅Si₃ would be the stable silicide in the Nb–24Ti–18Si–5Al–5Hf alloy [20].

2.2. Alloy Design

When we considered the requirement for zero volume fraction of Nb_{ss} (see (i) in the previous section), the alloy design methodology NICE gave the following values for the parameters $\Delta\chi$, VEC and δ : $\Delta\chi = 0.1543$, VEC = 4.263 and $\delta = 9.0075$. For these values the NICE gives the following concentrations: Ti = 24.2 at.%, Si = 21.5 at.% and Hf = 4.7 at.%. Next, we calculated the concentrations of these elements for the extreme (ideal) condition of $\Delta W/A$ (weight gain per unit area) equal to zero at 800 and 1200 °C, for which the NICE gave the following concentrations: Ti = 21.3 at.%, Si = 22.3 at.% and Hf = 4.4 at.%.

In view of the high but non-dissimilar concentrations of Si and Ti calculated from the two approaches based on NICE, we considered if Me₅Si₃ silicides could be in equilibrium with Al-rich aluminides. The available Ti–Al–Si phase equilibria data [25] shows that Ti₅Si₃ can be in equilibrium

with TiAl and TiAl₂ for Al ≈ 24 at.% and Si ≈ 24 at.% or in equilibrium with TiAl₃ and/or TiAl₂ for Al ≈ 30 at.% and Si ≈ 24 at.% or in equilibrium with TiAl₃ and Ti₅Si₄ for Al ≈ 35 at.% and Si ≈ 24 at.%.

The literature on the oxidation of Ti–Al alloys shows that protective Al₂O₃ scale does not necessarily form when alumina is thermodynamically stable in the alloy and that higher Al concentrations are required for kinetic reasons [26]. In other words, there are “two” Al concentrations, one required to thermodynamically stabilise Al₂O₃, we shall call this $C_{\text{ther}}^{\text{Al}}$, and the other, which we shall call $C_{\text{kin}}^{\text{Al}}$ ($C_{\text{kin}}^{\text{Al}} \geq C_{\text{ther}}^{\text{Al}}$), required to form a continuous protective oxide. Thermodynamics dominate alumina formation when $C_{\text{kin}}^{\text{Al}} = C_{\text{ther}}^{\text{Al}}$ and kinetics when $C_{\text{kin}}^{\text{Al}} > C_{\text{ther}}^{\text{Al}}$. The same is the case for Ti–Si alloys where the minimum Si concentration to form SiO₂ is about 40 to 45 at.% [26]. Alloying additions may change $C_{\text{ther}}^{\text{Al}}$, the oxygen solubility and the diffusivities of oxygen and Al in the alloy and thus may affect the concentration of Al at the oxide/alloy interface (see discussion). Kinetic factors would reduce $C_{\text{kin}}^{\text{Al}} - C_{\text{ther}}^{\text{Al}}$ (for example, see in previous section comment about the addition of Nb in Ti–48Al).

The calculated concentrations of Hf, Si and Ti from NICE, and the Al concentration for which Me₅Si₃ silicide is in equilibrium with TiAl and TiAl₂ (i.e., thermodynamics) were “guiding us” to consider an alloy of composition 23.75Nb–23.75Si–23.75Ti–23.75Al–5Hf (at.%). This could be considered to be a “High Entropy Alloy” (HEA) or a “Multi-Principle Element Alloy” (MPEA), or a “Complex Concentrated Alloy” (CCA). Then again, the oxidation literature was “guiding” us to increase the Al concentration.

We know that Nb–silicide based alloys with high vol.% Nb_{ss} exhibit lower Si macrosegregation compared with alloys with low vol.% Nb_{ss} for the reasons discussed in Reference [27]. For the (still to be decided) intermetallic alloys to be studied in this paper, because of the requirement for zero vol.% Nb_{ss} (see (i) at the beginning of this section), we would expect the Si macrosegregation to be high. When high Si macrosegregation was observed in Nb–silicide based alloys with high vol.% of intermetallics, the alloys had higher $\Delta H_m/T_m$ and T_m^{SP} values and lower T_m and $T_m^{\text{sd}}/T_m^{\text{SP}}$ values compared with the alloys with low Si macrosegregation (see Reference [27] for the definition of and equations for the parameters used for the study of macrosegregation). The low T_m accounts for the formation of undercooled melt near an effective heat sink, such as the walls of the water cooled copper crucibles used for the preparation of alloys. High melt undercooling is required for the growth of faceted S/L interfaces, like those of intermetallic compounds that have high entropy of fusion. High $\Delta H_m/T_m$ is consistent with high vol.% of intermetallic compounds in an alloy [27]. Zone(s) with different microstructure(s) can form from undercooled melts of Nb–silicide based alloys, for examples see References [28–31]. The high T_m^{SP} and low T_m and $T_m^{\text{sd}}/T_m^{\text{SP}}$ values steered us to high concentration of Al. Taking into consideration that Al and Ti in Nb alloy melts are “surface active” elements that tend to segregate to the surface [32], an increase in Al concentration with the accompanied changes in the aforementioned parameters that describe macrosegregation could lead to different zones forming in the alloy(s) from the bottom of the buttons (in contact with the heat sink) towards the bulk. In other words, the increase of the Al concentration and the solidification conditions at an effective heat sink could possibly result in some form of “functionally gradient microstructure”.

Next, we decided to select the following Si, Ti and Hf concentrations, Si = 23.75 at.%, Ti = 23.75 at.% and Hf = 5 at.%, and to opt for Al = 30 at.%, anticipating to avoid having stable TiAl in the microstructure. This approach gave the Nb concentration (balance) of 17.5 at.%. Thus, the nominal composition of our first alloy was 17Nb–24Si–24Ti–30Al–5Hf or Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5}. Subsequently, we decided to increase the volume fraction of tri-aluminide in the microstructure and also to exploit the presence of Ti₅Si₄ in it (see above in this section). This required us to increase the concentration of Al. We opted for Al = 35 at.% and Hf = 4 at.%. Thus, the nominal composition of our second alloy was 13Nb–24Si–24Ti–35Al–4Hf or Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}. Both alloys may be considered to be High Entropy Alloys (HEAs) or Multi-Principle Element Alloys (MPEAs) or Complex Concentrated Alloys (CCAs). For the aforementioned alloys we could not calculate the Al concentrations that correspond to $C_{\text{ther}}^{\text{Al}}$ or $C_{\text{kin}}^{\text{Al}}$ (see Section 5.3).

In summary, guided by the literature on the oxidation of intermetallic compounds, the alloy design methodology NICE, the available phase equilibria data and data about macrosegregation in Nb-Si based alloys, we selected two alloys, namely the alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$, which we wanted to have (i) zero vol.% Nb_{ss} and (ii) microstructures consisting of Me_xAl_y aluminides and Me_xSi_y silicides, and form alumina scales at 800 and 1200 °C. Also, we were interested to find out if zones of different microstructures would form in these alloys.

3. Experimental

Buttons (25 g) of the two alloys were prepared from high purity (better than 99.9 wt.%) elements by arc-melting in an argon atmosphere using a non-consumable tungsten electrode in a water cooled copper crucible. The melting procedure was repeated 5 times for each alloy. The samples for heat treatment were wrapped in Ta foil and placed in an alumina boat in the hot zone of a tube furnace. A crucible containing Ti-sponge was placed in the entrance of the tube furnace to ensure that the heat treatments were carried out in flowing Ti gettered argon. The alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ was heat treated at 1300 °C and the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ at 800 and 1200 °C. The latter temperatures were the same as those used for the isothermal oxidation experiments.

Cube specimens (approximately 0.4 cm × 0.4 cm × 0.4 cm) cut from the as cast buttons were prepared for isothermal oxidation. The specimens were polished to 300 grit. Isothermal oxidation experiments were performed at 800 and 1200 °C for 100 h using a NETZSCH STA 49 F3 Jupiter thermal analyser (NETZSCH GmbH, Selb, Germany) supported by the NETZSCH Proteus software. The instrument had a weight resolution of 0.1 µg over the entire weighing range (0–35,000 mg). We used a 3 degrees per minute heating rate from room temperature to 800 or 1200 °C. A Jeol 6400 scanning electron microscope (SEM, Jeol, Tokyo, Japan) and a Philips XL 30S FEG SEM (Philips-ThermoFisher Scientific, Hillsboro, OR, USA) were used for imaging and quantitative analysis. Both instruments were equipped with EDS detectors and Oxford Instrumentals INCA software for quantitative chemical analysis, and elemental standards of Nb, Ti, Al, Si, Hf. The Philips XL 30S FEG SEM was also equipped with Fe_2O_3 as the standard for oxygen. The X-ray maps of scales were taken in the latter instrument. All compositions in this paper are given in at.% unless stated differently.

A Siemens D5000 diffractometer with a $\text{Cu K}\alpha$ (Hiltonbrooks Ltd, Crew, UK) was used for phase identification in the as cast and heat treated specimen. The same diffractometer was used for glancing angle XRD to identify the oxides in the scales that formed on the oxidised specimens. The glancing angle XRD was performed at a scan speed of 2°/min over a 2θ range of 20° to 100° with a glancing angle of 5°. For phase analysis the ICDD (International Centre for Diffraction Data) PDF-4+ database and Sieve+ software (ICDD, Newtown Square, PA, USA) was used.

4. Results

4.1. Alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$

As cast: The actual composition of the alloy was Nb–23.4Ti–22.8Si–29.7Al–4.8Hf. This was the average composition of all EDS analyses taken from the top, bulk and bottom of the button. The standard deviations of the concentrations of all the elements with the exception of Hf were greater than one, indicating chemical inhomogeneity in the microstructure (see below). The cast microstructure is shown in Figure 1a,b. In all parts of the button there were large (bulky) faceted grains of a light contrast phase surrounded by a darker contrast microstructure, in which there were fine second phase(s) that were not easy to distinguish owing to similarities in contrast. The vol.% of the darker contrast microstructure was significantly reduced in the bottom of the button.

According to the XRD data (Figure 2a), silicides and TiAl_x ($x = 1, 3$) aluminides were present in the microstructure. In the X-ray diffractogram there were peaks that corresponded only to hexagonal $\gamma\text{Nb}_5\text{Si}_3$, or tetragonal $\beta\text{Nb}_5\text{Si}_3$ or TiAl_3 , and the peaks for TiAl coincided with those of other phases. The outline of some of the large lighter contrast grains in Figure 1a,b suggested hexagonal symmetry,

which is consistent with the crystal structure of $\gamma\text{Nb}_5\text{Si}_3$. The XRD data also suggested the presence of Ti_5Si_4 and TiSi . Peaks of the latter silicide coincided with peaks of other phases. The Ti_5Si_4 forms as thin layers on Ti_5Si_3 and the TiSi has similar contrast with Ti_5Si_4 (see Section 4.2 and discussion). Careful study of the cast alloy using EDS did not confirm the existence of Ti_5Si_4 and TiSi .

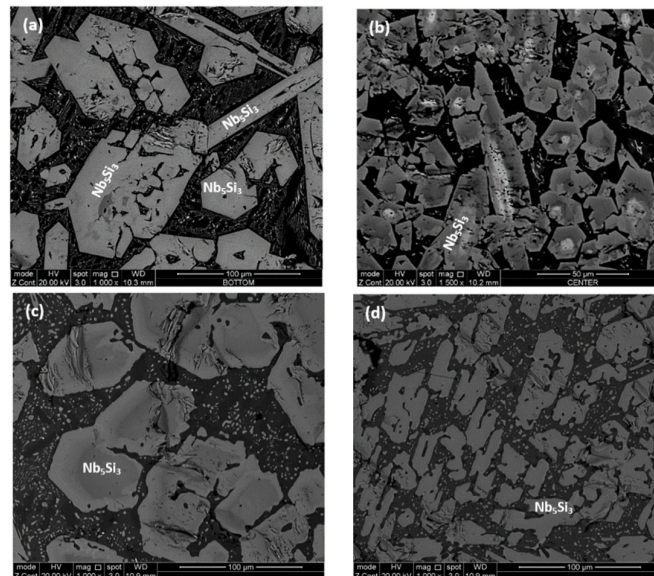


Figure 1. Scanning electron microscope (SEM) backscatter electron images of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$, (a,b) cast alloy; (c,d) heat treated alloy (1300 °C/100 h). (a,c) top; (b,d) bulk.

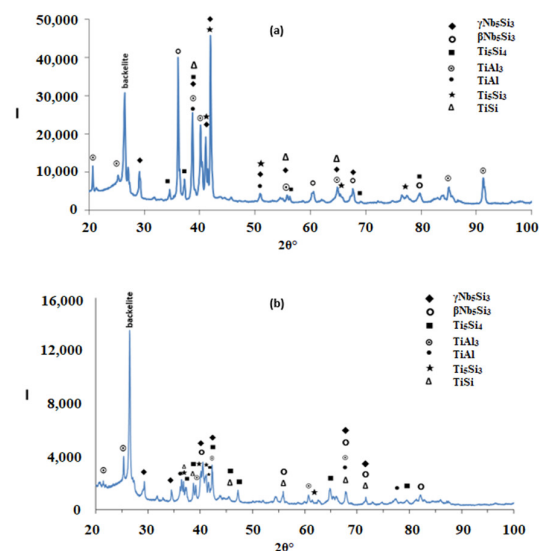


Figure 2. X-ray diffractograms of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$, (a) as cast; (b) heat treated (1300 °C/100 h).

Zones of different microstructure were not observed in the cross sections of the cast alloy even though there were differences in composition between bottom, bulk and top of the button, see Figure 3a. The bulk was poorer in Al compared with the bottom and top, the bottom was richer in Ti than the bulk and top and the top was poorer in Si than the bottom and bulk.

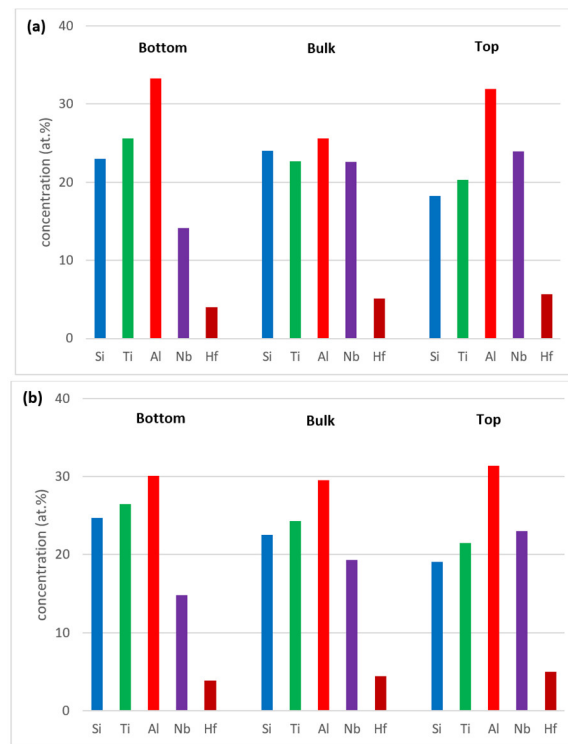


Figure 3. Comparison of the concentrations of elements in the bottom, bulk and top of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ (a) as cast; (b) heat treated at 1300 °C.

The EDS analysis confirmed that the large lighter contrast grains were Nb_5Si_3 with average composition 43.1Nb–31.2Si–12.8Ti–7Al–5.7Hf. There was segregation of Ti and Hf in the Nb_5Si_3 , some grains were Ti-rich with average composition 21.9Nb–38Si–31.2Ti–3Al–5.8Hf and others Hf rich with average composition 32.4Nb–35.9Si–18.5Ti–4.8Al–8.4Hf. Thus, owing to the partitioning of Ti and Hf some silicide grains had Nb/(Ti + Hf) ratio significantly less than 1 and others approximately equal to one or higher than one, which would indicate the presence of $\gamma\text{Nb}_5\text{Si}_3$ and tetragonal Nb_5Si_3 respectively [33]. This is consistent with the morphology of the silicides in Figure 1a,b, which shows hexagonal symmetry, and with the XRD data.

The microstructures surrounding the Nb_5Si_3 grains exhibited dark contrast but within these dark contrast areas there was also a slight variation in contrast which is not easy to reproduce in Figure 1. The EDS analyses confirmed different Al + Si concentration in different phases in these areas some of which were Ti rich, and others Ti and Nb rich. With the guidance of the XRD data (Figure 2a) and the works of Dezellus et al. [34], Bulanova et al. [35], Perrot [36] and Park et al. [37,38], these phases were identified to be aluminides, in particular TiAl_3 and $(\text{Ti,Nb})\text{Al}_3$, TiAl , Ti_2Al_5 , and the compounds $\text{TM}_{2.35}\text{Al}_{1.65}\text{Si}$ and $\text{TM}_{3.7}\text{Al}_3\text{Si}$. The average compositions of these phases were as follows: $\text{TiAl}_3 = 1.4\text{Nb} - 2.7\text{Si} - 22\text{Ti} - 71.9\text{Al} - 1.4\text{Hf}$, $(\text{Ti,Nb})\text{Al}_3 = 6.5\text{Nb} - 2.1\text{Si} - 17.5\text{Ti} - 72.1\text{Al} - 1.6\text{Hf}$, $\text{TiAl} = 16.2\text{Nb} - 0.9\text{Si} - 20.3\text{Ti} - 58.2\text{Al} - 4.2\text{Hf}$ and $18.8\text{Nb} - 3.5\text{Si} - 19.7\text{Ti} - 53.3\text{Al} - 4.6\text{Hf}$, $\text{Ti}_2\text{Al}_5 = 16\text{Nb} - 1.1\text{Si} - 10.8\text{Ti} - 70.8\text{Al} - 1.4\text{Hf}$, $\text{TM}_{2.35}\text{Al}_{1.65}\text{Si} = 13\text{Nb} - 19.8\text{Si} - 26.5\text{Ti} - 33.3\text{Al} - 7.1\text{Hf}$, and $\text{TM}_{3.7}\text{Al}_3\text{Si} = 18.7\text{Nb} - 12.9\text{Si} - 20.4\text{Ti} - 39.2\text{Al} - 8.8\text{Hf}$. The heat treatment confirmed that the latter two compounds were metastable phases that formed because of the strong chemical inhomogeneity that existed in the cast alloy. Finally, in the top of the button some of the microstructure in the dark contrast area was similar to that of a eutectic with average composition 19.8Nb–6.1Si–20.2Ti–49.4Al–4.5Hf. The Si and Al concentrations of the latter were in agreement with that of a eutectic between Nb_5Si_3 and TiAl reported in References [35,36].

In summary, different intermetallic compounds were present in different parts of the as cast button. The Hf rich Nb_5Si_3 and tetragonal Nb_5Si_3 , TiAl and $\text{TM}_{3.7}\text{Al}_3\text{Si}$ were observed in the top. In the bottom we found only TiAl_3 and $(\text{Ti,Nb})\text{Al}_3$ and the Ti rich Nb_5Si_3 and in the bulk we observed the Ti and Hf rich Nb_5Si_3 and TiAl , Ti_2Al_5 and $\text{Ti}_{2.35}\text{Al}_{1.65}\text{Si}$.

Heat treated: The average composition of the heat treated alloy (1300 °C/100 h) was 18.8Nb–22.3Si–24.3Ti–30.2Al–4.4Hf, and was close to that of the cast alloy. The standard deviations of the concentrations of all the elements with the exception of Hf were still high owing to the prevailing large scale chemical inhomogeneity after the heat treatment. The microstructure is shown in Figure 1c,d, and the XRD data in Figure 2b. After the heat treatment, zone(s) were not observed, and the average composition of the bottom, bulk and top areas had not changed significantly (Figure 3b).

The microstructure consisted of the Nb_5Si_3 , $(\text{Ti,Nb})\text{Al}_3$, TiAl and Ti_2Al_5 intermetallics and there was still segregation of Ti and Hf in the silicide. The average compositions were as follows: $\text{Nb}_5\text{Si}_3 = 29.9\text{Nb}–36.6\text{Si}–22.1\text{Ti}–4\text{Al}–7.4\text{Hf}$ and $20.7\text{Nb}–36.6\text{Si}–35.1\text{Ti}–2.6\text{Al}–5.1\text{Hf}$, $(\text{Ti,Nb})\text{Al}_3 = 17.8\text{Nb}–9.6\text{Ti}–71.7\text{Al}–1\text{Hf}$, $\text{TiAl} = 18.7\text{Nb}–1.8\text{Si}–20.8\text{Ti}–56.3\text{Al}–2.3\text{Hf}$ and $\text{Ti}_2\text{Al}_5 = 20.7\text{Nb}–0.6\text{Si}–7.3\text{Ti}–70.2\text{Al}–1\text{Hf}$. There were Nb_5Si_3 grains with $\text{Nb}/(\text{Ti} + \text{Hf}) \approx 0.5$, which would correspond to hexagonal Nb_5Si_3 [33]. The $\text{TM}_{2.35}\text{Al}_{1.65}\text{Si}$ and $\text{TM}_{3.7}\text{Al}_3\text{Si}$ phases were not observed.

The XRD data suggested the presence of TiAl and TMAl_3 , and tetragonal $\beta\text{Nb}_5\text{Si}_3$ and hexagonal $\gamma\text{Nb}_5\text{Si}_3$. However, the EDS data and the $\text{Nb}/(\text{Ti} + \text{Hf})$ ratio of the 5-3 silicide grains, which was reduced to less than 1 after the heat treatment, would suggest that the hexagonal $\gamma\text{Nb}_5\text{Si}_3$ is most likely the stable silicide in the microstructure of this alloy. The stable aluminides in this alloy were the TiAl , $(\text{Ti,Nb})\text{Al}_3$ and possibly the Ti_2Al_5 . There was no evidence of the prior eutectic but the microstructure that surrounded the bulky Nb_5Si_3 grains exhibited light contrast particles in the dark contrast matrix, which is consistent with coarsened $\text{Nb}_5\text{Si}_3 + \text{TiAl}$ prior eutectic. The XRD also indicated the presence of the Ti_5Si_4 and TiSi silicides, which were not confirmed by EDS analysis.

4.2. Alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$

As cast: The cast microstructure demonstrated the sensitivity of the solidification of this alloy to high temperature gradient(s) and/or cooling rate(s). Indeed, cross sections exhibited a “layered” structure separating the bottom from the bulk. The former consisted of two zones, namely Zone A and Zone B. There were differences in the contrasts of the zones A and B and the bulk and top of the cross section owing to differences in zone thickness, the scale and morphology of the microstructure, the chemical inhomogeneity and transitions in microstructure, see Figure 4a. Next to the water cooled copper crucible (highest temperature gradient(s) and/or cooling rate(s)) Zone A formed that had more or less a constant thickness. Then was Zone B the thickness of which varied slightly as the microstructure changed to that observed in the bulk.

The actual composition of the alloy was Nb–23.8Si–23.5Ti–35.9Al–3.3Hf. This was the average composition of all EDS analyses taken from the top, bulk and bottom of the button and was very close to the nominal one. However, the standard deviations of the concentrations of all the elements with the exception of Hf were greater than one, particularly those of Al and Si, owing to the changes (transitions) in microstructure and differences in the compositions of phases (see below). For the bulk and top of the button the standard deviations of all elements were smaller but still larger than one, and less and/or equal to one only for Hf and Ti.

The concentrations of each element in the two zones in the bottom, bulk and top of the cast alloy are shown by the blue colour vertical bars in Figure 5. The latter shows that Zone A was richer in Al and poorer in Hf, Nb, Si and Ti than the rest of the alloy and that there were not significant differences in the concentrations of all elements between Zone B, bulk and top. The solidification microstructures in the latter three areas were different, as shown in Figure 4. The Si and Al concentrations respectively increased from approx. 13 to 25.5 at.% and decreased from approx. 54 to 31 at.% from Zone A to Zone B. At the interface between Zone A and Zone B the Si concentration was about 36 at.%. At this interface the vol.% of Nb_5Si_3 was very high (Figure 4a). In the transition from Zone B to bulk the Si

and Al concentrations respectively increased from approx. 25 to 27 at.% and decreased from approx. 31 to 29 at.%, i.e., the changes were minor and within the error of analysis. In other words, significant changes in the concentrations of Al and Si occurred in the bottom of the button and near the transition from Zone A to Zone B.

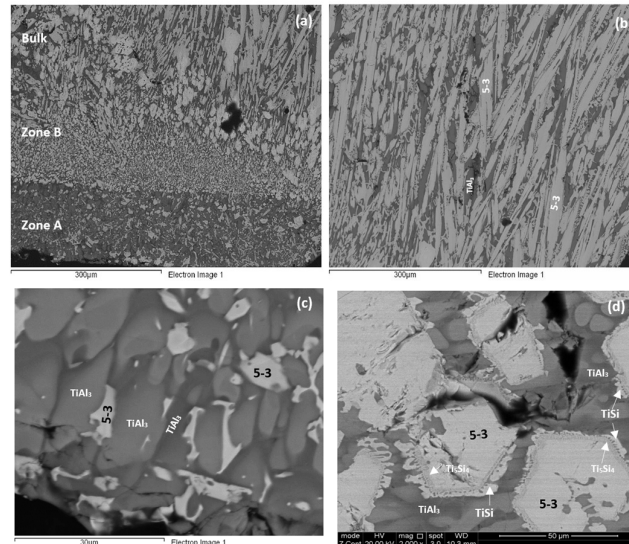


Figure 4. SEM backscatter electron images of the cast alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$. (a,b) low magnification images (a) showing zones A, B and transition to bulk microstructure; (b) bulk microstructure; (c,d) higher magnification images showing (c) details of microstructure in Zone A and (d) bulk microstructure.

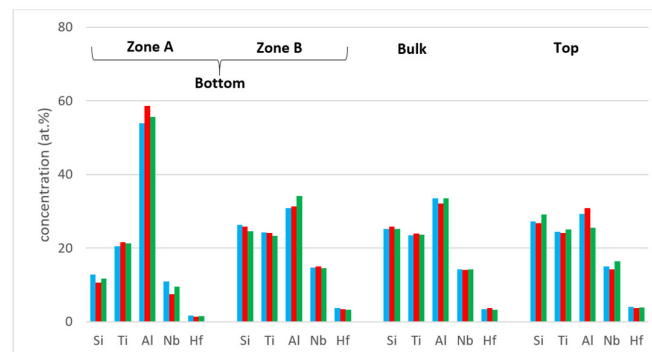


Figure 5. Comparison of the concentrations of elements in the bottom, bulk and top of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$. As cast—blue bars, heat treated at 800 °C—red bars and heat treated at 1200 °C—green bars.

According to the XRD data (Figure 6a) the aluminides TiAl and TiAl_3 and the silicides Ti_5Si_4 , Ti_5Si_3 , TiSi and hexagonal $\gamma\text{Nb}_5\text{Si}_3$ were present in the microstructure. The quantitative analysis data confirmed the presence of all the above phases in all parts of the button with the exception of TiAl . The average composition of $(\text{Ti,Nb})\text{Al}_3$ ($= 12.2\text{Nb}-2.4\text{Si}-12.7\text{Ti}-72.1\text{Al}-0.7\text{Hf}$) did not differ significantly along the cross section, the Al + Si sum was about 75 at.% but the standard deviations of each element with the exception of Hf were greater than one in the zones A and B. The contrast exhibited by the tri-aluminide grains (Figure 4c) varied depending on their Al content. Also, the average composition of TiSi ($= 12.2\text{Nb}-44.3\text{Si}-30.7\text{Ti}-6.6\text{Al}-6\text{Hf}$) did not differ significantly along the cross section, the Al + Si sum was about 50 at.% but the standard deviations of each element with the exception of Hf were greater than one in the bulk and top. The TiSi formed a thin “layer” between Ti_5Si_4 and tri-aluminide (Figure 4d). At the very bottom of Zone A, meaning in the areas that had been in direct contact with the crucible wall, we did not observe the Ti_5Si_4 and TiSi around the Nb_5Si_3 , but the latter

two silicides were observed around Nb_5Si_3 further in Zone A (i.e., further away from the crucible wall). The average composition of Ti_5Si_4 was different in the bottom (12Nb–46.1Si–33.6Ti–2.3Al–6Hf) and in the top and bulk (18.2Nb–47Si–24.3Ti–1.7Al–8.7Hf). This silicide was noticeably poor in Al. The average composition of Nb_5Si_3 ($= 22.3\text{Nb}–38.8\text{Si}–29.4\text{Ti}–4.6\text{Al}–4.9\text{Hf}$) did not differ significantly along the cross section and had $\text{Nb}/(\text{Ti} + \text{Hf}) \approx 0.66$ in the bottom, bulk and top but in the zones A and B we also observed Ti rich 5-3 silicide with $\text{Nb}/(\text{Ti} + \text{Hf}) \approx 0.36$ with average composition 15Nb–38.2Si–38.8Ti–5.1Al–2.9Hf. In Figure 4 the silicides are indicated as 5-3.

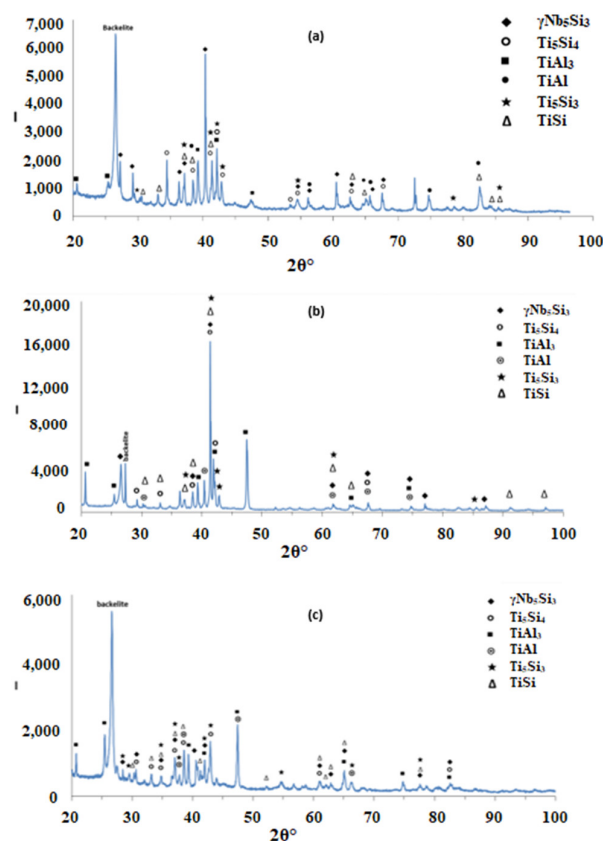


Figure 6. X ray diffractograms of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (a) as cast; (b) heat treated at 800 °C; (c) heat treated at 1200 °C.

Heat treated: After the 100 h heat treatments at 800 and 1200 °C the zones A and B were still observed in cross sections of the buttons. The actual compositions were 13.3Nb–23.2Si–23.6Ti–36.6Al–3.3Hf and 13.3Nb–21.6Si–23Ti–39.2Al–2.8Hf respectively for the 800 and 1200 °C heat treatment temperatures. These were the average compositions of all EDS analyses taken from the top, bulk and bottom of the heat treated buttons and were not significantly different from the actual composition of the cast alloy. The standard deviations for Si and Al were still high with that of the latter being higher, as was the case for the cast alloy. For the bulk and top of the heat treated button the standard deviations of all elements were smaller, and less and/or equal to one for Hf, Nb and Ti. The concentrations of each element in the bottom, bulk and top of the cast alloy are shown by the red and green colour vertical bars respectively for the 800 and 1200 °C temperatures in Figure 5.

According to the XRD data (Figure 6b,c) the aluminides TiAl and TiAl_3 and the silicides Ti_5Si_4 , Ti_5Si_3 , TiSi and hexagonal $\gamma\text{Nb}_5\text{Si}_3$ were present in the microstructure. The presence of TiAl at both heat treatment temperatures was confirmed by quantitative EDS. The TiAl was observed in the areas in-between the 5-3 silicide grains where TiAl_3 was also present. It was not easy to distinguish each phase using the contrast in back scatter electron imaging, because of the partitioning of Ti in both phases. The TiAl was scarcely present in the top and bulk of the button where at both temperatures

the TiAl had a similar average composition (11.4Nb–3.2Si–24.7Ti–59Al–1.6Hf) with Al + Si between 62 and 66 at.%. However, no TiAl was observed in the bottom of the alloy that was heat treated at 800 °C and in the bottom of the button that was heat treated at 1200 °C the TiAl was very poor in Nb (2.3Nb–10.4Si–29.9Ti–55.1Al–2.3Hf). The TMAI₃ had similar compositions for both temperatures with Al + Si between 73 and 75 at.% and with average composition similar to that given above for the as cast alloy. In the bottom, bulk and top of the alloy that was heat treated at 800 °C the Ti₅Si₄ silicide had a similar average composition (15.3Nb–45.6Si–30.6Ti–2Al–6.5Hf). However, after the heat treatment at 1200 °C the average compositions of the Ti₅Si₄ were different between the bottom (7.8Nb–46.5Si–38.5Ti–1.8Al–5.4Hf) and bulk and top (13.8Nb–45.2Si–32.4Ti–2.5Al–6.1Hf) and both were different from the as cast alloy but still poor in Al. With increasing heat treatment temperature, the Ti₅Si₄ became richer in Ti and poorer in Nb. At both heat treatment temperatures, the TiSi had similar composition with that given above for the as cast alloy. At 800 °C the Nb₅Si₃ had Nb/(Ti + Hf) ≈ 0.65 and average composition similar to the as cast alloy. However, at 1200 °C the 5-3 silicide had become richer in Ti with Nb/(Ti + Hf) ratios about 0.42 (17.3Nb–37.2Si–37.1Ti–4.1Al–4.1Hf) and 0.2 (9.7Nb–38.8Si–45.4Ti–2.8Al–3.2Hf).

The microstructures of the heat treated alloy are shown in Figure 7. After the heat treatment at 800 °C the microstructure had not changed significantly (compare Figure 4d and Figure 7a) but the 5-3 silicide grains exhibited severe cracking. After the heat treatment at 1200 °C the microstructure had changed considerably. There was precipitation of a second phase in the TMAI₃ grains. This phase exhibited bright contrast under back scatter electron imaging and its identity is unknown. There was also precipitation of a second phase inside 5-3 grains. This phase was present as finer particles compared with those observed in the bulk of TMAI₃ grains and their contrast was similar to that of TiSi. The latter had grown significantly compared with the cast microstructure. There was also growth of the Ti₅Si₄, some parts of which exhibited darker and others lighter contrast (owing to different Ti and Hf concentrations). Similar variations in contrast were also exhibited by 5-3 silicides depending on their Nb/(Ti + Hf) ratios.

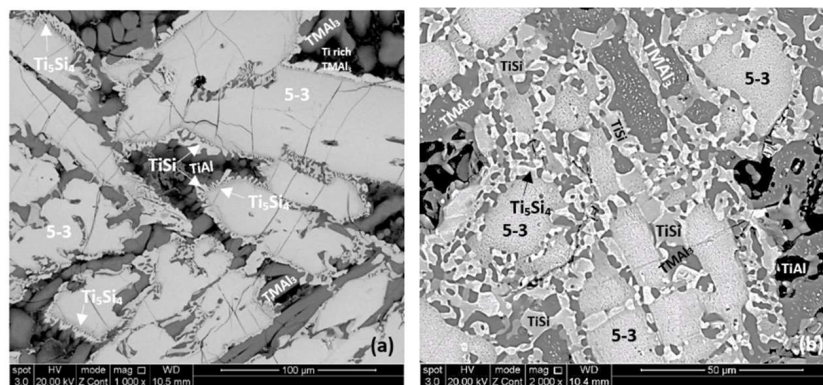


Figure 7. SEM backscatter electron images of the bulk microstructure of the heat treated alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} (a) 800 °C, (b) 1200 °C.

4.3. Isothermal Oxidation

4.3.1. Alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5}

The oxidised specimens after 100 h isothermal oxidation at each temperature are shown in Figure 8a,b. At 800 °C the alloy formed a thin scale and lost weight 0.74 mg/cm². At 1200 °C the alloy gained weight 8.5 mg/cm² and formed a thicker scale (see Figure 8c,d).

The microstructures just below the scale and in the bulk are shown in Figure 9. Figure 10 shows the glancing angle XRD data of the oxidised specimens. At 800 °C the XRD data suggested the presence of Ti niobates, Nb₂O₅, HfO₂, TiO₂, TiAl₂O₅ and SiO₂. The back scatter electron (BSE) imaging and analysis data confirmed the presence of discontinuous thin scale consisting of Al containing mixed

oxides, see Figure 9a. At 1200 °C the XRD data suggested the presence of the same oxides plus $\alpha\text{Al}_2\text{O}_3$. Figures 9c and 11 show a thicker “layered” scale that consisted of Ti-rich mixed oxide and Al and Ti rich mixed oxide at the top, beneath formed a Nb and Si-rich mixed oxide, beneath was Al and Ti rich mixed oxide and beneath the latter was a continuous mixture of Al_2O_3 (major phase) with dispersed oxide(s). The identity of the latter is not known. The dispersed oxide(s) exhibited a contrast similar to that of the Ti-rich oxides. There was also internal oxidation with Al_2O_3 forming at interfaces between Nb_5Si_3 and (Ti,Nb)Al (see Figures 9c and 11).

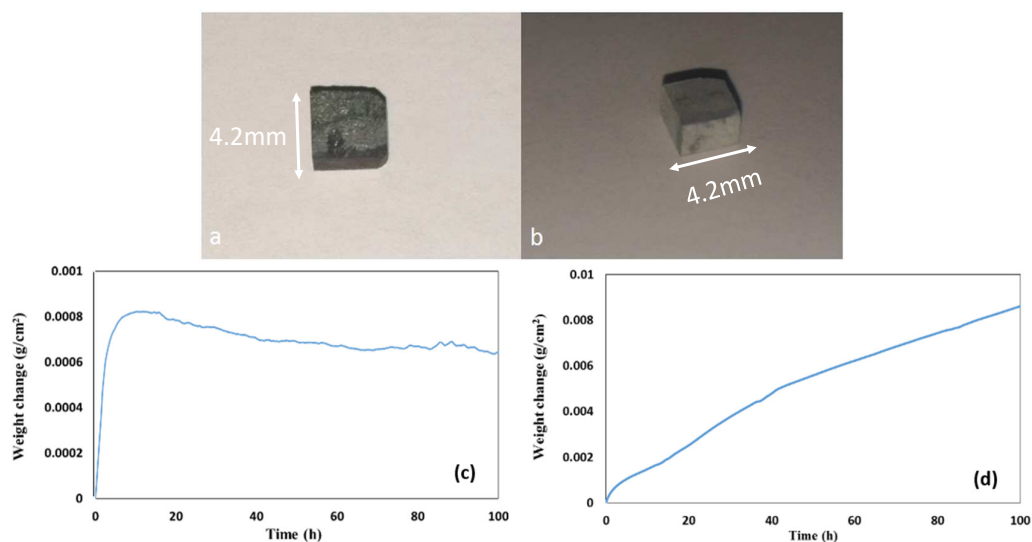


Figure 8. Oxidised specimens of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ (a) at 800 °C and (b) at 1200 °C and weight change versus time data (c) at 800 °C and (d) at 1200 °C.

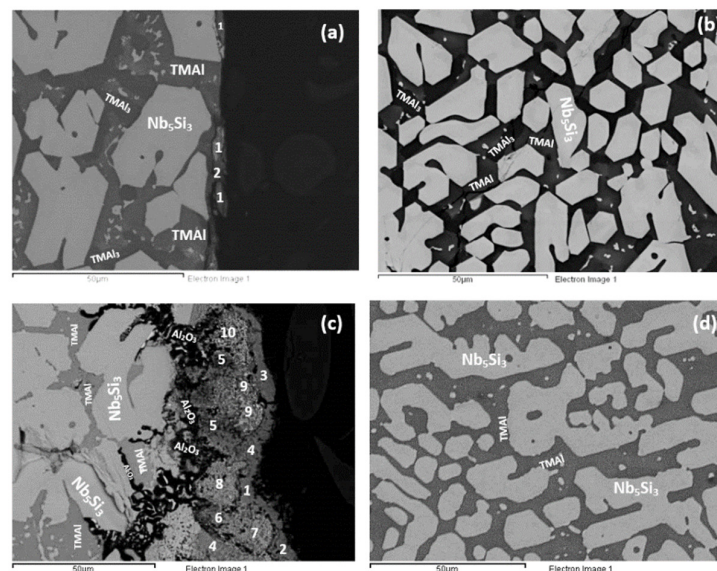


Figure 9. SEM backscatter electron images of the microstructure of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ after isothermal oxidation (a,b) at 800 °C; (c,d) at 1200 °C. (a,c) scale and substrate below scale; (b,d) bulk. In (a) 1 is Si rich oxide with Al,Nb,Ti, and 2 is Al rich oxide with Nb,Si,Ti. In (c) 1, 2, 3 indicate Ti rich mixed oxides, 4, 5 indicate Al and Ti rich mixed oxides, 6, 7, 8, 9, 10 indicate Si and Nb rich mixed oxides.

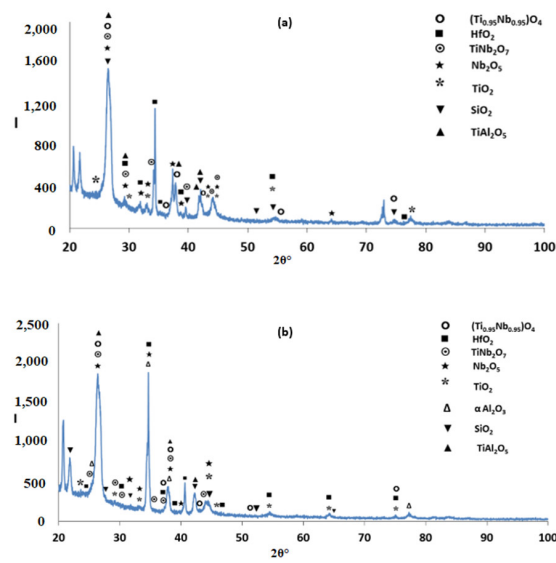


Figure 10. Glancing angle X ray diffractograms ($\theta = 5^\circ$) of the alloy $Nb_{1.7}Si_{2.4}Ti_{2.4}Al_3Hf_{0.5}$ after isothermal oxidation (a) at 800 °C; (b) at 1200 °C.

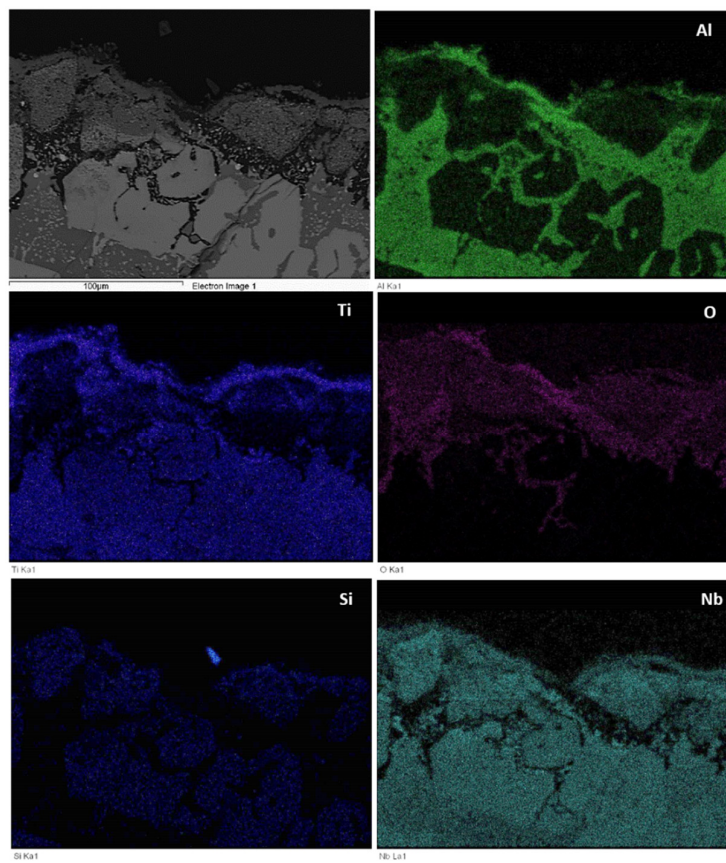


Figure 11. Cont.

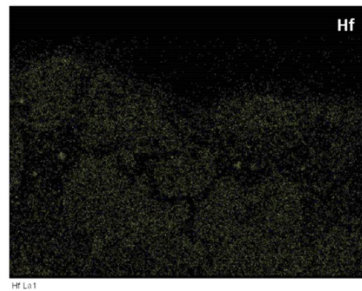


Figure 11. BSE image and X-ray elemental maps of scale formed on the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ at $1200\text{ }^\circ\text{C}$.

At both temperatures the Nb_5Si_3 , TiAl and TAl_3 were contaminated by oxygen both below the scale and in the bulk of the oxidised specimens. The contamination of Nb_5Si_3 was more severe than that of the TiAl . The TAl_3 exhibited the lower contamination. At $1200\text{ }^\circ\text{C}$ the contamination by oxygen of Nb_5Si_3 increased and the contamination by oxygen of the aluminides had not changed significantly.

4.3.2. Alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$

The oxidised specimens of this alloy after 100 h isothermal oxidation at each temperature are shown in Figure 12a,b. At $800\text{ }^\circ\text{C}$ the alloy formed a thin scale (Figure 13a,c) and gained weight 0.68 mg/cm^2 . At $1200\text{ }^\circ\text{C}$ it gained weight 2.6 mg/cm^2 , followed parabolic oxidation kinetics with the rate constant $K_p = 1 \times 10^{-11}\text{ g}^2\text{ cm}^{-4}\text{ s}^{-1}$, an order of magnitude lower than that of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and formed a continuous alumina scale (see Figure 13b,d).

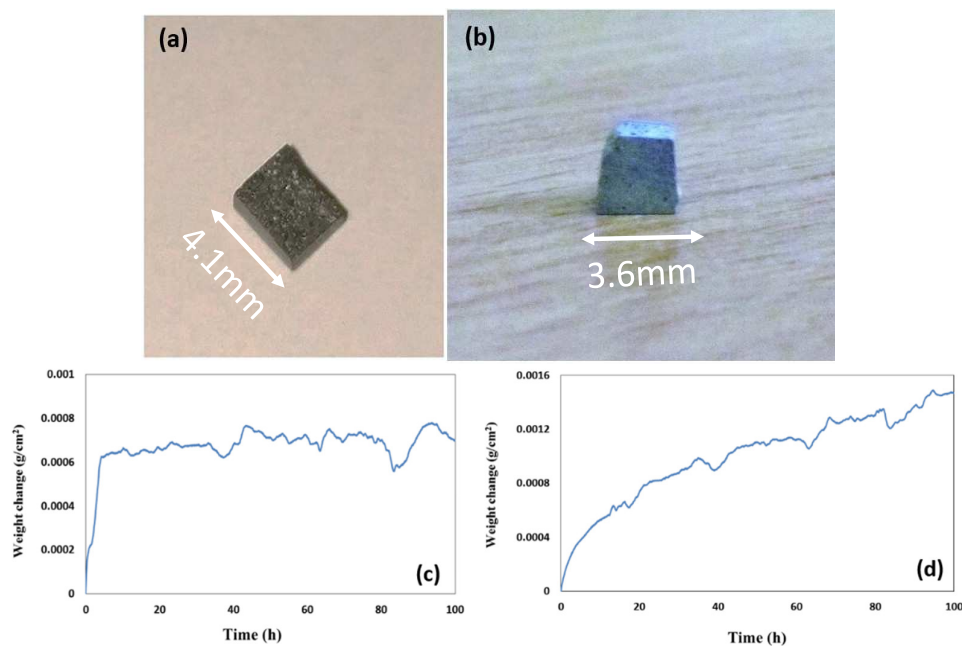


Figure 12. Oxidised specimens of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (a) at $800\text{ }^\circ\text{C}$ and (b) at $1200\text{ }^\circ\text{C}$ and weight change versus time (c) at $800\text{ }^\circ\text{C}$ and (d) at $1200\text{ }^\circ\text{C}$.

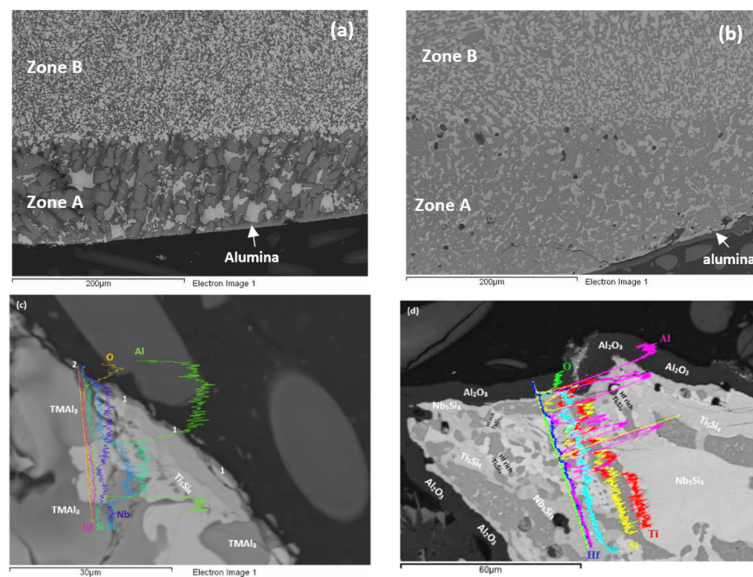


Figure 13. SEM back scatter electron images of cross sections of oxidised specimens of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (a) at 800 °C and (b) at 1200 °C; (c) line scan at 800 °C, 1 indicates Si containing Nb and Ti mixed oxide, 2 indicates Al_2O_3 ; (d) line scan at 1200 °C.

Cross sections of oxidised specimens are shown in Figure 13. At 800 °C a thin scale formed that consisted of “islands” of alumina, and Si containing mixed oxides (Figure 13a,c). At 1200 °C a thicker continuous alumina scale was formed, see Figure 13b,d. Figure 13c shows alumina formed on tri-aluminide grain and Figure 13a shows continuous thin alumina that formed on an area rich in tri-aluminide. Figure 13d shows thick continuous Al_2O_3 scale grown on a larger specimen that was oxidised in a muffle furnace at 1200 °C. Figure 14 shows that at 1200 °C the alumina scale was formed on top of $\gamma\text{-Nb}_5\text{Si}_3$, while in other parts (not shown) also it was formed on top of Si rich or Al rich intermetallics. In some parts there was a very thin Ti rich oxide on top of the 5 μm thick alumina (see Figure 13d). The microstructures in the bulk of these specimens were similar to those shown in Figure 7. In the bulk the contamination of the Nb_5Si_3 was slightly lower and of TiAl and TMAI_3 was similar to that of the same compounds in the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$.

Figure 15 shows the compositions of the different areas after the heat treatments at 800 and 1200 °C (red and green bars, these are the same as in Figure 5) and after the isothermal oxidation at the same temperatures. It shows small changes in Al concentrations in Zone B, the bulk and top and small decrease and increase, respectively, of Ti and Nb, in Zone A.

The average compositions of the phases at 800 °C were the same as after the heat treatment at the same temperature with the exception of the Ti_5Si_4 compound that became poorer (11.6Nb–46.8Si–32.1Ti–1.4Al–8Hf) and richer (17.1Nb–45.5Si–28.6Ti–2.5Al–6.2Hf) in Nb respectively in the bulk and top and in the bottom of the oxidised alloy. The average compositions of the phases at 1200 °C were the same with those after the heat treatment at the same temperature with the exception of $(\text{Ti,Nb})\text{Al}_3$ which became richer and poorer respectively in Nb and Ti in both the bottom (12.7Nb–1.1Si–13.8Ti–71.6Al–0.7Hf) and bulk and top (17.7Nb–2.6Si–9.8Ti–69.3Al–0.6Hf) and the Ti_5Si_4 which became richer and poorer respectively in Nb and Ti in the bottom and bulk and top with essentially the same composition throughout the oxidised alloy (15.9Nb–46.3Si–28.6Ti–1.8Al–7.4Hf). The Ti_5Si_4 silicide in the microstructures of the oxidised specimens at 800 and 1200 °C continued to be poor in Al.

The glancing angle XRD data in Figure 16 shows (i) that at 800 °C the scale consisted of Ti niobates and TiO_2 , SiO_2 , TiAl_2O_5 , Nb_2O_5 , HfO_2 (Figure 16a) and (ii) that the same oxides were present at 1200 °C plus $\alpha\text{-Al}_2\text{O}_3$ (Figure 16b). Compared with the $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ alloy (i) the glancing angle XRD had peaks that corresponded only to the aluminium titanate (TiAl_2O_5) and (ii) the weight gain

versus time data for both temperatures showed that the scale was not stable. Indeed, there were sudden changes in weight gain, particularly at 800 °C, compare Figure 8c,d with Figure 12c,d.

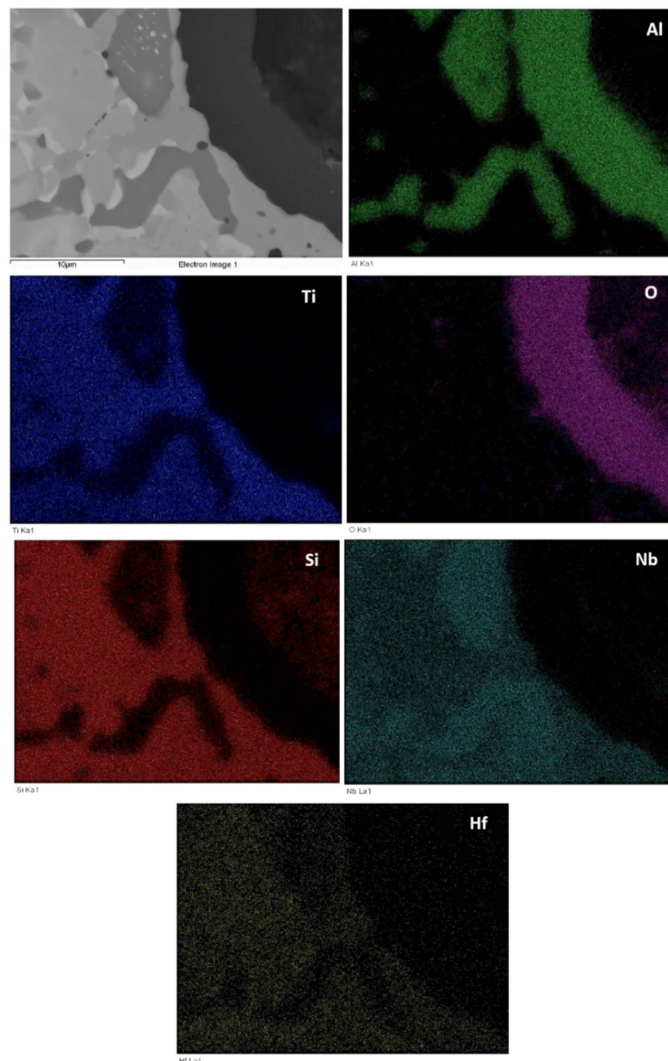


Figure 14. BSE image and X-ray elemental maps of scale formed on the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ at 1200 °C.

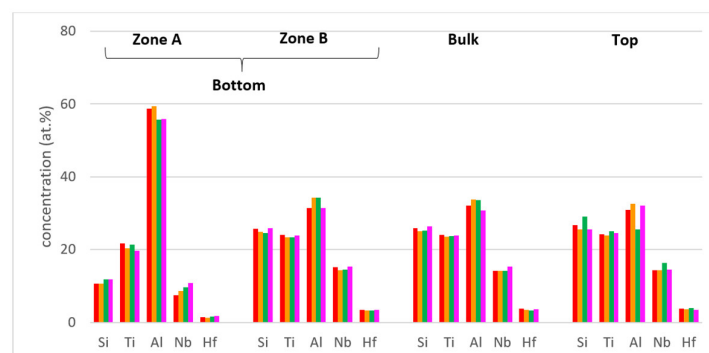


Figure 15. Comparison of the concentrations of elements in the bottom, bulk and top of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$. Heat treated at 800 °C—red bars (the same as in Figure 5), heat treated at 1200 °C—green bars (the same as in Figure 5), oxidised at 800 °C—orange bars, oxidised at 1200 °C—pink bars.

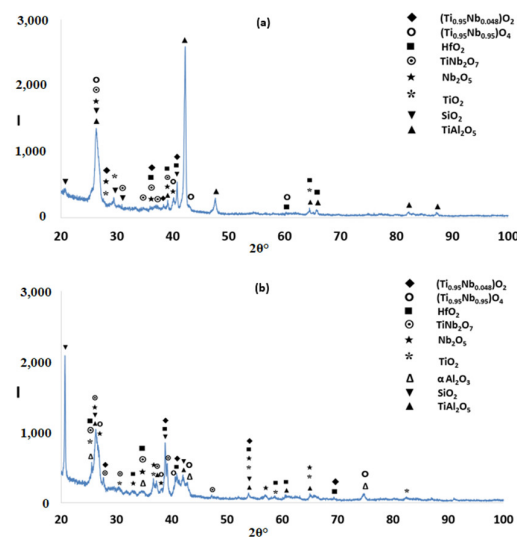


Figure 16. Glancing angle X ray diffractograms ($\theta = 5^\circ$) of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ after isothermal oxidation (a) at 800°C ; (b) at 1200°C .

5. Discussion

5.1. Macrosegregation

The as cast microstructures of both alloys were chemically inhomogeneous. Table 1 compares the parameters that describe macrosegregation of Si (MACSi) in the two alloys with those of the alloy NbSiTiHf-5Al (nominal composition $\text{Nb-24Ti-18Si-5Hf-5Al}$, [20]). In Reference [20] it was shown that Al increased MACSi and MACTi (macrosegregation of Ti) and that the chemical inhomogeneity of these elements persisted after heat treatment, which is supported by the results of this work. The data in Table 1 shows that MACSi increased as the parameters T_m , ΔH_m , ΔH_m^{sd} , T_m^{sd} decreased and the parameters $\Delta H_m/T_m$, ΔH_m^{sp} , T_m^{sp} increased, in agreement with [27]. Note that the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ has the lowest T_m of the three alloys, which increases the likelihood of forming a deeply undercooled melt in areas of high cooling rate (see Section 2 and [27]). Moreover, it has the highest $\Delta H_m/T_m$ value, which may indicate an increased difficulty for the growth of intermetallic compounds in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (see Section 5.2.2).

Table 1. Comparison of alloy parameters for the macrosegregation of Si in the cast alloys [27]. The arrows indicate “direction” of increase of specific parameter. The parameters were calculated as described in Reference [27].

Alloy	MACSi (at.%)	T_m (K)	ΔH_m (kJ/mol)	$\frac{\Delta H_m}{T_m}$ (J/molK)	ΔH_m^{sd} (kJ/mol)	ΔH_m^{sp} (kJ/mol)	T_m^{sd} (K)	T_m^{sp} (K)	$\frac{T_m^{\text{sd}}}{T_m^{\text{sp}}}$
MG1 *	7.4	2240	29.1	12.99	17.93	11.17	1838.7	401.3	4.58
MG2 +	12.8 ↓	1747 ↑	25.4 ↑	14.54 ↓	10.8 ↑	14.6 ↓	1085.3 ↑	661.7 ↓	1.64 ↑
MG7 **	21.8	1647	24.6	14.97	8.81	15.79 ↓	910	737	1.24

* $\text{Nb-18Si-24Ti-5Hf-5Al}$ or alloy NbSiTiHf-5Al in Reference [20]. + $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. ** $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$.

5.2. Microstructures

5.2.1. Alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$

The solid solution was not stable, as required by the alloy design criteria (see Section 2). The cast microstructure in the bottom of $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ consisted of hexagonal Ti rich Nb_5Si_3 and tri-aluminide $(\text{Ti,Nb})\text{Al}_3$ (see Section 4.1). As the Ti rich 5-3 silicide formed the melt became lean in Si, Ti, Hf and Nb, and rich in Al. As the solidification proceeded, from the aforementioned melt formed

the tri-aluminides with different transition metal content depending on the local melt chemistry. As the tri-aluminides formed, the melt became lean in Al and rich in Si and Nb, and the concentration of Ti in the melt either increased or did not change depending on the chemistry of the tri-aluminide. In the latter melt formed Ti and/or Hf rich Nb₅Si₃ and the melt near the silicide became lean in Si, Hf and Nb, rich in Al and either lean or rich in Ti depending on the chemistry of Nb₅Si₃. As the TiAl formed in this melt the latter became lean in Al, rich in Si, Hf and Nb with no significant change in Ti concentration. In this Si rich melt formed the Ti_{2.35}Al_{1.65}Si compound and then Ti₂Al₅ and thus the melt became rich in Ti, Nb, Hf and Si and lean in Al. As the solidification proceeded towards the top of the button, from the latter melt formed Nb₅Si₃ and the surrounding melt became lean in Si, Hf and Nb and rich in Al and Ti. Then the TiAl formed and the melt became lean in Al, rich in Si, Hf and Nb with no significant change in Ti concentration, and in this Si rich melt formed the TM_{3.7}Al₃Si compound. The solidification sequence discussed above indicates hexagonal Nb₅Si₃ as the primary phase. If the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} is considered as a (Ti,Nb,Hf)–Al–Si alloy, the above conclusion is in agreement with the liquidus projection of the Ti–Al–Si system [25] which shows that the average alloy composition is in the Ti₅Si₃ phase area. The formation of the tri-aluminide from the melt surrounding the hexagonal Nb₅Si₃ is in agreement with the Ti–Al–Si solidus projection [25]. Thus, based on the experimental results and the above discussion it is suggested that the solidification path in the bottom of the alloy was $L \rightarrow L + \gamma\text{Nb}_5\text{Si}_3 \rightarrow L + \gamma\text{Nb}_5\text{Si}_3 + \text{TMAI}_3$, in the bulk $L + \gamma\text{Nb}_5\text{Si}_3 + \beta\text{Nb}_5\text{Si}_3 \rightarrow L + \gamma\text{Nb}_5\text{Si}_3 + \beta\text{Nb}_5\text{Si}_3 + \text{TiAl} + \text{Ti}_{2.35}\text{Al}_{1.65}\text{Si} + \text{Ti}_2\text{Al}_5$ and in the top $L + \beta\text{Nb}_5\text{Si}_3 \rightarrow L + \beta\text{Nb}_5\text{Si}_3 + \text{TiAl} + \text{TM}_{3.7}\text{Al}_3\text{Si} + (\beta\text{Nb}_5\text{Si}_3 + \text{TiAl})_{\text{eutectic}}$.

The phases present in the microstructure of the heat treated alloy that were confirmed by both the XRD and EDS data were tetragonal βNb₅Si₃, hexagonal γNb₅Si₃, TMAI₃, TiAl and possibly Ti₂Al₅. This is in agreement with the 1250 °C isothermal section of the Ti–Al–Si system [25]. The composition of the Nb₅Si₃ had changed towards lower Nb/(Ti+Hf) ratios, which would suggest that the hexagonal Nb₅Si₃ is likely to be the stable 5-3 silicide in this alloy. The same was concluded for the Nb₅Si₃ in the alloy NbSiTiHf-5Al in Reference [20]. In the aluminides, the Si concentration was reduced to very low levels, which were in agreement with the literature.

5.2.2. Alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}

The solid solution also was not stable in this alloy, as required by the alloy design criteria (see Section 2). The same phases were present in all parts of the button of the alloy, namely the hexagonal γ(Nb,Ti)₅Si₃, the (Ti,Nb)₅Si₄, (Ti,Nb)Si silicides and (Ti,Nb)Al₃ aluminide. The vol.% of TMAI₃ was significantly higher in Zone A compared with Zone B, bulk and top of the button.

According to the Ti–Si binary phase diagram, in Si rich melts where, as the solidification starts, the Ti₅Si₃ is the primary phase there is a “cascade” of peritectic reactions, namely $L + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_5\text{Si}_4$, then $L + \text{Ti}_5\text{Si}_4 \rightarrow \text{TiSi}$. The microstructure of such a Si rich alloy would consist of the Ti₅Si₃ (primary) “surrounded” by the Ti₅Si₄ (first peritectic) and then Ti₅Si₄ “surrounded” by TiSi (second peritectic). This was observed in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} (Figure 4d).

The tri-aluminide formed in the areas between the “composite” silicide grains (composite here means Nb₅Si₃ (5-3) core surrounded by Ti₅Si₄, surrounded by TMSi), i.e., in the last melt to solidify. Thus, it was deduced that in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} the melting temperatures of the alloyed Nb₅Si₃, Ti₅Si₄ and TMSi silicides were higher than the tri-aluminide TMAI₃.

As the primary Nb₅Si₃ formed the surrounding melt became poor in Hf, Nb, Si and Ti and rich in Al, from this melt the Ti₅Si₄ formed around the 5-3 silicide via a peritectic reaction and the melt became poor in Hf, Si, Ti and richer in Al and Nb. Then from this melt the TiSi formed around the Ti₅Si₄ via a peritectic reaction and from Al rich and Si and Hf poor melt formed the TMAI₃. It is suggested that the solidification path of the alloy in Zone B, bulk and top of the button was $L \rightarrow L + \gamma\text{Nb}_5\text{Si}_3$ then $L + \gamma\text{Nb}_5\text{Si}_3 \rightarrow \text{TM}_5\text{Si}_4$, then $L + \text{TM}_5\text{Si}_4 \rightarrow \text{TMSi} \rightarrow \gamma\text{Nb}_5\text{Si}_3 + \text{TM}_5\text{Si}_4 + \text{TMSi} + \text{TMAI}_3$.

The average composition of Zone A was different than those of Zone B and the bulk and top (Figure 5). In the deeply undercooled melt next to the crucible wall the peritectic reactions that

would result in the growth of Ti_5Si_4 and $TiSi$ around the primary phase were suppressed. The melt surrounding the primary phase became less poor in Si and richer in Al than it would have been had the peritectic reactions occurred. Thus, as the primary Nb_5Si_3 nucleated and grew in the undercooled melt, the melt became rich in Al and poor in Nb, Si and Ti and from this melt formed the $TMAl_3$ making the melt poor in Al and rich in Si. The vol.% of $TMAl_3$ was very high in Zone A owing to the chemical composition of the latter, thus the melt became very rich in Si and poor in Al as the solidification advanced away from the cold crucible wall.

It is reasonable to assume that the growth velocity $V_{S/L}$ was “constant” during the solidification of Zone A (growth velocity “imposed” by the conditions near the crucible wall). The model of Tiller et al. [39] for the solute concentration (C_L^*) at the S/L interface during the initial transient solidification shows that the C_L^* is proportional to the solute concentration in the melt C_o . The undercooling ΔT_{CS} during the initial transient is given by the equation [40],

$$\Delta T_{CS} = m_L [C_o/k_o](1 - k_o)[1 - \exp(-k_o V_{S/L}^2 t/D_L)][1 - \exp(-V_{S/L} x/D_L)] - Gx$$

where t is time, x is the distance from S/L interface, D_L is diffusion coefficient in the melt, k_o is the partition coefficient, G is the temperature gradient and m_L is the liquidus slope. In other words, as the melt became rich in Si ahead of the advancing S/L front (i.e., C_o increased in the above equation) the ΔT_{CS} increased. Thus, as solidification proceeded in Zone A and latent heat was released from the solidifying compounds, the undercooling of the melt was enough to ensure the growth of the intermetallic compounds that formed in this zone, and as the thickness of the latter increased the melt ahead of the advancing solidification front became richer and richer in Si until it reached the concentration $Si \approx 36$ at.% and a high vol.% of Nb_5Si_3 formed. The latter resulted in the transition from Zone A to Zone B (see Section 4.2 and Figures 4a and 13a).

If the alloy is considered as an alloy of the (Ti,Nb,Hf)–Si–Al system, primary hexagonal 5-3 silicide is in agreement with the results reported in Reference [35]. If the alloy is considered as an alloy of the (Nb,Hf)-Ti-(Si,Al) system, then according to Bulanova and Fartushna [41] the reaction $L + (Ti,Nb)_5Si_3 \rightarrow \beta(Nb,Ti)_5Si_3 + (Ti,Nb)_5Si_4$ occurs at $T < 1815$ °C and then via $L + \beta(Nb,Ti)_5Si_3 \rightarrow (Ti,Nb)_5Si_4 + (Nb,Ti)Si_2$ and $L + (Ti,Nb)_5Si_4 \rightarrow (Nb,Ti)Si_2 + (Ti,Nb)Si$ the $TMSi$ is formed below 1570 °C. Note that we did not observe $(Nb,Ti)Si_2$ in the alloy $Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}$. The above would suggest that in the latter the formation of the $TMAl_3$ tri-aluminide was “controlled” by the Ti–Al–Si phase equilibria and that of the $TMSi$ silicide by the Nb–Ti–Si phase equilibria.

A characteristic feature of the microstructures observed in the cast, heat treated and oxidised conditions was the fibrous nature (structure) of Ti_5Si_4 , see Figures 4d and 7. Similar structure for Ti_5Si_4 has been reported by Gupta [42] and Park et al. [37]. Gupta described it as “wool like” and observed it in Ti–Al–Si diffusion couples air cooled after annealing at 800 or 900 °C for 3 or 6 h. The couples were made from pure Ti and eutectic Al–Si alloy. In the couples studied by Gupta the fibrous Ti_5Si_4 “grew” towards (“was over”, “formed in a matrix of”) $TiAl_3$ and was on top of (“sitting on”) Ti_5Si_3 that exhibited a brighter contrast than Ti_5Si_4 . The average Al concentration in Ti_5Si_4 given by Gupta [42] was approximately 7.5 to 8 at.%, and is higher than the average Al concentrations (about 2 at.%) analysed in this research, see Section 4.2, and the concentration reported in Reference [17] (about 0.2 to 0.4 at.% Al). Gupta did not observe $TiSi$ in his diffusion couples.

Park et al. [37] also reported about the formation of Ti_5Si_4 in diffusion couples annealed at 1100 °C for ≥ 200 h. They studied two couple types, one between $TiAl$ and $TiSi_2$ (type A, our notification) and the other was $TiAl/Ti/TiSi_2$ (type B, our notification). The type A and type B couples were referred to respectively as “direct interface reaction” and “biased interface reaction” couples by Park et al. [37]. In the type A couple the sequence of phases was $TiAl/TiAl_2/Ti_2Al_5/TiAl_3 + Ti_5Si_4/Ti_5Si_4/TiSi/TiSi_2$, i.e., the Ti_5Si_3 silicide did not form. The Ti_5Si_4 formed its own irregular “thick porous” layer. The solubility of Al was < 2 at.%. In our work the average Al concentrations in the Ti_5Si_4 in the cast and heat treated (800 and 1200 °C) alloy were ≈ 2 at.%. The Ti_5Si_4 also grew a columnar morphology through $TiAl_3$ and for this growth morphology, according to Park et al. [37],

the rate-limiting component was Ti ($D_{\text{Ti}(\text{TiAl}_3)} < D_{\text{Si}(\text{Ti}_5\text{Si}_4)}$), where D_i is diffusivity of species i ($= \text{Si, Ti}$) in the indicated intermetallic).

In the type B couple, the Ti_5Si_3 silicide formed. The Ti_5Si_4 also formed but it was not porous. The sequence of phases was $\text{TiAl}/\text{Ti}_3\text{Al}/\text{Ti}/\text{Ti}_3\text{Si}/\text{Ti}_5\text{Si}_3/\text{Ti}_5\text{Si}_4/\text{TiSi}/\text{TiSi}_2$. In the Ti_5Si_3 the Al concentration was about 5 at.%, the same as the average Al concentrations measured in this work in hexagonal 5-3 silicide in the cast, heat treated and oxidised alloy, see Section 4.2. The Al concentration in Ti_5Si_4 was the same as in the type A couple. Park et al. [37] suggested that in the type A couple the Ti flux was not enough for the formation of Ti_5Si_3 .

In this work, in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ the Ti_5Si_4 was observed in the cast, heat treated and oxidised conditions to be in contact with Ti_5Si_3 , with TMSi , and with TAl_3 . The Ti_5Si_4 formed a fibrous (columnar, wool like) structure. The formation of Ti_5Si_4 and the other phases was accompanied by partitioning of solute during solidification and solid state cooling of the ingot, and also during each heat treatment and during each oxidation experiment. Porosity was not observed in any of the 5-3/5-4/ TMSi microstructures in this work. Thus, on the basis of the results of this work and those of Gupta [42] and Park et al. [37], it is concluded that in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ the Ti_5Si_4 grew with a fibrous (columnar, wool like) morphology towards TAl_3 and that its growth was not accompanied by the formation of porosity.

The microstructure of the alloy after the heat treatment at 800 °C consisted of the hexagonal $\gamma\text{Nb}_5\text{Si}_3$, the aluminides TiAl and TAl_3 and the silicides Ti_5Si_4 and TMSi . Compared with the cast alloy, the TiAl was the new phase to form. The solubilities of Si and Al respectively in TiAl and Ti_5Si_4 were in agreement with the literature [35,37] but the solubility of Al in TMSi was higher than that reported by Park et al. [37]. The solubilities of Al, Hf and Ti in the Nb_5Si_3 were in agreement with the literature.

The microstructure of the alloy after the heat treatment at 1200 °C consisted of the hexagonal $\gamma\text{Nb}_5\text{Si}_3$, the aluminides TiAl and TAl_3 and the silicides Ti_5Si_4 and TMSi . Compared with the cast alloy, the TiAl was the new phase to form. Considering the results for the heat treatment at 800 °C it was concluded that the TiAl is a stable phase in this alloy. This conclusion is supported by the 1200 °C isothermal section for Ti-Al-Si in Reference [25], which shows that the average alloy composition falls in the three phase Ti_5Si_3 , TiAl and TiAl_3 area. The Al and Si concentrations respectively in Ti_5Si_4 and TiSi , and TiAl were close to those reported in the literature.

In the Nb_5Si_3 cracks were observed growing from one side of a grain to the other and often these cracks were parallel to each other, see Figure 7. In the cracked 5-3 silicide grains “lines” (sometimes curved) of darker contrast were observed mainly after the heat treatment at 800 °C (Figure 7) and a few were also observed after the heat treatment at 1200 °C. In the heat treated microstructure at 800 °C the growth of Ti_5Si_4 towards TAl_3 was noticeable (see above discussion, also Park et al. [37] reported that the growth rate of Ti_5Si_4 is higher than that of TiSi , TiAl_3 and TiAl_2 (decreasing growth rate sequence) with Ti_2Al_5 having the lowest growth rate from the aforementioned intermetallics). Furthermore, inside the Nb_5Si_3 and TAl_3 grains in the microstructure that was heat treated at 1200 °C there was evidence of precipitation of second phase(s), Figure 7b. Such precipitation was not observed at 800 °C.

The cracking of Nb_5Si_3 was attributed (a) to the enhanced anisotropy of the coefficient of thermal expansion with partitioning of Ti in the Nb_5Si_3 [43] and (b) to the large volume changes at the interfaces where the Ti_5Si_4 was formed [37]. The dark contrast in between the fibrous Ti_5Si_4 was the same as that exhibited by the tri-aluminide, but owing to the size of the growth features the latter could not be confirmed.

Agreement and/or disagreement with the literature regarding the Al concentration in Ti_5Si_4 and Nb_5Si_3 silicides was discussed above. The solubility of Si in TAl_3 (less than 3 at.% in the cast alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ and even lower in the heat treated alloys, respectively less than 1 and 3 at.%) is in agreement with Bulanova et al. [35], lower than the range reported by Park et al. [37] (up to 7 at.%) and significantly lower than the values reported by Gupta [42] (9.2 to 14.3 at.%). There are no reports about the solubility of Al in TiSi in higher order systems than

the ternary Ti-Al-Si where it is suggested to be very low or negligible [35,37]. However, the 700 and 1200 °C isothermal sections for the Ti-Al-Si system by Perrot [36] show solubility of Al in TiSi (about 10–12 at.% at 700 °C and about 5–7 at.% at 1200 °C). In this work, the solubility of Al in TiSi was about 16.7 at.% at 800 °C and 12.2 at.% at 1200 °C.

5.2.3. Comparison with High Entropy Alloys and Nb–Silicide Based Alloys

The actual compositions of the alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ met the “standard definition” of HEAs. Furthermore, the average compositions of the bottom, bulk and top of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and of Zone B, bulk, and top of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ met the “standard definition” of HEAs but not Zone A of the latter alloy.

The parameters $\Delta\chi$, δ and VEC of the alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ respectively were in the following ranges: $0.1464 < \Delta\chi < 0.158$, $8.6552 < \delta < 9.5275$, $3.808 < \text{VEC} < 3.97$ and $0.1063 < \Delta\chi < 0.1632$, $6.4897 < \delta < 10.1143$, $3.483 < \text{VEC} < 3.909$. The VEC of both alloys was outside the range of VEC values for bcc solid solution plus intermetallic(s) HEAs and outside the range of VEC values for Nb–silicide based alloys [44]. Both alloys had their δ values within the ranges of bcc solid solution plus intermetallic(s) HEAs. The parameter δ of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ was within the range of values for Nb–silicide based alloys but for the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ the δ values of Zone A were outside the lower end of the range for Nb–silicide based alloys [44].

The parameter $\Delta\chi$ of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ was within the range for bcc solid solution plus intermetallic(s) HEAs and within the range for Nb–silicide based alloys [44] and also was within the “forbidden range” of $\Delta\chi$ values for the Nb_{ss} in the latter alloys [1,44]. The parameter $\Delta\chi$ of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was outside the lower range of values for bcc solid solution and intermetallic(s) HEAs and Nb–silicide based alloys [1,44]. Furthermore, Zone A of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ had $\Delta\chi$ values outside the range for bcc solid solution plus intermetallic(s) HEAs and Nb–silicide based alloys [44] and the $\Delta\chi$ values of this alloy were within the “forbidden range” of $\Delta\chi$ values for the Nb_{ss} in Nb–silicide based alloys [1,44] with the exception of Zone A.

5.2.4. “Layered” Structure

Let us now return to the microstructures exhibited by the cross sections of the buttons of the alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$. Figure 17 shows plots of the parameters VEC, δ and $\Delta\chi$ for the microstructures of the cast and heat treated $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ (blue triangles) and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (green squares) alloys. Both alloys had similar concentrations of Hf, Si and Ti and both exhibited macrosegregation of Si that was more severe in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (see Table 1). The microstructure of the latter alloy also was sensitive to solidification conditions and was “layered” from bottom to top. This microstructure exhibited strong correlations ($R^2 > 0.987$) between the parameters $\Delta\chi$ and VEC, δ and VEC and $\Delta\chi$ and δ (Figure 17) and also “sampled” a wider range of values of each parameter compared with the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. The microstructure of the latter was not layered from bottom to top and exhibited no correlations ($R^2 < 0.039$) between the parameters δ and VEC and $\Delta\chi$ and VEC but there was a strong correlation between its parameters $\Delta\chi$ and δ with the data essentially parallel to that of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (Figure 17). Thus, the key to the “layering” of the microstructure of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was (i) its strong chemical inhomogeneity leading to severe macrosegregation of Si; (ii) its solidification that allowed it to sample (“experience”, “be exposed to”) a wide range of values of the parameters VEC, $\Delta\chi$ and δ that were strongly related to each other and (iii) its unique δ versus VEC and $\Delta\chi$ versus VEC relationships, which the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ could not form (Figure 17). It is concluded that the critical parameter of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was VEC. Remarkably, the latter alloy had the lowest VEC value (3.776 compared with 3.896 for the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$) and its Zone A had even lower VEC values (respectively 3.572, 3.488 and 3.539 for the as cast Zone A, and Zone A heat treated at 800 °C and heat treated at 1200 °C). The alloy design methodology NICE predicts that for good oxidation at 800 and 1200 °C the VEC value of the alloy should be low [4].

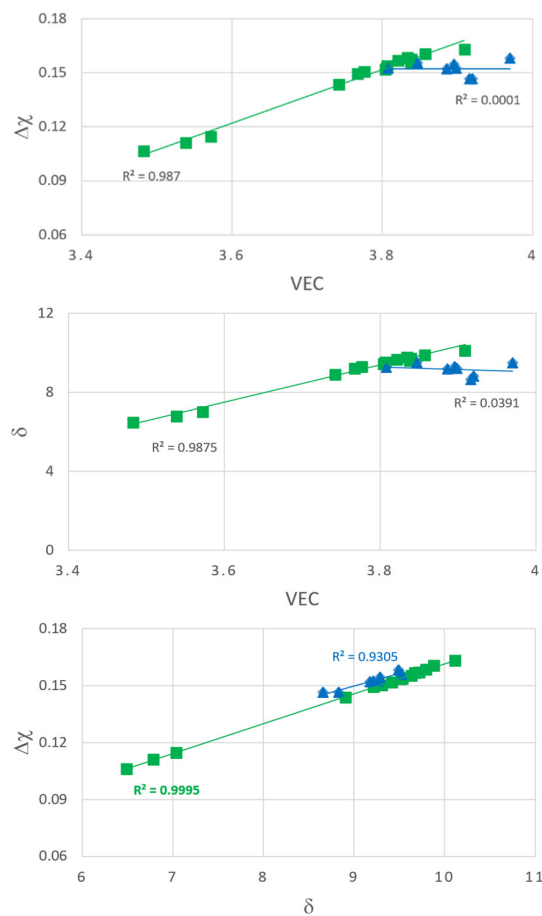


Figure 17. Plots of the parameters valence band (VEC), δ and $\Delta\chi$ for the microstructures of the cast and heat treated alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ (blue triangle) and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ (green squares).

5.3. Oxidation

The development of oxidation resistance in an alloy requires the presence of an alloying addition that oxidises selectively to produce a protective oxide. The latter requires the oxide to be more stable than that of the base metal. Therefore, a necessary but not sufficient requirement for the formation of a protective oxide on the surface on an alloy is that the oxide is more stable than all possible oxides. Al_2O_3 and SiO_2 are highly stable oxides owing to their low standard free energies of formation and are desirable for oxidation protection at $T > 1000$ °C. In terms of the standard free energy of oxide formation, the oxides of Nb and Ti are nearly as stable as Al_2O_3 and SiO_2 . Which oxide is stable on an alloy also depends on metal activities. Changes in the activities of the elements of an alloy can change the composition of oxidation products significantly.

For the oxide of an element to form, the latter must be available at the oxide/alloy or alloy/gas interface and the partial pressure of oxygen in contact with the alloy must exceed the equilibrium pressure for the oxidising reaction at that value of the activity of the element. The Si/ SiO_2 equilibrium pressure is several orders of magnitude higher than that of Al/ Al_2O_3 and Ti/ TiO_2 , both of which are similar [45]. Knowledge of the activity variation within the alloy system in which intermetallic phases exist is necessary to predict correctly the oxide stabilities.

There was internal oxidation in the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ but not in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$. According to Wagner, the critical solute concentration for the transition from internal to external oxidation increases with the solubility and diffusivity of oxygen and decreases with an increase in the solute diffusivity in the alloy [46]. When the oxide of the base metal can form and grow until the more stable oxide of the solute becomes stable and stops the growth of the transition oxide an excess solute above that calculated by Wagner is required [47]. The excess solute

concentration increases as the growth rate of the transient oxide increases. In intermetallics the rate of transient oxidation is a more significant factor in determining whether or not protective scale develops. Simulated transport kinetics of oxygen (oxygen penetration depths) in pure Nb and two Nb–Al and Nb–Al–Hf alloys showed significantly reduced oxygen penetration in the ternary alloy [48].

Wagner also showed that the concentration of solute that is required to maintain the growth of an external scale depends on the thermodynamic and diffusional properties of the alloy immediately beneath the oxide [49]. In the case of intermetallic compounds with narrow or no solubility ranges the consumption of the element that forms the external oxide results in the formation of the next intermetallic compound with a lower concentration of the consumed element next to the external oxide. The properties of the lower intermetallic compound determine the ability of the intermetallic to maintain the growth of the protective oxide. In the case of NbAl₃ the lower compound is Nb₂Al, which has poor oxidation (see Section 2). In the case of Ti₅Si₃ the lower compound is Ti₃Si which has inferior oxidation behaviour. In the case of TiAl₃ the lower compounds are Ti₂Al₅ and TiAl₂. In the case of alumina forming Al rich TiAl with $\alpha_{Al}/\alpha_{Ti} > 1$ the lower compound is titania forming Al poor TiAl with $\alpha_{Al}/\alpha_{Ti} < 1$ (α_i is the activity of element $i = Al, Ti$).

Some alloys can form protective oxide at low temperatures and others at high temperatures. The effect of temperature and alloying additions on the selective oxidation of an element is linked with how temperature and alloying element affect oxygen permeability and solute diffusivity in the alloy and the growth rate of transient oxide. Such data is not available for the Nb–Si–Ti–Al–Hf system.

The two alloys of this study do not have “a base metal”. The same is true for the intermetallic compounds in their microstructures, with the exception of TiAl₃ in the cast alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} (Section 4.1) and the Al rich TiAl (55 at.% Al) in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} that was heat treated at 1200 °C (Section 4.2). Both these compounds were very poor in Nb. In other words, it is not easy to indicate which would be the “lower compound” of the majority of the intermetallics in the microstructures of the two alloys as they oxidised. In addition, the solidification, solute partitioning and growth processes associated with the 5-3 silicide in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} resulted in a composite structure (see Section 5.2.2) where the 5-3 silicide core was surrounded by higher not lower compounds.

Do the oxidation responses of the two alloys at 800 °C, where they did not pest, and at 1200 °C, where the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} formed a continuous thin well adhering α -Al₂O₃ scale with no internal oxidation, point to some form of “cocktail effect” [50] and therefore unexpected synergies between elements and/or intermetallic phases in each alloy? Were the solubility and diffusivity of oxygen and the solute diffusivities in the alloys affected by synergies between elements and/or intermetallic phases? Which (if any) were the synergistic mixtures of elements and/or phases in each alloy at 800 °C? Why there were no synergies that resulted in exceptional oxidation for the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} at 1200 °C? Which were the synergistic mixtures of elements and/or intermetallic compounds that gave the exceptional oxidation of the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} at 1200 °C? Was the oxidation behaviour of the latter alloy greater than the sum of constituent parts? Was the oxidation at each temperature determined only by activities and partial pressures of oxygen? Was the oxidation of each alloy some combination of the above? We are not able to provide answers to these questions. We shall discuss the oxidation of the two alloys by referring to their starting and/or heat treated microstructures, current knowledge about the oxidation of binary or ternary intermetallic phases and data about the thermal expansion of compounds and oxides.

The starting microstructure of the oxidation specimens of the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} consisted of hexagonal and tetragonal Nb₅Si₃, TiAl₃ and (Ti,Nb)Al₃, TiAl, Ti₂Al₅ and TM_{2.35}Al_{1.65}Si and TM_{3.7}Al₃Si. Regarding the aluminides, only the tri-aluminide was present in the bottom and only the TiAl in the bulk and top of the cast alloy and the Ti₂Al₅ was found only in the bulk of the button. After the heat treatment the TM_{2.35}Al_{1.65}Si and TM_{3.7}Al₃Si compounds were not stable and the tri-aluminide had Nb/Ti > 1 (i.e., it was Nb rich). The fully intermetallic microstructure of this alloy was not free of micro cracks.

The aluminide (Ti,Nb)Al₃ with Nb/Ti ≈ 1 and the Ti₅Si₄, TiSi and hexagonal γNb₅Si₃ silicides were present in all parts of the starting microstructure of the oxidation specimens of the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}. The same phases were present after the heat treatments at 800 and 1200 °C and Nb poor TiAl at the latter temperature. Severe cracking of Nb₅Si₃ was observed in the microstructure of Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} particularly after the heat treatment at 800 °C. The vol.% of TMAI₃ was very high in Zone A compared with Zone B and the bulk and top of the button of this alloy.

The main difference between the starting microstructures of the two alloys for the isothermal oxidation experiments were (i) the absence of TiAl and the presence of Ti₅Si₄ and TiSi everywhere in the microstructure of the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}; (ii) the presence only of hexagonal 5-3 silicide in the microstructure of the latter alloy and (iii) the significantly higher vol.% of TMAI₃ in Zone A of this alloy compared with the bulk and top and the low vol.% of TMAI₃ formed in the bottom of the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5}. Furthermore, in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} (a) the TiAl was scarcely present in the bulk and top of the button after the two heat treatments and no TiAl was observed at 800 °C, but at 1200 °C the TiAl in Zone A was very poor in Nb (Ti/Nb = 13); (b) the Ti₅Si₄ became richer in Ti and poorer in Nb at 1200 °C compared with 800 °C and (c) at 1200 °C the TiSi had grown significantly compared with the cast microstructure. In both alloys no HfO₂ particles were observed in the as cast and heat treated conditions and after oxidation at 800 °C. In the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} probably there was some hafnia in the scale formed at 1200 °C (see BSE image and Hf and O maps in Figure 11). No hafnia was observed in or below the scale formed on the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4}.

Both alloys did not pest at 800 °C and both formed thin scales at this temperature. Remarkably, the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} did not pest even though its heat treatment at 800 °C indicated a heavily cracked microstructure (Figure 7a). According to the XRD data, at 800 °C the scales of the alloys Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} and Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} consisted of the same phases, namely Ti niobate(s), Nb, Ti, Si, Hf oxides and TiAl₂O₅ but the EDS data indicated “islands” of alumina in the latter, and Si containing mixed oxides in both alloys. In the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} there was tetragonal Nb₅Si₃, which is known to pest, and Nb rich tri-aluminide which also pests (see Section 2). The suppression of pest in this alloy could be attributed to the low vol.% of the aforementioned two phases. The presence of Ti in the oxide(s) in the scale of this alloy was attributed to the oxidation of Al poor TiAl and Nb rich tri-aluminide. The suppression of pest oxidation in the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} was attributed to the presence only of non-pesting intermetallic phases in its microstructure. The presence of alumina in the scale formed on this alloy was attributed to the high vol.% of tri-aluminide.

At 1200 °C the scale formed on the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} was thicker than that formed on the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} and exhibited a “layered” structure, (Figures 9c and 11), compared with the thin continuous scale that formed on the latter alloy (Figure 12c). The scale formed on the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} consisted of Ti-rich mixed oxide and Al and Ti-rich mixed oxide at the top, beneath it formed a Nb and Si-rich mixed oxide, beneath this was Al and Ti-rich mixed oxide and beneath the latter was a continuous mixture of Al₂O₃ (major phase) with dispersed (most likely) Ti-rich oxide. There was also internal oxidation with Al₂O₃ forming at interfaces between Nb₅Si₃ and TMAI. This oxidation behaviour was attributed to the oxidation of alloyed 5-3 silicides and TiAl forming first transient outer mixed oxides that were either Ti-rich or Ti and Al-rich, followed with inner Nb and Si-rich mixed oxides from the oxidation of silicides and then beneath them Al and Ti rich oxides from the oxidation of aluminides and alloyed 5-3 silicides and then alumina mixed with titania from the oxidation of aluminides. The internal oxidation was attributed to the oxidation of TMAI and alloyed 5-3 silicide (see Section 2).

The scale formed on the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} at 1200 °C consisted of a continuous αAl₂O₃ layer that was about 5 μm thick (Figures 13c and 14). Its formation was attributed to the oxidation of Al rich tri-aluminide, Nb poor and Al rich TiAl. The Ti₅Si₄ and TiSi that surrounded the hexagonal 5-3 silicide suppressed the formation of the lower Ti₃Si silicide and the formation of continuous Ti-rich oxide. The alloying of hexagonal 5-3 silicide with Al suppressed the formation of SiO₂ beneath the alumina scale (see Section 2).

There was a small weight loss of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ after about 18 h at 800 °C. The weight loss “levelled off” after about 70 h, then there was a small weight increase from 83 to 90 h and then again a small weight loss. Study of the isothermal oxidation of the alloy at 800 °C using thermo-gravimetric analysis coupled with mass spectrometry detected very low signals for species with atomic mass 27 and 44. The former and the latter could correspond respectively to Al and SiO. The SiO could be attributed to the reaction of Si in silicides with SiO_2 (at the silicide-oxide interface) that gives gaseous SiO [51]. The vapour pressures of SiO at 800 °C calculated from extrapolation of the data of Kubaschewski and Chart [51] and Ferguson and Nuth [52,53] respectively are 9.5×10^{-4} Pa and in the range 1.8×10^{-4} to 7.8×10^{-4} Pa. The Al could be attributed to Al loss from Al rich tri-aluminides. The NbO_2 , TiO and TiO_2 oxides have significant vapour pressures at significantly higher temperatures, which have been determined for the ranges 1739–1882 °C, 2027–2227 °C and 2027–2227 °C, respectively [54]. Extrapolation to 800 °C gives the vapour pressures of both Ti oxides approximately equal to 1.3×10^{-12} Pa, compared with 1.3×10^{-13} Pa for NbO_2 .

The weight gain versus time data of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ exhibited discontinuities (sharp changes in weight), that were more severe at 800 °C than at 1200 °C (Figure 12c,d) and more severe than those of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ at 800 °C. These were attributed to high stresses that built up in the scale and caused it to crack, thus exposing the substrate to the oxidising atmosphere (see below). Remarkably, even after the severe damage of the scales at 800 °C and 1200 °C this alloy did not pest, the scale was able to “repair” itself and formed alumina at both temperatures. The alumina scale was continuous and had uniform thickness at the higher oxidation temperature.

Oxide scales can be subjected to thermal, compositional and intrinsic stresses. Thermal stresses are caused by differences between coefficients of thermal expansion (CTEs) and compositional stresses can be important in non-stoichiometric oxides. Phase transformations, grain growth, coalescence of oxide islands, and changes in point defect concentrations (i.e., phenomena that induce dimensional changes) can build up intrinsic stresses during the growth of the scale.

The α -cristobalite is tetragonal with lattice constants close to the cubic form and is stable below 200 to 270 °C. The β -cristobalite is cubic and is stable above 200 to 270 °C [55]. The transition temperature depends on composition, defects and strains [56]. On heating, the reconstructive $\alpha \rightarrow \beta$ transformation is accompanied by an average volumetric change of 2.8%. On cooling, the displacive (martensitic) $\beta \rightarrow \alpha$ transformation [55] is accompanied by a approx. 5% reduction in volume, which causes the crystals to crack [56]. There is an overall expansion of about 0.8% from the temperature of the $\alpha \rightarrow \beta$ transformation up to 1027 °C [57]. Both α and β cristobalite are auxetic (i.e., have negative Poisson’s ratio) [55]. In cristobalite, Si can be substituted by Al, the substitution affects the stability of both the α and β cristobalite and the $\alpha \leftrightarrow \beta$ transitions. Al^{3+} occupies Si tetrahedral sites [56]. Up to 2.4 mol% of Al_2O_3 can substitute for SiO_2 in cristobalite [56].

In the oxidation of Ti the main product is TiO_2 (rutile) and oxides like TiO, Ti_2O_3 . The $\text{Ti}_x\text{O}_{2x-1}$ Magnelli phases oxidise rapidly to TiO_2 . TiO_2 can also form as anatase. Anatase I transforms to anatase II (both tetragonal) at 642 °C with no volume change, anatase II transforms to rutile (both tetragonal) at 915 °C with negative volume change. Anatase III transforms to rutile (both tetragonal) at 1150 °C with negative volume change and rutile (tetragonal) transforms to brookite (orthorhombic) at 1300 °C with positive volume change [58]. Niobium can form the NbO, NbO_2 and Nb_2O_5 oxides. TiO and NbO have cubic NaCl structure and large number of vacant sites in both the anionic and cationic sub-lattices. The vacancies in NbO are part of the structure and are very different in character from the random vacancies in TiO. The latter has a wide composition range but the composition range of NbO is very small (≈ 0.1 at.%) [59]. Rutile has a tetragonal crystal structure and two coefficients α_c and α_a are needed to represent the expansion of its crystals. Volume expansivity is given by $2\alpha_a + \alpha_c$ [60]. Micro-cracking of rutile depends on grain size [61] and the likelihood of micro-cracking is increased with grain size [62].

The different crystallographic forms of stoichiometric Nb₂O₅ all transform irreversibly above 1100 °C to monoclinic H-Nb₂O₅. The transformation of orthorhombic to monoclinic Nb₂O₅ is accompanied by a positive volume change [58]. The lattice thermal expansion of H-Nb₂O₅ is anisotropic, the “a” and “c” lattice parameters increase with increasing temperature whereas the “b” parameter and the angle β do not change [63]. This thermal expansion behaviour has been attributed to large variation in the Nb–O distances in the NbO₆ octahedra of Nb₂O₅ [4]. Anisotropy of the CTEs of the grains in a polycrystalline oxide may create internal stresses large enough to cause micro-cracking. The presence of micro-cracks will affect strength, elastic moduli and CTE. This is known to be the case in Nb₂O₅.

Aluminium oxide is known to exist in several structures, e.g., γ, δ, θ, α. The γ-Al₂O₃ is cubic and is stable up to 800 °C [64], or 1000 °C [65] and nano γ-Al₂O₃ up to 700 °C, the δ-Al₂O₃ is tetragonal or orthorhombic and forms above 800 °C, the θ-Al₂O₃ is monoclinic and forms above 900 [64] or 1050 °C [65] or 1100 °C and the α-Al₂O₃ (trigonal or hexagonal) forms above 1000 °C [66] or 1100 °C [65]. The γ-Al₂O₃ has low permeability to diffusing atoms and ions [67]. Si diffuses in Al₂O₃ at $T \geq 1100$ °C [67].

Mixtures of TiO₂ and Nb₂O₅ with Al₂O₃ can have low CTE values. The Ti₂Nb₁₀O₂₉ is orthorhombic, and both TiNb₂O₇ and AlNb₁₁O₂₉ have monoclinic structure. The thermal expansion of Ti₂Nb₁₀O₂₉ depends on its microstructure. The Nb₂O₅ content in TiNb₂O₇ also affects the thermal expansion of the latter. Similarly, the content of TiO₂ and Nb₂O₅ in Ti₂Nb₁₀O₂₉ and TiNb₂O₇ affects thermal expansion. In Ti₂Nb₁₀O₂₉ the Nb cations can be replaced by Al. In the mixed oxide 2Al₂O₃–98Nb₂O₅ the major phase was AlNb₁₁O₂₉ [68].

The TiAl₂O₅ is isomorphous with orthorhombic pseudo-brookite TiMe₂O₅. Compounds of the latter structure are highly anisotropic with extremely small CTE along the “a” direction and very large CTEs along the “c” direction [69]. The aluminium titanate has a very anisotropic CTE. Doping of this structure with Al₂O₃ and SiO₂ affects strength. The TiAl₂O₅ decomposes to α-Al₂O₃ and TiO₂ (rutile) between 800 and 1280 °C [70].

The microstructures of Nb-silicide based alloys contain phases with anisotropic CTEs. The CTE values of the alloys of this study are not known. Table 2 summarises data about the thermal expansion of oxides, silicides and aluminides that were observed in the alloys of this study. The CTE values of Nb₅Si₃, Ti₅Si₃, TiAl and Ti₅Si₃O_{0.4} are average values and that of TiAl₃ was calculated. Regarding the TiSi silicide, its CTE increases with temperature up to about 227–327 °C and after this temperature it does not change significantly [71]. Table 2 shows that the overall thermal expansion of Nb₂O₅ is small compared with the other oxides and most likely similar to that of TiAl₂O₅, which is very highly anisotropic.

Thermodynamics shows that both Ti₅Si₄ and TiSi or Ti₅Si₃ and Ti₅Si₄ can be in equilibrium with SiO₂, and that the Ti₅Si₃ can be in equilibrium with Ti₂O₃ and SiO₂ or with TiO and Ti₂O₃. There is some doubt about the Ti₅Si₃-Ti₅Si₄-SiO₂ equilibrium [26]. It has been suggested that the ternary oxides Ti₂O₃·5SiO₂ and 3Ti₂O₃·2SiO₂ may exist [45]. Ti rich and Nb and Si rich oxides can be present in the scales formed on Nb-silicide based alloys [31,72].

The CTE values of the intermetallic compounds that were present everywhere in the microstructure of the alloy Nb_{1.7}Si_{2.4}Ti_{2.4}Al₃Hf_{0.5} were similar or close to those of TiO₂ and α-cristobalite. At 800 °C the presence of Al in the thin scale formed on this alloy could be attributed to Al substituting Si in cristobalite. At 1200 °C there was evidence of cracks in the thicker scale in the “top layer” that consisted of Ti rich mixed oxides and Al and Ti rich mixed oxides and in the “layer” that consisted of Si and Nb mixed oxides (Figures 9c and 11). These cracks could be attributed to thermal, compositional and intrinsic stresses (see above and Table 2) and could have formed during the growth of the scale and/or during the cooling of the specimen.

In the case of the alloy Nb_{1.3}Si_{2.4}Ti_{2.4}Al_{3.5}Hf_{0.4} even though the scale was not stable (see above) alumina was formed at both temperatures. The alumina scale had uniform thickness and was continuous at 1200 °C (Figure 13d) but at 800 °C only islands of alumina were observed (Figure 13c).

It is likely that in this alloy the concentration of Al (C_{Al}) was larger than C_{ther}^{Al} or even $C_{Al} \approx C_{kin}^{Al}$. At 800 °C there were severe changes in weight (Figure 12c). The glancing angle XRD (Figure 16a) provided evidence for the presence of the low CTE and highly anisotropic aluminium titanate and the BES imaging indicated islands of alumina, probably $\gamma\text{Al}_2\text{O}_3$, which has a higher CTE compared with the phases that were present everywhere in the microstructure of the alloy (Table 2). The weight changes that occurred during the isothermal oxidation at 800 °C were attributed to the formation of TiAl_2O_5 that has highly anisotropic thermal expansion that causes severe micro-cracking, and the high CTE values of TiAl_3 and $\gamma\text{Al}_2\text{O}_3$. At 1200 °C the weight changes were not as severe (Figure 12d). This was attributed to the $\gamma\text{Al}_2\text{O}_3 \rightarrow \alpha\text{Al}_2\text{O}_3$ transformation, the transformation of TiAl_2O_5 to $\alpha\text{Al}_2\text{O}_3$ (see above), and the lower CTE of $\alpha\text{Al}_2\text{O}_3$.

Isothermal oxidation experiments allow one to determine the rate of growth of an oxide scale. This is a measure of the performance of an alloy but it is at best a poor yardstick. Oxidation resistance does not depend only on the rate at which an oxide scale thickens but must also consider the ability of the scale to resist the thermally induced stresses associated with cyclic behaviour. We plan to evaluate the latter for the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$, as well as its CTE and mechanical properties. The microstructures and isothermal oxidation of other alumina scale forming alloys of the same alloy system will be discussed in future publication.

Table 2. Coefficients of thermal expansion, volume thermal expansion, and thermal expansion anisotropy (α_c/α_a) of oxides, silicides and aluminides.

Oxide	CTE	T	Volume Thermal Expansion	Thermal Expansion Anisotropy	Ref.
	($\times 10^{-6} \text{ K}^{-1}$)	(°C)	($\times 10^{-6} \text{ K}^{-1}$)	α_c/α_a	
$\gamma\text{Al}_2\text{O}_3$	12.66	27–800	38.87	–	[67]
α -cristobalite	10.3	25	–	–	[55]
TiO_2	9	27–302	–	–	[73]
	8.4–11.8	–	–	–	[74]
TiO_2 (rutile)	–	25	23.57	1.28	[75]
	–	50	23.8	1.216	[60]
	–	280	26.78	1.30	[75]
	–	610	31.6	1.473	[60]
TiO_2 (anatase)	–	50	15.4	2.05	[60]
	–	690	39.4	2.147	[60]
$\alpha\text{Al}_2\text{O}_3$	7.5	1000–1600	–	–	[76]
	–	–	–	1.125	[67]
TiO	6.6	≤ 477	–	–	[59]
NbO	4.8	≤ 850	–	–	[59]
β -cristobalite	3.13	300	–	–	[57]
TiNb_2O_7	2.3	–	–	–	[77]
Nb_2O_5	2.19	25–1000	11.2	1.12	[63]
	1.66	25–1000	–	–	[63]
	1.59–0.48	25–1000	–	–	[78]
TiAl_2O_5	0.8–1.3	25–1000	–	–	[79]
$\alpha\text{Nb}_5\text{Si}_3$	8.75 **	–	–	1.254 *	[2]
$\beta\text{Nb}_5\text{Si}_3$	10.79 **	–	–	1.795 *	[2]
Ti_5Si_3	–	–	–	3.056 *	[2]
	8.5	800	–	–	[80]
	10.2 +	25	–	–	[81]
	9.25 +	1000	–	–	[81]
$\text{Ti}_5\text{Si}_3\text{O}_{0.4}$	10.47 +	25	–	2.5	[81]
TiAl ($\text{Ti}_{44}\text{Al}_{56}$)	10.87 +	27	32.6	0.934	[82]
TiAl_3	15	25	–	–	[83]

* average value using data from Reference [2]. + bulk coefficient of thermal expansion (CTE) calculated as $(2\alpha_a + \alpha_c)/3$.

6. Conclusions

We studied the intermetallic alloys $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ and $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ that were designed (i) not to have a solid solution in their microstructures; (ii) not to pest and (iii) to form alumina. Both alloys complied with (i) and (ii) and formed thin scales at 800 °C. At 1200 °C the former alloy suffered from internal oxidation and formed alumina intermixed with Ti rich oxide beneath a thick “layered” scale of mixed oxides that contained Ti and/or Al and/or Si and the latter alloy did not experience internal oxidation and formed a thin continuous well adhering $\alpha\text{-Al}_2\text{O}_3$ scale that was able to repair itself during oxidation at the same temperature.

There was severe macrosegregation of Si in both alloys, which in $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was almost double that in $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. The severe macrosegregation of Si contributed to the formation of a “layered” structure in the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$.

The microstructure of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ consisted of hexagonal and tetragonal Nb_5Si_3 , TiAl_3 and $(\text{Ti,Nb})\text{Al}_3$, TiAl , Ti_2Al_5 . Different aluminides were present in different parts of the button and the tri-aluminide had $\text{Nb/Ti} > 1$.

The $(\text{Ti,Nb})\text{Al}_3$ with $\text{Nb/Ti} \approx 1$ and the Ti_5Si_4 , TiSi and hexagonal $\gamma\text{Nb}_5\text{Si}_3$ silicides were present in all parts of the cast alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ and at 800 and 1200 °C, and Nb poor TiAl at the latter temperature. The “layered” structure of the cast alloy was retained at 800 and 1200 °C.

Both alloys met the “standard definition” of HEAs. The parameters VEC and δ of both alloys respectively were outside and within the range of VEC and δ values for bcc solid solution plus intermetallic(s) HEAs. The parameter $\Delta\chi$ of the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$ was within the range for bcc solid solution plus intermetallic(s) HEAs but the $\Delta\chi$ of the alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ was outside the lower range of values for bcc solid solution and intermetallic(s) HEAs.

The alloy $\text{Nb}_{1.3}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_{3.5}\text{Hf}_{0.4}$ exhibited strong correlations between the parameters $\Delta\chi$, δ and VEC, and also sampled a wider range of values of each parameter compared with the alloy $\text{Nb}_{1.7}\text{Si}_{2.4}\text{Ti}_{2.4}\text{Al}_3\text{Hf}_{0.5}$. There was a strong correlation only between the parameters $\Delta\chi$ and δ of the latter alloy that was similar to that of the former alloy, which also had the lowest VEC.

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