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On Nb silicide based alloys: Part II

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ABSTRACT

The paper examined alloying behaviour in cast and heat treated Nb-silicide based alloys where alloying additions were transition metals (Cr, Hf, Mo, Ta, Ti, W), and simple metal or metalloid elements (Al, B, Ge, Sn). The microstructures of the alloys consisted of bcc Nb_{ss} solid solution (which could be of three types, namely normal, Ti rich and with no Si) and intermetallic(s). The study used the parameters entropy (ΔS_{mix}) and enthalpy (ΔH_{mix}) of mixing, atomic size difference (δ), electronegativity difference ($\Delta\chi$), valence electron concentration (VEC), $\Omega = T_m\ \Delta S_{mix}/|\ \Delta H_{mix}\ |$ and the ratio sd/sp of sd over sp electronic configuration elements. The values of the parameters were in the ranges $-44.8 < \Delta H_{mix} < -32.7$ kJ/mol, $8.3 < \Delta S_{mix} < 14.7$ J/molK, $4.4 < VEC < 4.9$, $8.1 < \delta < 14.3$, $0.12 < \Delta\chi < 0.24$, $0.57 < \Omega < 0.95$ and $2.12 < sd/sp < 4.03$. Plots of $\Delta\chi$ versus δ and $\Delta\chi$ versus ΔH_{mix} separated the alloys in three groups according to alloying additions. In these plots the B containing alloys formed their own group. The data for Nb solid solutions from Part I (J Alloys Compd. 708 (2017) 961–971) was used to compare the parameters of the alloys and solid solutions. Plots of $\Delta\chi$ versus ΔH_{mix} and $\Delta\chi$ versus Ω separated the alloys and their bcc Nb solid solutions according to whether they contained B or not. The parameters ΔH_{mix}, ΔS_{mix}, δ and $\Delta\chi$ of some of the Nb-silicide based alloys were in the ranges reported for bcc solid solution + intermetallic(s) high entropy alloys. The values of the parameters ΔH_{mix}, ΔS_{mix}, VEC, δ and $\Delta\chi$ were in better agreement with those reported for amorphous alloys.

1. Introduction

Future aero-engines must comply with strict environmental and performance targets (e.g., reduction in average noise levels, reduction of CO_2 per passenger km, low NO_x emissions). Such targets can be met by changes of propulsive and thermal efficiency and require materials with capabilities beyond those of Ni-based superalloys. Property goals for high temperature alloys with capabilities beyond those of Ni-based superalloys have been discussed by Bewlay and co-workers [1]. Nb-silicide based alloys (also known as Nb *in situ* silicide composites) belong in the family of refractory metal intermetallic composites (RMICs) and have the potential to meet property targets for critical applications in future aero-engines. Reductions in rotor weight of more than 20% can be realized through the substitution of Nb-silicide based aerofoils for Ni-base superalloys aerofoils in present and advanced turbine designs [1].

Developmental Nb-silicide based alloys are multi-component alloys [1–11] and can have as many as 12 solute additions. The two most important phases in the microstructure of these alloys are the bcc Nb solid solution (Nb_{ss}) and the tetragonal Nb_5Si_3 silicide. Other intermetallics also can be stable in their microstructures, for example, the Nb_3Si silicide, the C14-$NbCr_2$ Laves phase [2,5] and A15 intermetallic compounds [11]. What is known about the role these phases play in the properties of Nb-silicide based alloys?

The Nb_{ss} has inferior creep and oxidation properties compared with the Nb_5Si_3 and Nb_3Si silicides, and the properties of the solid solution are crucial for meeting the property goals. The chemical composition, volume fraction, size, distribution and properties of the Nb_{ss} are crucial for achieving a balance of properties [1,4,12]. The volume fraction and spatial distribution of the Nb_{ss} are dependent on the macrosegregation of Si [13]. At temperatures above 1273 K the Nb_{ss} makes only a minor contribution to the creep strength [12].

In developmental Nb-silicide based alloys the Nb_{ss} can be with/out Si [8] and rich in Ti [2]. Transition (including refractory) metal additions substitute Nb and simple metal and/or metalloid element additions substitute Si in the Nb_5Si_3 [2,8–11,14] The unalloyed tetragonal Nb_5Si_3 has better creep and oxidation than the unalloyed tetragonal Nb_3Si. The creep of the alloyed tetragonal Nb_5Si_3 is inferior compared with the unalloyed silicide [15]. The toughness,

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strength and oxidation of the Nb_{ss} depend on the solute elements in the solid solution [1,4,12,16]. For example, the solutes Al, Cr, Hf or Ti can have positive and negative effect on the toughness of the Nb_{ss} depending on their concentration in the latter, the aforementioned elements with/out Mo, Ta or W provide solid solution strengthening, the solutes Al, B, Cr, Ge, Hf, Mo, Si, Sn, Ta, Ti, W individually and simultaneously as addition of two or more elements control the oxidation of the Nb_{ss} and B, Ge or Sn are essential solute additions for suppressing pest oxidation [1–3,16–18].

Alloying that can improve the properties of the Nb_{ss} can affect the type(s) of 5-3 silicide that is(are) stable in the microstructure of the alloys, meaning whether the tetragonal low temperature αNb_5Si_3 or the tetragonal high temperature βNb_5Si_3 or the hexagonal metastable γNb_5Si_3 will be stable [2,14], and the hardness, creep and oxidation of the silicide(s) [3,4,15].

A15 compounds play an important role in the oxidation of Nb-silicide based alloys [3] depending on their type, volume fraction and distribution in the microstructure and are crucial for achieving a balance of properties. The A15 intermetallic compounds Nb_3Al, Nb_3Ge, Nb_3Si (metastable 3-1 silicide) and Nb_3Sn can be stable in the microstructures of Nb-silicide based alloys [11,19]. Their properties were reported in Refs. [20–22] and compared with the tetragonal Nb_3Si, which is the stable 3-1 silicide in the Nb-Si binary [23].

The type and stability of the 3-1 silicide in Nb-silicide based alloys can depend on solidification conditions. For example, amorphous binary Nb-Si alloys of near – eutectic composition have been produced by rapid quenching from the melt [24] and formation of the A15-Nb_3Si (i.e., the metastable 3-1 silicide) proceeded the formation of the stable (tetragonal) Nb_3Si upon annealing [24]. Interstitials also stabilised the A15 structure [25]. Under rapid solidification conditions the eutectic $L \rightarrow Nb_{ss} + Nb_3Si$ in hypo and hyper-eutectic binary Nb-Si alloys can be replaced by the metastable eutectic $L \rightarrow Nb_{ss} + \beta Nb_5Si_3$ [26]. There is no phase equilibria data that includes the metastable A15-Nb_3Si. Even at homologous temperatures above 0.9, phase transformations in binary Nb-Si alloys are sluggish [27]. Nb-silicide based alloys are usually heat treated at $T \geq 1773$ K for $t \geq 100$ h [2,8,27].

In developmental Nb-silicide based alloys the alloying additions are transition metals (TM = Cr, Fe, Hf, Ti, V, Zr), refractory metals (RM = Mo, Ta, W) and simple metal or metalloid elements (Al, B, Ge, Si, Sn). Which of these elements should be added simultaneously to Nb-Si based alloys and at what concentrations in order to meet property goals? Calculation of phase diagrams (CALPHAD) is effective in alloy design provided there is reliable thermodynamic database for the system under investigation. Unfortunately, this is not the case for Nb-silicide based alloys, for which there is shortage of experimental data and disagreements about phase equilibria. This hampers alloy design and was discussed briefly in Part I [28].

Let us now briefly discuss what is known about the effects of alloying on the properties of binary Nb alloys and Nb-based alloys without Si addition. The ductile-brittle transition temperature (DBTT) of “pure” Nb is about 73 K and increases with interstitial elements, in particular nitrogen and oxygen and with substitutional alloying additions. The elements Al, Cr, Mo and W (group A1) have a strong effect on the DBTT of Nb, which is increased. Hf has a weak effect, while Ti and Ta (group A2) have no significant influence on the DBTT [29]. The ranking of substitutional alloying elements in binary Nb-X alloys in terms of decreasing effect on the DBTT is Al, Cr, W, Mo, V, Hf, Ti [29]. In terms of decreasing but positive effect on creep strength the ranking of substitutional solutes in binary Nb-X alloys is W, Mo, Ta, Cr (group A3). Hf, V and Ti (group A4) further decrease creep, and Ti has the strongest effect [30].

There is no data for the effect of the addition of two or more elements (a) from groups A1 and A2 on the DBTT of Nb_{ss}, (b) from groups A3 and A4 on the creep of Nb_{ss}, and (c) from groups A1 to A4 on the diffusivity of oxygen in the Nb_{ss}. Let us now briefly review what is known about the properties of Nb-based alloys where elements of the groups A1 to A4 are present simultaneously in an alloy.

There is data about the effect of alloying elements on the properties of the Nb_{ss} and Nb-based alloys from research on Nb intermetallic alloys and other Nb alloys without Si addition. This research has shown (i) that the toughness of Nb-Ti-Cr solid solution alloys increases with decreasing number of d + s electrons per atom in the alloy [31], (ii) that the simultaneous addition of Al and Cr in Nb-Ti-Cr-Al solid solution alloys leads to a reduction in fracture toughness and tensile ductility, (iii) that changing the number of d + s electrons through alloying additions can give a ductile solid solution alloy [32] and (iv) that the strength of Nb-Ti-Cr-Al solid solution alloys can be controlled by their Cr, Al and Ti concentrations and depends on their Al + Cr content and the Nb/Ti ratio [32].

Hafnium is an important addition in Nb alloys because it scavenges oxygen [3,4,16]. Furthermore, the addition of Hf improves the room temperature ductility of Nb-Ti-Hf solid solution alloys. Strength at room temperature and in the temperature range 1033–1473 K increases with an increase in Hf concentration. In Nb-Ti-Al alloys the addition of Hf increases strength in the temperature range 673–1173 K, and in Nb-Ti-Hf-Al alloys an increase in Al concentration results (a) to a decrease of ductility, (b) to an increase of strength up to 1033 K and (c) to a decrease of strength in the range 1253–1473 K below that of Nb-Ti-Hf alloys. Finally, in Nb-Ti-Al-Cr-Hf alloys an increase in Al concentration results to a decrease in ductility and the addition of Sn improves strength at low temperatures [33].

In Part I [28] it was shown (i) that the elements used as alloying additions in Nb-silicide based alloys belong in different groups regarding their activation energy and diffusivity in Nb, (ii) that some of the empirical parameters used to study the alloying of the so-called high entropy alloys (HEAs) can also describe the alloying behaviour of the bcc Nb solid solution in Nb-silicide based alloys, (iii) that the relationship between the enthalpy of mixing and atomic size (parameter δ) is the same as for HEAs, for which this relationship is considered to be very powerful [34] and (iv) that electronegativity (parameter $\Delta\chi$) and atomic size can differentiate the behaviour of sp and sd elements. Solid solutions with no B, Ta and V had $\Delta\chi > 0.179$ and solid solutions with no W had $\Delta\chi < 0.13$. Furthermore, Nb_{ss} rich in Ti had $\delta > 5$ and Nb_{ss} with no Si had $\delta < 5$. The partitioning of solutes between the phases (Nb_{ss} and intermetallic(s)) in Nb-silicide based alloys [2,6,8–11,14] was also considered and it was shown that Cr, Hf or Sn follow (“like”) Ti in the Nb_{ss} but B, Mo or W do not, and that the partitioning of Al depends on other alloying elements (i.e., “Al chooses how to behave”). Electronegativity and valence electron concentration (VEC) can also describe the alloying behaviour of tetragonal Nb_5Si_3 [15]. In $\Delta\chi$ versus VEC plots the B containing Nb_5Si_3 occupied a distinctly different area compared with Nb_5Si_3 without B [15].

Can Nb-silicide based alloys be differentiated depending on alloying additions? Do B containing Nb-silicide based alloys form their own district group? How are the bcc Nb solid solutions with/out B relate to Nb-silicide based alloys with/out B? Can we generate new data that could assist alloy design and alloy selection? The motivation for the research presented in this paper was to answer the above questions using the same empirical parameters as in Part I [28], where they were shown to be effective for separating the types of the Nb_{ss} that can form in Nb-silicide based alloys, and to compare them with those of the so-called high entropy alloys [35–40], concentrated solid solutions alloys [34] and amorphous alloys [41,42]. The empirical parameters are not used in this paper to “predict” which phase(s) is(are) stable in Nb-silicide based alloys.