The impact of Ti and temperature on the stability of Nb₅Si₃ phases: a first-principles study

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ABSTRACT

Nb-silicide based alloys could be used at T > 1423 K in future aero-engines. Titanium is an important additive to these new alloys where it improves oxidation, fracture toughness and reduces density. The microstructures of the new alloys consist of an Nb solid solution, and silicides and other intermetallics can be present. Three Nb₅Si₃ polymorphs are known, namely αNb₅Si₃ (tI₃2 Cr₅B₃-type, D8l), βNb₅Si₃ (tI₃2 W₅Si₃-type, D8m) and γNb₅Si₃ (hP₁₆ Mn₅Si₃-type, D88). In these 5–3 silicides Nb atoms can be substituted by Ti atoms. The type of stable Nb₅Si₃ depends on temperature and concentration of Ti addition and is important for the stability and properties of the alloys. The effect of increasing concentration of Ti on the transition temperature between the polymorphs has not been studied. In this work first-principles calculations were used to predict the stability and physical properties of the various Nb₅Si₃ silicides alloyed with Ti. Temperature-dependent enthalpies of formation were computed, and the transition temperature between the low (α) and high (β) temperature polymorphs of Nb₅Si₃ was found to decrease significantly with increasing Ti content. The γNb₅Si₃ was found to be stable only at high Ti concentrations, above approximately 50 at. % Ti. Calculation of physical properties and the Cauchy pressures, Pugh's index of ductility and Poisson ratio showed that as the Ti content increased, the bulk moduli of all silicides decreased, while the shear and elastic moduli and the Debye temperature increased for the αNb₅Si₃ and γNb₅Si₃ and decreased for βNb₅Si₃. With the addition of Ti the αNb₅Si₃ and γNb₅Si₃ became less ductile, whereas the βNb₅Si₃ became more ductile. When Ti was added in the αNb₅Si₃ and βNb₅Si₃ the linear thermal expansion coefficients of the silicides decreased, but the anisotropy of coefficient of thermal expansion did not change significantly.

1. Introduction

The development of high-temperature engineering alloys that can operate at temperatures above those of the latest generations of Ni-based superalloys is a priority in current metallurgical research to enable future gas turbine technologies to meet environmental and performance targets [1]. The Nb-silicide based alloys have higher melting temperatures, lower densities and better creep properties and are stable at higher temperatures than the Ni-based superalloys. These new alloys are also known as Nb in situ composites, and their microstructures consist of Nb solid solution that provides toughness and intermetallics that give low- and high-temperature strength and creep resistance [2]. Different alloying additions are used to achieve a balance of properties, in particular room-temperature fracture toughness, low- and high-temperature oxidation resistance and strength and creep [1,2].

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The Nb5Si3 is the desirable intermetallic in these new alloys. Three polymorphs of Nb5Si3 are reported, namely the αNb5Si3, (tI32 3CrB-type, D8h), βNb5Si3, (tI32 W2Si3-type, D8h) and γNb5Si3 (hP16 Mn5Si3-type, D8h). The αNb5Si3 and βNb5Si3 are the 5–3 silicides in the binary equilibrium Nb–Si phase diagram [3], both have tetragonal crystal structure, which contains 20 atoms of Nb and 12 atoms of Si, but crystallize in different atomic arrangements. The γNb5Si3 silicide is hexagonal with 10 Nb atoms and 6 Si atoms and is considered metastable [3]. In the Nb–Si binary phase diagram αNb5Si3 transforms to βNb5Si3 at 2208 K [3].

The addition of Ti in Nb-silicide based alloys not only reduces their density but also improves their fracture toughness and oxidation resistance [2,4,5]. To achieve a balance of properties, the concentration of Ti in Nb-silicide based alloys must be optimized because Ti (i) does not increase the ductile to brittle transition temperature (DBTT) of bcc Nb for concentrations up to 24 at. %, (ii) has the weakest effect of all additions X on the yield strength at T = 1095 °C and high-temperature strength at T = 1200 °C of Nb–X solid solution alloys, where X is transition (including refractory) metal [6] and (iii) substitutes for Nb in (Nb,Ti)5Si3 silicides and increases the toughness of unalloyed Nb5Si3 from about 3 MPa√m to about 10 MPa√m at T = 25 at. %, but at higher Ti contents the hexagonal (Ti,Nb)5Si3 is stabilized and the toughness drops to values below 3 MPa√m [4]. The stable structure for the fully Ti-substituted end member, i.e. the Ti5Si3, is hexagonal (hP16 Mn5Si3-type, D8h). The Ti5Si3 is isomorphous with γNb5Si3.

Even though Ti is an important addition, there is lack of data in the literature about the effect that Ti has on the stability of the different Nb5Si3 polymorphs. The effect of alloying with Ti on the transformation temperature between the two tetragonal polymorphs has not been reported, nor has the effect of Ti on their coefficient of thermal expansion (CTE). However, it has been shown that high concentrations of Ti in (Ti,Nb)5Si3 stabilized the 5–3 silicide in the hexagonal crystal structure in Nb-silicide based alloys at temperatures below 1500 °C [7,8]. The latter is undesirable because the hexagonal 5–3 silicide is reported to have inferior creep properties than the αNb5Si3 and βNb5Si3 [1,2]. The CTE of Ti5Si3 is also significantly more anisotropic [9].

The early data that were used to construct liquidus projection of the Nb–Ti–Si ternary system did not identify which was the structure of 5–3 compound(s) in the cast alloys (i.e. authors did not clarify which 5–3 polymorph was formed), and the projection gave a primary Nb5Si3 solidification area without specifying whether the primary silicide was the βNb5Si3, or the αNb5Si3, or the hexagonal Ti5Si3, based 5–3 silicide [10]. Geng et al. [11] proposed a liquidus projection for the Nb–Ti–Si ternary system with a large primary αNb5Si3 solidification area. Li et al. [12] revised the Nb–Ti–Si liquidus projection based on a study of ternary alloys in the Nb5Si3–Ti5Si3 region. The proposed liquidus projection by Li et al. shows that primary βNb5Si3 will form for Ti concentrations up to approximately 40 at. %, the liquidus projection has a very narrow primary αNb5Si3 solidification area and indicates that at higher concentrations primary hexagonal Ti5Si3 will form during solidification. A similar liquidus projection was proposed recently by Jânio Gigolotti et al. [13], with an extended βNb5Si3 region and narrow αNb5Si3 area. No primary αNb5Si3 solidification area is shown in the Nb–Ti–Si liquidus projection by Bulanova and Fartushna [14]. There are no data about the transformation temperature of 5–3 silicides alloyed with Ti below the liquidus.

In this work first-principles calculations are used to study the stability and physical properties of the three polymorphs, αNb5Si3, βNb5Si3 and γNb5Si3 alloyed with Ti (up to 12.5 at. % Ti for αNb5Si3 and βNb5Si3, and up to 50 at. % Ti for γNb5Si3). Density functional theory (DFT) is used to study the enthalpy of formation and properties of the αNb5Si3, βNb5Si3 and γNb5Si3 compounds with and without Ti additions at T = 0 K. To probe the effect of Ti on the transformation temperatures, the temperature dependence of the heats of formation of the compounds is computed by incorporating phonon calculations. The paper provides new data that advance current understanding of the stability of complex Nb-silicide based alloys and the design and development of new alloys.

2. Computational details

The CASTEP (Cambridge Serial Total Energy Package) code [15] was used for the calculations, as described by Papadimitriou et al. [16]. The valences for the atomic configurations were Nb-4s24p64d45s1, Ti-3s23p24s2 and Si-3s23p2. An energy cut-off of 500 eV was sufficient to reduce the error in the total energy to less than 1 meV/atom. A Monkhorst–Pack k-point grid separation of 0.03 Å−1 was used for the integration over the Brillouin zone according to the Monkhorst–Pack scheme [17]. Geometry optimizations of the structures were performed with thresholds for converged structures less than 1 × 10−7 eV, 1 × 10−3 eV/Å, 1 × 10−4 Å and 0.001 GPa, respectively, for energy change per atom, maximum residual force, maximum atomic displacement and maximum stress.

The method of finite displacements was used [16]. The forces on atoms were calculated when slightly perturbing the ionic positions [18]. The supercells used were as follows: 4 × 4 × 4 for Nb, 4 × 4 × 3 for Ti, 3 × 3 × 3 for Si, 2 × 2 × 2 for γNb5Si3 and Ti5Si3 and 2 × 2 × 1 for αNb5Si3 and βNb5Si3. The vibrational contributions to the enthalpy, entropy, free energy and heat capacity versus temperature and the Debye temperature were obtained using the quasiharmonic approximation [16]. The phonon density of states (DOS) of each element...
separately was calculated to obtain the finite temperature enthalpy of formation.

The linear thermal expansion coefficients (α) were obtained by generating structures with increasing the ratios a/a₀ and c/c₀ (a₀ and c₀ are the lattice parameters in the ground state) from 0.991 to 1.006 with an increment of 0.003 and conducting a phonon calculation for each volume. The equilibrium lattice parameters a(T,P) and c(T,P) were then calculated at every given temperature using the quasi-harmonic approximation by minimizing the total free energy with respect to volume, thus finding the equilibrium volume at each temperature. After calculating the a(T,P) and c(T,P) the linear thermal expansion coefficients αₐ and αₖ were obtained. This procedure was repeated for αNB₁₆Si₁₆, βNB₂₅Si₁₅, αNB₁₆Ti₄Si₁₂, and βNB₁₆Ti₅Si₁₂.

The elastic constants and properties were calculated as described in Papadimitriou et al. [16]. The calculation method consisted of applying a given strain and calculating the stress. At each deformation the unit cell was kept fixed, and the internal coordinates were optimized. The matrix of the linear elastic constants was reduced according to the crystal structure of each phase. The maximum number of strain patterns (sets of distortions) for a tetragonal or hexagonal structure is two and one for cubic cells. Six strain steps (varying from –0.003 to 0.003) were used [16].

For the cubic (Nb) and diamond (Si) structures a series of six geometry optimizations were done to evaluate the three independent elastic constants C₁₁, C₁₂ and C₄₄ whereas for the tetragonal αNB₁₆Si₁₆, βNB₂₅Si₁₅, and γNB₂₅Si₁₅ and hexagonal Ti, γNB₁₆Si₁₆, and Ti₅Si₃ structures the corresponding number was twelve, with the six independent elastic constants being C₁₁, C₁₂, C₁₃, C₃₃, C₄₄ and C₆₆ for the tetragonal and C₁₁, C₁₂, C₁₃, C₃₃, and C₄₄ for the hexagonal. After acquiring the matrix of the elastic constants and confirming that the mechanical stability criteria [19] are satisfied, the bulk (B), Young’s (E) and shear (G) moduli, Poisson’s ratio (ν) and Debye temperature were obtained as described in Papadimitriou et al. [16].

3. Results and discussion

3.1. Site occupancies, lattice constants and densities of states

Twelve structures in total were investigated in the current study, four for each of the αNB₁₆Si₁₆, βNB₂₅Si₁₅, and γNB₂₅Si₁₅ silicides. In all cases, each of the four structures contained an increasing number of Ti atoms, starting from 1 and increasing to 4. Thus, from the structure with the lowest Ti content to that with the highest, the corresponding percentages were 3.125, 6.25, 9.375 and 12.5 at. % Ti for the αNB₁₆Si₁₆, and βNB₂₅Si₁₅ and 6.25, 12.5, 18.75 and 25 at. % for γNB₂₅Si₁₅. Higher Ti concentrations of 37.5 at. % and 50 at. % were considered in order to study the effect of the Ti concentration on the stability of the hexagonal silicide, and provide an estimation of the critical Ti concentration to form γNBₓSi₁₋ₓ. Ab initio technique has been used previously to study the effects of alloying on stability and mechanical properties of αNB₁₆Si₁₆ [20–22]. The first-principles study by Chen et al. [21] considered the effect of the substitution of Nb by Ti on the stability of Nb₁₆Si₁₆. Chen et al. studied only the substitution of one atom of Nb with Ti (i.e. alloying with 3.125 at. % Ti) on different atomic positions at 0 K.

Figure 1 shows the crystal structures of the 5–3 silicide polymorphs. Ti can substitute Nb in all three polymorphs and occupies the more closely packed Nb sites in αNB₁₆Si₁₆ and the less closely packed Nb sites in βNB₂₅Si₁₅ and γNB₂₅Si₁₅ [21,22]. In Figure 1, M and L, respectively, represent the more and the less closely packed sites. In the work presented in this paper, in order to investigate the order of the site occupancies of Ti atoms with increasing Ti concentration, separate geometry optimizations were made, and the enthalpies of formation at 0 K were computed (Table 1). In the case of γNB₁₆Si₁₆, the enthalpies of formation for different combinations of occupancies were found to be approximately equal. The enthalpies of the most stable structures are indicated by bold numbers in Table 1.

| Table 1. Enthalpies of formation at 0 K (kJ/mol) for all combinations of site occupancies of Ti substituting Nb atoms in αNB₁₆Si₁₆ and βNB₂₅Si₁₅ for Ti addition from 1 to 4 atoms. See also Figure 1 for reference to atom positions. The bold values are the enthalpies of the most stable structures. |
|---------------------------------|-----------------|-----------------|
|                                | αNB₁₆Si₁₆        | βNB₂₅Si₁₅        |
| Ti atom (Nb 1)                 | −64.513          | −60.771          |
| Ti atom (Nb 2)                 | −64.481          | −60.770          |
| Ti atom (Nb 3)                 | −64.456          | −60.770          |
| Ti atom (Nb 4)                 | −64.461          | −60.770          |
| 2 Ti atoms (Nb 1, Nb 2)        | −66.125          | −61.956          |
| 2 Ti atoms (Nb 1, Nb 3)        | −65.981          | −61.284          |
| 2 Ti atoms (Nb 1, Nb 4)        | −66.105          | −61.287          |
| 3 Ti atoms (Nb 1, Nb 2, Nb 3)  | −67.533          | −62.528          |
| 3 Ti atoms (Nb 1, Nb 2, Nb 4)  | −67.535          | −62.527          |
| 4 Ti atoms (Nb 1, Nb 2, Nb 3, Nb 4) | −68.894      | −63.143          |
Using the enthalpies of formation and equation 1 [21], the impurity formation energies $E_{f}^{M-im}$ were calculated and are shown in Table 2.

$$E_{f}^{M-im} = E_{f}^{M-im} - E_{f}^{M} = E_{t}^{M-im} - E_{t}^{M} = E_{sol}^{X} + E_{sol}^{im} \tag{1}$$

In equation 1 $M$ and $X$ denote the silicide and the substituted atom, respectively. The $E_{f}^{M}$ and $E_{f}^{M-im}$ refer to the pure $M$ (unalloyed) and impurity-doped (alloyed) $M$ structures. $E_{sol}^{X}$ and $E_{sol}^{im}$ are the total energies of $X$ and impurity atoms in their bulk states, respectively, and $E_{t}^{M}$ and $E_{t}^{M-im}$ denote the total energies of the unit cell of $M$ and impurity-doped $M$ at their equilibrium state.

Negative impurity formation energy means that the impurity-doped (alloyed) phase is more stable than the unalloyed phase, while the lower the impurity formation energy, the more stable, the lower the impurity formation energy for all polymorphs were negative. The alloyed phase is more stable than the unalloyed phase, while the lower the impurity formation energy is, the more stable the doped (alloyed) phase.

The Ti-doped structures exhibited negative impurity formation energies, which confirmed the study by Chen et al. [21], where the impurity formation energies for Ti in Nb$_5$Si$_3$ at $T = 0$ K were calculated. It can be seen in Table 2 that all the impurity formation energy values for all polymorphs were negative. The alloyed phase is more stable, the lower the impurity formation energy is. In all cases the impurity formation energy became more negative with each additional Ti atom, indicating increasing stability with increasing Ti substitution for all polymorphs.

The lattice constants and the volumes of the crystal structures of the 5–3 silicide polymorphs in the present study were calculated (Table 3). The $a$ and $c$ lattice parameters of the αNb$_5$Si$_3$ decreased and increased, respectively, as the Ti concentration increased. In the case of the γNb$_5$Si$_3$ and γNb$_5$Si$_3$ polymorphs both lattice parameters decreased as the Ti content increased. The lowest lattice parameters for the γNb$_5$Si$_3$ polymorph were for the case where all the Nb atoms are substituted by Ti atoms (i.e. for the Ti$_5$Si$_3$). The volume of all the 5–3 silicide polymorphs decreased as the Ti content increased, which is expected as Nb has a larger atomic radius than Ti [23,24].

The partial (PDOS) and total (TDOS) electronic densities of states are shown in Figures 2 to 4 for the α, β and γ 5–3 silicide structures. It can be seen that for all structures the main contribution to the TDOS was the PDOS of d electron states, followed by the p electron states, while the s electron states contribute the least to the TDOS of all structures.

The location of the Fermi level is indicative of phase stability. If the Fermi level is located in a deep valley of the TDOS, this indicates phase stability, whereas the opposite is the case if the Fermi level is located near peaks of the TDOS. It is clear that for the unalloyed compounds the valleys near the Fermi levels were deeper in αNb$_5$Si$_3$ (Figure 2(a)) than βNb$_5$Si$_3$ (Figure 2(f)), whereas for the γNb$_5$Si$_3$ (Figure 3(a)) the Fermi level is situated near one of the high peaks of the TDOS. This explains the gradual decrease of phase stability from α to β to γ 5–3 silicide.

The addition of Ti in the αNb$_5$Si$_3$ slightly moves the Fermi level to the bottom of the deepest valley (Figure 2(b)–(e)), making the silicide even more stable, while in the case of βNb$_5$Si$_3$, the Fermi level moves slightly towards one of the small peaks (Figure 2(g)–(j)) rendering the silicide somewhat less stable. This confirms that the difference between the formation enthalpies of the α and β phases is increased as the aforementioned phases are alloyed (doped) with Ti. In the case of γNb$_5$Si$_3$, the Ti addition also moves the Fermi level slightly closer to one of the peaks (Figure 3(c)–(f)).

The evolution of the TDOS as the Ti concentration in γNb$_5$Si$_3$ increases shows that the Fermi level would pass the large peak and move towards the valley below, as the

### Table 2. Enthalpies of formation and impurity formation energies at 0 K of the silicides of this study.

| Silicide       | Enthalpy of formation (kJ/mole) | Impurity formation energy (eV) |
|----------------|---------------------------------|-------------------------------|
| αNb$_5$Si$_3$  | -62.841                         |                               |
| βNb$_5$Si$_3$  | -59.654                         |                               |
| γNb$_5$Si$_3$  | -53.739                         |                               |
| αNb$_5$Si$_3$  | -60.1                           |                               |
| βNb$_5$Si$_3$  | -61.25                          | -0.01733                      |
| γNb$_5$Si$_3$  | -67.533                         | -0.01499                      |
| αNb$_5$Si$_3$  | -68.88                          | -0.01400                      |
| βNb$_5$Si$_3$  | -69.306                         |                               |
| γNb$_5$Si$_3$  | -69.242                         |                               |
| αNb$_5$Si$_3$  | -70.757                         | -0.00593                      |
| βNb$_5$Si$_3$  | -73.143                         | -0.00567                      |
| γNb$_5$Si$_3$  | -76.057                         |                               |
| αNb$_5$Si$_3$  | -76.938                         |                               |
| βNb$_5$Si$_3$  | -78.278                         |                               |
| γNb$_5$Si$_3$  | -79.016                         |                               |

### Table 3. Lattice parameters and volumes of the studied intermetallic structures.

| Silicide       | Lattice parameter (Å) | Volume (Å$^3$) |
|----------------|-----------------------|----------------|
| αNb$_5$Si$_3$  | 6.6281                | 11.7973        | 518.283        |
| βNb$_5$Si$_3$  | 10.0686               | 5.0828         | 515.278        |
| γNb$_5$Si$_3$  | 7.5706               | 5.2696         | 515.536        |
| αNb$_5$Si$_3$  | 6.8584               | 5.1753         | 509.074        |
| βNb$_5$Si$_3$  | 6.5704               | 5.0610         | 513.08         |
| γNb$_5$Si$_3$  | 6.5565               | 5.0468         | 511.426        |
| αNb$_5$Si$_3$  | 6.5427               | 5.0023         | 507.271        |
| βNb$_5$Si$_3$  | 7.5953               | 5.2335         | 259.082        |
| γNb$_5$Si$_3$  | 7.5479               | 5.1977         | 256.447        |
| αNb$_5$Si$_3$  | 7.535                | 5.1753         | 254.465        |
| βNb$_5$Si$_3$  | 7.5207               | 5.1513         | 252.331        |
| γNb$_5$Si$_3$  | 7.464                | 5.1387         | 247.926        |
with the enthalpies of formation of the aforementioned phases (see Table 2), confirms that the hexagonal γ-Nb$_5$Si$_3$ silicide becomes stable compared with the other two tetragonal silicides when the Ti concentration reaches Ti content increases above 37.5 at. % (Figure 4(e), (f)). On the other hand, it can be seen in Figure 4(a), (b) and (c), (d) that the Fermi level moves away from the respective pseudo-gaps for the α and β polymorphs. This, combined

Figure 2. Partial and total density of states of (a) α-Nb$_5$Si$_3$, (b) α-Nb$_{19}$Ti$_{12}$Si$_{12}$, (c) α-Nb$_{18}$Ti$_2$Si$_{12}$, (d) α-Nb$_{17}$Ti$_3$Si$_{12}$, (e) α-Nb$_{16}$Ti$_4$Si$_{12}$, (f) β-Nb$_5$Si$_3$, (g) β-Nb$_{19}$Ti$_{12}$Si$_{12}$, (h) β-Nb$_{18}$Ti$_2$Si$_{12}$, (i) β-Nb$_{17}$Ti$_3$Si$_{12}$ and (j) β-Nb$_{16}$Ti$_4$Si$_{12}$.
Figure 3. Partial and total density of states of (a) γ-Nb$_3$Si$_3$, (b) Ti$_5$Si$_3$, (c) γ-Nb$_9$TiSi$_6$, (d) γ-Nb$_8$Ti$_2$Si$_6$, (e) γ-Nb$_7$Ti$_3$Si$_6$, (f) γ-Nb$_6$Ti$_4$Si$_6$. 
50 at. %. Li et al. [12] reported that in a cast Nb-25Si-40Ti (at. %) alloy, the $\beta$Nb$_{5-x}$Ti$_x$Si$_3$ was the primary phase, whereas in the cast Nb-30Si-45Ti (at. %), Nb-25Si-45Ti (at. %) and Nb-25Si-60Ti (at. %) alloys the $\gamma$Ti$_{5-x}$ (Nb)$_x$Si$_3$ was the primary phase formed during solidification. The microstructures of the alloys studied by Li et al. [12] were not at equilibrium, nevertheless their data suggest that the hexagonal 5–3 silicide becomes stable at high Ti concentrations in excess of 40–45 at. %, which is in agreement with the present study.

### 3.2. Elastic properties

The results of the calculations of the independent elastic constants ($C_{ij}$), bulk moduli (B) from elastic constants according to the Voigt–Reuss–Hill (VRH) scheme and bulk moduli and first pressure derivatives of bulk moduli (B') from the Birch–Murnaghan equation of state (B-M EOS) for all compounds and elements are shown in Table 4. The mechanical stability criteria [19] were met for all phases. The elastic constants for the pure elements were in agreement with the experimental data [25–27]. The property data for the un-doped $\alpha$Nb$_5$Si$_3$, $\beta$Nb$_5$Si$_3$ and $\gamma$Nb$_5$Si$_3$ from the literature [16] are also given in Table 4. Compared with the VRH scheme, the values obtained by the B-M EOS tend to be larger. There is good agreement between the values from the two calculations. The bulk modulus tends to decrease with increasing Ti concentration in all 5–3 silicides. The calculated values of shear modulus (G) and Young’s modulus (E) are given in Table 5. For the $\alpha$Nb$_5$Si$_3$ and $\gamma$Nb$_5$Si$_3$ silicides the shear and Young’s moduli tend to increase with increasing Ti addition. In the case of $\beta$Nb$_5$Si$_3$ the corresponding values decrease.

Figure 4. Partial and total density of states of (a) $\alpha$Nb$_8$Ti$_{12}$Si$_{12}$ (37.5 at. % Ti), (b) $\alpha$Nb$_{4}$Ti$_{16}$Si$_{12}$ (50 at. % Ti), (c) $\beta$Nb$_8$Ti$_{12}$Si$_{12}$ (37.5 at. % Ti), (d) $\beta$Nb$_8$Ti$_{16}$Si$_{12}$ (50 at. % Ti), (e) $\gamma$Nb$_8$Ti$_{12}$Si$_{12}$ (37.5 at. % Ti), (f) $\gamma$Nb$_8$Ti$_{16}$Si$_{12}$ (50 at. % Ti).
The Cauchy pressures (C_{12}-C_{44} for cubic and C_{13}-C_{44} and C_{12}-C_{66} for tetragonal and hexagonal structures), Pugh’s [33] index of ductility (ratio of shear modulus over bulk modulus (G/B)) and Poisson’s ratio (ν) were calculated. The values of the aforementioned properties are given in Table 5. These parameters are often used as ‘predictors’ of the ductile or brittle behavior of inter-metallics. For metallic bonding, a positive or negative value of Cauchy pressures means respectively a ductile or brittle material [34]. The other two conditions for brittle behavior are G/B > 0.57 and ν < 0.26. The results of the present study would suggest that the most ductile of the unalloyed silicides is the γ Nb_5Si_3, and the least ductile is the α Nb_5Si_3. The α Nb_5Si_3 and γ Nb_5Si_3 silicides become more brittle as the Ti content increases, whereas the β Nb_5Si_3 becomes more ductile.

Table 4. Elastic constants (C_{ij}) and bulk modulus (B) in GPa for elements and silicides of this study.

| Element     | C_{11}  | C_{12}  | C_{13}  | C_{33}  | C_{44}  | C_{66}  | B      | B’      |
|-------------|---------|---------|---------|---------|---------|---------|--------|---------|
| Nb          | 241     | 126.3   |         |         |         |         | 164.5  | 165.1   |
| Si          | 151.2   | 57.4    |         |         |         |         | 87.8   | 91.2    |
| Ti          | 149.6   | 97.5    | 79.7    | 186.1   | 33      |         | 110.9  | 118.4   |
| α Nb_5Si_3  | 374.1   | 94.1    | 115.6   | 321.7   | 120.3   | 109.9   | 91.9   | 194.4   |
| γ Nb_5Si_3  | 370.4   | 91.3    | 114.3   | 322.9   | 133.5   | 122.5   | 189.2  | 192.8   |
| α Nb_5Si_3  | 373.1   | 90.6    | 112.9   | 322.4   | 134.1   | 124.4   | 187.9  | 190.5   |

Table 5. Calculated shear (G) and elastic (E) moduli in GPa, Poisson’s ratio (ν), Cauchy pressures (C_{12}-C_{44} for cubic, C_{13}-C_{44} and C_{12}-C_{66} for tetragonal and hexagonal) in GPa, G/B ratio and Debye temperature (Θ_d) from elastic constants and phonon DOS for elements and silicides.

| Element     | G       | E       | ν       | C_{12}-C_{44} | C_{13}-C_{44} | C_{12}-C_{66} | G/B    | Phonon DOS | Θ_d (K) |
|-------------|---------|---------|---------|-------------|-------------|-------------|--------|------------|---------|
| Nb          | 36.5    | 101.9   | 0.396   | 99.6        |             |             | 0.228  | 277        | 268     |
| Si          | 61.2    | 149.2   | 0.216   |             |             |             | 0.701  | 647        | 628     |
| Ti          | 32.7    | 89.3    | 0.366   |             |             |             | 0.295  | 369        | 346     |

The Cauchy pressures (C_{12}-C_{44} for cubic and C_{13}-C_{44} and C_{12}-C_{66} for tetragonal and hexagonal structures), Pugh’s [33] index of ductility (ratio of shear modulus over bulk modulus (G/B)) and Poisson’s ratio (ν) were calculated. The values of the aforementioned properties are given in Table 5. These parameters are often used as ‘predictors’ of the ductile or brittle behavior of inter-metallics. For metallic bonding, a positive or negative value of Cauchy pressures means respectively a ductile or brittle material [34]. The other two conditions for brittle behavior are G/B > 0.57 and ν < 0.26. The results of the present study would suggest that the most ductile of the unalloyed silicides is the γ Nb_5Si_3, and the least ductile is the α Nb_5Si_3. The α Nb_5Si_3 and γ Nb_5Si_3 silicides become more brittle as the Ti content increases, whereas the β Nb_5Si_3 becomes more ductile.
The elastic moduli for different Ti concentrations in 5–3 silicides are given in Table 5. Elastic moduli reflect the cohesion in a crystal structure. For αNb5Si3 and γNb5Si3, the elastic modulus increases with increasing Ti concentration, whereas for βNb5Si3, the elastic moduli decrease. This suggests that the addition of Ti strengthens atomic bonding in αNb5Si3 and γNb5Si3, and reduces bond strength in βNb5Si3.

3.3. Enthalpies of formation, transition temperatures and thermal expansion coefficients

The vibrational density of states (DOS) for the elements and silicides of this study were calculated. All the eigenfrequencies were found to be real, hence it was confirmed that the silicides are mechanically stable. After inserting the computed phonon DOS in the relevant formulae the vibrational contribution to free energies per atom (Fphon(T)) was calculated for the D8l, D8m, and D8s structures. Data for the pure elements were shown previously in Papadimitriou et al. [16]. The Fphonon for both αNb5Si3 and βNb5Si3 silicides decreased faster as the Ti addition increased, whereas for the γNb5Si3, the Fphonon decreased more slowly as the Ti addition increased.

After taking Fphonon into account, the phonon contribution to the enthalpy of formation (ΔHfphonon(T)) was evaluated for the D8l, D8m, and D8s structures (Figure 5). For all the silicides the slope increased with increasing Ti addition. Comparison of the D8l and D8m structures shows that all values are significantly lower for the D8m. This shows that the temperature dependence of the phonon contribution favors the stability of the βNb5Si3 over αNb5Si3 with increasing temperature, which is expected from the binary phase diagram [3] and the experimental data for binary Nb-Si alloys. This trend is also followed by the Ti-alloyed phases, thus indicating that a Ti-alloyed βNb5Si3 should become more stable than the Ti-alloyed αNb5Si3 as the temperature increases.

After acquiring the ΔHf(T) for all unalloyed and alloyed phases, the phase equilibrium at finite temperatures was investigated. Figure 6 shows the enthalpy of formation of the γNb5Si3 for Ti content between 0 and 25 at. % and the enthalpy of formation of Ti5Si3. The slope of each curve increases as the Ti content increases from 0 at. % to fully Ti-alloyed 5–3 silicide, i.e. Ti5Si3. In all cases, over the whole temperature range, the Ti5Si3 has the lowest enthalpy of formation.

The enthalpy of formation against temperature of the D8l, D8m and D8s structures for up to 12.5 at. % Ti is shown in Figure 7. For all phases the enthalpy of formation increases with increasing temperature owing to the phonon contributions. Between 0 and 12.5 at. % Ti the γNb5Si3 is not expected to be stable. This is in agreement with experiments that show that this phase is metastable at low Ti contents. In Figure 7, for 0 at. % Ti, the γNb5Si3 curve does cross the βNb5Si3 curve; however, this occurs at a temperature above the melting temperature of both phases. Here the stable phase would be the liquid.

Figure 5. Vibrational contribution to the enthalpies of formation of the (a) D8l, (b) D8m, (c) D8s silicides with Ti substitution.
Figure 6. Enthalpies of formation of the D8\textsubscript{8} silicides.

Figure 7. Enthalpies of formation of the alpha, beta and gamma silicides doped with 0 to 12.5 at. % Ti.
Comparing the unalloyed α Nb₅Si₃ with the β Nb₅Si₃ silicide, the former is stable up to 2085 K where its heat of formation curve crosses that of β Nb₅Si₃, which becomes stable above this temperature (Figure 7(a)). This value is in good agreement with the transition temperature reported in the accepted Nb-Si binary phase diagram [3], as discussed in Papadimitriou et al. [16]. After adding Ti to the aforementioned structures this transition temperature decreases significantly to 1431 K for Nb₃Ti₅Si₁₂, 1361 K for Nb₁₈Ti₁₂Si₁₂, 1358 K for Nb₁₆Ti₄Si₁₂, and finally to 1222 K for Nb₆₄Ti₅Si₁₂ (Figure 7(a–e)). The contribution from the vibrational entropy is much greater for α Nb₅Si₃ with increasing temperature, compared with β Nb₅Si₃. Hence, the addition of Ti appears to have a larger effect on the phonon contribution of α Nb₅Si₃, which drives the transition temperature lower. For the Nb-Si-Ti ternary system there are no experimental data with which to compare the calculated transition temperatures given above. In early experimental isothermal sections for similar temperatures [10,35] the prototype of Nb₅Si₃ was not stated. The error of finite temperature ab initio calculations can be large in some cases due to anharmonicity. Confidence in the above values is justified by the good agreement of the α Nb₅Si₃ → βNb₅Si₃ transition temperature in the binary Nb-Si system with the literature.

Chen et al. [21] studied the stability of α Nb₅Si₃ and β Nb₅Si₃ when one Nb atom was substituted by a single Ti atom in its preferred site (e.g. the site with the lowest impurity energy) by comparing the differences in the calculated formation energies of the two silicides. They suggested that the larger the difference in formation energy, the higher the temperature of the phase transition. The difference between the enthalpy of formation at 0 K for unalloyed α Nb₅Si₃ and β Nb₅Si₃ and alloyed with 3.25 at.% Ti α and β Nb₅Si₃ (1 Nb atom replaced by Ti) increases with the Ti addition and is comparable with the results in Chen et al. [21]. Thus, based on the assumption of Chen et al., this would suggest that Ti will stabilize α Nb₅Si₃ over β Nb₅Si₃, and therefore the transition temperature would be expected to be pushed to higher values. Our results indicate the opposite trend, with Ti addition stabilizing β Nb₅Si₃ and decreasing the transition temperature. For α Nb₅Si₃ alloyed with Ti the temperature dependence of the phonon contribution to the heat of formation is much greater than that for β Nb₅Si₃ alloyed with Ti, and therefore the slope of the ΔH(T) curve for α Nb₅Si₃ increases more dramatically with increasing temperature than for β Nb₅Si₃. This indicates the importance of entropic contributions on phase stability that should be accounted for when considering the effect of alloying on transformation temperatures. In a thermodynamic assessment of the Nb-Ti–Si ternary system [11] the model used suggests that the stability of α Nb₅Si₃ increases with increasing Ti content, and that α Nb₅Si₃ alloyed with Ti becomes stable above the melting temperature of unalloyed α Nb₅Si₃. The results of the present study suggest that a new assessment of the Nb-Ti–Si ternary system is needed.

The linear thermal expansion coefficients of the stable (tetragonal α and β) unalloyed Nb₅Si₃ and two Ti-alloyed silicides, namely the α Nb₅₄Ti₅Si₁₂ and β Nb₆₄Ti₅Si₁₂, are shown in Table 6. Also included in Table 6 are experimental values for Ti₅Si₃ [9]. There is good agreement between the calculated values and the available data in the literature. The CTE of all the silicides is anisotropic. The Ti₅Si₃ is the most anisotropic, whereas α Nb₅Si₃ is the least. Alloying with 12.5 at.% Ti decreases the thermal expansion coefficients of both α Nb₅Si₃ and β Nb₅Si₃ silicides. However, the addition of Ti does not have a strong effect on the CTE anisotropy of both the α and β Nb₅Si₃.

### 3.4. Debye temperatures

The phonon DOS was used to calculate the Debye temperature, as described in Papadimitriou et al. [16]. The calculated values (Table 5) are in good agreement with those calculated using the elastic constants. For the elements the results from the calculations based on phonon DOS and the elastic constants are in good agreement with the literature. Regarding the silicides studied in this paper, the Debye temperatures that were calculated using the two methods are also in good agreement. For the α Nb₅Si₃ and γ Nb₅Si₃ silicides the Debye temperature increases with increasing Ti content, but for the β Nb₅Si₃ the opposite is the case, and the Debye temperature decreases slightly as more Nb atoms are substituted by Ti atoms.

Referring to the study by Chen et al. [30], according to which at the same temperature the number of the excited acoustic modes responsible for the stabilization of β Nb₅Si₃ with respect to α Nb₅Si₃ increases with the Ti content, it is the softer shear modulus of the Ti-alloyed β Nb₅Si₃ compared with the Ti-alloyed α Nb₅Si₃, that leads to the stability of this phase. For example, in Table 5 the shear moduli (G) of unalloyed α and β Nb₅Si₃, respectively, are 116.8 and 106.4 GPa. Alloying α Nb₅Si₃ with Ti increases the shear modulus from 126.1 to 128.7 GPa when the Ti content increases from 1 to 4 atoms, whereas for β Nb₅Si₃ the shear modulus decreases from 98.5 to 93.1 GPa when the Ti content increases from

| Phase          | α₅ | α₇ | α₅/α₇ |
|----------------|----|----|-------|
| α Nb₅Si₃ (this work) | 8.691 | 11.095 | 0.783 |
| Experimental [36] | 6.310 | 8.140 | 0.799 |
| Experimental [9] | 8.638 | 12.359 | 0.699 |
| Experimental [37] | 7.264 | 8.657 | 0.839 |
| Theoretical [38] | 9.210 | 10.336 | 0.891 |
| β Nb₅Si₃ (this work) | 8.777 | 13.331 | 0.658 |
| Theoretical [38] | 8.328 | 15.211 | 0.484 |
| α Nb₅Si₃ Ti₅Si₃ (this work) | 8.510 | 10.682 | 0.797 |
| β Nb₅Si₃ Ti₅Si₃ (this work) | 6.709 | 10.980 | 0.611 |

### Table 6. Linear thermal expansion coefficients (α₅ and α₇) for α Nb₅Si₃, β Nb₅Si₃, α Nb₅₄Ti₅Si₁₂ and β Nb₆₄Ti₅Si₁₂ at 298 K in 10⁻⁶/K.
1 to 4 atoms. Therefore, as the concentration of Ti is increased, the difference in the shear moduli values also increases, and this results in a decrease of the transition temperature.

4. Conclusions

First-principles calculations were carried out for the D8\textsubscript{l}, D8\textsubscript{m} and D8\textsubscript{g} polymorphs of Nb\textsubscript{5}Si\textsubscript{3} alloyed with Ti, and the constituent elements. The volume of all structures contracted as the Ti addition increased. Elastic constants, bulk, shear and Young's moduli, Poisson's ratio and Debye temperature were calculated. These calculations showed that as the Ti content increased the bulk moduli of all silicides decreased, while the shear and elastic moduli increased for α\textsubscript{Nb5Si3} and γ\textsubscript{Nb5Si3} and decreased for β\textsubscript{Nb5Si3}. The Debye temperatures of α\textsubscript{Nb5Si3} and γ\textsubscript{Nb5Si3}, and β\textsubscript{Nb5Si3}, respectively, increased and decreased as the Ti addition increased. The calculations suggested that the γ\textsubscript{Nb5Si3} is the most ductile polymorph. The elastic properties of this silicide are reported in this paper. The alloying with Ti makes the α\textsubscript{Nb5Si3} and γ\textsubscript{Nb5Si3} silicides less ductile and β\textsubscript{Nb5Si3} more ductile. The transition temperature between the α and β structure decreases as more Ti is added, and at about 50 at. % Ti content the hexagonal silicide becomes stable over its tetragonal polymorphs. The α\textsubscript{Nb5Si3} and β\textsubscript{Nb5Si3} exhibit anisotropy of their coefficients of thermal expansion, with the latter being more anisotropic than the former.

Alloying the aforementioned compounds with 12.5 at. % Ti content the hexagonal silicide becomes stable over its tetragonal polymorphs. The α\textsubscript{Nb5Si3} and γ\textsubscript{Nb5Si3} exhibit anisotropy of their coefficients of thermal expansion, with the latter being more anisotropic than the former.

Alloying the aforementioned compounds with 12.5 at. % Ti content the hexagonal silicide becomes stable over its tetragonal polymorphs. The α\textsubscript{Nb5Si3} and γ\textsubscript{Nb5Si3} exhibit anisotropy of their coefficients of thermal expansion, with the latter being more anisotropic than the former.

Structural intermetallics 2001. Warrendale: TMS; 2001. p. 99–108.

Tsakiropoulos P, Beyond nickel based superalloys. In: Blockley R, Shyu W, editors. Encyclopedia of aerospace engineering. John Wiley & Sons, Ltd; 2010.

Schlesinger ME, Okamoto H, Gokhale AB, et al. The Nb-Si (Niobium-Silicon) system. J Phase Equilib. 1993;14:502–509.

Chan KS. Alloying effects on fracture mechanisms in Nb-based intermetallic in-situ composites. Mater Sci Eng A. 2002;329-331:513–522.

Geng J, Tsakiropoulos P, Shao G. Oxidation of Nb-Si-Cr-Al in situ composites with Mo, Ti and Hf additions. Mater Sci Eng A. 2006;441:26–38.

Begley RT. Colombium alloy development at Westinghouse. In: Dalcer ENC, Grobstein T, Olsen CS, editors. Evolution of refractory metals and alloys. Warrendale, PA: TMS; 1994. p. 29–48.

Vellios N, Tsakiropoulos P. The role of Fe and Ti additions in the microstructure of Nb-185Si-5Sn silicide-based alloys. Intermetallics. 2007;15:1529–1537.

Li ZF, Tsakiropoulos P. Study of the effect of Ti and Ge in the microstructure of Nb-24Ti-18Si-5Ge in situ composite. Intermetallics. 2011;19:1291–1297.

Zhang LT, Wu JS. Thermal expansion and elastic moduli of the silicide based intermetallic alloys Ti\textsubscript{5}Si\textsubscript{3}(X) and Nb\textsubscript{5}Si\textsubscript{3}, Scr Mater. 1997;38:307–313.

Liang H, Chang YA. Thermodynamic modeling of the Nb-Ti-Si ternary system. Intermetallics. 1999;7:561–570.

Geng T, Li C, Bao J, et al. Thermodynamic assessment of the Nb-Si-Ti system. Intermetallics. 2009;17:343–357.

Li Y, Li CR, Du ZM, et al. As-cast microstructures and solidification paths of the Nb-Si-Ti ternary alloys in Nb\textsubscript{5}Si\textsubscript{3}–Ti\textsubscript{5}Si\textsubscript{3} region. Rare Metals. 2013;32:502–511.

Jânio Gigolotti JC, Coelho GC, Nunes CA, et al. Experimental evaluation of the Nb-Si-Ti system from as-cast alloys. Intermetallics. 2017;82(1):76–92.

Bulanova M, Fartushina I. Nb-Si-Ti, Landolt-Börnstein New Series IV/11E3. Berlin Heidelberg: Springer; 2010.

Clark SJ, Segall MD, Pickard CJ, et al. First principles methods using CASTEP, Z. Kristall. 2005;220:567–570.

Papadimitriou I, Utton C, Scott A, et al. Ab initio study of the intermetallics in Nb-Si binary system. Intermetallics. 2014;54:125–132.

Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. Phys Rev B. 1976;13:5188–5192.

Montanari B, Harrison NM. Lattice dynamics of TiO\textsubscript{2} rutile: influence of gradient corrections in density functional calculations. Chem Phys Lett. 2002;364:528–534.

Born M, Huang K. Dynamical theory of crystal lattices. Oxford: Oxford University Press; 1956.

Shi S, Zhu L, Jia L, et al. Ab-initio study of alloying effects on structure stability and mechanical properties of α-Nb\textsubscript{5}Si\textsubscript{3}. Comput Mater Sci. 2015;108:121–127.

Chen Y, Shang J-X, Zhang Y. Bonding characteristics and site occupancies of alloying elements in different Nb\textsubscript{5}Si\textsubscript{3} phases from first principles. Phys. Rev. B. 2007;76:184–204.

Chen Y, Shang J-X, Zhang Y. Effects of alloying element Ti on alpha-Nb\textsubscript{5}Si\textsubscript{3} and Nb\textsubscript{5}Al from first principles. J Phys Condens Matter. 2007;19:016213–16218.

Slater JC. Atomic radii in crystals. J Chem Phys. 1964;41:3199.

Clementi E, Raimondi DL, Reinhardt WP. Atomic screening constants from SCF functions. II. atoms with 37 to 86 electrons. J Chem Phys. 1967;47:1300–1307.
[25] Tromans D. Elastic anisotropy of hcp metal crystals and polycrystals. Int J Res Rev Appl Sci. 2011;6:462–483.
[26] Soderlind P, Eriksson O, Wills JM, et al. Theory of elastic-constants of cubic transition-metals and alloys. Phys Rev B. 1993;48:5844–5851.
[27] Simmons G, Wang H. Single crystal elastic constants and calculated aggregate properties: a handbook. 2nd ed. London: The M.I.T Press; 1971.
[28] Smithells CJ. Metal references book. 5th ed. London: Butterworth; 1976.

[29] Chu F, Lei M, Maloy SA, et al. Elastic properties of C40 transition metal disilicides. Acta Mater. 1996;44:3035–3048.
[30] Chen Y, Hammerschmidt T, Pettifor DG, Shang J-X, Zhang Y. Influence of vibrational entropy on structural stability of Nb–Si and Mo–Si systems at elevated temperatures. Acta Mater. 2009;57:2657–2664.
[31] Kittel C. Introduction to solid state physics. 7th ed. New York, NY: John Wiley & Sons; 1996.
[32] Chen X, Zeng M, Wang R, et al. First-principles study of (Ti5−xMgx)Si3 phases with the hexagonal D8h structure: Elastic properties and electronic structure. Comput Mater Sci. 2012;54:287–292.
[33] Pugh SF. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. Philos Mag. 1954;45:823–843.

[34] Pettifor DG. Theoretical predictions of structure and related properties of intermetallics. Mater Sci Technol. 1992;8:345–349.
[35] Zhao J-C, Jackson MR, Peluso LA. Mapping of the Nb-Ti-Si phase diagram using diffusion multiples. Mater Sci Eng. 2004;372:21–27.
[36] Schneibel JH, Rawn CJ, Watkins TR, Payzant EA. Thermal expansion anisotropy of ternary molybdenum silicides based on Mo5Si3. Phys Rev B. 2002;65:8725–134115.
[37] Rodrigues G, Nunes CA, Suzuki PA, Coelho GC. Lattice parameters and thermal expansion of the T-2-phase of the Nb-Si-B system investigated by high-temperature X-ray diffraction. Intermetallics. 2004;12:181–188.
[38] Xu WW, Han JJ, Wang CP, et al. Temperature-dependent mechanical properties of alpha-/beta-Nb5Si3 phases from first-principles calculations. Intermetallics. 2014;46:72–79.
[39] Parthé E, Nowotny H. Strukturuntersuchungen an Siliziden [Structural studies for silicides]. Monatsh Chem. 1955;86:385–396.
[40] Meschel SV, Kleppa OJ. Standard enthalpies of formation of some 3d transition metal silicides by high temperature direct synthesis calorimetry. J Alloys Compounds. 1998;267:128–135.