Effect of Mo Addition on Phase Stability and High-Temperature Strength of NbSi$_2$/Nb$_5$Si$_3$ Composites

Wei Li*, Haibo Yang, Aidang Shan, Lanting Zhang and Jiansheng Wu

Key Laboratory of Ministry of Education for High Temperature Materials and Tests, Shanghai Jiao Tong University, Shanghai, 200030, P.R.China

Directionally solidified NbSi$_2$/Nb$_5$Si$_3$ in-situ composites have been prepared. Scanning Electron Microscopes (SEM) and X-ray diffraction (XRD) have been used to investigate phase constitution and microstructure. It was found that microstructure and phase stability of directionally solidified alloys depended on growth rate, heat-treatment and alloying element. Compression strength was tested in the temperature range from 1473 to 1773 K and compression axes parallel to growth direction was chosen. High-temperature strength of NbSi$_2$/Nb$_5$Si$_3$ composites increased from 222.9 to 593.77 MPa at 1773 K due to Mo addition.

(Received August 17, 2004; Accepted October 4, 2004)

Keywords: directionally solidification, NbSi$_2$/Nb$_5$Si$_3$ composites, phase transformation, alloying element, high temperature strength

1. Introduction

Nb$_5$Si$_3$ is an attractive structural material at high temperature due to its high creep resistance and strength over 1473 K. As a reinforcement phase at high temperature, Nb$_5$Si$_3$ has been compounded with Nb to acquire a balance between high temperature strength and room temperature fracture toughness. Moreover, creep resistance of directionally solidified MoSi$_2$/Mo$_5$Si$_3$ eutectics has been reported to be far better than that of single phase MoSi$_2$. Hence, it is expected that high temperature strength of NbSi$_2$ can be improved by incorporation with Nb$_5$Si$_3$.

Nb$_5$Si$_3$ displays a complex tetragonal structure with 32 atoms per cell in both of its allotropic forms. The lattice parameters are $a = 0.657$ nm and $c = 1.1884$ nm for $\alpha$-Nb$_5$Si$_3$ (D8$_1$) and $a = 1.0018$ nm and $c = 0.5072$ nm for $\beta$-Nb$_5$Si$_3$ (D8$_m$). According to phase diagram of Nb-Si system, a reaction of $\beta$-Nb$_5$Si$_3$ + Nb$_3$Si$_2$ to $\alpha$-Nb$_5$Si$_3$ takes place at 2220 K in low Si region where Si content is in the range from 25 to 37.5% (at.). However, work of Kim et al. indicates that transformation temperature from $\alpha$-Nb$_5$Si$_3$ to $\beta$-Nb$_5$Si$_3$ declines to 1918 K in the Nb/Nb$_5$Si$_3$ composites due to Mo addition. It was assumed that the selective substitution behavior of Mo for Nb is responsible for the shortening of $c$ axis and extension of a axis in $\alpha$-Nb$_5$Si$_3$. As a result, $\beta$-Nb$_5$Si$_3$ is more stable in Nb/Nb$_5$Si$_3$ composites with Mo. However, the reason of change in the crystal structure and the stability of $\beta$-Nb$_5$Si$_3$ has not yet been clearly interpreted. $\beta$-Nb$_5$Si$_3$ performs a lower yield stress than $\alpha$-Nb$_5$Si$_3$ in Nb/Nb$_5$Si$_3$ composites. Moreover, Mo addition effectively increases the height and temperature of anomalous strengthening peak of Nb$_5$Si$_2$. Thereby, it’s very necessary to make clear the effect of Mo addition on phase stability and high temperature strength of NbSi$_2$/Nb$_5$Si$_3$ composites. The purpose of this paper is to study the effect of growth rate, heat-treatment and Mo addition on microstructure and phase stability and mechanical properties of NbSi$_2$/Nb$_5$Si$_3$ composites.

2. Experiment Procedure

Nb-57(at)Si-x(at)Mo (x = 0.1, 0.2, 3) alloys were prepared in the form of ~80 g bar by arc-melting in a water-cooled copper crucible. The purity of raw materials is 99.93 mass% for Nb and 99.999 mass% for Si. Hereafter alloy composition will be abbreviated as Nb-57Si instead of Nb-57(at)Si. Directionally solidified materials were produced using a Floating Zone (FZ) method at growth rates of 5 mm/h and 10 mm/h, and then annealed under Ar at 1473 K for 100 h. The crystal structure and volume fraction of constituent phases were determined by X-ray diffraction (XRD) method using the copper K$_\alpha$ radiation. Differential thermal analysis (DTA) experiment was performed up to 1723 K in an argon atmosphere. The microstructure of directionally solidified materials was observed using back scattered electron images (BEI) with energy dispersive spectroscopy (EDS) to identify the constituent phase. Compression specimens with 2.7 $\times$ 2.7 $\times$ 5 mm$^3$ were prepared by electro-discharge machining (EDM) and then mechanically polished. Compression tests were conducted on a Shimadzu AG-500 testing machine in vacuum in the temperature range from 1473 to 1773 K at a strain rate of $1 \times 10^{-4}$ s$^{-1}$. Compression axes is parallel to growth direction.

3. Results

3.1 X-ray diffraction

Table 1 shows the experimental composition of $\alpha$-Nb$_5$Si$_3$, $\beta$-Nb$_5$Si$_3$ and Nb$_5$Si$_2$ which was calculated from the results of XRD. Figure 1 shows XRD spectra of NbSi$_2$/Nb$_5$Si$_3$ composites. These results indicate that $\beta$-Nb$_5$Si$_3$ and Nb$_5$Si$_2$ appear in the as-cast alloys with growth rate of 10 mm/h. No $\alpha$-Nb$_5$Si$_3$ phase was found. With the decrease of growth rate from 10 mm/h to 5 mm/h, both $\alpha$-Nb$_5$Si$_3$ and $\beta$-Nb$_5$Si$_3$ were observed in the as-cast alloys. Heat treatment at 1473 K for 100 h is responsible for complete transformation from $\beta$-Nb$_5$Si$_3$ to $\alpha$-Nb$_5$Si$_3$. But $\alpha$-Nb$_5$Si$_3$ was not observed in Nb-57Si-2Mo alloys even after heat-treatment at 1473 K for 100 h. At 1918 K, a reaction of $\beta$-Nb$_5$Si$_3$ $\to$ $\alpha$-Nb$_5$Si$_3$ +
NbSi$_2$ takes place in rich Si region where Si content is in the range from 39.5 to 66.7\% (at.). However, $\beta$-Nb$_5$Si$_3$ was stable below 1473 K when the content of Mo was higher than 2 at%.

Figure 2 shows the result of DTA of Nb-57Si and Nb-57Si-2Mo alloys. The reaction of $\beta$-Nb$_5$Si$_3$ $\rightarrow$ $\alpha$-Nb$_5$Si$_3$ + NbSi$_2$ can be observed in Nb-57Si, while this reaction does not present in the temperature range from 1593 to 1723 K in Nb-57Si-2Mo alloys.

### 3.2 Microstructure

Figures 3(a) and (b) show microstructure of directionally solidified binary and ternary NbSi$_2$/Nb$_5$Si$_3$ composites annealed at 1473 K for 100 h. Dark and bright regions correspond to NbSi$_2$ and Nb$_5$Si$_3$ phase, respectively. Precipitation of NbSi$_2$ can be observed in the Nb$_5$Si$_3$ phase of Nb-57Si alloys annealed at 1473 K for 100 h in Fig. 4(a). In Fig. 4(b), NbSi$_2$ precipitation does not occur in Nb$_5$Si$_3$ phase of annealed Nb-57Si-2Mo alloys. The concentration of Nb, Si and Mo is shown in Table 2.

### 3.3 High-temperature compression behavior

Elevated temperature compression strength of Nb-57Si and Nb-57Si-2Mo in the temperature range from 1473 to 1773 K is shown in Fig. 5. The compression strength of NbSi$_2$/Nb$_5$Si$_3$ composites at 1773 K increased from 222.9 to 593.77 MPa due to Mo addition.

---

### Table 1 The volume fraction of constituent phase in NbSi$_2$/Nb$_5$Si$_3$.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Nb</th>
<th>Si</th>
<th>Mo</th>
<th>Heat treatment</th>
<th>Growth rate</th>
<th>$\alpha$-Nb$_5$Si$_3$ (at%)</th>
<th>$\beta$-Nb$_5$Si$_3$ (at%)</th>
<th>NbSi$_2$ (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>43</td>
<td>57</td>
<td>—</td>
<td>—</td>
<td>10 mm/h</td>
<td>0</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>b</td>
<td>43</td>
<td>57</td>
<td>—</td>
<td>—</td>
<td>5 mm/h</td>
<td>18</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>c</td>
<td>43</td>
<td>57</td>
<td>—</td>
<td>1473 K for 100 h</td>
<td>10 mm/h</td>
<td>33</td>
<td>0</td>
<td>67</td>
</tr>
<tr>
<td>d</td>
<td>43</td>
<td>57</td>
<td>—</td>
<td>1473 K for 100 h</td>
<td>5 mm/h</td>
<td>32</td>
<td>0</td>
<td>68</td>
</tr>
<tr>
<td>e</td>
<td>41</td>
<td>57</td>
<td>2</td>
<td>1473 K for 100 h</td>
<td>10 mm/h</td>
<td>0</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>f</td>
<td>41</td>
<td>57</td>
<td>2</td>
<td>1473 K for 100 h</td>
<td>5 mm/h</td>
<td>0</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>g</td>
<td>42</td>
<td>57</td>
<td>1</td>
<td>1473 K for 100 h</td>
<td>10 mm/h</td>
<td>22</td>
<td>11</td>
<td>67</td>
</tr>
<tr>
<td>h</td>
<td>40</td>
<td>57</td>
<td>3</td>
<td>1473 K for 100 h</td>
<td>10 mm/h</td>
<td>0</td>
<td>34</td>
<td>66</td>
</tr>
</tbody>
</table>

---

**Fig. 1** X-ray diffraction pattern of NbSi$_2$/Nb$_5$Si$_3$ composites.

**Fig. 2** DTA thermogram of Nb-57Si and Nb-57Si-2Mo alloys.
4. Discussion

Nb$_5$Si$_3$ has two allotropes: $\beta$-Nb$_5$Si$_3$ (D$_{8m}$) and $\alpha$-Nb$_5$Si$_3$ (D$_{81}$). In Kim’s report,$^6$ $\alpha$-Nb$_5$Si$_3$ is observed in as-cast Nb/Nb$_5$Si$_3$ composites prepared by arc melting. In contrast, only when cooling rate is rather low, $\beta$-Nb$_5$Si$_3$ can be found in as-cast Nb$_5$Si$_2$/Nb$_5$Si$_3$ composites. The reason is that the reaction of $\beta$-Nb$_5$Si$_3$ + Nb$_3$Si $\rightarrow$ $\alpha$-Nb$_5$Si$_3$ easily takes place at 2220 K because it is easy for Nb and Si atoms to diffuse at this temperature. At 1918 K, a reaction of $\beta$-Nb$_5$Si$_3$ $\rightarrow$ $\alpha$-Nb$_5$Si$_3$ + NbSi$_2$ takes place in rich Si region where Si content is in the range from 39.5 to 66.7(at.%). The decrease of diffusivity of Nb atom due to lower temperature restrains the reaction of $\beta$-Nb$_5$Si$_3$ $\rightarrow$ $\alpha$-Nb$_5$Si$_3$ + NbSi$_2$.

According to phase diagram of Nb-Si system, Si content is 37.5% (at) in $\alpha$-Nb$_5$Si$_3$ and 39.6% (at) in $\beta$-Nb$_5$Si$_3$ respectively. In $\beta$-Nb$_5$Si$_3$, Si content is higher than the stoichiometry composition. The former researcher reported$^{13}$ that there are two assumptions for the excess Si: 1) Si atoms substitute for Nb atoms: (Nb)$_4$(NbSi)(Si)$_3$; 2) vacancies in the Nb position: (Nb)$_4$(NbVa)(Si)$_3$. In Table 2, with Mo addition, the content of Nb does not distinctly change, while Si content decreases close to the content of Si in $\alpha$-Nb$_5$Si$_3$. And Mo content is equal to the decrement of Si content in $\beta$-

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Concentration of Nb, Si and Mo in Nb$_5$Si$_3$ in Nb-57Si and Nb-57Si-2Mo alloys.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb (at%)</td>
</tr>
<tr>
<td>$\beta$-Nb$_5$Si$_3$ in as-cast binary Nb-Si alloys</td>
<td>59.78</td>
</tr>
<tr>
<td>$\alpha$-Nb$_5$Si$_3$ in annealed binary Nb-Si alloys</td>
<td>63.75</td>
</tr>
<tr>
<td>$\beta$-Nb$_5$Si$_3$ in annealed ternary Nb-Si-Mo alloys</td>
<td>60.51</td>
</tr>
<tr>
<td>$\alpha$-Nb$_5$Si$_3$</td>
<td>62.5</td>
</tr>
<tr>
<td>$\beta$-Nb$_5$Si$_3$</td>
<td>60.4</td>
</tr>
</tbody>
</table>

Fig. 3  BEI of Nb$_5$Si$_2$/Nb$_5$Si$_3$ composites annealed at 1473 K for 100 h: a) Nb-57Si b) Nb-57Si-2Mo.

Fig. 4  Microstructure of directionally solidified Nb$_5$Si$_2$/Nb$_5$Si$_3$ composites. (a) Nb-57Si annealed at 1473 K for 100 h (b) Nb-57Si-2Mo annealed at 1473 K for 100 h.
Effect of Mo Addition on Phase Stability and High-Temperature Strength of NbSi$_2$/Nb$_5$Si$_3$ Composites

Fig. 5 Compression strength of NbSi$_2$/Nb$_5$Si$_3$ composites deformed at an initial strain rate of $1 \times 10^{-4}$.

Nb$_5$Si$_3$. So Mo atoms substitute for Si atoms in Nb-57Si-2Mo. Due to the size of Nb atom similar to Mo atom, Mo atoms always substitute for Nb position in Nb$_5$Si$_3$. Therefore, it is more possible that Si substituting for Nb results in the increase of Si content in $\beta$-Nb$_5$Si$_3$. Moreover, a reasonable assumption can be obtained that Mo atoms substitute for the sites of Si$_{Nb}$, where Si$_{Nb}$ denotes Si atom substituting Nb position. As a result, the -Si-Mo-Si- chains replace the -Si-Si- and -Mo-Mo- chains to -Si-Mo-Si- chains. Hence, in Nb-57Si-2Mo alloys, substitution of Mo for the sites of Si$_{Nb}$ and formation of the strongly bonded -Si-Mo-Si- chains are responsible for the stabilization of $\beta$-Nb$_5$Si$_3$. Similar to Mo$_5$Si$_3$, the bond of -Si-Nb-Si- chains is stronger than -Si-Si- and -Nb-Nb- chains. After Nb-57Si alloys are annealed at 1473 K, the weakly bonded -Si-Si- chains are broken down and the strongly bonded -Si-Nb-Si- chains form. Consequently, $\beta$-Nb$_5$Si$_3$ transforms to -Nb$_5$Si$_3$ in Nb-57Si alloys.

Because Nb$_5$Si$_3$ performs more complex crystal structure and higher melting point than NbSi$_2$, it’s more difficult for dislocation to move in Nb$_5$Si$_3$ than in NbSi$_2$. Then, strength of NbSi$_2$ can obviously affect on the high temperature yield strength of NbSi$_2$/Nb$_5$Si$_3$. Nb$_5$Si$_3$ shows an anomalous strengthening peak in temperature range from 1673 to 1873 K, which was reported to be due to the formation of the dragging atmosphere around the moving dislocation by interstitial and solute atoms. These interstitial atoms are impurity in binary NbSi$_2$, such as oxygen. When the impurity atoms segregate around dislocation and form dragging atmosphere, an additional stress is required for the motion of dislocations to leave the atmosphere. Umakoshi et al. reported that Mo atoms easily gather near the stacking fault between two 1/6(1210) and form the dragging atmosphere. Thus, the addition of Mo in NbSi$_2$ assisted the anomalous strengthening. As a result, the compression strength of Nb-57Si-2Mo alloys at 1773 is up to 593 MPa, far higher than that of Nb-57Si alloys. In addition, the diffusion ability of Mo is lower than that of interstitial atoms. Higher temperature is needed to form the atoms atmosphere around the moving dislocation. As a result, Mo addition changes the anomalous peak temperature of NbSi$_2$ from 1573 to 1773 K. Therefore, the anomalous strengthening of NbSi$_2$ results in the increase of strength of binary Nb-57Si alloys at 1573 K, while that of NbSi$_2$ with Mo is responsible for the increase of strength of ternary Nb-57Si-2Mo at 1773 K.

5. Conclusion

NbSi$_2$/Nb$_5$Si$_3$ composites were produced using a Floating Zone (FZ) method at growth rates of 5 mm/h and 10 mm/h. Low growth rate and heat-treatment result in the transformation from $\beta$-Nb$_5$Si$_3$ to $\alpha$-Nb$_5$Si$_3$ in NbSi$_2$/Nb$_5$Si$_3$ composites. The addition of 2 at% Mo makes $\beta$-Nb$_5$Si$_3$ stable below 1473 K in the NbSi$_2$/Nb$_5$Si$_3$ composites. The strength of ternary Nb-Si-Mo alloys at 1673 K and 1773 K significantly higher than that of binary Nb-Si alloys.

Acknowledgements

This work is supported by the National Natural Science Foundation of China under contract No. 50131030. Part of the experiment is carried out at Kyoto University.

REFERENCES