Microstructure and Oxidation Behavior of Boron-Added WSi$_2$ Compact$^{*1}$

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In order to improve the oxidation resistance of WSi$_2$ at 873–1473 K, B-added WSi$_2$ was fabricated by a spark plasma sintering method and oxidation tests were carried out in air. The fabricated B-added WSi$_2$ consists of WSi$_2$, Si, and W$_2$B$_5$. The addition of B into WSi$_2$ leads to the formation of a protective borosilicate scale, resulting in improvement of the oxidation resistance. Requisite concentration of B for the formation of a protective borosilicate scale decreases as the temperature is raised. Consequently, the addition of 2 or 3 mass% B is the most effective for improvement of the oxidation resistance of WSi$_2$ in the temperature range of 873–1473 K. Such effect of B on high-temperature oxidation of WSi$_2$ is also discussed. [doi:10.2320/matertrans.MRA2008002]

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1. Introduction

From the viewpoint of energy resource saving and reduction in CO$_2$ emissions, we have to attain high efficiency for energy conversion systems such as gas turbine and jet engine systems. However, at present this depends much on the high-temperature performance of Ni-base superalloys. Future high-temperature structural applications will require materials with increasing performances. This is the reason why intermetallics,$^{1–4}$ ceramics,$^5$ carbon composites,$^{6–8}$ and refractory metals,$^{9,10}$ are candidates for replacing the current Ni-base superalloys. Silicide becomes one of the above candidates, because it has high strength and can form a protective SiO$_2$ scale at very high temperature.

When metal disilicides form a protective SiO$_2$ scale, they show excellent oxidation resistance. The structures of oxide scales formed on metal disilicides are classified into three groups: (1) silica scale, (2) mixed oxide (silica + metal oxide) scale, and (3) double layered (silica/outer side)/metal oxide scale.$^{13}$

On WSi$_2$, it has been reported that its oxidation behavior is complicated, and the structures of their scales show the 3 types,$^{13–16}$ depending on temperature ranges. At temperatures below 1073 K, the scales consist of mixed oxides of WO$_3$ and SiO$_2$, indicating a low oxidation rate. In an intermediate temperature range (1073–1473 K), scales having double-layer structure are formed. The outer and inner layers are consisting of SiO$_2$ and mixed oxides of WO$_3$ and SiO$_2$, respectively. The outer porous SiO$_2$ layer must be formed by evaporation of WO$_3$. Consequently, at these temperatures, WSi$_2$ forms the thick and porous oxide scales and thus shows an extremely poor oxidation resistance. On the other hands, at temperatures above 1573 K, WSi$_2$ shows excellent oxidation resistance because of the formation of a thin and dense SiO$_2$ scale on it. Therefore, understanding the classification of oxidation behavior in silicides is essential for investigating the oxidation resistance of next generation’s ultra high temperature material.

A few papers demonstrated the improvement of oxidation resistance by the addition of B to metal silicide. Meyer et al. reported that Mo$_5$Si$_3$ formed a protective borosilicate scale by the addition of B and thus showed a good oxidation resistance.$^{17}$ According to Kurokawa et al., the oxidation resistance of NbSi$_2$ is dramatically improved by the addition of B with concentrations of 2 mass% or higher at temperatures ranging from 1073 to 1673 K in air.$^{11}$ Consequently, their results suggested that the formation of a borosilicate scale having high plasticity suppressed the high porosity of the scale, making the scale much more protective.$^{4,17,18}$

The purpose of this work is to clarify the effect of B addition on the improvement of oxidation resistance for WSi$_2$ compacts, especially at intermediate temperatures (1073–1473 K).

2. Experimental Procedures

The starting materials were WSi$_2$ powder (purity: 99.5 mass%, average grain size: 2.5 µm, Japan New Metals Co., LTD) and B powder (purity: 99 mass%, average grain size: 40 µm, Kojundo Chemical Laboratory Co., LTD). Percent in this paper means mass percent, unless otherwise stated. B and WSi$_2$ mixed powders consisting of WSi$_2$:0.5, 1.0, 2.0 and 3.0% B were ball-milled for 1.8 ks at a rate of 150 rpm. These powder mixtures were sintered by using a spark plasma sintering (SPS) method. The sintering conditions are shown in Table 1.

The specimens for oxidation tests were cut into 10 × 3.5 × 1 mm pieces from the compacts. Their surfaces were polished with SiC paper of up to #1500, and then polished with a 1 µm diamond abrasive for mirror finishing. Prior to oxidation tests, the specimens were ultrasonically cleaned in ethanol.

<table>
<thead>
<tr>
<th>Table 1 Sintering conditions of B added WSi$_2$ powders.</th>
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<td>Sintering process</td>
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<td>Compressive stress</td>
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<td>Atmosphere</td>
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cleaned in ethanol, and the mass and the surface area were measured.

Isothermal oxidation tests were performed at temperatures ranging from 873 to 1473 K for up to 360 ks in the laboratory air. The oxidation kinetics was obtained by measuring the difference in masses before and after the oxidation. The oxidized specimens were characterized by using X-ray diffractometer (XRD), field-emission scanning electron microscope (FE-SEM) and electron probe microanalyzer (EPMA).

3. Results and Discussion

3.1 Microstructure of B added WSi₂ compact

Figure 1 shows the microstructures of B added WSi₂ compacts (B-WSi₂) fabricated by SPS. The analysis by XRD

![Figure 1](image1)

**Fig. 1** Microstructures of sintered B added WSi₂. (a) 0.5 mass%B, (b) 1.0 mass%B, (c) 2.0 mass%B, and (d) 3.0 mass%B.

![Figure 2](image2)

**Fig. 2** (a) X-ray diffraction patterns of B added WSi₂, and (b) SEM micrograph and EPMA analysis of 3.0 mass%B added WSi₂.

<table>
<thead>
<tr>
<th>mol%</th>
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<tr>
<td>W</td>
<td>Si</td>
</tr>
<tr>
<td>0.16</td>
<td>99.84</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>64.66</td>
<td>35.34</td>
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<td></td>
<td>66.29</td>
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<td>1.25</td>
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and EPMA (Fig. 2) showed that the matrix of the compact is WSi$_2$, the dark-colored second phase is Si, and the third phase around Si is W$_2$B$_5$. The amount of the second phase increases with an increase in the B concentration. The reaction between B and WSi$_2$ at their interface can be expressed as

$$5B + 2WSi_2 \rightarrow 4Si + W_2B_5.$$  

3.2 Oxidation behavior

Figure 3 shows the temperature dependence of mass changes of WSi$_2$ and B-WSi$_2$ oxidized for 180 and 360 ks in the temperature range. In the oxidation of WSi$_2$, W and Si are simultaneously oxidized to form WO$_3$ and SiO$_2$ in the temperature range of 873 K to 1473 K.$^{13,14}$ As the temperature increases, the mass gain increases and then reaches a maximum value at about 1300 K. Above 1300 K, a remarkable decrease in mass change occurs. At 1473 K a pro-
nounced mass loss of WSi$_2$ is confirmed for the oxidation time of 36 ks. This mass loss is attributable to the evaporation of WO$_3$.\textsuperscript{13,14)"

On the other hand, the addition of B leads to outstanding suppression of the severe mass loss of WSi$_2$. At 1073 K, 0.5 and 1.0\% of B-WSi$_2$ show the almost same mass change for the 180 ks oxidation as WSi$_2$. Their mass changes for the 360 ks oxidation are larger than those of WSi$_2$ for the same oxidation time. In comparison, the mass changes of 2.0 and 3.0\% of B-WSi$_2$ are negligible even for the 360 ks oxidation, showing an excellent oxidation resistance. As the temperature is increased, the effect of B concentration on the mass change of the compacts diminishes. In other words, the B concentration necessary to improve the oxidation resistance decreases as the temperature increases.

3.3 Structure and composition of oxide scale

Figure 4 shows the cross-sectional SEM micrographs of WSi$_2$ containing various B concentrations which were oxidized at 1073 K for 180 ks. As shown in Figs. 4(a) and (b), many pores are formed in the scales for 0.5 and 1.0\% of B-WSi$_2$. The thickness of their scales consisting of yellow oxide is 100\,\mu m or larger. On the contrary, the scales formed on 2.0 and 3.0\% of B-WSi$_2$ are about 2\,\mu m in thickness and dense.

The scales formed at higher temperatures were similarly observed. The cross-sectional SEM micrographs of the various B-WSi$_2$ oxidized at 1473 K for 180 ks are shown in Fig. 5. For all the specimens the scales are about 1–2\,\mu m in thickness and dense. Thus, the influence of B concentration on the growth rate of scales decreases as the oxidation temperature increases. This is attributable to the fact that the viscosity of the SiO$_2$ scale with B (probably borosilicate) decreases with increasing the B concentration and temperature,\textsuperscript{19,20)} and the SiO$_2$ scale is easily formed due to the evaporation of WO$_3$ in the initial oxidation stage.\textsuperscript{13)"

Since the evaporation of WO$_3$ affects the oxidation kinetics of WSi$_2$,\textsuperscript{13,14)} there is a possibility that the temperature dependence of mass change by the oxidation (Fig. 3)

Fig. 5 Fractured oxide scales formed on B added WSi$_2$, after oxidation for 180 ks at 1473 K in air. (a) 0.5 mass% B, (b) 1.0 mass% B, (c) 2.0 mass% B, and (d) 3.0 mass% B.

Fig. 6 Change of the thickness of scales formed on B added WSi$_2$ with temperature for 180 ks oxidation in air.
will be inconsistent with that of the scale thickness. Therefore, the thicknesses of scales formed at various temperatures were measured on the SEM photographs. Figure 6 indicates the temperature dependence of the scale thickness formed by the 180 ks oxidation. The temperature dependence in Fig. 6 is in good agreement with that in Fig. 3. Furthermore, it was found that the negligible mass change in the high temperature range is due to the formation of SiO$_2$ scale, not owing to the evaporation of WO$_3$ but owing to the effect of the B addition.

Next, the B concentration in the scale was examined. Figure 7 shows the cross-sectional SEM micrograph and concentration profiles of W, Si, B and O in the scale formed on 1.0% of B-WSi$_2$ oxidized at 1073 K for 360 ks. WO$_3$ and SiO$_2$ are uniformly distributed throughout the scale. In addition, the atomic ratio of Si to W in the scale is close to 2. Regarding B, the whole scale has the uniform B concentration of about 1.1%. These results mean that the effect of the B addition on the oxidation of WSi$_2$ containing low B concentration at 1073 K is very little. It is concluded that W and Si must be simultaneously oxidized to form WO$_3$ and SiO$_2$, and a thick scale is formed similarly with WSi$_2$.

At this temperature, WO$_3$ evaporated hardly. Moreover, the changes of composition of the scales formed on B-WSi$_2$ with high B concentration and oxidation temperature were investigated. Table 2 summarizes the results of EPMA for the scales formed on 1.0 and 3.0% of B-WSi$_2$ oxidized for 360 ks in the temperature range of 1073–1473 K. Though these concentrations are mean values analyzed by EPMA, the distributions of each element are almost uniform throughout the scale regardless of its thickness. These results demonstrate that the B concentration in the scale tends to decrease as the oxidation temperature increases. In addition, these results indicate that the content of WO$_3$ in the scale formed at the intermediate temperatures decreases outstandingly with an increase in the B concentration. Consequently it can be concluded that increasing B concentration leads to the formation of a protective oxide scale having little content of WO$_3$.

### 3.4 Formation of SiO$_2$ scale containing B$_2$O$_3$

B-WSi$_2$ showed excellent oxidation resistance except for the compacts having 0.5 and 1.0% B oxidized at 1073 K. It must be emphasized that the scales formed on B-WSi$_2$ showing excellent oxidation resistance consist of SiO$_2$ with B and their thicknesses are about 1–2 μm. In order to clarify the growth mechanism of the SiO$_2$ scale with B, the morphologies of protective scales formed at high temperatures during the short time were examined. Figure 8 shows the surface features of the scales formed on WSi$_2$ containing the various B concentrations in the oxidation at 1473 K for 180 ks. The observation revealed that the ratio of surface area covered with the circular black oxide increases with the B concentration for the same oxidation time. The EPMA analysis indicated that this black-colored oxide consists of SiO$_2$ with B. Figure 9 shows the cross section of the SiO$_2$ scale with B formed on B-WSi$_2$. The relatively thick SiO$_2$ scale with B is locally formed on the region where Si and W:B phases coexist. It was observed that this oxide widens with oxidation time because of its low viscosity. In the case of high B concentrations...
compacts, dense SiO$_2$ scales with B were readily formed throughout the surface during the initial stage of oxidation, because of the homogeneous distribution of W$_2$B$_5$ over the whole specimen surface.

3.5 Effect of B on improvement of oxidation resistance of WSi$_2$

The effect of B on the high temperature oxidation resistance of WSi$_2$ has been considered on the basis of the results, in which high temperature oxidation behavior of WSi$_2$ was classified according to the temperature range as follows.

1. $T \leq 1273$ K: Formation of the scales consisting of mixed oxides of WO$_3$ and SiO$_2$ results in a large mass gain.

2. $1473$ K $\leq T < 1673$ K: In the initial stage of oxidation, scales consisting of WO$_3$ and SiO$_2$ are formed, and then SiO$_2$ only is left in the scales owing to the evaporation of WO$_3$. However, these scales are porous.

3. $T \geq 1673$ K: Protective scales consisting of only SiO$_2$ are formed at 1673 K and above, from the initial stage because of their low viscosity.

At temperatures below 1573 K, WSi$_2$ shows a poor oxidation resistance because of the formation of either porous scale or mixed oxides scale consisting of WO$_3$ and SiO$_2$. Therefore, it is needed to form a protective oxide scale below this temperature for the suppression of inward oxygen diffusion by densifying the oxide scale by B addition.

The effect of B addition on the improvement of oxidation resistance of metal silicides such as Mo$_5$Si$_3$, NbSi$_2$, and ReSi$_{1.75}$ has been confirmed. Such an effect results from densifying the scale due to the formation of borosilicate phase having low viscosity. Though the equilibrium dissociation oxygen pressure of borosilicate is not identified, that of WO$_3$ is eight orders of magnitude higher than that of SiO$_2$ over the whole temperature range. That of borosilicate was estimated to be the almost same as that of SiO$_2$. Therefore, when the surface of B-WSi$_2$ was entirely covered with a

Fig. 8 Surface features of B added WSi$_2$ oxidized for 90 ks at 1473 K in air. (a) 0.5 mass%B, (b) 1.0 mass%B, (c) 2.0 mass%B, and (d) 3.0 mass%B.

Fig. 9 Cross-sectional micrograph of scale formed on 0.5 mass%B added WSi$_2$ by oxidation at 1473 K for 180 ks in air.
dense SiO₂ (or borosilicate) scale, oxidation of W at the scale/substrate interface could not take place. In other words, selective oxidation of Si proceeds.

The composition of borosilicate has been shown as \( (\text{SiO}_2)_{1-x} (\text{B}_2\text{O}_3)_x \), and increasing \( x \) leads to decreasing its viscosity.\(^{19,20}\) In this study, the formation of borosilicate phase was not verified by XRD, probably because this phase was amorphous. However, the EPMA analysis confirmed that the presence of B in the scale (see Table 2). The formation of a borosilicate scale having low viscosity would lead to sealing pores in the scale and consequently improves the oxidation resistance of WSi₂. The high concentration of B is required for showing this effect at low temperatures. In other words, at higher temperatures the addition of smaller amounts of B is sufficient to give WSi₂ excellent oxidation resistance. Thus, this result implies that the increasing temperature could cause SiO₂ with B to soften easily. Moreover, it is well-known that B₂O₃ evaporates heavily above 1273 K.\(^{23}\) Consequently this causes a decrease in the concentration of B in the oxide scale formed at higher temperatures.

4. Conclusions

In the present study, the oxidation behavior of B-WSi₂ (WSi₂-0.5, 1.0, 2.0, 3.0%B) was investigated in a temperature range of 873 to 1473 K. The following results were obtained.

(1) The oxidation resistances of WSi₂ containing B concentrations above 2.0% are remarkably improved owing to the formation of the dense SiO₂ scale with B in a temperature range of 1073 to 1473 K.
(2) The B concentration of WSi₂ to form the dense SiO₂ scale with B decreases with an increase in the oxidation temperature. The structural features of the scales formed on B-WSi₂ at 1273 K and above are almost the same irrespective of B concentration.
(3) The formation of a SiO₂ scale with B progresses around the Si and W₂B₃ phases. The covering rate of the surface with the oxide scale increases with temperature and B concentration.

REFERENCES