Synthesis and high temperature oxidation of Mo–Si–B–O pseudo in situ composites

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Abstract

In this paper, the new concept of ‘pseudo in situ composites’ is introduced into artificial composites for ultra-high temperature applications, composed of five phases, Mo, Mo₅Si, Mo₅Si₂, Mo₅SiB₂ and SiO₂. Among these phases, Mo and Mo₅Si are not thermodynamically stable with each other, but they are locally equilibrated in the composites due to the formation of Mo₅Si as their reactant. Using the spark plasma sintering (SPS) technique, the Mo–Si–B–O pseudo in situ composites are successfully synthesized from Mo₅Si/Mo₅Si₂/Mo₅SiB₂ in situ composite powder, Mo and/or SiO₂ powders. The consolidated compacts are sound and fully dense, indicating that the SPS is a promising technique to synthesize the Mo–Si–B–O pseudo in situ composites. High temperature oxidation properties of the composites were examined up to 1673 K. The temperature range is divided into three with respect to the oxidation behavior; i.e. (I) below 1000 K, (II) between 1000 and 1400 K, and (III) above 1400 K. In the range II, the oxidation resistance of the composites is significantly improved by SiO₂ addition. In the range III, the oxidation resistance of the composites is good enough even at 1673 K in spite of the existence of Mo, displaying high potential for ultra-high temperature applications. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Molybdenum silicides are very attractive intermetallic-base materials for high temperature applications not only as structural components but also as heating elements and oxidation resistant surface coating materials. In particular, since discovery of remarkable improvement of oxidation resistance of D₈₈₃₇-type Mo₅Si₃ with a tetragonal structure of 14/mcm symmetry by a small addition of boron [1,2], anticipation has increased on the silicides containing higher Mo concentrations. Recently, molybdenum borosilicide of Mo₅SiB₂ (D₈₇₈₇-type structure, space group I4/mmm) has also attracted attention as an ultra-high temperature structural material because of its melting point higher than 2500 K and relatively low density (8.864 g/cm³). Ito et al. investigated high temperature strength and creep properties of Mo₅SiB₂ using single crystals, and showed that it has more excellent high temperature performance than that of Mo₅Si₂ and Mo₅Si₃ single crystals and their composites [3].

Of significance is that the Mo₅SiB₂ phase is in equilibrium with several phases of Mo solid solution (Moₙ), A15-type Mo₅Si, Mo₅Si₃ mentioned earlier [4]. In other words, Mo₅SiB₂ has some options to harmonically design material properties such as low temperature toughness, high temperature strength, high temperature oxidation resistance and so on by incorporating these thermodynamically stable phases.

In our previous work [5], oxidation resistance of Mo₅SiB₂-based alloy at high temperature was found not to be as good as B-added Mo₅Si₁₋ₓ-basal alloys [1,2]. This deterioration of oxidation resistance may be due to low viscosity of silicate scale formed on Mo₅SiB₂ [5]. During the oxidation of Mo₅SiB₂ at the ambient oxygen pressure, two layers are developed onto the substrate; i.e. top layer is silicate and interlayer Moₙ including silicate dispersions [5]. Since the viscosity of silicate drastically decreases with increasing B concentration [6], the silicate of the top layer on the Mo₅SiB₂ substrate is considered to be much fluid at high temperature due to the B concentration of Mo₅SiB₂ (B/Si ratio = 2). If Mo–Si–B in situ composites were designated as reducing the B/Si ratio, for an example, to be in the triangle of Mo₅Si/Mo₅Si₂/Mo₅SiB₂ in the ternary phase diagram [4], oxide scale formed onto the in situ

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composites would get more protective, consequently the oxidation resistance being modified. However, toughness of the in situ composites will be still poor, because the monolithic phases of these three silicides are brittle even at elevated temperatures [3,7–9]. Furthermore, coefficients of thermal expansion of Mo₃Si₂ are much anisotropic and different from those of Mo₃SiB₂ [3,10,11], so that the composites will be readily embrittled by thermal stress. Quite recently, Yoshimi et al. suggested that the toughness of Mo₃SiB₂ could be modified by incorporating Mo [12]. Therefore, it is possible to incorporate the ductile Mo phase [13] into Mo₃Si/Mo₂Si/Mo₂SiB₂ in situ composites, the toughness may be improved. Mo, fortunately, can be in equilibrium with Mo₃Si and Mo₃SiB₂ [4]. Even if Mo contacts Mo₃Si, the reactant will be Mo₃Si. Eventually, the constituent phases in the composites would be Mo, Mo₃Si, Mo₃Si₃ and Mo₂SiB₂, being locally equilibrated. We call this kind of composites ‘pseudo in situ composites’.

The purpose of this work is to synthesize Mo/Mo₃Si/ Mo₂Si/Mo₂SiB₂ pseudo in situ composites in the Mo–Si–B system and examine their high temperature oxidation properties. In this work, SiO₂ is further added into the pseudo in situ composites in anticipation of better oxidation resistance. SiO₂ is also thermodynamically stable with, at least, Mo, Mo₃Si and Mo₃Si₃ [13]. Thus, SiO₂ can be considered as one of components in Mo–Si–B–O pseudo in situ composites.

2. Experimental procedure

2.1. Sample synthesis

A Mo–25 mol% Si–8.35 mol% B alloy was produced by arc-melting in an Ar atmosphere from 99.9 mass% Mo, 99.999 mass% Si and 99.8 mass% B. After homogenizing at 2073 K for 24 h in an Ar gas atmosphere, the ingot was pulverized by hand-milling, and powder under #270 mesh was obtained by sieving. The sieved powder was mixed with Mo and/or SiO₂ powders of 1.43 and 4 μm in size, and three kinds of mixed powders were prepared with different volume fractions of Mo–Si–B, Mo and/or SiO₂: i.e. (A) Mo–Si–B/Mo = 7:2, (B) Mo–Si–B/Mo = 3:2 and (C) Mo–Si–B/Mo/SiO₂ = 7:2:1. The mixed powder was well blended by a cross-rotary blender for 24 h, and consolidated by a spark plasma sintering (SPS) method at 1773 K and 53 MPa for 600 s. Microstructure of the consolidated bodies observed by scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS), and constituent phases were identified by X-ray diffractometry (XRD).

2.2. Oxidation test

Plate-state specimens with 6 × 5 × 0.6 mm in size were cut from the consolidated bodies by an electro-discharge machine. Top and bottom surfaces were polished with SiC paper up to #3000, and then vibratorily polished in a Buehler Vibromet 2 with 0.3 μm Al₂O₃. Thermogravimetry and differential thermal analysis (TG–DTA) were performed to observe oxidation behavior of the pseudo in situ composites. The measurement condition was at a heating rate of 10 K/min in a mixed gas atmosphere of high-purity Ar and O₂ gas (gas flow rates; Ar: 200 ml/min, O₂: 50 ml/min) in a Netsch STA409C using Al₂O₃ crucibles. Isothermal oxidation tests were also performed at 873, 1273, 1473 and 1673 K in the same instrument. In the isothermal oxidation tests, specimens were kept in a high-purity Ar gas atmosphere (gas flow rate: 200 ml/min) until furnace temperature reached a desired test temperature and held for 30 min at the temperature, then high purity O₂ gas began to flow at the rate of 50 ml/min. Oxidized surfaces were examined by XRD and SEM–EDS, and cross-section microstructure of the specimens was observed by optical microscopy (OM) and SEM–EDS.

3. Results

3.1. Microstructure of Mo–Si–B–O pseudo in situ composites

Fig. 1 shows back-scattered electron (BSE) micrographs.

Fig. 1. BSE micrographs of composites A, B and C synthesized by the SPS technique. (a) Mo–Si–B/Mo = 7:2, (b) Mo–Si–B/Mo = 3:2 and (c) Mo–Si–B/ Mo/SiO₂ = 7:2:1.
of consolidated compacts of composites A, B and C. Few residual voids formed by insufficient sintering are observed, and these compacts look sound and fully dense. A white and three gray phases in different contrasts can be seen in each micrograph, corresponding to Mo<sub>3</sub>Si, Mo<sub>5</sub>Si<sub>3</sub>, Mo<sub>5</sub>Si<sub>2</sub>, and Mo<sub>5</sub>Si<sub>2</sub>B<sub>2</sub>, respectively. At black regions, silicon and oxygen were detected by EDS. Although it was difficult to quantify its composition, this phase was suggested to be SiO<sub>2</sub>, SiO<sub>2</sub> in composites A and B is considered to be formed during the SPS process. The existence of Mo<sub>3</sub>Si and these molybdenum silicides was confirmed by XRD, as shown in Fig. 2. There are no peaks corresponding to crystalline SiO<sub>2</sub>, indicating that SiO<sub>2</sub> becomes amorphous. Therefore, the SPS technique is a promising way to produce Mo–Si–B–O pseudo in situ composites.

3.2. Oxidation behavior

Fig. 3 shows TG–DTA curves of the pseudo in situ composites obtained at the heating rate of 10 K/min in the atmosphere of Ar/O<sub>2</sub> = 4:1. Mass and heat change behavior is very similar for the three composites below about 1400 K.
Below about 1000 K, mass change is of slight gain, but TG curves are almost flat. DTA curves change to be exothermic around 650 K with increasing temperature, but heat change rates are very slow. Around 1000 K, mass and heat change values become larger. DTA curves show an exothermic peak around 1030 K, and then turn slowly endothermic with a few small fluctuations. TG curves show a mass gain peak around 1100 K, and then large mass loss up to 1400 K. Above 1400 K, in composites A and C, the mass and heat changes become small. The quantity of mass loss around 1400 K is larger in composite B than in composites A and C, and TG–DTA curves still show small fluctuations. In any case, the temperature dependence of the change in TG–DTA curves shows similar tendency for the three composites in the temperature range investigated. Accordingly, we can divide the temperature range into three with
respect to the oxidation behavior along the earlier results; i.e. (I) below 1000 K, (II) between 1000 and 1400 K, and (III) above 1400 K.

Isothermal oxidation tests were performed at 873, 1273, 1473 and 1673 K. 873 K is in the temperature range I, 1273 K in the range II, and 1473 and 1673 K in the range III, respectively. Figs. 4–6 show isothermal oxidation curves obtained at the test temperatures. At 873 K, oxidation curves exhibit mild mass gain for the three composites. The oxidation rate of composite B is slightly higher than those of composites A and C. At 1273 K, composites A and B exhibit poor oxidation resistance. At the beginning of the tests, the oxidation curves show a rapid mass loss. Although the rapid mass loss turns to mass gain once in a short while, a rapid decrease in the mass starts again, and the rapid loss never stops within the test periods. After testing, a large amount of MoO₃ was adhered in flakes on the wall of an exhaust pipe of the test apparatus. Furthermore, since the test specimens were put in an Al₂O₃ crucible during the oxidation tests, the mass change due to spalling never occurred. Consequently, the mass loss observed earlier is not due to spalling of oxide, but due to volatilization of

Fig. 6. Isothermal oxidation curves of composite C obtained at 873, 1273, 1473 and 1673 K in the atmosphere of Ar/O₂ = 4:1.

![Graph showing isothermal oxidation curves of composite C](image)

Fig. 7. SE images of surface of composite A isothermally oxidized at (a) 873 K, (b) 1273 K, (c) 1473 K and (d) 1673 K.
MoO$_3$. For composite C, a rapid mass loss occurs at the initial oxidation in the similar manner to the others, and then the mass loss rate suddenly changes to be very slow. This mass change behavior is the so-called ‘transient and steady state oxidation’, observed in B-added Mo$_5$Si$_3$ alloys and a Mo$_5$SiB$_2$-based alloy [1,2,5,12,14]. Thus, it is found that SiO$_2$ addition is effective in improving the oxidation resistance around 1273 K of the pseudo in situ composites. At and above 1473 K, the transient and steady state oxidation behavior was observed in any test. At 1473 K, the quantity of mass loss in the transient oxidation is much different between composites, which is in the order of C < A < B. On the contrary, at 1673 K, oxidation rates are nearly the same in not only the transient period but also the steady-state regime. It should be noted that the quantity of mass loss in the transient oxidation is smaller at 1673 K than at 1473 K for any composite. This suggests that protective oxide scale forms faster on the substrate at higher temperature.

3.3. Characterization of oxide scale

Figs. 7–9 show secondary electron (SE) images of surfaces of the three composites oxidized at the test temperatures for 24 h. On composites A, B and C oxidized at 873 K, two types of oxides are observed. One is elongated plate-like flake, and the other is fine-particle agglomerate. SEM–EDS analysis demonstrated that the elongated

![Fig. 8. SE images of surface of composite B isothermally oxidized at (a) 873 K, (b) 1273 K, (c) 1473 K and (d) 1673 K.](image)

![Fig. 9. SE images of surface of composite C isothermally oxidized at (a) 873 K, (b) 1273 K, (c) 1473 K and (d) 1673 K.](image)
plate-like oxide seems to be MoO$_3$ containing B, and the fine-particle agglomerate is complex oxide containing molybdenum, silicon and boron. In the XRD profiles (Figs. 10–12), peaks from MoO$_3$ are seen in addition to those from MoO$_5$. The fine-particle agglomerates might be composed of crystalline MoO$_3$ and amorphous SiO$_2$. Boron seems to be distributed homogeneously into the agglomerates. At 1273 K in the range II, glassy oxide having some defects was developed on specimen surfaces for the three composites. On composites A and B, pores are clearly open, and large plate-like oxide remains in the glassy oxide. In the XRD profiles, small peaks from MoO$_2$ and Mo$_5$Si$_3$ are still seen for the composites A and B, but no molybdenum oxide peak for the composite C. Element mapping (EM) images by SEM-EDS of composite A show that the plate-like oxide is molybdenum boro-oxide, and the glassy oxide is silicate (Fig. 13). At and above 1473 K in the range III, specimen surfaces were perfectly sealed by sound amorphous silicate without defects. This formation of sound silicate would be the cause why each composite exhibits the excellent oxidation resistance in this temperature range.

It is obvious that the oxidation resistance of the pseudo in situ composites in the range II can be improved by SiO$_2$ addition. To investigate how the protective oxide scale
Fig. 12. XRD profiles of surface of composite C isothermally oxidized at 873, 1273, 1473 and 1673 K. Solid circles indicate peaks from bcc Mo, open circles Mo$_3$Si, open squares Mo$_5$Si$_3$, open triangles Mo$_5$Si$_2$, solid squares MoO$_3$ and solid triangles MoO$_2$, respectively.

Fig. 13. SE and EM images of surface of composite A oxidized at 1273 K for 1.5 h. (a) SE image, (b) Mo, (c) Si, (d) B and (e) O mapping images.
formation was induced by the SiO₂ addition in more detail, cross-section microstructure of oxide scale developed at 1273 K was examined by SEM-EDS for composites A and C. Fig. 14 shows SE and EM images of cross-section of composite A. As shown in the SE (Fig. 14(a)) and EM images (Fig. 14(b)–(e)), the substrate is covered with complicated oxide. The condensation of only silicon is observed in the area marked by W, whereas only molybdenum in the area marked by Z. On the other hand, the area marked by X is complex oxide of silicon and boron, and the area marked by Y of molybdenum and silicon. These oxides were defective and/or porous. Fig. 15 is SE and EM images of cross-section of composite C. In contrast to composite A, composite C is entirely covered by one layer. Top layer is dense oxide mainly consisting of silicon and oxygen (Figs. 15(a), (c) and (e)), and Mo-rich dispersions are included there. From the XRD results (Fig. 12), it is deduced that the matrix of the top layer is amorphous silicate and the inclusions are bcc Mo₃C. Between the top layer and the substrate, there is a Mo-interlayer that is also dense and defect-free. An amount of boron comparable to the concentration of the substrate was detected there, but no silicon and oxygen. Thus, the scales developed on the substrates are considerably different between composites A and C, and that of composite C looks sound and protective. This would be the reason why composite C exhibits the good oxidation resistance in the range II.

4. Discussion

In this study, it has been demonstrated that Mo–Si–B–O pseudo in situ composites are successfully produced by the SPS technique, and volume fractions of Mo, Mo₃Si, Mo₂Si, Mo₂SiB, and/or SiO₂ are flexibly variable in the composites. Microstructure controlling should be also feasible with ease by changing powder size. Therefore, on the basis of the concept of the so-called harmonious design of materials functions, and using this powder-metallurgical method, we can readily modify its coefficient of thermal expansion, thermal conductivity, strength, toughness, oxidation resistance and so on, to meet development targets.

Concerning oxidation behavior of Mo–Si–B alloys, in general, molybdenum, silicon and boron are simultaneously oxidized under the ambient oxygen pressure, and then MoO₃ and B₂O₃ volatilize if the temperature is high enough.
[1,2,5,15]. Consequently, silicate scale is developed on the substrate accompanied by large mass loss. This silicate scale formation process is necessary for providing Mo–Si–B alloys with high temperature oxidation resistance [5,15]. For the present pseudo in situ composites, the silicate scale formation was observed in the temperature ranges II and III (Figs. 7–9). However, the silicate formation was insufficient at 1273 K for composites A and B, as shown in Figs. 7 and 8, so that their oxidation resistance was considerably poor at the condition. Added SiO₂ should accelerate protective silicate scale formation in the transient period at lower temperature (range II) (Figs. 9 and 15).

Interestingly, apparent oxidation rates at 1673 K are nearly the same for the three composites. The effect of the SiO₂ addition and/or Mo volume fraction was not detectable at this temperature within the test period. The B/Si ratio in the Mo–Si–B powder might be definitive at higher temperature in the range III. The amount of mass loss in the transient period is smaller at 1673 K than at 1473 K for each composite. This inverse temperature dependence of the mass loss suggests that the substrates are sealed with protective silicate scale faster at 1673 K than at 1473 K. The coverage of the substrates is considered to have proceeded by lateral flow of the silicate, and the lateral flow rate is controlled by viscosity of the silicate [15]. The viscosity of the silicate strongly depends on temperature and the B/Si ratio [6]. On the other hand, at 1473 K, the amount of mass loss in the transient period is much different among the composites, which is in the order of C < A < B. This would be caused by the difference in Mo volume fraction.

As mentioned earlier, the mass change during this silicate scale formation process is the sum total of mass increment due to binding with oxygen and mass decrement due to the volatilization of MoO₃ and B₂O₃. Thus, the mass change curves in Figs. 4–6 do not show true oxidation rates. To evaluate true oxidation rates precisely, change in thickness of the plate-shape specimens was measured for composite C oxidized at 1273 and 1673 K as a function of time. A half of the change in thickness corresponds to corroded depth of the substrate (Fig. 16). The oxidation rate is always slower at 1673 K than at 1273 K through the transient and steady-state oxidation regimes, similar to that seen in Fig. 6. Furthermore, the corroded depth–time curves in the steady-state regime are found to obey the parabolic law. The estimated values of rate constant are approximately

Fig. 15. SE and EM images of cross-section of composite C oxidized at 1273 K for 3 h. (a) SE image, (b) Mo, (c) Si, (d) B and (e) O mapping images.
$4.8 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$ at 1273 K and $1.2 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$ at 1673 K that is still three-order higher than that of oxygen diffusion in SiO$_2$ at the same temperature [16]. To enhance the high temperature oxidation resistance, as seen in B-added Mo$_x$Si$_y$ [1,2], it would be needed to decrease the B/Si ratio more.

5. Conclusions

In this work, the Mo–Si–B–O pseudo in situ composites based on the new concept were successfully synthesized from Mo$_x$Si/Mo$_x$Si$_y$/Mo$_x$SiB$_z$ in situ composite powders, Mo and/or SiO$_2$ powders by the SPS technique. The consolidated compacts are sound and fully dense, indicating that the SPS is a promising technique to synthesize the Mo–Si–B–O pseudo in situ composites. High temperature oxidation properties of the composites were examined by oxidation tests at the heating rate of 10K/min up to 1673 K and isothermal oxidation ones. Based on the obtained results, the temperature range is divided into three; i.e. (I) below 1000 K, (II) between 1000 and 1400 K, and (III) above 1400 K. In the range II, simultaneous oxidation of molybdenum, silicon and boron is accelerated for the composites that SiO$_2$ is not added, thereby reducing their oxidation resistance. Of importance is that the oxidation resistance in the range II is well improved by SiO$_2$ addition. The effect of SiO$_2$ on the oxidation resistance is interpreted in terms of the acceleration of protective silicate scale formation in the transient oxidation period. In the range III, the oxidation resistance of the composites is good even at 1673 K in spite of the existence of Mo, displaying high potential for ultra-high temperature applications. By means of this powder-metallurgical method, not only oxidation resistance but also other material properties such as coefficient of thermal expansion, thermal conductivity, strength, toughness, and so on are controllable in the Mo–Si–B–O pseudo in situ composites.

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