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## Microstructure of Nb/Nb<sub>5</sub>Si<sub>3</sub> in situ composites<sup>①</sup>

QU Shi-yu(曲士昱), WANG Rong-ming(王荣明), HAN Ya-fang(韩雅芳)  
(Beijing Institute of Aeronautical Materials, Beijing 100095, China)

**[Abstract]** The Nb-10Si (mole fraction, %) alloy was fabricated using the vacuum arc melting method and heat-treated at 1850 °C and 1550 °C for 2~ 100 h in Ar atmosphere. The microstructure of the alloy has been investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM) equipped with X-ray energy dispersive spectrometry (EDS) and transmission electron microscopy (TEM). The results show that 1550 °C, 100 h is an optimum heat-treatment condition to acquire the equilibrium Nb+ Nb<sub>5</sub>Si<sub>3</sub> two phase microstructure. The microstructure of Nb-10Si alloy in the as-cast condition consists of continuous Nb<sub>3</sub>Si matrix and dispersed Nb particles, which implies that the alloy is in the metastable equilibrium state. In the case of 1850 °C, 2 h heat-treatment the Nb particles are coarsened evidently. However, in the heat-treatment condition of 1550 °C for 25~ 100 h the growth of Nb particles is unobvious. After heat-treated at 1550 °C, Nb<sub>3</sub>Si phase transforms into the equilibrium Nb<sub>5</sub>Si<sub>3</sub> and Nb phase with the increase of heat-treatment time gradually. TEM observations reveal that the interface of Nb phase and Nb<sub>5</sub>Si<sub>3</sub> phase is clean and some twins with about 10 nm in width are found.

**[Key words]** silicides; composites; heat treatment; microstructure

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### 1 INTRODUCTION

Refractory metal silicides have attracted considerable interest as potential high temperature structural materials for future turbine engines since the operating temperature of nickel-based superalloys has only an upper limit of about 1100 °C<sup>[1, 2]</sup>. The transition metal silicides with  $x(\text{Metal})/x(\text{Si})$  ratio of 5:3 in particular are attractive since they have higher melting temperatures and lower densities. Among them, Nb<sub>5</sub>Si<sub>3</sub> has the highest melting temperature (2484 °C) and has a density below that of the nickel-based superalloys<sup>[3]</sup>. The Nb-Si system has been of interest as a model experimental system to study the mechanical behavior of in situ composites and the concept of ductile-phase toughening<sup>[4]</sup>. Recent studies have shown that in Nb-Si system the two phase Nb/Nb<sub>5</sub>Si<sub>3</sub> in situ composites exhibit a good balance in mechanical properties, having a reasonably high strength at temperatures up to 1500 °C and high toughness at room temperature<sup>[5, 6]</sup>. These combined properties of the composites provide an attractive basis for developing high temperature structural materials. However, by common casting processing we can only acquire the metastable Nb+ Nb<sub>3</sub>Si phase. To acquire the equilibrium Nb+ Nb<sub>5</sub>Si<sub>3</sub> phase, heat-treatment is needed to transform Nb<sub>3</sub>Si phase to Nb+ Nb<sub>5</sub>Si<sub>3</sub> phase by an eutectoid reaction, i. e. Nb<sub>3</sub>Si → Nb+ Nb<sub>5</sub>Si<sub>3</sub>. So it is important to choose an appropriate heat-treatment system. Though the environmental resistance of Nb-Si alloy under oxidizing environments is catastrophic, it can be improved by alloy-

ing of both the base composite and the coating<sup>[7]</sup>. In present investigation, the microstructure of Nb-10% Si (mole fraction) alloy is investigated.

### 2 EXPERIMENTAL

The raw materials used were high purity Nb (99.5%) and Si (99.9%). The alloy was fabricated in form of 250 g buttons using vacuum arc melting for three times. The heat-treatment was carried out in Ar atmosphere at (1850 ± 5) °C for 2 h and (1550 ± 5) °C for 25, 50, 75 and 100 h, respectively. The samples were cooled down with furnace.

The sample with size of 10 mm × 10 mm × 10 mm cut from the button was polished, then corroded in the water solution of 15% H<sub>2</sub>SO<sub>4</sub>+ 15% HCl+ 8% HNO<sub>3</sub>. The microstructures were investigated using JSM-5600HV/LV scanning electron microscope (SEM) equipped with X-ray energy dispersive spectrometer (EDS). The thin foil with thickness of about 250 μm was manually polished to 50 μm and dimpled to 30 μm in the center, then performed by ion milling polisher. The samples were examined using H-800 and JEOL-2010 transmission electron microscopes (TEM). The structure of various phases were identified by X-ray diffraction (XRD) method using a MXP-AHF18 type X-ray diffractometer.

### 3 RESULTS AND DISCUSSION

The microstructures of Nb-10% Si (mole fraction) alloy in as-cast condition are shown in Fig. 1. It can be seen that the bright particles with size of 1~

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10  $\mu\text{m}$  are dispersed in the continuous matrix. X-ray EDS results show that the matrix is  $\text{Nb}_3\text{Si}$  phase and the bright particles are Nb phase. Two types of bright particles were distinguished by further observation. The larger particles (about 10  $\mu\text{m}$ ) are the primary-Nb phases formed during solidification and the finer particles (about 1  $\mu\text{m}$ ) are the secondary-Nb phases formed during the eutectic reaction. No  $\text{Nb}_5\text{Si}_3$  phase was found by element line distribution scanning analysis. TEM observations confirmed that the matrix is the tetragonal  $\text{Nb}_3\text{Si}$  phase (space group is  $\text{Im}3\text{m}$  and  $a = 0.330656 \text{ nm}$ ) and the spherical particle is the BCC-type Nb phase (space group is  $\text{P}4_2/\text{n}$ ,  $a = 1.021 \text{ nm}$  and  $c = 0.519 \text{ nm}$ ), which is in agreement with SEM results. XRD results were further confirmed that no other phases exist except the  $\text{Nb}_3\text{Si}$  and Nb phases in as-cast Nb-10Si alloy.

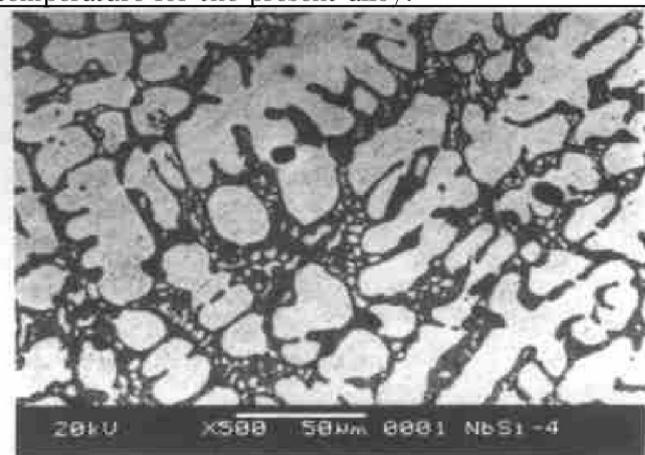


**Fig. 1** SEM back scattered electron image of as-cast Nb-10Si alloy

According to the Nb-Si binary phase diagram, the equilibrium microstructure of Nb-10Si alloy should be composed of Nb and  $\text{Nb}_5\text{Si}_3$  phases. The fact that the Nb+  $\text{Nb}_3\text{Si}$  phase instead of the equilibrium Nb+  $\text{Nb}_5\text{Si}_3$  phase formed in Nb-10Si alloy indicated that as-cast alloy is in the metastable equilibrium.

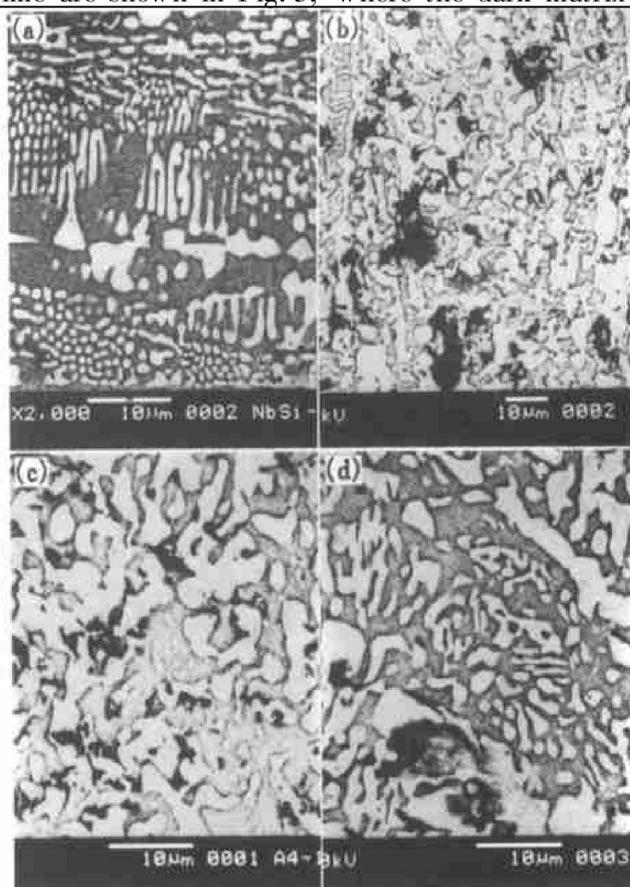
In order to acquire the equilibrium Nb+  $\text{Nb}_5\text{Si}_3$  two-phase microstructure, Nb-10Si alloy must be heat-treated. Heat-treatment temperature of 1850  $^{\circ}\text{C}$  upon the eutectoid transformation temperature (1783  $^{\circ}\text{C}$ ) of the  $\text{Nb}_3\text{Si}$  was first selected to decrease the length of heat-treatment time. The microstructure of Nb-10Si alloy heat-treated at 1850  $^{\circ}\text{C}$  for 2 h is shown in Fig. 2. It can be seen that the primary-Nb particles are markedly coarsened up to 20~30  $\mu\text{m}$  and connected each other, forming an interconnectional system. X-ray EDS analysis revealed that the matrix is still  $\text{Nb}_3\text{Si}$  phase, indicating that the metastable equilibrium  $\text{Nb}_3\text{Si}$  phase cannot be decomposed to equilibrium  $\text{Nb}_5\text{Si}_3$  phase under the heat-treatment of 1850  $^{\circ}\text{C}$ , 2 h due to the shorter heat-treatment time. As prolonging the duration of heat-treatment at high

temperature is not denefit to the equipment and the coarsening of Nb particles due to too high heat-treatment temperature (as shown in Fig. 2) will result in the decrease of mechanical property, it is considered that 1850  $^{\circ}\text{C}$  may not be a suitable heat-treatment temperature for the present alloy.



**Fig. 2** SEM back scattered electron image of Nb-10Si alloy heat-treated at 1850  $^{\circ}\text{C}$  for 2 h

According to the reasons mentioned above, the heat-treatment condition of lower temperature of 1550  $^{\circ}\text{C}$  for longer periods from 25 h to 100 h was chosen for the alloy. The microstructures of Nb-10Si alloy heat-treated at 1550  $^{\circ}\text{C}$  for various periods of time are shown in Fig. 3, where the dark matrix is



**Fig. 3** SEM back scattered electron images of Nb-10Si alloy heat-treated at 1550  $^{\circ}\text{C}$  for different time  
(a) —25 h; (b) —50 h; (c) —75 h; (d) —100 h

niobium silicide and bright secondary phase is Nb phase. It can be seen that the Nb particles remain almost the same size when the heat-treatment time changes from 25 h to 100 h. X-ray EDS results indicated that the matrix of Nb-10Si alloy heat-treated at 1 550 °C for 25 h is still Nb<sub>3</sub>Si phase mainly and with the increase of heat-treatment time the Nb<sub>3</sub>Si matrix transforms to Nb<sub>5</sub>Si<sub>3</sub> phase gradually.

XRD patterns of Nb-10Si alloy heat-treated at 1 550 °C for various time are shown in Fig. 4. After 1 550 °C, 25 h heat-treatment, the stronger peaks of Nb and Nb<sub>3</sub>Si accompanied with the weaker Nb<sub>5</sub>Si<sub>3</sub> peaks exist. With the increase of heat-treatment time, the Nb<sub>5</sub>Si<sub>3</sub> peaks become stronger; while Nb<sub>3</sub>Si peaks become weaker. After 1 550 °C, 100 h heat-

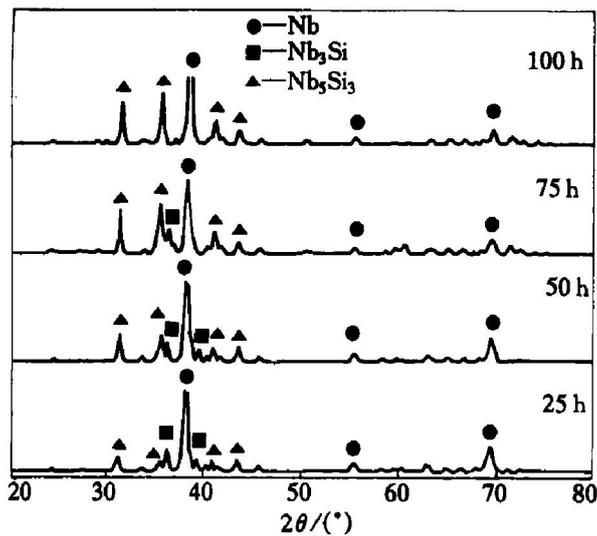


Fig. 4 XRD patterns of Nb-10Si alloy heat-treated at 1 550 °C for different time

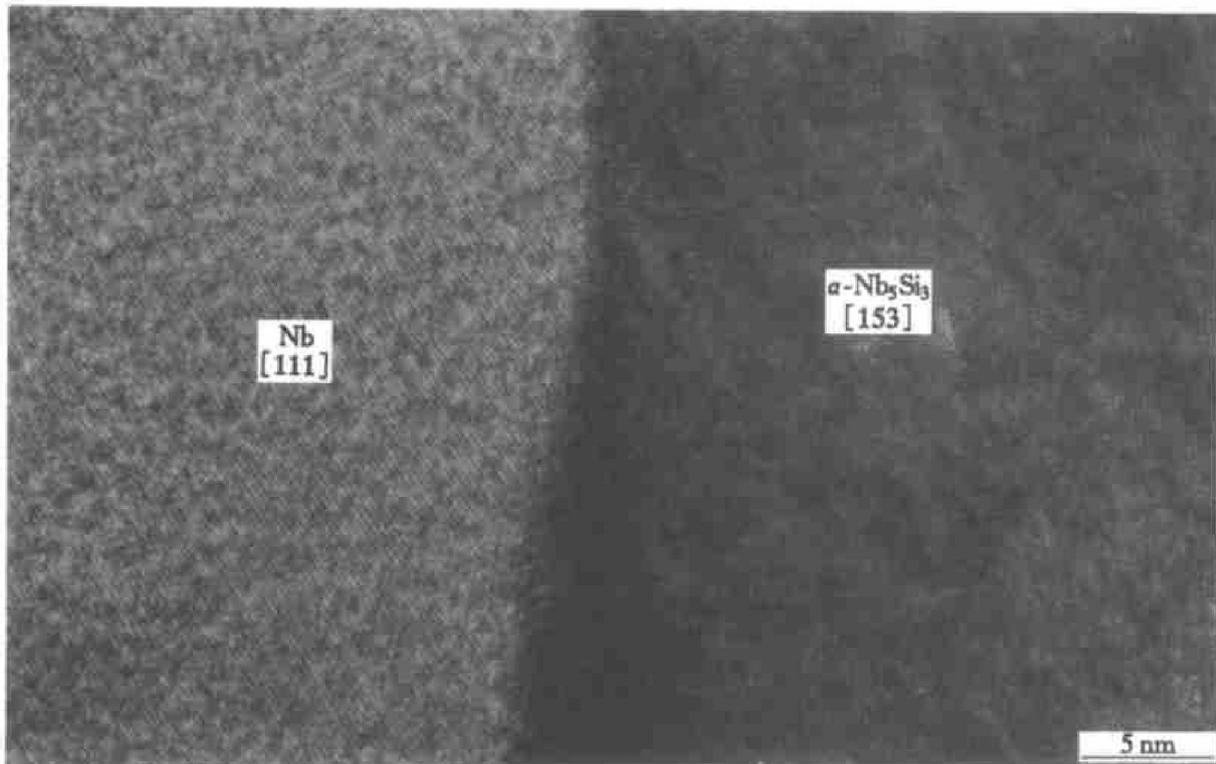


Fig. 5 HREM image of interface of Nb phase and Nb<sub>5</sub>Si<sub>3</sub> phase in Nb-10Si alloy heat-treated at 1550 °C for 100 h

treatment, the Nb<sub>3</sub>Si peaks entirely transformed into Nb<sub>5</sub>Si<sub>3</sub> peaks, which is consistent with the SEM results.

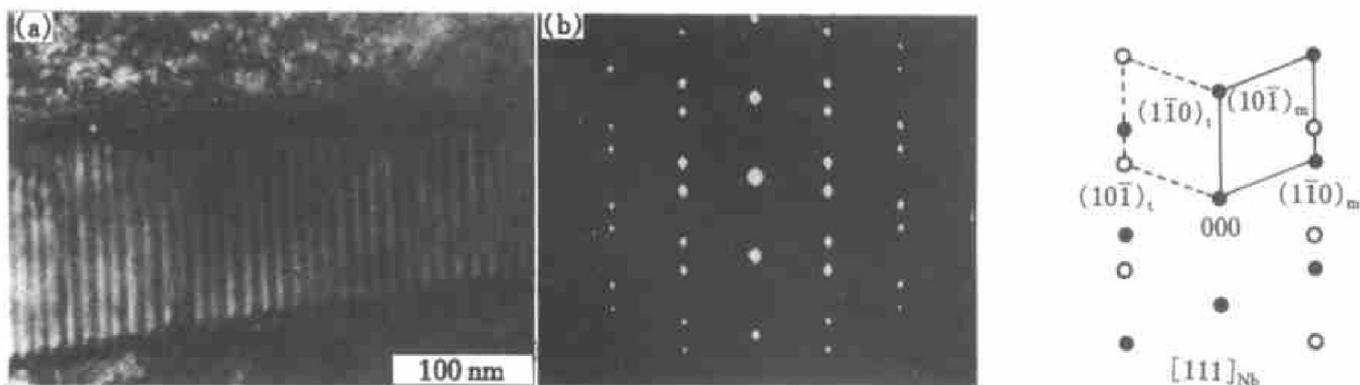
The results in Fig. 3 and Fig. 4 indicate that during the heat-treatment at 1 550 °C the Nb<sub>3</sub>Si phase transforms into Nb<sub>5</sub>Si<sub>3</sub> phase gradually via an eutectoid reaction: Nb<sub>3</sub>Si → Nb + Nb<sub>5</sub>Si<sub>3</sub>. After 1 550 °C, 100 h heat-treatment, the microstructure of Nb-10Si alloy consists of the continuous Nb<sub>5</sub>Si<sub>3</sub> matrix and the dispersed Nb particles, while no remarkable growth of Nb particles occurred. This illuminated that the 1550 °C, 100 h is an optimum heat-treatment condition for Nb-10Si alloy.

HREM image of interface between Nb phase and Nb<sub>5</sub>Si<sub>3</sub> phase in Nb-10Si alloy heat-treated at 1 550 °C for 100 h is shown in Fig. 5. It can be seen that the interface between Nb phase and Nb<sub>5</sub>Si<sub>3</sub> phase is clean. Selected-area electron diffraction pattern analysis revealed that there is no definite orientation relationship between Nb and Nb<sub>5</sub>Si<sub>3</sub> phase.

TEM study showed that some twins with about 10 nm in width occurred in Nb-10Si alloy heat-treated at 1 550 °C for 100 h, as shown in Fig. 6(a). SAD pattern analysis showed that this is [111] twins of Nb, as shown in Fig. 6(b).

#### 4 CONCLUSIONS

- 1) The 1 550 °C, 100 h heat-treatment condition is an optimum one for Nb-10Si alloy to acquire the equilibrium Nb + Nb<sub>5</sub>Si<sub>3</sub> two-phase microstructure.
- 2) For Nb-10Si alloy heat-treated at 1 550 °C for



**Fig. 6** Twins in Nb-10Si alloy heat-treated at 1 550 °C for 100 h

(a) —Bright-field image; (b) —SAD pattern; (c) —Demarcation

100 h, the interface between Nb phase and Nb<sub>5</sub>Si<sub>3</sub> phase is clean and some twins with about 10 nm in width occur.

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