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Improvement of Oxidation Resistance of NbSi$_2$ by Addition of Boron

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Abstract. NbSi$_2$ is a promising candidate as a coating material for Nb-base alloys. However, it shows complicated oxidation behavior, depending on oxidation temperature. In the present study, in order to clarify the oxidation resistance of NbSi$_2$, oxidation tests of sintered NbSi$_2$ were carried out at temperatures ranging from 773 to 1673 K in air. Moreover, the effect of addition of boron on oxidation resistance of NbSi$_2$ was clarified. NbSi$_2$ showed accelerated oxidation at temperatures of 1073 K and above. The accelerated oxidation was caused by formation of a porous oxide layer, which may be due to the phase transformation from amorphous to crystalline SiO$_2$. The addition of boron to NbSi$_2$ leads to the formation of a protective borosilicate layer, resulting in great improvement of the oxidation resistance. Consequently, NbSi$_2$ added with boron shows excellent oxidation resistance up to at least 1673 K.

Introduction

Nb-base alloys are promising candidates for applications at ultra-high temperatures, because of the high melting point and high temperature strength. 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. NbSi$_2$ possesses a thermal expansion coefficient closed to those of Nb-base alloys and probably shows excellent oxidation resistance if selective oxidation of Si occurs. Thus, it is expected that NbSi$_2$-coating offers outstanding improvement of the oxidation resistance of Nb-base alloys.

Some refractory metal disilicides, for example MoSi$_2$ [1-3] and WSi$_2$ [4,5], show excellent oxidation resistance at high temperatures. This is due to the formation of a protective SiO$_2$ scale by selective oxidation of Si. On the other hand, Nb silicides show poor oxidation resistance at high temperatures and its oxidation behavior is complicated [6-8]. Therefore, the improvement of oxidation resistance of NbSi$_2$ is required for actual services.

It has been reported that the addition of boron to metal disilicides leads to improvement of their oxidation resistance [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. However, as shown in oxidation of Nb$_5$Si$_3$B$_2$ [11], addition of excessive amounts of boron often leads to evaporation of B$_2$O$_3$, resulting in degradation of oxidation resistance.

In the present study, in order to determine the optimum composition of boron in oxidation resistance of B-NbSi$_2$ alloys, oxidation tests of some B added NbSi$_2$ (B-NbSi$_2$) alloys were carried out in air, and the oxidation behavior and the structures of oxide scales were clarified.

Experimental

Fabrication of specimen: The mixed powders consisting of NbSi$_2$ and B were ball-milled for 5 min at a rate of 300 rpm. The compositions of starting mixed powders are shown in Table 1. As a reference, the composition of Nb$_5$Si$_3$B$_2$ is also shown in table 1. In all specimens used in the present study, the atomic ratio of Si to Nb was 2. The mixed powders were sintered by using a spark plasma sintering (SPS)

Table.1 Composition of starting mixed powders.

wt.%B	at. %		
	Nb	Si	B
0.5	31.2	62.3	6.5
2.0	26.0	52.0	22.0
3.0	23.4	46.7	29.9
$Nb_5Si_3B_2$	50.0	30.0	20.0

method. In this sintering method, the mixed powders were packed in a graphite die (outer diameter is 25 mm and inner diameter 15 mm) under a compressive stress of 40 MPa, and then a pulsating current was passed through the mixed powders and the graphite die in an evacuated chamber of 6 Pa. The heating rate was 0.33 K/sec, and the maximum pulsating current of about 800 A was passed to heat up to 1673 K. The densities of $NbSi_2$ and B-$NbSi_2$ measured by Archimedean method were about 98-99%. The sintered specimens were characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), and an electron probe microanalyzer (EPMA).

Oxidation tests: Specimens for oxidation tests were cut into about 4x7x1 mm pieces from the sintered compacts. The surfaces were polished to 1 micrometer diamond finish, and then cleaned ultrasonically in acetone bath. Oxidation tests were carried out in air at temperatures ranging from 773 to 1673 K. Oxidation kinetics was evaluated by measuring the mass before and after oxidation. The oxidized specimens were characterized by using XRD, SEM, and EPMA.

Results and Discussion

Oxidation of NbSi₂

Oxidation kinetics: Fig. 1 shows oxidation kinetics of $NbSi_2$ at various temperatures in air. The mass gain by oxidation, especially at 1073 K and temperatures above 1373K, increases almost linearly with oxidation time, and the temperature dependence of mass gain is very complicated. To understand the temperature dependence, the mass gains after oxidation for 360 ks (100 hr) are plotted as a function of temperature in Fig. 2. The mass gains below about 1000 K are negligible, forming a protective oxide scale. As temperature increases, the mass gain rapidly increased and reached a maximum value at 1073 K. Then, it decreases with increasing temperature and reaches a minimum value. Further increase in temperature leads to abrupt increase in mass gain. Thus, $NbSi_2$ shows complex oxidation behavior, depending on temperature.
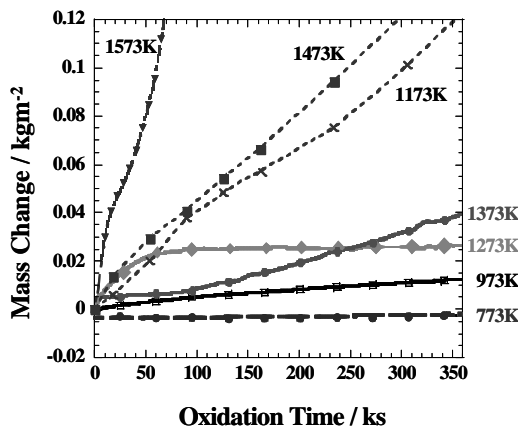

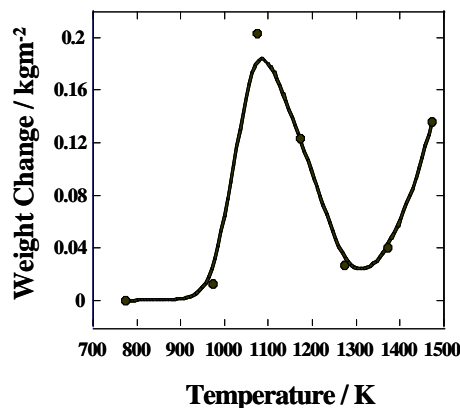
Fig.1 Oxidation kinetics of NbSi₂

Fig.2 Mass gain after 360 ks-oxidation of NbSi₂ in air

Structure of oxide scale: To clarify oxidation mechanism of $NbSi_2$, SEM observation and EPMA analysis of oxide scales were carried out. Fig. 3 shows cross-sectional SEM images and concentration profiles of Nb, Si and O in the oxide scales formed in oxidation for 360ks at various temperatures. A dense and thin scale is formed at 973 K, whereas the formation of a porous and thick oxide scale at 1073 K is observed. The oxide scale formed at 1273 K is appreciably thinner than that at 1073 K, and further increase in temperature leads to the formation of thicker oxide scales. All oxide scales consist of mixed oxides of Nb_2O_5 and SiO_2, and these oxides are uniformly distributed in the oxide scale. In addition, the atomic ratio of Si to Nb in the oxide scales is close to 2, which implies that the oxide scale was non-protective against the inward transport of oxygen. In other words, these results demonstrate that high oxygen potential at the interface of oxide scale/$NbSi_2$-substrate results in simultaneous oxidation of Nb and Si.
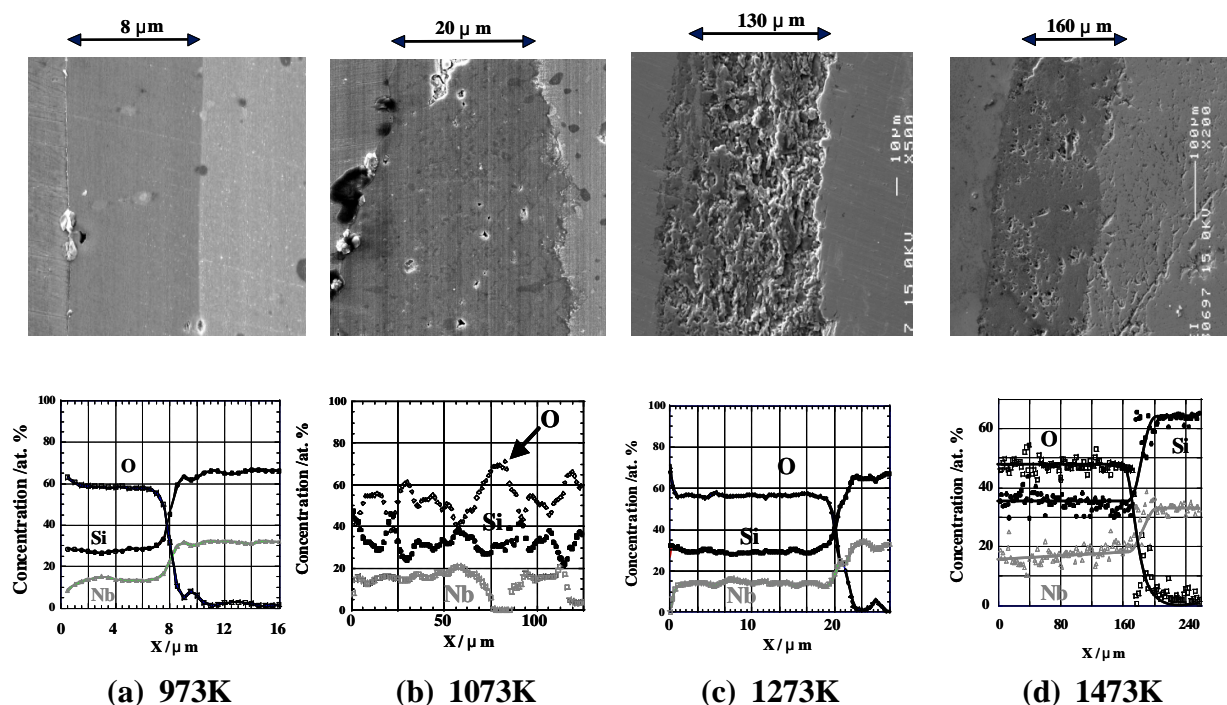

Fig.3 Cross-sectional SEM images of scales formed on $NbSi_2$ for 360 ks at various temperatures.

Cause of strong temperature dependence: As described above, oxidation behavior of $NbSi_2$ strongly depends on oxidation temperature. In particular, oxidation at 1073 K leads to formation of a porous oxide scale. XRD results did not show a cristobalite phase at temperatures below 973 K, and the spectrum of cristobalite at 1073 K was broad. Namely, 1073 K may be the transition temperature from amorphous phase to crystalline phase of SiO_2 forming on $NbSi_2$. The formation of a porous oxide scale at 1073 K, therefore, is probably caused by reduction in volume by crystallization of SiO_2 during oxidation. At medium temperatures (1273-1373 K), relatively-dense oxide scales are formed. This is speculated to be due to sintering of SiO_2 and Nb_2O_5 grains. However, the oxide scales at higher temperatures grow in high oxidation rates. This demonstrates that the oxide scales are still non-protective against inward transport of oxygen at high temperatures and oxygen potential at the interface of oxide scale/$NbSi_2$ substrate is enough high to oxidize Nb. This is supported by the distribution profiles of Nb_2O_5 and SiO_2 in the oxide scales.

Oxidation of B-NbSi$_2$

The poor oxidation resistance of NbSi$_2$ is probably caused by porosity in the oxide scale. Therefore, decrease in porosity leads to improvement of oxidation resistance of NbSi$_2$. It is known that the addition of boron into SiO$_2$-forming silicides, such as Mo$_5$Si$_3$ [9] and ReSi$_{1.75}$ [10], improve the oxidation resistance, because of sealing of pores due to high plasticity of borosilicate, namely formation of a dense oxide scale.

In this section, results on effect of addition of boron to NbSi$_2$ on oxidation behavior are described.

Structure of sintered B-NbSi$_2$: Fig. 4 shows microstructures of sintered B-NbSi$_2$ having various boron concentrations. The reaction products in the sintering of the mixed powders of boron and NbSi$_2$ powders are shown in Table 2. These products were determined from the results of XRD and EPMA analysis. In all sintered B-NbSi$_2$ bodies, a major phase is NbSi$_2$ dissolved minute amounts of B, and small amounts of NbB$_2$ (white colored phase) are surrounding free Si grains (black colored phase) or SiO$_2$ grains. In addition, SiO$_2$ inclusions were not observed in high B NbSi$_2$. This may be caused by formation and subsequent evaporation of B$_2$O$_3$.

Table.2 Products in sintering of B and NbSi$_2$ powder.

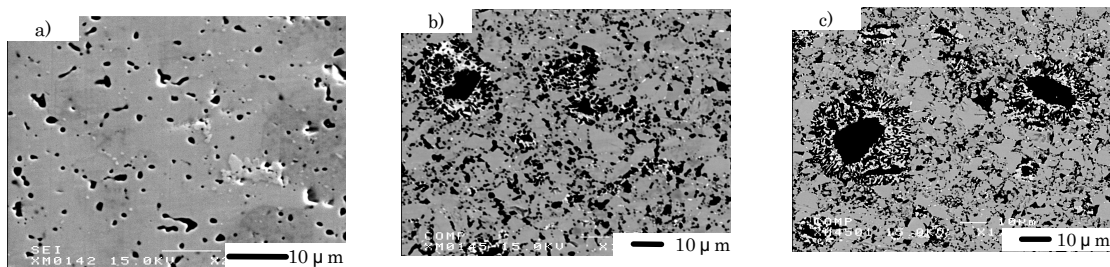| Color of phase	NbSi$_2$	NbSi$_2$-0.5wt%B	NbSi$_2$-2.0wt%B	NbSi$_2$-3.0wt%B
Black	SiO$_2$	SiO$_2$	Si (+B)	Si (+B)
Gray	NbSi$_2$	NbSi$_2$ (+B)	NbSi$_2$ (+B)	NbSi$_2$ (+B)
White	-	NbB$_2$	NbB$_2$	NbB$_2$

Fig.4 Microstructures of sintered B-NbSi$_2$. (a) 0.5wt%B (b) 2.0wt%B (c) 3.0wt%B

Oxidation behavior: Fig. 5 shows the temperature dependence of mass gain in oxidation for 360 ks (100 hr) of various B-NbSi$_2$. Though the mass gains in B-NbSi$_2$ at 973 K increase more than that in NbSi$_2$, remarkable improvement of oxidation resistance by the addition of boron is recognized at higher temperatures. In particular, abrupt increase in mass gain at 1073 K in NbSi$_2$ is completely suppressed in B-NbSi$_2$ having boron concentration above 3.0 wt%. Further, B-NbSi$_2$ specimens demonstrate excellent
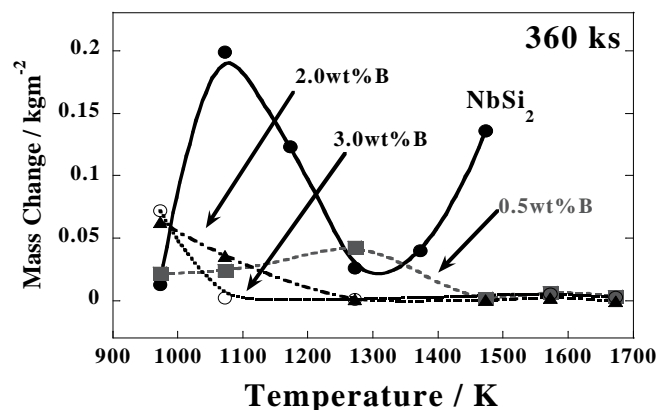

Fig.5 Mass gain after 360 ks-oxidation of B-NbSi$_2$ in air.

oxidation resistance even at 1673 K. On a relationship between boron concentration and oxidation resistance, boron concentration requiring for improvement of oxidation resistance is liable to decrease with increasing temperature. For example, the boron concentrations of 3.0 wt% at 1073 K, 2.0 wt% at 1273 K, and 0.5 wt% at 1473 K are required for remarkable improvement of oxidation resistance of $NbSi_2$.

Structure of oxide scale: As demonstrated above, B-$NbSi_2$ shows excellent oxidation resistance. This is speculated to be due to change in the structure of oxide scale. Therefore, the structures were observed using SEM. Fig. 6 shows the cross-sectional SEM photographs of the oxide scales formed on 3 wt%B-$NbSi_2$ in oxidation for 360 ks at 973, 1273, and 1673 K. The oxide scale formed at 973 K is porous, whereas the scales formed at higher temperatures are remarkably thin and dense. In addition, the
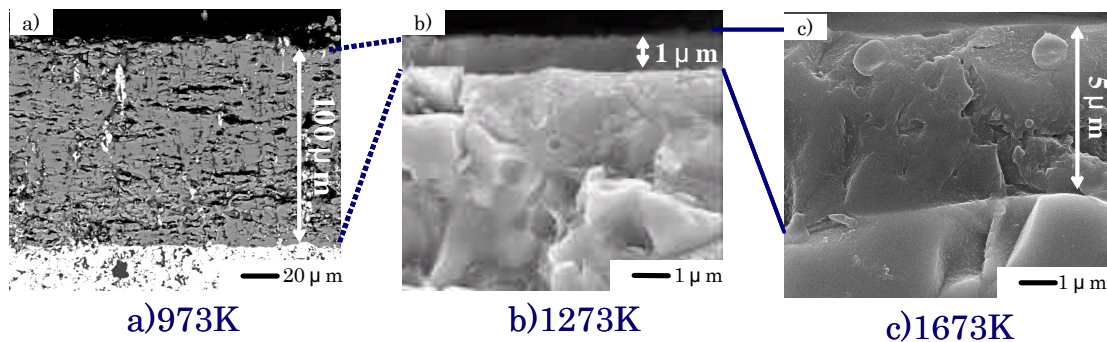

a)973K   b)1273K   c)1673K

Fig.6 Cross-sectional SEM images of scales formed on 3.0wt%B-$NbSi_2$ in oxidation for 360 ks in air.
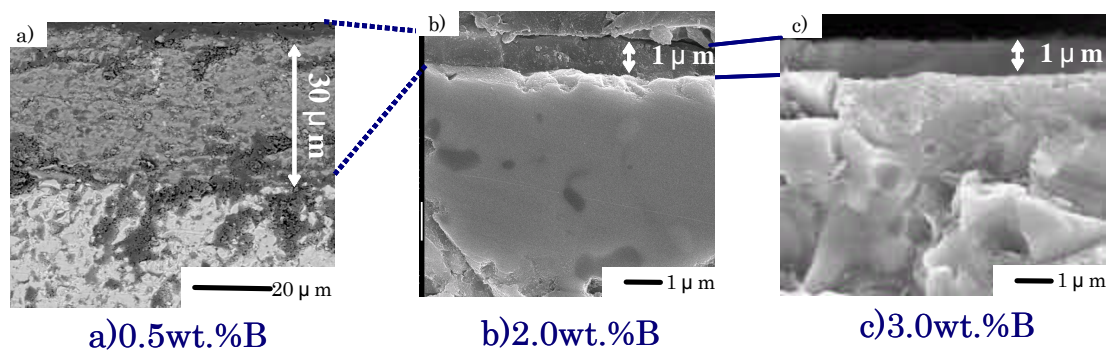

a)0.5wt.%B   b)2.0wt.%B   c)3.0wt.%B

Fig.7 Cross-sectional SEM images of scales formed on B-$NbSi_2$ in oxidation for 360 ks at 1273 K.

structures of oxide scales formed on 0.5, 2.0, and 3.0 wt%B-$NbSi_2$ for 360 ks at 1273 K are shown in Fig. 7. At this temperature, it is observed that B-$NbSi_2$ specimens having boron concentration of 2 wt% and above form a thin and dense oxide scale. These results correspond to temperature dependence of oxidation behavior.

Effect of boron addition: It can be concluded that the boron addition leads to remarkable improvement of oxidation resistance of $NbSi_2$. According to EPMA analysis, it was fpund that the Nb concentration in a porous thick oxide scale was about 15 at%, whereas that in a protective (thin and dense) was below 3 at%. These results demonstrate that the formation of a borosilicate layer, which has higher plasticity than crystalline SiO_2, leads to selective oxidation of Si and B, because the dense borosilicate layer lowers the oxygen potential at the interface of oxide scale/substrate to the value below the equilibrium dissociation pressure of Nb_2O_5.

Conclusions

Oxidation tests of sintered $NbSi_2$ and B-$NbSi_2$ were carried out at temperatures ranging from 773 to 1673 K in air, and the effect of boron addition on oxidation resistance of $NbSi_2$ was clarified. Based on the

oxidation tests, the following conclusions were obtained.

(1) NbSi$_2$ shows accelerated oxidation at temperatures of 1073 K and above. The accelerated oxidation was caused by formation of porous oxide layer.

(2) The addition of boron to NbSi$_2$ leads to the formation of a protective borosilicate layer, resulting in remarkable improvement of the oxidation resistance.

(3) NbSi$_2$ with boron is serviceable up to at least 1673 K in the view of oxidation resistance.

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