Oxidation Behavior of the Si-B-X (X = Mo, Cr, or Ti) Alloys in the Temperature Range of 1000–1400 °C

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ABSTRACT: Low-melting-point silicon–boron system alloys are promising for low-temperature reactive melt infiltration to reduce high-temperature damage to silicon carbide fibers during the densification of SiC/SiC composites. Meanwhile, the oxidation resistance of the alloys will have a large impact on the intrinsic oxidation resistance of the composite. Herein, three alloys, Si-14.88B-7Mo, Si-14.88B-7Ti, and Si-14.88B-7Cr, were fabricated to investigate the oxidation behavior in air at 1000–1400 °C. The results showed that the oxidation weight gains of the Si-B-Mo alloy after oxidation at 1400 °C for 100 h were 0.9 mg/cm², which were only 50 and 1.5% of those of Si-B-Ti and Si-B-Cr alloys, respectively. The excellent oxidation resistance of Si-B-Mo alloys at 1000–1400 °C was attributed to the formation of glassy-surface layers and the dense internal oxide layer. The dense oxide layer and the low solubility of Mo ions in SiO₂ inhibit the volatilization of MoO₃ and the oxidation reaction, reducing the oxidation rate of the Si-B-Mo alloy. The difference in the coefficients of thermal expansion for SiO₂ and TiO₂ led to penetrating cracks in the oxide layer of the Si-B-Ti alloy during cooling, thereby reducing the oxidation resistance. In addition, the rate of volatilization of Cr₂O₃ as CrO₃ in an oxidation atmosphere above 1200 °C increased significantly in the Si-B-Cr alloy. The simultaneous volatilization of B₂O₃ and CrO₃ resulted in the formation of loose oxide layers in the CrB₂ region of the Si-B-Cr alloy, leading to severe oxidation.

1. INTRODUCTION

The increasing flight speeds and distances of various aircraft with the development of the aerospace industry have placed more stringent requirements on high-performance thermal protection materials. Silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC) are considered to be one of the most promising thermal structural materials in the aerospace field due to their low density, high specific modulus, thermal shock resistance, and excellent oxidation resistance and ablation resistance. Currently, the densification methods of SiC/SiC composites mainly include chemical vapor infiltration (CVI), polymer impregnation pyrolysis (PIP), and reactive melt infiltration (RMI). Among these, the RMI process displays significant advantages of a short preparation time, simple process, low cost, and the ability to prepare complex materials with a low porosity. Thus, it has great potential in the development of low-porosity SiC/SiC composites that can be applied in engineering.

However, the temperature of the RMI process generally exceeds 1600 °C. The relatively high reaction temperatures would damage the fiber, resulting in a decrease in the mechanical properties of the composite. Chen et al. investigated the effects of heat treatment temperature on Kansas-III SiC fibers (Leaoasia New Material Co., Ltd.). They determined that the average tensile strength of the SiC fiber was approximately 1.81 GPa before heat treatment and decreased to 1.13 GPa after heat treatment at 1700 °C for 1 h. The strength retention rate was only 62.4% at 1700 °C. Therefore, it is essential to develop low-melting alloys for the RMI process. Meanwhile, the decrease in temperature of the RMI process must consequently lead to a decrease in the reaction rate for the formation of SiC, which can result in more residual alloys in the composite. The intrinsic oxidation resistance of the composites will therefore be greatly affected if the alloys have an inferior oxidation resistance. Therefore, the alloys used in the RMI process should also have an excellent oxidation resistance.

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The Ti, Mo, and Cr elements are generally added as antioxidant components in ultra-high temperature ceramics, coatings, and composites, which exhibit excellent antioxidant properties in the materials.\textsuperscript{19–22} Meanwhile, the addition of Ti, Mo, and Cr to silicon alloys will have no significant increase in the melting point of the silicon alloy.

Thus, in this work, three alloys with a melting point of approximately 1400–1500 °C, Si-14.88B-7Mo, Si-14.88B-7Ti, and Si-14.88B-7Cr, were subjected to isothermal oxidation at 1000, 1200, and 1400 °C in air to investigate their oxidation behaviors. The alloys with the optimal oxidation resistance were identified, and the oxidation mechanisms of the alloys were analyzed via volatility diagrams. This will provide data and theoretical support for subsequent studies on the oxidation behavior of SiC/SiC composites.

2. EXPERIMENTAL PROCEDURES

2.1. Material Preparation. Three alloys with relatively low melting points, namely, Si-14.88B-7Mo, Si-14.88B-7Ti, and Si-14.88B-7Cr (the compositions are given in at. %), were designed according to the phase diagram.\textsuperscript{23–25} The three alloys were produced using an arc-melting method in an Ar atmosphere from elemental powder mixtures of Si, B, Mo, Ti, and Cr at 99.99, 99.9, 99.95, 99.95, and 99.95% purity levels, respectively. Melted button ingots were flipped over and remelted more than five times. The detected chemical compositions of the three alloys are listed in Table 1. Each sample was processed into a uniform dimension of 6 × 6 × 8 mm from the as-melted ingots. To ensure a uniform oxidation, all surfaces of the samples were carefully ground using a P1500 SiC sandpaper and then ultrasonically cleaned in ethanol. In addition, all samples prepared for the oxidation experiments were accurately weighed, and the surface area was measured prior to the oxidation experiment to calculate the change in mass per unit area.

2.2. Isothermal Oxidation and Microstructural Characterization. The isothermal oxidation experiments were performed in a vertical tubular furnace (Tongcoco TCGC1800-41, Shanghai, China) at 1000, 1200, and 1400 °C for 100 h. The samples were extracted after 1, 5, 10, 20, 40, 60, 80, and 100 h of oxidation and cooled to room temperature for weighing. The oxidation atmosphere consisted of 79 vol % nitrogen and 21 vol % oxygen. The flow rate was 200 mL/min, and the total pressure was 0.1 MPa (1 atm). In particular, each sample was hung in an alumina crucible with a platinum wire to expose all surfaces.

To examine the microstructure of the as-cast samples before oxidation, the samples were mechanically ground using a P2000 SiC sandpaper and polished using a 1.5 μm diamond solution. The microstructures were then examined via scanning electron microscopy (SEM, Phenom ProX, Netherlands) in back-scattered and secondary electron imaging modes (SEI and BSI, respectively) with an X-ray energy-dispersive spectrometer (EDS) analyzer. The phase composition of the samples was analyzed via X-ray diffraction (XRD, Rigaku D/max-2550VB, Tokyo, Japan) using Cu Kα radiation. The diffraction angle ranged from 5 to 80° with a scanning speed of 5°/min. The Gibbs energy minimization principle and Factage software were used to calculate the volatility diagrams for the three alloys with temperature and equilibrium oxygen partial pressure.

3. RESULTS AND DISCUSSION

3.1. Microstructures of the As-Cast Alloys. The XRD patterns, SEM images, and elemental distribution of the three alloys are shown in Figures 1 and 2. It can be observed that the Si-14.88B-7Mo alloy is mainly composed of Si, MoSi\textsubscript{2}, SiB\textsubscript{6}, and a small amount of Mo\textsubscript{2}B\textsubscript{3}, Mo\textsubscript{3}B\textsubscript{4}, predominantly embedded in MoSi\textsubscript{2}, MoSi\textsubscript{2}, and SiB. The three alloys were designed to its low content, but an EDS analysis shows that the black phase contains more boron. The Si-14.88B-7Ti alloy consists of Si, TiB\textsubscript{2}, and TiB\textsubscript{7}. The Si-14.88B-7Cr alloy possesses Si, CrSi\textsubscript{2}, and CrB\textsubscript{2}. In the Si-14.88B-7Mo and Si-14.88B-7Cr alloys, the microstructure morphologies of TiB\textsubscript{2} and CrB\textsubscript{2} are distributed in a columnar-like or massive-like structure in the silicon matrix. There is also a lamellar eutectic structure in the Si-14.88B-7Ti and Si-14.88B-7Cr alloys. Overall, the main phase of the three alloys is silicon. The volume fraction of silicon in the as-received alloys was found to be 72, 81, and 83% in the Si-14.88B-7Mo, Si-14.88B-7Ti, and Si-14.88B-7Cr alloys, respectively.

3.2. Oxidation Kinetics. Figure 3 shows the cyclic oxidation weight gain for the three alloys at different temperatures for 100 h. It can be observed that the oxidation weight increase per unit area of the alloy increases with temperature for the same oxidation times. The three alloys initially exhibit a rapid weight gain at all oxidation temperatures. With an increasing oxidation time, the oxidation weight gain gradually slows down and tends to stabilize. The Si-14.88B-7Mo and Si-14.88B-7Ti alloys have a parabolic or near-parabolic curve shape. In the early stages of oxidation, the reason for the faster oxidation rate is that oxygen molecules are more likely to react directly with the surface of the alloy, and it is easy for oxide grains to nucleate at grain boundaries and defects on the surface of the alloy. When the oxide layer covers the alloy, the oxide layer inhibits an inward diffusion of oxygen, and the oxidation rate begins to decrease. The Si-14.88B-7Mo and Si-14.88B-7Cr alloys show an increasing oxidation weight gain per unit area of the alloy with an increasing temperature for the same oxidation time. However, the Si-14.88B-7Cr alloy shows a reduced oxidation weight gain in the alloy when oxidized at 1200 °C compared to oxidation at 1000 °C. This is due to the significant increase in the rate of volatilization of CrO\textsubscript{3} and B\textsubscript{2}O\textsubscript{3} generated by the oxidation of the alloy when oxidized at temperatures in excess of 1200 °C. After oxidation at 1400 °C, the oxidation weight gains of the Si-B-Mo and Si-B-Ti alloys were 0.9 and 1.8 mg/cm\textsuperscript{2}, respectively, whereas that of the Si-B-Cr alloy was 62 mg/cm\textsuperscript{2}.

Figure 4 presents the squared oxidation weight gain per unit area versus time (M\textsuperscript{2}) for the Si-14.88B-7Mo alloy over a temperature range from 1000 to 1400 °C. As can be observed from the graph, M\textsuperscript{2} of the oxidized specimen at temperatures of 1000–1400 °C exhibits a linear relationship with respect to the duration of oxidation, i.e., ΔM\textsuperscript{2} = kt. It can therefore be concluded that the isothermal oxidation behavior of the Si-14.88B-7Mo and Si-14.88B-7Ti alloys follows a parabolic pattern, which is controlled by a diffusion mechanism.

### Table 1. Chemical Compositions of the As-Cast Alloys

| alloy notation | Mo (at. %) | Ti (at. %) | Cr (at. %) | B (at. %) | Si (at. %) |
|---------------|-----------|-----------|-----------|---------|-----------|
| Si-14.88B-7Mo | 7.26      | 15.02     | bal.      | 72.42   | bal.      |
| Si-14.88B-7Ti | 7.13      | 14.68     | bal.      | 70.86   | bal.      |
| Si-14.88B-7Cr | 7.31      | 15.11     | bal.      | 69.10   | bal.      |
model-fitting method was widely used to obtain the kinetic triplet (the activation energy, the pre-exponential factor, and the reacted fraction) and evaluate the kinetic mechanism of the gas−solid reaction. A variety of kinetic models have been widely used to describe the kinetic mechanisms of gas−solid reactions. The kinetic analysis of the oxidation resistance of the alloy can be performed according to the Wagner theory and the Arrhenius equation, and the parabolic law can be described using the following equation:

\[
\left( \frac{\Delta m}{A} \right)^2 = kt
\]

where \(\Delta m\) is the oxidation weight gain per unit area after oxidation, \(A\) is the surface area of the sample, and \(k\) is the parabolic reaction rate constant. The slope of the linear fit in Figure 4 gives the reaction rate constant \(k\) for the oxidation of the alloy. Thus, the parabolic rate constants for the Si-14.88B-7Mo alloy at 1000, 1200, and 1400 °C are 4.98 \times 10^{-3}, 2.12 \times 10^{-3}, and 1.12 \times 10^{-2} \text{ mg}^2/(\text{cm}^4 \cdot \text{h})$, respectively, while the parabolic rate constants for the Si-14.88B-7Ti alloy were 0.00258, 0.0052, and 0.02725 \text{ mg}^2/(\text{cm}^4 \cdot \text{h}) at 1000, 1200, and 1400 °C, respectively. In addition, the parabolic rate constant of the alloy during oxidation is exponentially related to temperature, i.e.,

\[
k = k_0 \exp\left( -\frac{Q}{RT} \right)
\]

where \(k_0\) is a constant, \(R\) is the gas constant, \(T\) is the temperature, and \(Q\) is the activation energy of the reaction. Figure 5 shows the temperature dependence of the parabolic rate constant for alloy oxidation, obtained by plotting \(\ln(k)\) as the vertical coordinate and \((1/T)\) as the horizontal coordinate. The calculated slope gives an activation energy of \(\sim 136.64 \text{ kJ/mol}\) for the oxidation of the Si-14.88B-7Mo alloy and \(\sim 101.81 \text{ kJ/mol}\) for the oxidation of the Si-14.88B-7Ti alloy from 1000 to 1400 °C. The oxidation activation energy of the Si-14.88B-7Mo alloy is higher than that of the Si-14.88B-7Ti alloy, indicating that the oxidation rate of the Si-14.88B-7Mo alloy is lower than that of the Si-14.88B-7Ti alloy.

Due to the presence of volatile substances in the oxide product, the oxidation weight gain does not accurately determine the oxidation resistance of the alloys. Therefore, the thickness of the oxide layer must be measured (Figure 6). From the oxide layer thickness curves, the difference between the oxide layer thicknesses of the three alloys after oxidation at 1000 and 1200 °C was small, while the difference in the thickness after oxidation at 1400 °C was large. It can therefore be concluded from the oxide layer thickness and oxidation weight gain that the Si-14.88B-7Mo alloy shows an excellent oxidation resistance compared with the other two alloys in the 1000−1400 °C range.

3.3. Microstructures of the Alloys after Oxidation. Figure 7 shows the XRD of the surface of alloys oxidized at 1000, 1200, and 1400 °C for 100 h. It can be seen from the XRD patterns that the surface oxide layer compositions of the same
alloy oxidized at 1000, 1200, and 1400 °C for 100 h are essentially identical. The XRD results of the Si-14.88B-7Mo alloy after oxidation show diffraction peaks of SiO₂ as well as diffraction peaks of the matrix phase, without MoO₃ or other oxides of molybdenum. MoO₃ shows a high vapor pressure and is extremely volatile above 1000 °C, which means that the Si-14.88B-7Mo alloy is more likely to form a single protective oxide layer of SiO₂ after oxidation. As the oxidation temperature increases, the intensity of the diffraction peak of SiO₂ gradually increases, indicating that a thicker oxide layer is formed on the surface of the Si-14.88B-7Mo alloy. After oxidation at 1000−1400 °C for 100 h, the composition of the oxide layer was mainly SiO₂ and Cr₂O₃ for the Si-14.88B-7Cr alloy and SiO₂ and TiO₂ for the Si-14.88B-7Ti alloy. The XRD analysis of the Si-14.88B-7Cr and Si-14.88B-7Ti alloys after oxidation at 1400 °C for 100 h reveals the strong SiO₂ diffraction peaks and the absence of matrix diffraction peaks, indicating that the oxidation of the two alloys at 1400 °C is more severe. B₂O₃ is mainly in the amorphous glass phase or in the gas phase at temperatures above 1000 °C; therefore, it is not detected in any of the XRD patterns.

The surface microstructure of the three alloys after oxidation at 1000, 1200, and 1400 °C for 100 h in air is shown in Figures 8−10. As shown in Figure 8, the Si-14.88B-7Mo alloy was covered with an oxide layer after oxidation from 1000 to 1400 °C. There were no obvious cracks in the oxide layer on the surface of the alloy, but some honeycomb structures were attached to the oxide layer, presumably due to the volatilization of B₂O₃ generated by the oxidation of boron-rich borosilicate compounds. The Si-14.88B-7Mo alloy had an oxide layer on the surface after oxidation at 1000 °C, and the MoSi₂ phase could still be observed. In addition, the surface of the alloy was covered with many nodules, ranging from a few microns to tens of microns in diameter, after oxidation at 1000 and 1200 °C, and the EDS results showed that it was a borosilicate glass phase. After oxidation at 1400 °C, these glassy nodules disappeared, and the surface of the alloy was completely covered by a layer of glassy phases.

Figure 9 illustrates the surface oxide layer morphology of the Si-14.88B-7Cr alloy. The surface morphology of the Si-14.88B-7Cr alloy varied after oxidation at different temperatures. The surface of the alloy remained relatively flat after oxidation at 1000 °C. The oxide layer undergoes significant oxide layer bulging (Figure 9a) and the presence of cracks after oxidation in the CrB₂ phase area, while a distinct glassy phase was formed in the CrSi₂ phase area. A large number of holes appeared on the surface of the alloy after oxidation at 1200 °C and were mainly concentrated in the CrB₂ phase area. This is mainly due to the high oxidation temperature and the oxidation of CrB₂ to produce B₂O₃(g) and CrO₃(g). After oxidation at 1400 °C, a thick oxide layer was formed on the surface of the alloy. The surface of the oxide layer was loose with large oxide particles and large cracks.

The surface oxide layer morphology of the Si-14.88B-7Ti alloy after oxidation at 1000−1400 °C for 100 h is shown in Figure 10. The surface of the alloy was covered with an oxide layer after oxidation at 1000 °C, but the oxide layer was not dense, with the matrix exposed and with cracks in some areas.
The alloy was partially covered by a SiO₂ glass phase, with a few TiO₂ crystals embedded in an amorphous SiO₂ matrix, which acted as a filler for surface defects. Due to the difference in the coefficient of thermal expansion of the oxides and the rapid cooling of the alloy from the oxidation temperature to room temperature during cooling, the oxide layer on the surface of the alloy cracked after oxidation at 1200 °C. The entire oxide layer exhibited a fish scale shape, and an increasing number of TiO₂ grains could be seen forming on the surface of the alloy. When the oxidation temperature was increased to 1400 °C, the Si-14.88B-7Ti alloy was completely covered by a layer of the glass phase. However, there were still a large number of cracks in the oxide layer.

SEM images of the cross sections of the Si-14.88B-7Mo alloy after oxidation for 100 h at 1000 °C (a), 1200 °C (b), and 1400 °C (c) are shown in Figure 11. The Si-14.88B-7Mo alloy

Figure 3. The cyclic oxidation weight gain for the three alloys at different temperatures for 100 h. (a) Si-14.88B-7Mo, (b) Si-14.88B-7Ti, and (c) Si-14.88B-7Cr.

Figure 4. Square of the weight gain per unit area versus time for an alloy oxidized in the temperature range from 1000 to 1400 °C. (a) Si-14.88B-7Mo and (b) Si-14.88B-7Ti.
produced a continuous dense oxide layer on the surface after 100 h of oxidation at 1000° C to 1400° C. The thickness of the oxide layer on the surface of the alloy increased gradually with an increasing oxidation temperature. The oxide layer on the surface of the oxidized specimens showed a poor thickness uniformity, but none of the oxide layers were found to be flaking or cracked.

Figure 11c shows that the surface oxide layer formed by Si-poor Si11B31 had a thicker oxide layer. This was due to the oxidation of Si-poor borosilicate compounds themselves to generate more B2O3 and a small amount of SiO2. After the volatilization of B2O3, the surface oxide layer was very loose and could not be filled with SiO2 in time.

Figure 12 shows the cross-sectional BSE image of the Si-14.88B-7Ti alloy for 100 h of oxidation. As shown in Figure 12a, a dense and complete oxide layer was formed on the surface of the specimen after oxidation at 1000 °C, with a thickness of approximately 1–2 μm. After oxidation at 1200 °C, the oxide layer on the surface of the alloy grew significantly. Figure 12c shows a cross section of a specimen oxidized for 100 h at 1400 °C. The scale, which was 20–25 μm, consisted of two partial layers: an inner layer of rather pure SiO2 and an outer layer. The outer one consisted of a mixture of Si and Ti oxides. It was determined that there are visible penetrating cracks in the oxide layer.

Figure 13 shows the cross-sectional SEM images and EDS mapping results of the Si-14.88B-7Cr alloy oxidized at 1000, 1200, and 1400 °C for 100 h. The thicknesses of the oxide layer after oxidation at 1000 and 1200 °C were approximately <1 and 3.12 μm, respectively. The EDS analysis showed that the Cr element was mainly distributed on the surface of the oxide layer, and the Cr content in the oxide layer gradually decreased from the outside to the inside, while the Si content gradually increased. The cross-sectional morphology of the oxide layer of the Si-14.88B-7Cr alloy after 100 h of oxidation at 1400 °C is shown in Figure 13c. It can be seen that the Si-14.88B-7Cr alloy underwent severe oxidation, with a dramatic increase in the oxide layer thickness to several hundred microns and the presence of penetrating cracks and tiny holes. These provided channels for the internal diffusion of oxygen gas, resulting in internal oxidation and the formation of large oxidation pores within the alloy.

3.4. Oxidation Mechanism. The oxidation weight gain curves of the Si-14.88B-7Mo and Si-14.88B-7Ti alloys follow an increasing parabolic law. It can be concluded that the oxidation rates of the Si-14.88B-7Mo and Si-14.88B-7Ti alloys are mainly controlled by the diffusion rate of oxygen in the oxide layer. As a valuable tool for oxidation behavior studies, volatility diagrams show the thermodynamically predicted stable solid phase, the concomitant gaseous species, and their vapor pressures at different oxygen partial pressures and temperatures.31 As shown in Figure 14a, when the partial pressure of oxygen is 104 Pa (i.e., the partial pressure of oxygen at 1 atm), the Si-B-Mo alloy mainly has SiO2(cr) and B2O3(l) in the condensed phase and MoO3(g) and B2O3(g) in the vapor phase after oxidation at 1400 °C, with partial pressures of ~9.66 and ~32.89 Pa, respectively. Research has demonstrated that there are two scenarios for the oxidation of MoSi2 in air:

a. Selective oxidation of Si in MoSi2 to a pure SiO2 oxide layer, while Mo forms the transition phase Mo5Si3 at the MoSi2/SiO2 interface.

b. Selective oxidation of Si to SiO2 and complete evaporation of Mo to MoO3 in oxidized MoSi2.

In this study, no transition phase was found in any of the MoSi2 phases of the Si-14.88B-7Mo alloy after oxidation. It can therefore be assumed that Mo in the Si-14.88B-7Mo alloy is completely volatilized to MoO3. Thus, the formation process of
the Si-14.88B-7Mo oxide layer can be explained as follows: The oxygen in the air is rapidly adsorbed onto the surface of the substrate, and the adsorbed oxygen anion reacts with the alloy to produce the corresponding oxide. Due to the difference in the vapor pressure (Figure 14a), SiO₂ grows on the surface to form a protective oxide layer, while MoO₃ rapidly evaporates and B₂O₃ partly evaporates and partly dissolves in the SiO₂ to form a low-viscosity borosilicate glass phase. The oxidation reactions of the Si-B-Mo alloy in air can be summarized as follows:

\[
\text{Si} (s) + \text{O}_2 (g) = \text{SiO}_2 (s) \quad (3)
\]

\[
2\text{MoSi}_2 (s) + 7\text{O}_2 (g) = 4\text{SiO}_2 (s) + 2\text{MoO}_3 (g) \quad (4)
\]

\[
4\text{Mo}_2\text{B}_3 (s) + 27\text{O}_2 (g) = 10\text{B}_2\text{O}_3 (g) + 8\text{MoO}_3 (g) \quad (5)
\]

Figure 7. Surface XRD patterns of the three alloys after oxidation at 1000, 1200, and 1400 °C. (a) Si-14.88B-7Mo, (b) Si-14.88B-7Ti, and (c) Si-14.88B-7Cr.

Figure 8. SEM images of the Si-14.88B-7Mo alloy surface after oxidation. (a) 1000 °C, (b) 1200 °C, and (c) 1400 °C.
Rahul Mitra\textsuperscript{34} showed that when MoSi\textsubscript{2} was oxidized at temperatures $\geq 1000 \, ^\circ\text{C}$, the growth rate of SiO\textsubscript{2} was sufficient to fill the pores formed by the volatilization of MoO\textsubscript{3}, leading to a continuous SiO\textsubscript{2} protective layer. The oxidation of Mo and its diffusion mechanism in the Mo-Si-O system ensured the integrity of the alloy oxide layer. Becker et al.\textsuperscript{35} indicated that MoO\textsubscript{3} and MoO\textsubscript{2} have a certain solubility in SiO\textsubscript{2}, which is consistent with this work, as shown in Figure 11. Due to the low oxygen equilibrium pressure at the alloy/SiO\textsubscript{2} interface, MoSi\textsubscript{2} cannot be directly oxidized to form the MoO\textsubscript{3} phase. Instead, Mo\textsuperscript{4+}(MoO\textsubscript{2}) is first dissolved in SiO\textsubscript{2} and migrates outward through the SiO\textsubscript{2} layer. When $p(\text{O}_2)$ in SiO\textsubscript{2} is higher than the equilibrium pressure MoO\textsubscript{2}-MoO\textsubscript{3} for the activities of these species in SiO\textsubscript{2}, Mo\textsuperscript{4+} is oxidized to Mo\textsuperscript{6+} and volatilized as MoO\textsubscript{3} at the SiO\textsubscript{2}/gas interface. The diffusion of Mo ions into the SiO\textsubscript{2}/gas interface avoids the formation of MoO\textsubscript{3}(g) at the alloy/SiO\textsubscript{2} interface, indicating that volatilization of MoO\textsubscript{3} basically occurs on the surface of the oxide layer and further reduces the internal defects formed in the oxide layer due to gas evaporation. The sealing ability of the glass phase also ensures the denseness and continuity of the oxide layer. Thus, MoO\textsubscript{3} can only diffuse slowly outward through the SiO\textsubscript{2} continuous protective layer due to the lack of fast overflow channels. Meanwhile, the Mo ions have a low solubility in SiO\textsubscript{2}.\textsuperscript{35} These significantly inhibit reactions 4 and 5, which further reduce the oxidation rate of the alloy.

The XRD and EDS results indicate that the oxide layer of the Si-14.88B-7Ti alloy is mainly composed of SiO\textsubscript{2} and TiO\textsubscript{2}. From the volatility diagrams (Figure 14b), it can be seen that TiO\textsubscript{2} and SiO\textsubscript{2} possess a low gas partial pressure, and TiO\textsubscript{2} and SiO\textsubscript{2} can form a protective oxide layer on the surface of the alloy, which can effectively slow the diffusion of oxygen into the substrate. Figure 12 shows that the distribution of Si, Ti, and O elements in the oxide layer is not uniform. Ti is enriched on the surface of the

\[
\text{SiB}_2(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + \text{B}_2\text{O}_3(g) \quad (6)
\]
oxide layer. The Ti content in the outer oxide layer increases as the oxidation temperature increases. When the oxidation temperature reached 1400 °C, the oxide layer showed a clear delamination with an outer layer of SiO₂-TiO₂ and an inner layer of SiO₂. During the oxidation process, the Si-14.88B-7Ti alloy has a high silicon content on the surface in the early stages and preferentially oxidizes to SiO₂. Silicon atoms in oxide films are relatively immobile, which is consistent with the higher bond

Figure 11. SEM (BSE) micrographs of the cross sections of the Si-14.88B-7Mo alloys after oxidation. (a)1000 °C, (b)1200 °C, and (c)1400 °C.

Figure 12. SEM (BSE) micrographs of the cross sections of the Si-14.88B-7Ti alloys after oxidation. (a)1000 °C, (b)1200 °C, and (c)1400 °C.
energy of Si\(^{4+}\)-O (465 kJ/mol) compared with Ti\(^{4+}\)-O (323 kJ/mol).\(^{36}\) The migration rate of Ti\(^{4+}\) to the outer layer is greater than that of Si\(^{4+}\). With an increasing oxidation temperature and time, the oxide layer structure of SiO\(_2\)-TiO\(_2\) in the outer layer and SiO\(_2\) in the inner layer is gradually formed.

The weight change and oxide layer thickness show that the Si-14.88B-7Ti alloy has an inferior oxidation resistance compared to the Si-14.88B-7Mo alloy. The reason for this is that the difference between the thermal expansion coefficients of SiO\(_2\) (0.2 \(\times \) 10\(^{-6}\) K\(^{-1}\)) and TiO\(_2\) (8.0 \(\times \) 10\(^{-6}\) K\(^{-1}\)) during rapid cooling from the oxidation temperature to room temperature leads to cracks in the oxide layer. TiO\(_2\) is an n-type oxide with two types of structural defects, i.e., interstitial metal ions and oxygen ion vacancies, and Ti dioxide is more susceptible to oxidation by the diffusion of cations and anions.\(^{37}\) SiO\(_2\) has a relatively low oxygen diffusivity compared to TiO\(_2\).\(^{38}\) Thus, there is a faster rate of oxygen transport in TiO\(_2\) than in SiO\(_2\).\(^{39}\) Meanwhile, the migration rate of Ti\(^{4+}\) to the outer layer is greater than that of Si\(^{4+}\); thus, the growth rate of the TiO\(_2\) oxide layer is faster than that of SiO\(_2\). The SiO\(_2\)-TiO\(_2\) oxide layer acts as an "oxygen pipe", resulting in an increase in the rate of oxygen transfer through the oxide layer, significantly reducing the oxidation resistance of the alloy. In addition, the oxidation activation energy of the Si-14.88B-7Ti alloy is lower than that of the Si-14.88B-7Mo alloy, indicating that the Si-14.88B-7Ti alloy is more easily activated by oxidation than the Si-14.88B-7Mo.

Figure 14c–e shows the volatility diagrams of the Si-B-Cr alloy calculated at 1000, 1200, and 1400 °C. The Si-B-Mo alloy has Cr\(_2\)O\(_3\)(cr), SiO\(_2\)(cr), and B\(_2\)O\(_3\)(l) in the condensed phase and B\(_2\)O\(_3\)(g), BO\(_2\)(g), and CrO\(_3\)(g) in the vapor phase after oxidation at 1000 °C, with partial pressures of \(~3.2 \times 10^{-3}\), \(~3.2 \times 10^{-3}\), and \(~1.9 \times 10^{-4}\) Pa, respectively. The calculated pressures of the other species were all dramatically lower (Figure 16). The partial pressures of the various gases gradually increase as the oxidation temperature increases. Based on the increase by 2–4 orders of magnitude in the pressure of the dominant species compared to 1000 °C, the rate of B\(_2\)O\(_3\) and CrO\(_3\) vaporization would be expected to be significantly higher at 1400 °C. The partial pressure of CrO\(_3\)(g) during oxidation of the Si-B-Cr alloy at 1400 °C is up to 6 \(\times\) 10\(^{-2}\) Pa, which has an important negative impact on the formation of the protective oxide layer of Cr\(_2\)O\(_3\). Studies have indicated that during the oxidation of Cr at high temperatures, the oxidative volatilization of Cr\(_2\)O\(_3\) as CrO\(_3\) occurs under an oxidizing atmosphere.\(^{40}\) Comparing the cross-sectional morphology of the Cr\(_2\) phase in Si-14.88B-7Cr oxidized at 1000 and 1200 °C, it can be seen that the alloy can form a relatively dense oxide layer that is oxidized at 1000 °C (Figure 15). However, the corresponding region of the alloy forms a thick, porous, loose, and unprotected oxide layer after oxidation at 1200 °C. As the oxidation temperature increases, there is an increase in the rate of volatilization of B\(_2\)O\(_3\) and CrO\(_3\) generated by the oxidation of the alloy, which destroys the integrity of the oxide layer. This situation is even more
Figure 14. Calculated volatility diagrams for the (a) Si-B-Mo alloy at 1400 °C, (b) Si-B-Ti alloy at 1400 °C, (c) Si-B-Cr alloy at 1000 °C, (d) Si-B-Cr alloy at 1200 °C, and (e) Si-B-Cr alloy at 1400 °C.

Figure 15. SEM image of the CrB$_2$ phase in the Si-14.88B-7Cr alloy after 100 h of oxidation. (a) 1000 °C and (b) 1200 °C.
pronounced in the CrB<sub>2</sub> phase region. The simultaneous volatilization of B<sub>2</sub>O<sub>3</sub> and CrO<sub>3</sub> makes it easy to form loose oxide layers in the CrB<sub>2</sub> region of the Si-B-Cr alloy, making the CrB<sub>2</sub> phase region of the alloy more susceptible to oxidation compared to other regions. Oxygen diffuses inward along the columnar CrB<sub>2</sub> phase, resulting in severe oxidation within the alloy. Therefore, the cross-sectional view of the alloy shows that severe internal oxidation has occurred and that large oxidation holes have been created within the alloy after oxidation at 1400 °C.

4. CONCLUSIONS

In summary, Si-B-X (X = Mo, Cr, or Ti) alloys were fabricated to investigate the oxidation behavior in air at 1000—1400 °C. The oxidation behavior of the Si-14.88B-7Mo and Si-14.88B-7Ti alloys essentially follows a parabolic law, and the oxidation reaction is controlled by a diffusion process, with activation energies of ~136.64 and ~101.81 kJ/mol, respectively. The oxidation weight gains of the Si-B-Mo alloy after oxidation at 1400 °C for 100 h were 0.9 mg/cm<sup>2</sup>, while the Si-B-Ti and Si-B-Cr alloys reached 1.8 and 62 mg/cm<sup>2</sup>, respectively. The formation of glassy-surface layers and a dense internal oxide layer results in the excellent oxidation resistance of Si-B-Mo alloys at 1000—1400 °C. During the oxidation of the Si-B-Mo alloy, the oxidation and diffusion mechanism of Mo in the Mo-Si-O system ensures the integrity and continuity of the oxide layer. The dense oxide layer and the low solubility of Mo ions in SiO<sub>2</sub> inhibit the volatilization of MoO<sub>3</sub> and the oxidation reaction, reducing the oxidation rate of the Si-B-Mo alloy. The oxide layer of the Si-14.88B-7Ti alloy showed a SiO<sub>2</sub>-TiO<sub>2</sub> oxide layer structure in the outer layer and SiO<sub>2</sub> in the inner layer. The difference in the coefficients of thermal expansion for SiO<sub>2</sub> and TiO<sub>2</sub> led to penetrating cracks in the oxide layer of the Si-B-Ti alloy during cooling, thereby reducing the oxidation resistance. The Si-B-Cr alloy can form a continuous and dense protective oxide layer during oxidation at 1000 °C because there is less oxide volatilization. However, the rate of volatilization of CrO<sub>3</sub> as CrO<sub>3</sub> in an oxidation atmosphere above 1200 °C increased significantly in the Si-B-Cr alloy. The simultaneous volatilization of B<sub>2</sub>O<sub>3</sub> and CrO<sub>3</sub> resulted in the formation of loose oxide layers in the CrB<sub>2</sub> region of the Si-B-Cr alloy, leading to severe oxidation.

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