Effect of Cr Addition on Microstructure and Mechanical Properties in Nb–Si–Mo Base Multiphase Alloys

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The effects of Cr addition to Nb–22Si–5Mo alloy on phase equilibria, microstructures and mechanical properties are investigated by metallography, X-ray diffraction, scanning electron microscopy equipped with wavelength dispersive X-ray fluorescence spectroscopy and compression test at temperatures from room temperature to 1773 K. With increasing Cr content a duplex microstructure consisting of Nb5Si3 and Nbss (niobium solid solution) is changed to three-phase microstructure consisting of Nb5Si3, Nbss and NbC2. Chromium addition does not change the volume fraction of constituent phases in the two-phase alloys, whereas it increases the volume fraction of NbC2, C14 Laves phase, at the expense of mostly Nbss in the three-phase alloys. The c/a axis ratio of α-Nb5Si3 phase increases with increasing (Cr + Mo) content. It is found that Cr alloying in Nbss increases the room temperature strength due to atomic size misfit and decreases high temperature strength due to accelerated diffusion. The existence of C14 Laves phase increases high temperature strength, but degrades room temperature deformability. High temperature strength is found to be sensitive to the volume fraction and crystal structure of constituent phases as well as microstructure.

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Keywords: microstructure, mechanical property, niobium silicide, alloying element, phase equilibria, high temperature strength

1. Introduction

Niobium silicide Nb5Si3 based alloys have a high potential for high temperature structural applications because of high melting point (2527 K) and low density (7.1 g/cm3) of the silicide. Therefore, the alloys can be good candidates to be used at temperatures above 1473 K as a replacement for Ni-base superalloys whose attainable maximum temperature is around 1273 K.1–9 Since the monolithic Nbss phase has been found to be very brittle at ambient temperatures, Nbss-based multiphase alloy systems containing a ductile niobium solid solution (Nbss) phase would be of a technological interest in the field of high temperature structural materials. Considering the inherent difficulty in ductilizing this silicide, it is essential that an incorporation of the ductile phase into the brittle silicide is necessarily required in order to improve the room temperature deformability and fracture toughness.10–21 Thus, high temperature strength can be held by the silicide, and low temperature deformability and fracture toughness can be enhanced by the incorporated ductile phase.

From the microstructural viewpoint, the presence of the eutectic and eutectoid reactions in the binary Nb–Si alloy system would allow us to improve mechanical properties by optimizing the microstructures through a proper control of processing conditions.22,23 While an alternative way to satisfy the required properties such as room temperature deformability and fracture toughness and high temperature strength is allowing by which microstructural and crystal structural modifications of constituent phases can be achieved. In previous studies,22–25 we have found that Mo alloying is effective in improving room temperature fracture toughness through the microstructural modification, and high temperature strength through both the solid solution hardening of Nbss phase and the control of volume fraction and crystal structure of Nb5Si3 phase. Especially, Nb–22Si–5Mo ternary alloy has been shown to have a reasonable balance between room temperature fracture toughness and high temperature strength. In the present study, Cr is added to Nb–22Si–5Mo ternary alloy to form Cr5Si3 phase which possesses a complex tetragonal structure (D8h structure type) in the binary Cr–Si system. The Cr5Si3 phase undergoes phase transformation from γ-Cr5Si3 to β-Cr5Si3 at around 1773 K. If a pseudo-binary between Cr5Si3 and Nbss is formed and phase transformation is closely related to diffusion-driven process, Cr may have a positive role to enhance the phase stability of β-Nb5Si3 in the present quaternary alloy system, since the transformation temperature of Nb5Si3 from α to β is higher than that of Cr5Si3 phase. In our previous studies, α-Nb5Si3 has been found to be favorable from the viewpoint of high temperature strength than β-Nb5Si3.23 These reports indicate that phase stability of Nb5Si3 is directly correlated with mechanical property. Moreover, another intermetallic phase, C14 Laves phase NbC2, can be expected to form in the Nb-rich composition range of this alloy system.

We aim at understanding the alloying behavior of chromium on microstructural formation, crystal structure of constituents and mechanical properties in a wide temperature range from room temperature to 1773 K.

2. Experimental Procedure

The purities of starting raw materials were 99.9 mass%Nb, 99.999 mass%Si, 99.9 mass%Mo and 99.999 mass%Cr, respectively. Small alloy buttons of 20 mm in diameter were prepared by arc melting on a water-cooled copper hearth under an argon gas atmosphere with a non-consumable tungsten
10th Avenue, New York, NY 10001

Table 1 Nominal compositions (mol%) of six alloys used in this study.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Nb</th>
<th>Si</th>
<th>Mo</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, a1</td>
<td>73</td>
<td>22</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>b, b1</td>
<td>68</td>
<td>22</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>c, c1</td>
<td>63</td>
<td>22</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>d, d1</td>
<td>58</td>
<td>22</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>e, e1</td>
<td>53</td>
<td>22</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>f, f1</td>
<td>48</td>
<td>22</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

The button ingots were re-melted at least five times for chemical homogeneity. The ingots were then heat treated under an argon atmosphere at 1773 K for 100 h followed by furnace cooling to room temperature at a rate of 200 K/min in the high temperature region (1773 to 773 K) and then at a rate of 10 K/min in the low temperature region (773 K to room temperature). Samples for chemical composition analysis, microstructural observation and compression test were made by electro-discharge machining (EDM) from both the as-cast and heat treated buttons. The nominal compositions for all of the samples studied here are listed in Table 1. X-ray diffraction (XRD) analysis was conducted on bulk samples to determine the crystal structures and lattice parameters of constituent phases. Lattice parameters were determined by the well-known least square method. Samples for metallographic observations were mechanically polished with SiC paper and Al2O3 particles with water. Scanning electron microscopy (SEM) equipped with wavelength-dispersive X-ray fluorescence spectroscopy (WDS) was used for determining the chemical composition of each constituent phase. Phase analysis by XRD was performed on finely polished bulk samples. The measurement of volume fraction of constituent phases was carried out using image analyzer equipped with computer system. Compression test specimens with 2.5 mm × 2.5 mm cross-section and 6 mm height were prepared by EDM and then mechanically polished. Compression test was carried out using an Instron model 8500 mechanical testing machine at room temperature to 1773 K in Ar atmosphere and at an initial strain rate of $3 \times 10^{-3}$ s$^{-1}$.

3. Results

3.1 Phase analysis and lattice parameter

The result of phase analysis by XRD of both the as-cast and the heat treated alloys indicate that all samples are either two phases with α-Nb5Si3 (D8h) or β- (D8m) tetragonal structure and bcc Nb$_{57}$ (alloys a, b, a1, b1), or three phases composed of the α- or β-Nb$_5$Si$_3$, NbCr$_2$ (C14 hexagonal Laves crystal structure) and bcc Nb$_{57}$ (alloys c, d, e, f, c1, d1, e1, f1). In Fig. 1, Results of XRD on six samples of as-cast alloys a to f are shown. Filled circles and squares in Fig. 1 indicate peaks from Nb$_{57}$ and β-Nb$_5$Si$_3$, respectively. The C14 Laves phase is marked as filled triangles. No discernible peaks are identified as meta-stable Nb$_3$Si, which appears as an intermediate phase in the Nb–Si binary alloy phase diagram, and as cubic C15 Laves phase which is stable in the low temperature region in the Cr–Nb binary alloy phase diagram. The XRD spectra clearly show that alloys a and b are composed of duplex structure with β-Nb$_5$Si$_3$ and Nb$_{57}$, whereas alloys c, d, e and f additionally contain the C14 hexagonal Laves phase. The six alloys a to f in Fig. 1 have the same Si and Mo contents with the Cr concentrations from 0 to 25 mol% as listed in Table 1. No significant change is exhibited in the diffraction spectra by increasing Cr content from 0 to 5 mol%. On further increasing Cr content in alloys c to f, microstructure observations indicated that the C14 Laves phase appears and its volume fraction increases, while the volume fraction of Nb$_{57}$ decreases.
Fig. 2 X-ray diffraction spectra for six heat treated alloys at constant Si and Mo contents. The alloy \( a_1 \) is ternary and the others are quaternary.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Constituent phases</th>
<th>Volume fractions (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 )</td>
<td>46 ( \text{Nb}_{54} ), 54 ( \text{Nb}_5\text{Si}_3 )</td>
<td>—</td>
</tr>
<tr>
<td>b</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 )</td>
<td>45 ( \text{Nb}_{54} ), 55 ( \text{Nb}_5\text{Si}_3 )</td>
<td>—</td>
</tr>
<tr>
<td>c</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>32 ( \text{Nb}_{54} ), 55 ( \text{Nb}_5\text{Si}_3 )</td>
<td>13</td>
</tr>
<tr>
<td>d</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>23 ( \text{Nb}_{54} ), 51 ( \text{Nb}_5\text{Si}_3 )</td>
<td>16</td>
</tr>
<tr>
<td>e</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>24 ( \text{Nb}_{54} ), 45 ( \text{Nb}_5\text{Si}_3 )</td>
<td>31</td>
</tr>
<tr>
<td>f</td>
<td>( \text{Nb}_{54} + \beta - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>11 ( \text{Nb}_{54} ), 44 ( \text{Nb}_5\text{Si}_3 )</td>
<td>45</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 )</td>
<td>43 ( \text{Nb}_{54} ), 57 ( \text{Nb}_5\text{Si}_3 )</td>
<td>—</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 )</td>
<td>45 ( \text{Nb}_{54} ), 55 ( \text{Nb}_5\text{Si}_3 )</td>
<td>—</td>
</tr>
<tr>
<td>( c_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>36 ( \text{Nb}_{54} ), 52 ( \text{Nb}_5\text{Si}_3 )</td>
<td>12</td>
</tr>
<tr>
<td>( d_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>23 ( \text{Nb}_{54} ), 49 ( \text{Nb}_5\text{Si}_3 )</td>
<td>28</td>
</tr>
<tr>
<td>( e_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>20 ( \text{Nb}_{54} ), 46 ( \text{Nb}_5\text{Si}_3 )</td>
<td>34</td>
</tr>
<tr>
<td>( f_1 )</td>
<td>( \text{Nb}_{54} + \alpha - \text{Nb}_5\text{Si}_3 + \text{C}14 \text{ NbCr}_2 )</td>
<td>12 ( \text{Nb}_{54} ), 44 ( \text{Nb}_5\text{Si}_3 )</td>
<td>44</td>
</tr>
</tbody>
</table>

creases. Another noticeable change caused by the increase in Cr content is the shift of the bcc diffraction peaks to higher 2\( \theta \) indicating a contraction of the lattice parameter. This contraction seen in Fig. 1 is dependent on Cr content. XRD results on six alloys \( a_l \) to \( f_l \), which were heat-treated at 1773 K for 100 h, are shown in Fig. 2. Basically, the diffraction spectra for the heat-treated alloys are observed to be similar to those for the as-cast alloys. The alloys \( a_l \) and \( b_l \) are composed of duplex phases, and the others appear to be of three-phase. An obvious difference, however, is found in the crystal structure of \( \text{Nb}_5\text{Si}_3 \). The silicide is \( \beta - \text{Nb}_5\text{Si}_3 \) phase in the as-cast alloys, while it is \( \alpha - \text{Nb}_5\text{Si}_3 \) in the heat-treated alloys. In Fig. 3, the lattice parameters of \( \text{Nb}_{a_l} \) phase in the heat-treated alloys \( a_l \) to \( f_l \) are plotted as a function of (Cr + Mo) content in \( \text{Nb}_{a_l} \). The lattice parameter decreases rapidly with increasing (Cr + Mo) content up to 15 mol\%, and then it gradually decreases with a linear slope. SEM-WDS analysis indicates that the decrease in lattice parameter of the \( \text{Nb}_{a_l} \) phase originates from a concurrent increase in Cr and Mo contents in the alloys \( a_l \) to \( b_l \), and from a decrease in Cr content at almost constant content of Mo in the alloys \( c_l \) to \( f_l \). Since the atomic sizes of Cr, Mo and Nb are 0.128, 0.140 and 0.147 nm, respectively, the above decrease in lattice parameter will be explained by the substitution of Cr and Mo for Nb in their content to \( \text{Nb}_{a_l} \).

Figure 4 shows the \( c/a \) axis ratio of \( \alpha - \text{Nb}_5\text{Si}_3 \) phase as a function of (Cr + Mo) content. The \( c/a \) axis ratio increases sharply with increasing content of (Cr + Mo) especially at small contents, and it finally saturates.

3.2 Microstructures of as-cast and heat treated alloys

Back scattered electron images (BEI) of as-cast alloys \( a \) to \( f \) are shown in Fig. 5. It is revealed from XRD and SEM-
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3.3 Mechanical properties

Compression tests were carried out to ascertain the effect of Cr addition on the mechanical properties of as-cast and heat treated alloys in the wide temperature range from room temperature to 1773 K. Yield stress or fracture stress, and compressive ductility are summarized in Table 3 for five as-cast and four heat treated samples tested at room temperature at an initial strain rate of 3 × 10⁻⁴ s⁻¹. The addition of 5 mol% Cr increases the yield stress of as-cast two-phase alloys (see alloys a and b), and the heat treatment increases the compressive ductility without decreasing yield stress (see alloys b and b'). The increase in yield stress at room temperature is attributable to solid solution strengthening of Nb₃s, because the lattice parameter of Nb₃s decreases significantly by 5 mol% Cr addition, as shown in Fig. 3, with almost no change in the volume fraction of Nb₃s, as shown in Table 2. The increased compressive ductility of 5 mol% Cr added two phase alloy by the
heat treatment would be associated with the formation of eutectic structure and the increase in thickness of the constituent Nbss phase, since the crack propagation is retarded by thick Nbss phase. No compressive ductility is shown in three-phase alloys with high Cr contents irrespective of heat treatment. This may be closely related to the decrease in volume fraction of ductile Nbss and the presence of very brittle C14 NbCr2 Laves phase.27–29)

The 0.2% offset yield stress at 1773 K is presented in Fig. 7 as a function of Cr content for both the as-cast and the heat treated alloys. At all compositions investigated, the yield stress of the heat treated alloys is seen to be higher than that of the as-cast alloys. With increasing Cr content, yield stress exhibits the minimum at around 15 mol% Cr and then increases in both the as-cast and heat treated alloys. Fracture or yield stress of the heat treated two-phase and the three-phase alloys is plotted against test temperature in Fig. 8. The two- and three-phase alloys exhibit very high yield stress at room temperature, but are remarkably weakened above 1500 K. The high Cr content alloys containing Laves phase are very brittle at room temperature, and especially Nb–22Si–5Mo–25Cr (alloy f1) fractures without showing yielding at room temperature to 1473 K. This brittleness would be ascribed to the intrinsic brittleness of Laves phase and the decrease in the volume fraction of Nbss with an increase in Cr content.

4. Discussion

The microstructure, phase equilibria, mechanical and physical properties are often sensitive to a small change in com-
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Fig. 6 BEI micrographs of the alloys heat treated at 1773 K for 100 h. (a) Nb–22Si–5Mo, (b) Nb–22Si–5Mo–5Cr, (c) Nb–22Si–5Mo–10Cr, (d) Nb–22Si–5Mo–15Cr, (e) Nb–22Si–5Mo–20Cr, (f) Nb–22Si–5Mo–25Cr.

In previous studies, we have correlated the phase equilibrium and microstructure with the mechanical properties in the temperature range from room temperature to 1773 K in the Nb–Si–Mo ternary alloy system.

In the present study, we have investigated the phase formation on the Nb–22Si–5Mo alloy containing Cr, which was the heat treated at 1773 K for 100 h, using XRD and SEM-WDS. Interestingly, we found that the constituent phases are different between Nb–Si–Mo and Nb–Si–Mo–Cr systems. In the quaternary system the C14 NbCr$_2$ Laves phase is formed along with Nb$_{ss}$ and Nb$_5$Si$_3$ phases at Cr contents of 10 to 25 mol%, indicating that the maximum solubility limit of Cr to Nb$_{ss}$ is between 5 and 10 mol% in this alloy system. From the results of Figs. 1 and 2, it is found that $\beta$-Nb$_5$Si$_3$, which is stable at high temperature, transforms to $\alpha$-Nb$_5$Si$_3$ at 1773 K, which is stable at low temperature. No intermediate phase such as Nb$_3$Si or Cr$_3$Si is found, suggesting that Mo has the effect to make A$_3$B-type compound unstable in this alloy system. Considering the facts that the atomic sizes of Mo and Cr are smaller than Nb, and if Mo and Cr atoms were substituted for Nb atoms and there was no anisotropy in the site occupancy, the unit cell size of the silicide would become compact and the $c/a$ ratio would not be changed. However, the measured $c/a$ axis ratio is somewhat different from our expectation as shown in Fig. 4. The $c/a$ axis ratio of $\alpha$-Nb$_5$Si$_3$ phase shows a significant increase up to about 5 mol% of (Cr + Mo) content. Kim et al. have reported that the $c/a$ axis ratio of $\alpha$-Nb$_5$Si$_3$ phase increases with increasing Mo content and phase transformation from $\alpha$-Nb$_5$Si$_3$ to $\beta$-Nb$_5$Si$_3$ takes place at around 5 mol%Mo at 1973 K. Therefore, the present result is similar to the previous result by Kim et al. This may be related to the site preference arising from the anisotropy in inter-atomic bonding force depending on crystallographic orientation. Correspondingly, Chu et al. have found that the thermal expansion is strongly anisotropic along the $a$ and $c$ directions in a Mo$_5$Si$_3$ single crystal.
Table 3 Summary of 0.2% offset yield or fracture stress and compressive ductility of alloys used in this study.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Yield or fracture stress (MPa)</th>
<th>Compressive ductility (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1888(Y)</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>2504(Y)</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>2627(F)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>2855(F)</td>
<td>0.5</td>
<td>as-cast</td>
</tr>
<tr>
<td>e</td>
<td>2576(F)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>2196(F)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>a1</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>b1</td>
<td>2209(Y)</td>
<td>3</td>
<td>heat</td>
</tr>
<tr>
<td>c1</td>
<td>2231(Y)</td>
<td>2.1</td>
<td>treatment at 1773 K for 100 h</td>
</tr>
<tr>
<td>d1</td>
<td>2496(F)</td>
<td>0</td>
<td>1773 K for 100 h</td>
</tr>
<tr>
<td>e1</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>f1</td>
<td>1178(F)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7 0.2% offset yield stress plotted as a function of Cr content in the as-cast and the heat treated alloys.

However, the present observations of the extended solubility of alloying elements Mo and Cr and no phase transformation in α-Nb5Si3 heat treated at 1773 K are different from the previous results obtained in the Nb–Si–Mo ternary system in which phase transformation from α-Nb5Si3 to β-Nb5Si3 took place at around 5 mol% Mo at 1733 K, indicating maximum solubility of Mo in the α-Nb5Si3. It is very interesting to note that the constituent phases change from two to three phases at the transition composition, as seen in Figs. 1 and 2 and Table 2. The (Cr + Mo) content dependence of lattice parameter of Nb ns in Fig. 3 results from the distribution of alloying elements into the constituent phases. Using SEM-WDS analysis, we have found that the contents of Cr and Mo in Nb ns increase concurrently with increasing Cr content in the two-phase equilibrium, whereas the content of Mo is kept constant in the three-phase equilibrium in this study. This means that the sharp decrease of the lattice parameter seen in Fig. 3 is due to the increase of (Cr + Mo) content in Nb ns, while the gradual decrease is attributable to the increase of Cr content at the constant Mo content. These differences therefore, could be explained by considering the role of Cr alloying which stabilizes α-Nb5Si3 stable. As shown in Fig. 3, the lattice parameter of Nb ns decreases along the two combined slopes, as (Cr + Mo) content increases. The composition at the transition of the slopes is found to be about 14.5 mol% for the (Cr + Mo) content in Nb ns.

The room temperature compression tests revealed that the two-phase alloys show plastic yielding and appreciable ductility, while the three-phase alloys fracture before yielding with high fracture stress. This difference may result simply from the volume fraction of ductile Nb ns. As shown in Table 2 for both as-cast and heat treated conditions, the volume fractions of Nb ns in the two-phase alloys are higher than 40%, while those of the three phase alloys are less than 32%. Here, it is noted that the as-cast three-phase alloy c shows no ductility, while the heat treated alloy c shows yielding, where the volume fractions of Nb ns in the as-cast and heat treated alloys are 32 and 36%, respectively. Therefore, the volume fraction of a ductile phase would play an important role to provide the compressive ductility.

In view of plastic deformation, more ductile phase would be favorable to increase ductility. The compressive ductility is larger in the alloy a than in the alloy b. This is because the Nb ns of alloy b is solid solution hardened by Cr alloying, which is confirmed by the significant decrease in the lattice parameter, as shown in Fig. 3. At present, it is not easy to detect the difference in room temperature deformability between monolithic Nb5Si3 and NbCr2 phases, because both the intermetallics are completely brittle even in compression. However, it has been shown that a duplex Nb ns/Nb5Si3 alloy with a similar volume fraction of Nb ns phase to alloy c deforms plastically at room temperature. This result suggests that Nb ns/Nb5Si3 alloy has deformability superior to Nb ns/Nb5Si3/NbCr2 alloy at room temperature. Much more
works would be required to understand the room temperature deformability of those complex intermetallic phases in the relation to microstructures as well as volume fractions of constituent phases.

The yield stress at 1773 K changes dramatically with Cr content as shown in Fig. 7. The rapid decrease of yield stress by 5 mol% Cr addition would be associated with weakening of Nbα, since the volume fractions ratio of the constituent phases is identical in alloys α and β. As shown in Fig. 3, the lattice parameter of Nbα decreases with increasing (Cr + Mo) content in Nb–22Si–5Mo–xCr alloys. Even though solid solution strengthening due to Cr addition occurs at room temperature in the alloys, Cr is well known to have high diffusivity in Nbα at high temperature, which can accelerate the deformation controlled by a thermally activated process and thereby high temperature strength would be decreased. In contrast, the rapid increase of yield stress by 25 mol% Cr addition would be ascribed to the increase in volume fraction of NbC2 and the decrease in volume fraction of Nbα. As seen in Fig. 7, yield stress is always higher in the heat treated alloys than in the as-cast alloys. Although a strict explanation for the difference is difficult because of microstructure changes by heat treatment, the decrease in the volume fraction of Nbα (Table 2) should be responsible.

As can be seen in Fig. 8, yield stress is still very high even at around 1500 K, which results from high strength of Nb5Si3 and NbC2. The abrupt decrease of yield stress above 1700 K may be due to intrinsic nature of the constituent phases.

5. Conclusions

The phase equilibria, crystal structures of constituent phases, microstructures and mechanical properties were investigated at room temperature to 1773 K for Cr-added Nb–22Si–5Mo–xCr alloys consisting of two-phase Nbα/Nb5Si3 or three-phase Nbα/Nb5Si3/NbC2. The obtained results are summarized as follows.

(1) The Cr addition to Nb–22Si–5Mo ternary system gives rise to a shift of eutectic line toward Si-rich corner being related to the two-phase Nbα/Nb5Si3 region, while three-phase, Nbα, Nb5Si3 and NbC2 Laves phase, are formed by Cr addition higher than 5 mol%. The volume fraction of NbC2 increases at the expense of mostly Nbα with increasing Cr content.

(2) Lattice parameter of Nbα phase decreases with increasing Cr content at constant Si and Mo contents. The decrease in the lattice parameter of Nbα can be related to partitioning of Mo and Cr in the constituent phases. The c/a axis ratio increases with increasing content of (Cr + Mo) up to 5.9 mol% and then is saturated.

(3) Phase transformation from β-Nb5Si3 to α-Nb5Si3 exists at temperature above 1773 K in the present alloys.

(4) With increasing Cr content yield stress increases but compressive ductility decreases at room temperature in the two-phase alloys. The presence of C14 Laves phase is not beneficial for improving deformability at room temperature in this alloy system.

(5) The 0.2% offset yield stress at 1773 K increases with increasing the volume fraction of Nb5Si3 or C14 Laves phase but decreases with increasing the volume fraction of bcc solid solution or increasing Cr content in Nbα.

Acknowledgements

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