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On Nb silicide based alloys: Part II

P Tsakiropoulos

Department of Materials Science and Engineering,
The University of Sheffield, Sheffield S1 3JD, UK

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.

Keywords: A – High temperature alloys, Intermetallics, solid solutions

*p.tsakiropoulos@sheffield.ac.uk, fax: +44 114 222 5943

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, 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 [–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 [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 to 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 to 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 to 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. The alloys Nb-24Ti-18Si-5Cr-5Al [alloy KZ5 in ref. 2] and Nb-20Si-5Hf-5Mo-3W [alloy YG8 in ref. 8] (nominal compositions, (at. %)) were used as "basis alloys" because they meet the toughness (≥ 21 MPa$\sqrt{}$m) and creep property goals, respectively. Indeed, at 1473 K the creep rates of the latter polycrystalline alloy were in the range 4.9 10^{-8} s^{-1} to 3.1 10^{-7} s^{-1} for stresses in the range 150 MPa to 300 MPa, compared with 6.3 10^{-5} s^{-1} at σ = 150 MPa for the single crystal superalloy

CMSX-4 while at 1323 K and σ = 200 MPa the creep rate was 9 10^{-9} s^{-1} compared with 1.3 10^{-7} s^{-1} for CMSX-4.

The structure of the paper is as follows. First the values of the empirical parameters are calculated for Nb-silicide based alloys. The bcc Nb solid solutions studied in Part I [28] belonged to these alloys. Then these parameters are compared with data for so-called high entropy alloys and amorphous alloys. Finally, the data for the alloys and their bcc Nb solid solutions is compared.

Method of Analysis of Data

The parameters used in this paper were the same as in the Part I [28], namely the entropy (ΔS_{mix}) and enthalpy (ΔH_{mix}) of mixing, the parameter $\Omega = T_m\Delta S_{mix} / |\Delta H_{mix}|$, the atomic size difference (δ), electronegativity difference ($\Delta\chi$) and valence electron concentration (VEC [43]). The equations for these parameters were given in Part I [28]. The ratio sd/sp of the sd electronic configuration elements over the sp electronic configuration elements in the alloy was used in this paper as an additional parameter. (The capital letter Q was used instead of Ω (capital omega) for the ratio $T_m\Delta S_{mix} / |\Delta H_{mix}|$ in [28] to avoid confusion with the term Ω_{ij} in the definition of ΔH_{mix}. The parameter Ω is used in the study of the so-called high entropy alloys, for example see refs [35-41]).

The multicomponent Nb-silicide based alloys considered in this paper were based either on the first or the second "basis alloy" (see introduction) with Si and Ti respectively in the ranges 16 to 22 at. % and 10 to 26 at. % and with additions (at. %) of Al (≤ 5), B (≤ 10), Cr (≤ 8), Ge (≤ 5), Hf (≤ 5) Mo (≤ 8), Sn (≤ 5), Ta (≤ 6), and W (≤ 4) [2,3,6,8-11,14,19,44-47]. The $Nb(Ti+Hf)^{-1}$ ratio of the alloys was in the range 1.13 to 4.87. This ratio for the alloy and the Nb_5Si_3 is considered to be important because it is thought to "define" the structure of the latter (tetragonal or hexagonal) in the alloy.

The alloys studied in this paper were prepared in earlier research, meaning no new alloys were made for this study. As described elsewhere [2], the alloys were made using high purity (better than 99.99 wt.%) elements and arc melting in water cooled copper hearths and were heat treated in an Argon atmosphere at 1773 K for 100 h. The chemical composition of each alloy was determined in the cast (AC) and heat treated (HT) conditions using EPMA (electron probe microanalysis). Readers that are interested to know more about the chemistries, microstructures and properties of Nb-silicide based alloys could refer to the refs [1-11,14,17,19,33,44-47].

The actual average chemical composition of each alloy determined by EPMA was used to calculate the aforementioned parameters using data for the elements from [41,48] and the equations given in Part I [28]. The enthalpy values were calculated using data from Miedema's model. More reliable enthalpy data is essential but not available for the alloys of this study.

Results and Discussion

The ΔH_{mix} ($kJmol^{-1}$), ΔS_{mix} ($Jmol^{-1}K^{-1}$), VEC, δ, $\Delta\chi$, Ω, and sd/sp values for different alloys are given in the Table 1. In the latter there is more than one entry for an alloy series when there is data for more than one alloy. In the Table 1 and the Figures 1 and 2 the series 2 data is for alloys with refractory metals (RMs), transition metals (TMs), and Sn but no Al, the series 3 data is for alloys with RMs, TMs, Ge or Sn and with/out Al or Cr, the series 4 data is for alloys with TMs, Al, with/out Hf, no RMs and no B, Ge, Sn, the series 5 data is for alloys with TMs, Al and B, with/out Hf, the series 6 data is for alloys with TMs, Al and with/out B, Ge, Hf or Sn, the series 7 data is for alloys with RMs, TMs with/out Al and with no B, Ge, Sn and the series 8 data is for alloys with TMs, Al with/out RMs, B or Sn and with no Ge. Alloy compositions for series 2 to 8 are given in the Table 1. The bcc Nb_{ss} solid solutions that were studied in Part I [28] belonged to alloys of the series 2 to 8 in this paper. Chemical compositions of the solid solutions are given in the Table 1 of Part I [28].

Plots of $\Delta\chi$ versus δ and $\Delta\chi$ versus ΔH_{mix} (Figures 1 and 2) separated the alloys in three groups (areas) that are shown by ellipses in the Figures 1 and 2. The Nb-silicide based alloys without B addition that are based on the “basis alloy” YG8 fall in area B, and the alloys that are based on the “basis alloy” KZ5 fall in areas A and C. Only B containing Nb-silicide based alloys belong in area C. The two “basis alloys” are indicated by asterisks in areas A (alloy KZ5) and B (alloy YG8). Alloys that contain Ge and Sn simultaneously are in area B. Alloys with RMs can be found in all three areas. Alloys in which Ge or Sn were added individually are only in area A. Alloys without Al addition are in area B. Separation of the alloys of this study in the same three groups (areas) was also observed in plots of VEC versus ΔH_{mix} and VEC versus δ (Figures not shown). However, separation of the alloys in three groups (areas) was not possible in plots of $\Delta\chi$ versus ΔS_{mix}, ΔH_{mix} versus Ω, Ω versus δ and ΔH_{mix} versus δ (Figures not shown).

None of the alloys studied in this paper satisfy the standard definition of a HEA [40]. The ranges of the values of the parameters are summarised in Table 2 together with the data (a) for the bcc Nb_{ss} solid solutions in Nb-silicide based alloys from Part I [28], (b) for single phase solid solutions from [34], (c) for bcc solid solution + intermetallic(s) HEAs from [–35-39] and (d) for amorphous alloys from [41,48]. The Table 2 gives minimum and maximum values of the parameters reported in the literature. The very negative values of ΔH_{mix} in the Tables 1 and 2 for Nb-silicide based alloys are consistent with the presence of stable intermetallic(s) in their microstructures.

The ΔH_{mix} (kJ/mol) is reported to be in the range of 2.5 to - 25 kJ/mol [37] for bcc solid solution + intermetallic(s) HEAs, in the ranges of - 15 to - 35 and - 7.5 to - 17.5, respectively for cast and heat treated bcc solid solution + intermetallic(s) HEAs [35], and about - 5 kJ/mol in bcc + Laves phase HEAs [38]. For amorphous alloys the ΔH_{mix} range of - 12 to - 40 kJ/mol was given in [42], and the ranges of 0 to - 50 kJ/mol and - 9 to - 36 kJ/mol respectively for equiatomic and non-equiatomic amorphous alloys [41]. The enthalpy of mixing of Nb-silicide based alloys is more negative than that of the bcc Nb_{ss} solid solution and the enthalpies of mixing reported for bcc solid solution + intermetallic(s) HEAs, but falls within the range of the more negative enthalpies of mixing of amorphous alloys.

The entropy of mixing ΔS_{mix} for equiatomic and non-equiatomic amorphous alloys has been reported to be in the ranges of 6 to 17.5 and 7.25 to 13.5 J/molK, respectively [41]. The lower values of ΔS_{mix} of Nb-silicide based alloys fall outside the range of bcc + Laves phase HEAs but are within the range of values for the bcc Nb_{ss} solid solution and amorphous phases. Some Nb-silicide based alloys have ΔS_{mix} close to those of stainless steels and Ni-based superalloys, which are about 9.56 and 11.39 J/molK, respectively. Most multiphase alloys have $\Delta S_{mix} \geq 14$ J/molK [34].

VEC values for bcc solid solution + intermetallic(s) HEAs [35-37,39] are reported to be in the ranges of 6 to 7.8 [35] and 5.7 to 8 [37], or less than 6.7 [36]. Furthermore, the VEC value of 6.9 was reported for bcc solid solution + Laves phase HEAs [39] and the value of 4.4 for a rapidly solidified TiVCrAlSi HEA with microstructure consisting of bcc solid solution + $(Ti,V)_5Si_3$ silicide [39]. The ranges of 4.5 to 7.5 and 4 to 9.5 have been reported respectively for equiatomic and non-equiatomic amorphous alloys [41]. The VEC of Nb-silicide based alloys is outside the range reported for bcc solid solution + intermetallic(s) HEAs but falls in the range of values for the bcc Nb_{ss} solid solutions and the lower range of values of amorphous alloys.

The δ values for bcc solid solution + intermetallic(s) HEAs [–35-38] were reported to be in the ranges of 6.6 to 11 and 4.3 to 6.6 respectively for the cast and heat treated conditions [35], or less than 4.6 [36], and in the ranges 5.5 to 10.5 [37] and 6.8 to 7.2 for bcc solid solution + Laves phase HEAs [38]. For equiatomic amorphous alloys the δ parameter has been reported to be in the ranges of 4.6 to 15.4 and 6.5 to 18 [42] and for non-equiatomic amorphous alloys to be in the range of 8.9 to 18.5 [41]. The δ values for Nb-silicide based alloys are mostly outside the range of the bcc Nb_{ss} solid solution and the bcc solid solution + intermetallic(s) HEAs but fall within the range of amorphous alloys.

The $\Delta\chi$ values for equiatomic and non-equiatomic amorphous alloys, respectively are in the ranges of 0.1 to 0.35 and 0.14 to 0.30 [41]. The $\Delta\chi$ values for the Nb-silicide based alloys fall within the range for the bcc Nb_{ss} solid solution and the amorphous alloys and cover the range for bcc solid solution + intermetallic(s) HEAs. The gap in $\Delta\chi$ values of the bcc Nb_{ss} solid solution that was discussed in Part I [28] was not observed for the $\Delta\chi$ values of Nb-silicide based alloys.

The parameter Ω values were reported to be in the ranges of 4.9 to 7.1 and 1 to 10 respectively for bcc solid solution + Laves phase HEAs [38] and bcc solid solution + intermetallic(s) HEAs [37]. The Ω values of Nb-silicide based alloys are outside the ranges for bcc Nb_{ss} solid solutions and bcc solid solution + intermetallic(s) HEAs.

In summary, some values of the parameters ΔH_{mix}, ΔS_{mix}, δ and $\Delta\chi$ of Nb-silicide based alloys fall in the ranges reported for bcc solid solution + intermetallic(s) HEAs. The values of the parameters ΔH_{mix}, ΔS_{mix}, VEC, δ and $\Delta\chi$ of Nb-silicide based alloys are in better agreement with those reported for amorphous alloys.

The alloys in group (area) C, i.e., the alloys with B addition had $-44.8 < \Delta H_{mix}$ (kJ/mol) < -41.7, $12.4 < \Delta S_{mix}$ (J/molK) < 13.5, $4.374 < VEC < 4.477$, $12.57 < \delta < 14.27$, $0.155 < \Delta\chi < 0.172$ and $0.624 < \Omega < 0.734$. Compared with the Nb-silicide based alloys in groups (areas) A and B, the B containing alloys had more negative ΔH_{mix}, higher values of ΔS_{mix} and δ, and lower values of VEC and $\Delta\chi$. The B containing alloys (i) had more negative ΔH_{mix} and higher δ values than bcc solid solution + intermetallic(s) HEAs, (ii) their ΔS_{mix} and $\Delta\chi$ values were within the ranges of these parameters for bcc solid solution + intermetallic(s) HEAs and (iii) their VEC values were outside the range for bcc solid solution + intermetallic(s) HEAs.

Nb-silicide based alloys without Al addition (i.e., the alloys belonging in group (area) B) had $-41.5 < \Delta H_{mix}$ (kJ/mol) < -36.5, $11.55 < \Delta S_{mix}$ (J/molK) < 13.29, $4.605 < VEC < 4.896$, $8.7 < \delta < 9.9$, $0.196 < \Delta\chi < 0.237$ and $0.69 < \Omega < 0.84$, and compared with the B containing alloys they had less negative ΔH_{mix}, higher values of VEC, Ω and $\Delta\chi$ and lower values of δ. The non-Al containing alloys had more negative ΔH_{mix} and their parameters δ and ΔS_{mix} were in the ranges of bcc solid solution + intermetallic(s) HEAs.

Data for the Nb-silicide based alloys was compared with that for the bcc Nb solid solutions, see Figures 3 to 5. In these Figures the series 2, 3, 4, 5, 6, 7 and 8 data are for the bcc Nb_{ss} solid solutions studied in Part I [28] and the series 2a, 3a, 4a, 5a, 6a, 7a and 8a data is for Nb-silicide based alloys studied in this paper. Note that the solid solutions that were studied in the Part I [28] belonged to Nb-silicide based alloys studied in this paper. In the Figures 3 to 5 the series 2 and 2a data is for alloys with RMs, TMs, and Sn but no Al, the series 3 and 3a data is for alloys with RMs, TMs, Ge and Sn and with/out Al or Cr, the series 4 and 4a data is for alloys with TMs, Al, with/out Hf, no RMs and no B, Ge, Sn, the series 5 and 5a data is for alloys with TMs, Al and B, with/out Hf, the series 6 and 6a data is for alloys with TMs, Al and with/out B, Ge, Hf or Sn, the series 7 and 7a data is for alloys with RMs, TMs with/out Al and with no B, Ge, Sn and the series 8 and 8a data is for alloys with TMs, Al with/out RMs, B or Sn and with no Ge.

In each of the Figures 3 to 5 the data for alloys and bcc Nb solid solutions is shown in ellipses or circles where full lines are used for the solid solutions and dashed lines for the alloys. Red colour lines are used for alloys and bcc Nb solid solutions that do not have B as an alloying addition. Green colour lines are used for alloys and bcc Nb solid solutions that contain B. In Figures 3 and 4 a line is drawn to emphasise (help the eye to note) the separation between these groups. The position of this line in the Figures is arbitrary. In Figure 3 above the black line in the right hand side ellipse are the series 2, 3 and 7 bcc Nb solid solutions and in the left hand side ellipse are the 2a, 3a and 7a series of Nb silicide based alloys of this study. In the Figures 3 to 5 the data for Nb_{ss} with no Si from Part I [28] is only in the red full line ellipses and the data for normal Nb_{ss} and Ti rich Nb_{ss} from Part I [28] is in the red and green full line ellipses. The clear separation of data in four separate areas, as shown in Figure 3 and Figure 4, was also possible in the plot of VEC versus ΔH_{mix} (Figure not shown).

For the alloys and their solid solutions the Figures 3, 4 and 5 clearly show the gap in $\Delta\chi$ values of the bcc Nb_{ss} solid solutions that was discussed in Part I [28]. The plots of $\Delta\chi$ versus ΔH_{mix} and $\Delta\chi$ versus Ω (Figures 3 and 4) show clear separation between the data for alloys and bcc Nb_{ss} solid solutions. The same is the case in the plot of VEC versus ΔH_{mix} (Figure not shown). Figure 5 and the plot of $\Delta\chi$ versus VEC (Figure not shown) show that the alloys with no B addition fall within the wider areas occupied by the bcc Nb solid solutions. In these figures the data for Nb_{ss} with no Si is outside the dashed line red ellipses.

The separation of alloys and bcc Nb solid solutions that contain B was clear, particularly in the $\Delta\chi$ versus ΔH_{mix} (Figure 3) $\Delta\chi$ versus Ω (Figure 4) and VEC versus ΔH_{mix} (Figure not shown) plots. The data would suggest that future research on the bcc Nb_{ss} solid solutions formed in Nb-silicide based alloys should use the $\Delta\chi$ versus ΔH_{mix}, $\Delta\chi$ versus Ω and VEC versus ΔH_{mix} plots for the selection of solute additions.

Figures 1 and 2 demonstrated that the plots of $\Delta\chi$ versus δ and $\Delta\chi$ versus ΔH_{mix} (and VEC versus ΔH_{mix} and VEC versus δ, Figures not shown) can separate the Nb-silicide based alloys in groups according to alloying additions. The data for the parameters studied in this paper can be used to derive relationships between them. For example, data for series 4 alloys gives the following relationships $\Delta\chi = 0.05\delta - 0.3$ with $R^2 = 0.988$, $\Delta H_{mix} = - 118.4\Delta\chi - 20.23$ with $R^2 = 0.989$, $\Delta H_{mix} = 48.4(VEC) - 255$ with $R^2 = 0.998$ and $VEC = - 0.12\delta + 5.5$ with $R^2 = 0.988$.

In this paper the ratio sd/sp of the sd electronic configuration elements over the sp electronic configuration elements in an alloy was also used (Table 1). Plots of each of the other six parameters versus sd/sp did not separate the alloys in three groups (areas), like those shown in Figures 1 and 2. However, the sd/sp data is useful for selecting alloys. For example, data for series 4 alloys gives the following relationships $\Delta\chi = - 0.07(sd/sp) + 0.37$ with $R^2 = 0.969$, $\Delta H_{mix} = 8.21(sd/sp) - 64.3$ with $R^2 = 0.989$, $\Omega = 0.073(sd/sp) + 0.47$ with $R^2 = 0.986$ and $\delta = - 1.46(sd/sp) + 13.47$ with $R^2 = 0.948$. These relationships allow one to quickly check the values of the six parameters for an alloy composition selected by other means, for example using CALPHAD. All the aforementioned equations, which are ONLY for series 4 alloys, should be used with caution because of the limited available data.

Figures 6 and 7 show the ranges of the parameters considered in this paper for Nb-silicide based alloys that exhibit best isothermal oxidation at 1073 K and 1473 K or creep at 1473 K and 210 MPa. The Figures use data that was available at the time of writing the paper. It is possible that the ranges might be modified slightly as new experimental data about oxidation and creep becomes available. The bars give the minimum and maximum value of each parameter. It should be noted that in these two Figures, to aid presentation and comparison of data between them, the ranges of the enthalpy and entropy of mixing are given as $|\Delta H_{mix}|/100$ and $\Delta S_{mix}/100$ and the data for VEC, sd/sp and δ is presented as VEC/10, (sd/sp)/10 and $\delta/10$.

In Figure 6 data is plotted for the parameters of polycrystalline Nb silicide based alloys that do not pest and have k_p values in the range 10^{-12} to 10^{-13} $g^2cm^{-4}s^{-1}$ at 1073 K and k_p about 10^{-10} $g^2cm^{-4}s^{-1}$ at 1473 K, compared with 4 10^{-14} and 1 10^{-11} $g^2cm^{-4}s^{-1}$, respectively at 1088 K and 1473 K for single crystal CMSX-4 Ni based superalloy. Figure 7 includes data for the alloys 55.5Nb-21Ti-16Si-7.5Hf (creep rate 3.2 10^{-8} s^{-1}) and 48Nb-25Ti-16Si-8Hf-3Mo (creep rate 6.4 10^{-8} s^{-1}) [49].

The parameters of the alloy Nb-16Si-5Hf-5Mo-15W, which was suggested to meet target mechanical properties [50], do not fall in any of the ranges shown in Figure 6 but are in the ranges of the $|\Delta H_{mix}|$, ΔS_{mix}, δ, and sd/sp in Figure 7. This is not surprising as the alloy does not have solute elements that are known to improve the oxidation of Nb-silicide based alloys. This alloy belongs in the family of Nb-silicide based alloys for which the relationship $\Delta H_{mix} = 5.08(sd/sp) - 57$ with $R^2 = 0.989$ holds. The alloy has sd/sp = 5.25 and for this value the above equation gives $\Delta H_{mix} = - 30.3$ kJ/mol. The ΔH_{mix} of the alloy is - 31 kJ/mol.

It is suggested that the parameters $\Delta\chi$, VEC, δ, Ω and sd/sp can assist the design (selection) of Nb-silicide based alloys. If more data were to become available for a particular family (series) of alloys then equations linking the empirical parameters of this study should be useful for alloy design purposes, particularly when reliable phase equilibria data is available to guide alloy design based on CALPHAD modelling. The use of the above parameters to design new Nb-silicide based alloys will be demonstrated in a future publication.

Conclusions

In this paper Nb-silicide based alloys with microstructures consisting of bcc Nb_{ss} solid solution and intermetallic(s) were studied in the cast and heat treated conditions using the parameters ΔH_{mix}, VEC, δ, $\Delta\chi$, Ω, ΔS_{mix} and sd/sp. The alloys could be separated in three groups according to alloying additions in plots of $\Delta\chi$ versus δ, and $\Delta\chi$ versus ΔH_{mix}, where the B containing alloys formed their own group. Plots of $\Delta\chi$ versus ΔH_{mix} and $\Delta\chi$ versus Ω could separate the alloys and their bcc 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) HEAs but the values of the above parameters and VEC were in better agreement with those reported for amorphous alloys.

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