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Citation	Vacuum, 83(1), 157-160 https://doi.org/10.1016/j.vacuum.2008.04.080
Issue Date	2008-09-04
Doc URL	http://hdl.handle.net/2115/35633
Type	article (author version)
File Information	Vacuum2008.pdf

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Title:

Interfacial reactions in Nb/NbSi₂ and Nb/NbSi₂-B systems

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Abstract:

For the use of Nb-base alloys at high temperatures, a high oxidation resistant coating such as a NbSi₂ coating is required. In the present study, to clarify the physico-chemical compatibility between Nb and NbSi₂, the extent of the interfacial reaction and the reaction products were studied at temperatures ranging from 1573 to 1773 K. Growth of the reaction layer formed in the interfacial reactions was caused by the preferential diffusion of Si towards to the Nb side, leading to the formation of a Nb₅Si₃ layer. The growth followed a parabolic rate law, and the growth rate constant was expressed by $k_p \text{ (m}^2 \text{ s}^{-1}\text{)} = 7.98 \times 10^{-10} \exp(-131.84 \text{ kJmol}^{-1}/RT)$. In addition, behavior of boron in the Nb/NbSi₂ interfacial reaction was clarified.

Keywords: Nb/NbSi₂ reaction, Boron, Reaction mechanism, Growth kinetics

1. Introduction

Nb-base alloys are promising candidates for structural materials at ultra-high temperatures, because of the high melting point and superior mechanical properties. However, it is well known that they have poor oxidation resistance. Therefore, for the use of Nb-base alloys at high temperatures, a high oxidation resistant coating is required. NbSi₂ possesses a thermal expansion coefficient closed to those of Nb-base alloys. If selective oxidation of Si occurs in NbSi₂, it could show excellent oxidation resistance and NbSi₂-coating could offer outstanding improvement of the oxidation resistance of Nb-base alloys.

Some of refractory metal disilicides, for example MoSi₂ [1-3] and WSi₂ [4, 5], show excellent oxidation resistance at high temperatures. This is due to the formation of a protective SiO₂ scale by selective oxidation of Si. On the other hand, NbSi₂ shows relatively poor oxidation resistance

and its oxidation behavior is complex [6-8]. However, it has been reported that the addition of boron to metal disilicides leads to improvement of oxidation resistance of them [9-10]. This is probably due to the formation of a borosilicate layer having higher plasticity than silica, in addition to improvement of adhesive bonding of oxide scale to substrate. In fact, we demonstrated that addition of boron into NbSi₂ leads to outstanding improvement of oxidation resistance of NbSi₂ [11]. Therefore, Nb-base alloys coated with NbSi₂-B can be fully recognized to be promising candidate materials for ultra-high temperature applications. However, the physico-chemical compatibility between Nb-base alloys and NbSi₂-B has not been clarified.

In the present study, as a fundamental study for the Nb-based alloy/NbSi₂-B system, the physico-chemical compatibility between Nb and NbSi₂, that is, the extent of the interfacial reaction, the reaction products and reaction mechanism were studied at temperatures ranging from 1573 to 1773 K. Similarly, the interfacial reaction between Nb and NbSi₂-B was studied in the same temperature range, and the differences in the reaction mechanisms between Nb-NbSi₂ and Nb/NbSi₂-B systems were discussed.

2. Experimental

As starting materials, Nb, Si, and B powders (purity of 99.9%) were used. After pressed Nb powder and Nb-Si mixed powder (atomic ratio of Si to Nb is 2) or Nb-Si mixed powder containing 2 weight% B (the atomic ratio of NbSi₂-2wt%B is Nb-52at%Si-22at%B) in a carbon die belonging to a spark plasma sintering equipment, the reaction couples were heated up to 1573, 1673, or 1773 K with a heating rate of 20 K/min under a compressive stress of 40 MPa. Here, the temperatures were measured on the surface of graphite die by using a noncontact infrared temperature sensor. So, it is supposed that there is a little difference in temperature between sample and outer surface of graphite die. The holding times at each temperature were 0, 1, and 4 hours. After the heating, the diffusion couple was cooled in the sintering equipment, and NbSi₂-B was composed of NbSi₂,

NbB₂ and Si phases.

The cross-sections of the reacted specimens were observed and analyzed using a scanning electron microscope (SEM) and an electron microprobe analyzer (EPMA).

3. Results and discussion

3.1 Structure and growth behavior of reaction layer

3.1.1 Nb/NbSi₂ system

Figure 1 shows SEM photographs of the cross-sections of the reaction layers formed in the Nb/NbSi₂ interfaces at 1673 K for 0, 1 and 4 hours. In this system, uniform reaction layers in thickness were formed. These compounds were identified to be Nb₅Si₃ by EPMA analysis. These results are well corresponded to the Nb-Si phase diagram because there is only one compound, Nb₅Si₃, between Nb and NbSi₂.

The marker experiments with alumina powders demonstrated that formation of Nb₅Si₃ layers was caused by the preferential diffusions of Si from NbSi₂ phase to Nb phase.

Change in thickness of the reaction layers (Nb₅Si₃) with time at various temperatures is shown in **Fig. 2** in which the thickness at 0 hr corresponds to that of the reaction layer formed during heating process to each temperature. The curves roughly follow the parabolic rate law. This means that diffusion of Si through the reaction layer may be the rate-determining step in growth of the reaction layer.

3.1.2 Nb/NbSi₂-B system

Figure 3 shows SEM photographs in the cross-sections of the reaction layers formed in the Nb/B-NbSi₂ interfaces at 1673 K for 0, 1 and 4 hours. The EPMA analysis indicated that reaction layers formed between Nb and B-NbSi₂ may be composed of the Nb₅(Si, B)₃ phase. At 0 hr, the reaction layer grows perpendicular to the interface and as the result is parallel to it, whereas at 1

hour and 4 hours, the B-NbSi₂/reaction layer interfaces have irregular and roughened appearance. Such irregularity in the B-NbSi₂/reaction layer interface was not observed at 1573 K.

EPMA analysis indicated that the composition of reaction product in the irregular part was almost identical with that in the part near Nb. Therefore, such coarse irregularities may be caused by the existence of NbB₂ and Si phases dispersed in the sintered B-NbSi₂. Namely, the NbB₂ grains contacted with a reaction layer (Nb₅Si₃) transforms to Nb₅(Si, B)₃ via following steps:

As the result, NbB₂ grains existed in sintered NbSi₂-B lead to localized formation of Nb₅(Si, B)₃ on the Nb₅Si₃ reaction layer, resulted in the formation of irregular reaction layer/NbSi₂-B interface.

Figure 4 shows growth behavior of the reaction layer composed of Nb₅(Si, B)₃. We measured two kind of thickness of the reaction layers; the thickness of Nb₅(Si, B)₃ layer approximately parallel to the interface, namely the thickness of uniform reaction zone (in other wards, minimum thickness of reaction layer), and the total thickness including the locally-grown reaction layer (in other wards, total thickness of reaction zone). The results demonstrate that the addition of B leads to the formation of thicker total reaction zone, but on the contrary, that the growth of Nb₅(Si, B)₃ layer having uniform reaction zone is slightly suppressed. This means that the Si diffusion towards Nb side is suppressed by adding boron. According to EPMA analysis, a region of quite high B concentration in the Nb/Nb₅(Si, B)₃ interface were observed, as shown in **Fig. 5**. The B rich layer (probably Nb boride) plays a role of a barrier for diffusion of Si toward Nb side, as pointed out by Tsirlin et al. [12].

3.2 Growth kinetics of reaction layer

A plot of the square thickness of reaction layer against reaction time in the Nb/NbSi₂ system indicated that the growth of reaction layer obeys a parabolic rate law, $d^2=k_p t$, where d , k_p and t are the thickness of reaction layer, the parabolic rate constant and the reaction time, respectively. **Figure 6** shows Arrhenius plot of the parabolic rate constants estimated from the slope of d^2 - t plot. From this figure, the growth rate of the reaction layer can be represented as follows:

$$k_p(\text{m}^2\text{s}^{-1})= 7.98 \times 10^{-10} \exp(-131.84 \text{ kJmol}^{-1}/RT).$$

Marker experiments demonstrated that Si diffusion from the NbSi₂ side toward the Nb side controlled the growth of the reaction layer. Hence, using Fick's first law, the diffusion coefficient of Si, D , in the reaction layer was represented by

$$D=d^2\pi/4t$$

where d is the thickness of the grown Nb₅Si₃ and t is the duration time. By substituting the experimental values for this equation, we can obtain the diffusion coefficient. Arrhenius plot is shown in **Fig. 7**. Consequently, the diffusion coefficient of Si in the Nb₅Si₃ phase can be represented by the following equation.

$$D (\text{m}^2\text{s}^{-1}) = 4.23 \times 10^{-14} \exp (-97.59 \text{ kJmol}^{-1}/ RT)$$

4. Conclusions

In both of the interfacial reactions in the Nb/NbSi₂ and Nb/NbSi₂-B systems, the growth of the reaction layer was caused by the preferential diffusion of Si toward the Nb side, leading to the formation of Nb₅Si₃ and Nb₅(Si, B)₃ layer, respectively.

(1) The reaction layer formed in the Nb/NbSi₂ interface grew perpendicular to the interface with a uniform thickness of reaction layer. On the other hand, the addition of B to NbSi₂ led to formation of a rough interface of B-NbSi₂ and the reaction layer. This was related to the existence of NbB₂ and Si phases in as-sintered B-NbSi₂.

(2) The growth of reaction layer obeyed a parabolic rate law, and the growth rate constant and the

diffusion coefficient of Si in Nb₅Si₃ were represented by $k_p \text{ (m}^2 \text{ s}^{-1}\text{)} = 7.98 \times 10^{-10} \exp(-131.84 \text{ kJmol}^{-1}/RT)$ and $D \text{ (m}^2 \text{ s}^{-1}\text{)} = 4.23 \times 10^{-14} \exp(-97.59 \text{ kJmol}^{-1}/RT)$, respectively.

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Figure captions

Fig. 1 Cross-sectional photographs of reaction layers formed in the Nb/NbSi₂ interfaces at 1673 K for (a)0h (b)1h (c)4hrs.

Fig. 2 Thickness of the Nb₅Si₃ layer as a function of reaction time.

Fig. 3 Cross-sectional photographs of reaction layers formed in the Nb/B-NbSi₂ interfaces at 1673 K for (a)0h (b)1h (c)4hrs.

Fig 4 Thickness of the Nb₅(Si,B)₃ layer as a function of reaction time (the broken lines show the total thickness include partial Nb₅(Si,B)₃).

Fig. 5 Element mapping in the cross-section of the Nb/B-NbSi₂ interface.

Fig. 6 Arrhenius plot of the parabolic rate constant of reaction layer in the Nb/NbSi₂ system.

Fig. 7 Arrhenius plot of the diffusion coefficient of Si in Nb₅Si₃.

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Fig. 7 Arrhenius plot of the diffusion coefficient of Si in Nb_5Si_3 .