Study of three-phase equilibrium in the Nb-rich corner of Nb–Si–Cr system

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Abstract

The full understanding of the Nb–Si–Cr ternary system is important for the development of Nb silicide based composites, which show great potential for high temperature applications. There was, however, disparity in experimental observations of phase equilibrium in the vicinity of the Nb-corner. Two kinds of three-phase equilibrium, NbssC14Cnb5Si3 and NbssCrNbSiCnb5Si3, in the Nb corner of the Nb–Si–Cr system have been reported in the literature. This work aims to clarify the three-phase equilibrium near the Nb-corner, by studying phase equilibrium in the Nb–18Si–15Cr ingot. Such a composition was chosen with the assistance of CALPHAD calculations to avoid unnecessary load of work. The alloy ingot was prepared by clean melting followed by heat treatment at 1000 and 1500 °C. The C14 Laves phase formed in all the samples and was stable at both temperatures. The results confirmed that Si has the effect of stabilising the C14 Laves phase down to at least 1000 °C. The three-phase equilibrium NbssC14Cnb5Si3, instead of NbssCrNbSiCnb5Si3, was observed in this work. The current work demonstrates that ingot metallurgy is necessary to check the reliability of the information obtained about the ternary and higher-order phase diagrams, especially for the regions where the exact phase boundaries are in question. The investigation of the selected alloy was greatly helpful to clarify the confusion of the three-phase field near the Nb corner in the Nb–Si–Cr ternary system. The work confirmed the CALPHAD prediction of phase equilibrium near the Nb corner, showing the power to combine phase diagram predictions with experimental work for cost effective alloy development.

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1. Introduction

Development of high temperature intermetallics has been driven by promising combinations of low density with elevated temperature mechanical properties. Ultra-high temperature materials are needed which can survive well beyond the 1200 °C limit to metal surface temperature that appears to be a major barrier for Ni-base superalloys. Ideally, a new family of materials will have high melting point, low density, good oxidation resistance, and exceptional high-temperature strength. Niobium silicide based intermetallic composites are being developed toward these goals, although these materials suffer from catastrophic oxidation resistance and poor ductility and toughness at room temperature [1–7]. A balance of low temperature fracture toughness, good oxidation resistance and high creep strength is required for the potential applications of these materials at elevated temperatures.

Multi-alloying of Nb–Si with both transition metal elements such as Cr, Hf, Ti and Al has resulted in significant improvement of the properties of the composites [3,8,9]. Alloying with Al, Ti and Cr can significantly improve the oxidation resistance, and the Cr effect on enhancing oxidation resistance can be attributed to stabilisation of the NbCr2 Laves phase [10]. For the purpose of advanced design of the Cr-rich Laves phase containing Nb–Si based composites, one needs a good understanding of phase equilibria and thermodynamic properties of the Nb–Si–Cr–Hf–Ti–Al system, with Nb–Si–Cr being the most important.

Experimental data on phase equilibria in the Nb–Si–Cr ternary alloy system are limited. In the early 1960s, Goldschmidt and Brand [11] reported a 1000 °C isothermal section of the Nb–Si–Cr system, which was based on phase equilibrium data in 220 cast alloys which were annealed for 336 h for equilibration. Zhao et al. [12] have recently reinvestigated the Nb–Si–Cr ternary, using a high efficiency diffusion-multiple approach and electron-probe micro-analysis (EPMA). Summarising both work, the major difference is that the former work showed that the niobium solid solution (Nbss) cannot be in direct equilibrin with the ternary CrNbSi phase, giving a ternary-phase field of NbssC14+Nb2Si3, which...
corresponds well with the thermodynamic description of the Nb–Si–Cr system established by Shao [13], using the calculation of phase diagram (CALPHAD) method. On the other hand, Zhao et al. suggested the existence of a different ternary-phase field \( \text{Nb}_{ss} \text{CrNbSi} \text{Nb}_{5Si3} \) [12].

It is worth noticing that the diffusion-multiple approach that was used by Zhao et al. [12] was on the basis of local equilibrium at interfacial regions. While it is a powerful and generally acceptable tool for efficient study of phase equilibria in multi-component alloys, it is also necessary to use such a technique with other approaches in order to check the reliability of the information obtained about the ternary and higher order phase diagrams, especially for the regions where the exact phase boundaries are in question, since due to unclear reasons one of the equilibrium phases could not form by interdiffusion reaction in some occasions [12, 14]. Recently, new experimental evidence in layered structures [15] and multi-component silicide billets [16, 17] seems to be consistent, though inconclusive, with the CALPHAD predicted \( \text{Nb}_{ss} + \text{CrNbSi} + \text{Nb}_{5Si3} \) region according to Ref. [12] but in the \( \text{Nb}_{ss} + \text{C14} + \text{Nb}_{5Si3} \) region according to Ref. [13].

This work aims to clarify the debatable, yet very important, ternary phase equilibrium near the Nb corner. An alloy composition of Nb–18Si–15Cr (all compositions are given in atomic percent in this paper) was chosen, Fig. 1, so that such debate on phase equilibrium could be readily clarified, as this composition is located in the middle of the \( \text{Nb}_{ss} + \text{CrNbSi} + \text{Nb}_{5Si3} \) region according to Ref. [12] but in the \( \text{Nb}_{ss} + \text{C14} + \text{Nb}_{5Si3} \) region according to Ref. [13].

2. Experimental

The alloy with nominal composition Nb–18Si–15Cr was prepared from high purity elements by arc-melting under an argon atmosphere in a water-cooled copper hearth using a non-consumable tungsten electrode. The alloy was remelted five times in order to ensure homogeneity. Heat treatment were carried out at 1000 and 1500 °C (named HT1000C and HT1500C, respectively) for 100 h in flowing argon, with samples wrapped in Ta foil to be buried in Ti chips. All samples were furnace cooled. The actual chemical compositions of the solidified and heat treated samples, which were determined by EPMA, are given in Table 1.

X-ray diffraction (XRD) was used to identify the phases present in the samples. We used a Philips diffractometer with monochromatic Cu K\( \lambda \) (\( \lambda = 1.540562 \) Å). The microstructures were observed by scanning electron microscopy (SEM) and the chemical compositions of the constituent phases were analysed by electron-probe microanalysis (EPMA) using a JEOL JXA 8600 superprobe with energy-dispersive and wave-dispersive X-ray (EDX and WDX) analysis facilities.
EPMA was operated using a 15 kV accelerating voltage, under which the spatial resolution was about 1 μm with the studied materials. Taking this into consideration, analysis was only performed on particles of size > 5 μm in diameter (the depth resolution is a lesser concern for EDX analysis). High purity of Nb, Si and Cr were used as standards and ZAF (Z, atomic number effect; A, absorption; F, fluorescence) iterative corrections were used to calculate the weight percentage compositions from measured X-ray intensities. The errors in the Nb, Si and Cr measurements were ~1.0, 0.1 and 0.3% relative, respectively.

3. Results and discussion

The typical backscattered electron (BSE) micrographs of the solidified ternary Nb–18Si–15Cr are shown in Fig. 2. The microstructure consisted of large primary Nb5Si3 particles, faceted Nb3 and a fine-scale lamellar eutectic of Nb3 and (Cr, Si)2Nb Laves phase in the Nb5Si3 matrix. The crystal structures of these phases were identified using XRD. Fig. 3 presents the X-ray diffractograms of the samples. The Nb5Si3 formed in the solidified alloy was found to be the W5Si3-type βNb5Si3, which has a tetragonal D8m structure. The Si-containing Laves phase (Cr, Si)2Nb has a hexagonal MgZn2 (C14) type crystal structure. The compositions of individual phases were determined using EPMA, as shown in Table 2. The Si concentration of the 5–3 silicide was 34.2 at.%, which was lean of the stoichiometric composition. Cr has a solubility of 10.3 at.% in Nb3. The C14 Laves phase, which has a volume fraction of 9.3%, contained 11.1 at.% Si.

After heat treatment at 1000 °C for 100 h, the microstructure, as shown in Fig. 4, was similar to that of the as-cast alloy (Fig. 2). Three phases, Nb3, Nb5Si3 and (Cr, Si)2Nb Laves, were present in the annealed microstructure. The Laves phase was found to be C14 Laves by XRD (Fig. 3b). This confirmed

<table>
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<th>Condition</th>
<th>Nb</th>
<th>Si</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>67.4 (66.7–67.8)</td>
<td>17.6 (16.6–18.7)</td>
<td>15.0 (14.5–15.7)</td>
</tr>
<tr>
<td>As-cast + 1000 °C/100 h</td>
<td>67.8 (66.4–69.1)</td>
<td>17.6 (15.7–19.4)</td>
<td>14.6 (14.0–15.5)</td>
</tr>
<tr>
<td>As-cast + 1500 °C/100 h</td>
<td>67.0 (66.3–67.7)</td>
<td>18.7 (17.9–19.4)</td>
<td>14.3 (14.0–14.9)</td>
</tr>
</tbody>
</table>

Fig. 2. BSE images of the as-cast Nb–18Si–15Cr alloy: (a) low magnification image and (b) high magnification image. The white phase is Nb3, the grey phase is Nb5Si3 and the black phase is (Cr, Si)2Nb.

Fig. 3. XRD diffractograms of the samples studied in this work: (a) as-cast; (b) 1000 °C/100 h; and (c) 1500 °C/100 h.
that the C14 Laves phase, which is only stable at temperatures above 1585 °C in the binary Cr–Nb system [18], was stabilised by Si to lower temperatures (at least 1000 °C). Moreover, XRD data revealed the existence of both the \( \beta \)\( \text{Nb}_5\text{Si}_3 \) and \( \alpha \)\( \text{Nb}_5\text{Si}_3 \) phases. However, the strongest peaks of the X-ray diffractogram corresponded to the \( \beta \)\( \text{Nb}_5\text{Si}_3 \) phase. It seems that a solid-state transformation took place via which the \( \beta \)\( \text{Nb}_5\text{Si}_3 \) phase transformed to \( \alpha \)\( \text{Nb}_5\text{Si}_3 \). Furthermore, this indicates that the decomposition process of the primary solidified \( \beta \)\( \text{Nb}_5\text{Si}_3 \) phase had not completed and the equilibrium at 1000 °C had not been reached. The compositions of individual phases are listed in Table 2. The composition of \( \beta \)\( \text{Nb}_5\text{Si}_3 \) phase did not change significantly by heat treatment at 1000 °C. The Cr contents in the \( \text{Nb}_{ss} \) and C14 Laves had increased by 16.5 and 10.1%, respectively, compared to the as-cast condition. This suggests that the change of the microstructure is mainly attributed to the partitioning of Cr. The grain growth of C14 Laves had taken place during annealing, with the composition of the Laves phase being changed towards the theoretical composition (Fig. 1). As shown in Table 2, the volume fraction of the C14 Laves phase had increased from 9.3% in the as-solidified microstructure to 16.3% in the sample HT1000C. There was no evidence of the formation of the \( \text{CrNbSi} \) phase in the annealed microstructure at 1000 °C.

The microstructure also coarsened after annealing at 1500 °C for 100 h and still consisted of three phases, namely \( \text{Nb}_{ss} \), \( \text{Nb}_5\text{Si}_3 \) and \( \text{(Cr, Si)}_2\text{Nb} \) Laves phases. A typical BSE micrograph of the sample HT1500C is shown in Fig. 5. Again, it was noticed that the Laves phase coarsened evidently and there were well defined triple junctions between the three phases. XRD results (Fig. 3c) indicated the Laves phase had a hexagonal C14 structure and the niobium silicide was the low temperature form \( \alpha \)\( \text{Nb}_5\text{Si}_3 \). The decomposition of primary

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Nb</th>
<th>Si</th>
<th>Cr</th>
<th>Volume fraction (%)</th>
</tr>
</thead>
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<tr>
<td>As-cast</td>
<td>( \text{Nb}_{ss} )</td>
<td>87.7</td>
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<td>10.3</td>
<td>44.5</td>
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<td></td>
<td>( \beta \text{Nb}_5\text{Si}_3 )</td>
<td>62.3</td>
<td>34.2</td>
<td>3.5</td>
<td>46.2</td>
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<tr>
<td></td>
<td>( \text{(Cr, Si)}_2\text{Nb} )</td>
<td>43.3</td>
<td>11.1</td>
<td>45.6</td>
<td>9.3</td>
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<tr>
<td>HT1000C</td>
<td>( \text{Nb}_{ss} )</td>
<td>86.0</td>
<td>2.0</td>
<td>12.0</td>
<td>41.8</td>
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<tr>
<td></td>
<td>( \beta \text{Nb}_5\text{Si}_3 )</td>
<td>61.5</td>
<td>35.1</td>
<td>3.4</td>
<td>41.9</td>
</tr>
<tr>
<td></td>
<td>( \text{(Cr, Si)}_2\text{Nb} )</td>
<td>38.3</td>
<td>11.5</td>
<td>50.2</td>
<td>16.3</td>
</tr>
<tr>
<td>HT1500C</td>
<td>( \text{Nb}_{ss} )</td>
<td>89.7</td>
<td>0.0</td>
<td>10.3</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>( \beta \text{Nb}_5\text{Si}_3 )</td>
<td>62.6</td>
<td>35.8</td>
<td>1.6</td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td>( \text{(Cr, Si)}_2\text{Nb} )</td>
<td>35.5</td>
<td>52.5</td>
<td>2.0</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Fig. 4. BSE images of the Nb–18Si–15Cr alloy after heat treatment at 1000 °C for 100 h: (a) low magnification image and (b) high magnification image.

Fig. 5. BSE image of the Nb–18Si–15Cr alloy after heat treatment at 1500 °C for 100 h.
solidified $\beta$Nb$_5$Si$_3$ phase had completed and the full equilibrium had reached after heat treatment at 1500 $^\circ$C for 100 h. EPMA results, as shown in Table 2, show that the Cr content in the Nb$_5$Si$_3$ decreased by $\sim$54.3% with a slight increase of Si concentration. Since, the Nb$_5$Si$_3$ formed in the HT1500$^\circ$C was $\alpha$Nb$_5$Si$_3$, it is suggested that the $\beta$Nb$_5$Si$_3$ phase has a higher solubility of Cr than $\alpha$Nb$_5$Si$_3$. Little Si was dissolved in the Nb$_{ss}$ in agreement with the low equilibrium solid solubility of Si in Nb. The Nb and Cr contents in the C14 Laves had significantly changed after heat treatment at 1500 $^\circ$C for 100 h. Compared to the as-cast sample, the Cr content had increased by 15.1% whilst the Nb concentration had decreased by 18.0% to approach the 'ideal' full sublattice occupancy of 1/3, accompanied by a slight increase of Si content. The compositions of the three phases after annealing at 1500 $^\circ$C are superimposed on the calculated corresponding equilibrium isothermal section, showing excellent agreement with the theoretical prediction (Fig. 6). The Si solubility in the C14 Laves phase did not change much with temperature varying from 1000 to 1500 $^\circ$C (11.5 at.% at 1000 $^\circ$C and 12.0 at.% at 1500 $^\circ$C, as shown in Table 2). It suggests that the formation of equilibrium microstructure was accompanied by partitioning of Cr to the C14 Laves phase. As shown in Figs. 2 and 5, the C14 Laves became much coarser after annealing at 1500 $^\circ$C and its volume fraction was more than two times as that in the as-cast sample. This indicates that the C14 Laves is stable at 1500 $^\circ$C.

The changes of phase morphology and composition of C14 Laves after heat treatment at 1000 and 1500 $^\circ$C for 100 h indicated that this phase is stable in this temperature range. The CrNbSi phase was not observed in any samples. While the equilibration was not completed in the sample annealed 1000 $^\circ$C, the coarsening of the Laves phase and the change of compositions towards the CALPHAD predicted ones are strong evidence to support the modelling results that the Laves phase is stable in the alloy of interest [13]. The microstructure of the sample annealed at 1500 $^\circ$C is apparently fully equilibrated. Therefore, the Nb$_{ss}$+CrNbSi+$\alpha$Nb$_5$Si$_3$ phase equilibrium suggested by Zhao et al. [12] cannot comply with our results, which showed experimental support for the Nb$_{ss}$+C14+$\alpha$Nb$_5$Si$_3$ three-phase equilibrium in the Nb–Si–Cr system [11,13].

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It should be noted that the C14 Laves phase could have an effectively extended metastable composition range (see also the work of Goldschmidt and Brand [11]). In refractory silicide alloys where solid state diffusion is slow, equilibration is a sluggish process, and extra care should be taken in studying phase equilibria when such phases are involved. Also, the disappearance of the $\alpha$Nb$_5$Si$_3$ phase after prolonged annealing at 1500 $^\circ$C is supportive to the suggestion that the appearance of $\beta$(Cr, Nb)$_5$Si$_3$ (or $\alpha$CrNb$_4$Si$_3$ [11]) in ternary alloys is a metastable phenomenon [12,13].

![Fig. 6. The calculated isothermal section of the Nb–Si–Cr system at 1500 $^\circ$C. The phase compositions in the as-cast ingot are shown as stars, and these after annealing at 1500 $^\circ$C are shown as circles. Notice that annealing at 1000 $^\circ$C makes the Laves phase approach equilibrium composition.](image-url)
3.1. Conclusions

Alloy Nb–18Si–15Cr, which locates in the disputable three-phase fields near the Nb corner, was selected and prepared by clean melting followed by heat treatment at 1000 and 1500 °C. The C14 Laves formed in both the as-cast and heat treated samples. The results confirmed that the C14 Laves phase in the binary Nb–Cr system was stabilised by Si to lower temperatures. \( \text{Nb}_{5} + \text{C14} + \alpha \text{Nb}_{5} \text{Si}_{3} \) instead of \( \text{Nb}_{5} \alpha + \text{CrNbSi} \), three-phase equilibrium was observed in this work.

The current work demonstrates that it is necessary to use ingot metallurgy to check the reliability of the information obtained about the ternary and higher-order phase diagrams using the diffusion-multiple technique, especially for the regions where the exact phase boundaries are in question. The investigation of the selected alloy is greatly helpful to clarify the confusion of the three-phase field near the Nb corner in the Nb–Si–Cr ternary system, and the work confirms the CALPHAD prediction of phase equilibrium near the Nb corner, showing the power to combine phase diagram predictions with experimental work for cost effective alloy development.

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