Oxidation behavior of Mo-Si-B *in-situ* Composites

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Abstract. Isothermal oxidation behavior of Al added Mo-Si-B *in-situ* composites was investigated under Ar-20%O_2 and air atmosphere over the temperature range of 1073–1673 K. The Al added Mo-Si-B composites ((Mo-8.7mol%Si-17.4mol%B)-1mol%Al) were prepared by arc-melting, and homogenized at 2073 K for 24 h in an Ar-flow atmosphere. The ternary Mo-Si-B *in-situ* composite exhibited a rapid mass loss at the initial oxidation stage and then the passive oxidation after the substrates were sealed with borosilicate glass in the temperature range of 1173–1473 K, whereas it exhibited a rapid mass gain around 1073 K. On the other hand, the Al addition significantly improved the oxidation resistance of Mo-Si-B *in-situ* composites at temperatures from 1073–1573 K. These excellent oxidation resistances are considered to be due to the rapid formation of a continuous, dense scale of Al-Si-O complex oxides.

Introduction

Mo-based composites are attractive materials for high-temperature structural applications to achieve high energy efficiency. Especially, Mo-Si-B alloys have high potential as heat-resistant materials at ultra-high temperature [1-5]. Akinc *et al.* reported that the oxidation resistance of Mo_5Si_3 is dramatically improved by the addition of boron at temperatures ranging from 1073 to 1773 K in air [6]. However, it would not be possible to use monolithic Mo_5Si_3 for structural applications because of its fatal brittleness and strong anisotropy of thermal expansion coefficient [7]. Mo_5SiB_2 is only one ternary compound in the Mo-Si-B system. Ito *et al.* reported that the single crystal of Mo_5SiB_2 shows excellent strength at high temperature for a few orientations [8-9]. With respect to the oxidation resistance of Mo_5SiB_2, Yoshimi *et al.* [10] studied the oxidation behavior of Mo_5SiB_2-based alloy at elevated temperatures, and concluded that the oxidation resistance of Mo_5SiB_2-based alloy is not as good as that of boron-added Mo_5Si_3-based alloys. Furthermore, they worked on thermal expansion, strength and oxidation resistance of Mo/Mo_5SiB_2 *in-situ* composites, and reported that the Mo/Mo_5SiB_2 *in-situ* composite having a eutectic microstructure shows superior high temperature strength even at 1773 K [11]. However, the oxidation resistance of the Mo/Mo_5SiB_2 *in-situ* composites is worse than that of Mo_5SiB_2 [12]. Therefore, the improvement of oxidation resistance is a key to develop Mo-Si-B alloys for ultra-high temperature applications.

Yanagihara *et al.* reported the effect of third elements on the oxidation resistance of $MoSi_2$ [13-14]. The third elements having a larger affinity to oxygen than Si show the advantages not only for the oxidation resistance at high temperature but also for the suppression of the pesting phenomenon in a temperature range from 673 to 973 K. Consequently, their results suggested that the effective fourth elements have the

potential to improve the oxidation resistance of Mo/Mo_5SiB_2 *in-situ* composites. The purpose of this work is to investigate the effect of Al addition on the oxidation behavior of Mo/Mo_5SiB_2 *in-situ* composites. Isothermal mass change is examined at several elevated temperatures, and cross-section microstructure and morphology of oxide scale are characterized. Based on the obtained results, the oxidation behavior of the Al added Mo/Mo_5SiB_2 *in-situ* composite is discussed.

Experimental Procedure

The nominal composition of a ternary Mo/Mo_5SiB_2 in-situ composite used in this study is Mo-8.7mol%Si-17.4mol%B. The Mo-Si-B alloy was produced by an arc-melting method in an Ar atmosphere from 99.9 mass% molybdenum, 99.9999 mass% silicon, and 99.8 mass% boron. Melted button ingots were flipped over and re-melted more than 5 times. And then three Mo/Mo_5SiB_2 in-situ composites having different aluminum concentrations were produced by the arc-melting method from the Mo-Si-B alloy ingots and 99.99mass% aluminum. Homogenization heat treatment was carried out at 2073 K for 86.4 ks in an Ar gas atmosphere. Nominal and chemically analyzed compositions of the present four composites are listed in Table 1.

Table 1 Compositions of the Al-doped Mo/Mo_5SiB_2 *in-situ* composites

Composite	Nominal Composition	Chemical Composition
A	Mo-8.7Si-17.4B	Mo-9.0Si-17.2B
B	(Mo-8.7Si-17.4B)-1Al	Mo-9.4Si-16.8B-1Al
C	(Mo-8.7Si-17.4B)-3Al	Mo-9.3Si-16.2B-3Al
D	(Mo-8.7Si-17.4B)-5Al	Mo-8.6Si-16.4B-5Al

Specimens for oxidation tests were cut into 5×5×1 mm pieces from the homogenized ingots by electrospark machining. Surfaces were polished with SiC paper up to No.1500, and then polished with a 0.3 μm Al_2O_3 and fine diamond abrasive for finishing. Prior to oxidation tests, the specimens were ultrasonically cleaned in acetone, and the mass and the surface area were measured. Isothermal oxidation tests were performed at temperatures raging from 1073 to 1673 K for 86.4 ks in a Netzsch STA409A thermogravimeter using Al_2O_3 crucibles. In the isothermal oxidation tests, the specimen was kept in a high purity Ar gas atmosphere (Ar gas flow rate: 6.67ml s^{-1}) until the furnace temperature reached a desired test temperature. After 900 s passed for the temperature stabilization, high purity oxygen gas began to flow at 0.83ml s^{-1}, and simultaneously the mass change was recorded. After the oxidation test, surface morphology and cross section of the oxidized specimens were examined by SEM, XRD, AES, and EPMA.

RESULTS AND DISCUSSION

Oxidation behavior of Al added Mo/Mo_5SiB_2 in-situ composites. The isothermal mass change curves are shown in Fig. 1 As shown Fig. 1 (1), no Al added, ternary Mo/Mo_5SiB_2 *in-situ* composite (composite a) exhibits a rapid mass gain at 1073 K. In the higher temperature range, i.e., 1173-1473 K, a rapid mass loss occurs at the initial oxidation stage, and then suddenly changes to the steady state oxidation in which the oxidation rate is slow and almost constant. As reported in the previous studies, this mass loss is interpreted as the volatilization of MoO_3 [10-12]. On the other hand, the Al addition considerably improves the oxidation resistance of the Mo/Mo_5SiB_2 *in-situ* composite in the temperature range between 1073 and 1573 K. The Al addition, especially 1mol% addition, suppresses the initial mass loss more than 50%. The trends of the oxidation behavior of the Al-added Mo/Mo_5SiB_2 *in-situ* composites appear to be similar irrespective of Al concentration.

These results suggest that oxidation mechanism(s) is (are) quite similar for all the Al added Mo/Mo_5SiB_2 *in-situ* composites. At and above 1673 K, however, the oxidation resistances of all the composites are drastically degraded.

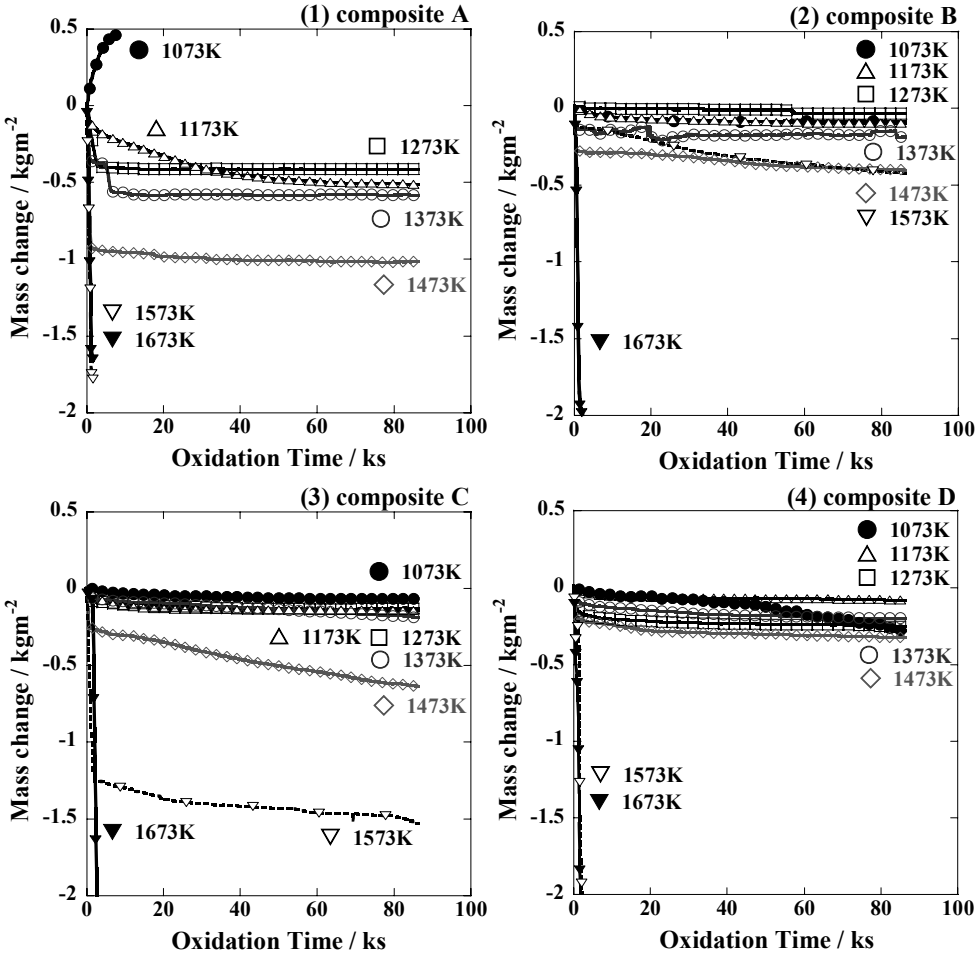

Fig. 1 Isothermal mass change curves of the composite 1, 2, 3, and 4 oxidized at temperatures between 1073 and 1673 K in an atmosphere of Ar-20%O_2.

Scale morphology of Al added Mo/Mo_5SiB_2 in-situ composites. Fig. 2 shows the surface morphologies of the four composites oxidized for 86.4 ks at 1273 K. As shown in Fig. 2 (1), the formation of a continuous scale with many pores is observed for composite A (ternary). XRD and EPMA analyses show that the scale formed on the ternary composite consists of borosilicate glass. In contrast, continuous protective scales having no pores are formed onto composite B and C (see in Fig. 2 (2) and (3)). The results of XRD analysis show that main products among the protective scales are Al_2SiO_5 and SiO_2. In addition, AES analysis shows only the peaks of Al and O from the scale surfaces. These results suggest that the protective scales mainly consist of Al-Si-O compounds and Al_2O_3 might exist on the top of the surfaces. Moreover, it is clear in composite D (highest Al concentration) that a large amount of needle-like oxides was markedly formed in the scale.

The surface morphologies of composites oxidized at 1473 K for 86.4 ks are shown in Fig. 3. The formation of a dense and continuous scale is observed for composite A. On the other hands, protective scales having needle-like crystalline Al-Si oxide are remarkably formed on Al added composites (B, C and D). The needle-like oxide increases with Al concentration. An EPMA analysis indicates that the compositions of scales formed on Al-doped Mo/Mo_5SiB_2 *in-situ* composites change with temperature and Al concentaration (see the Table 2). As the oxidation temperature is increased, Mo concentration in the scale formed on the composites decreases.

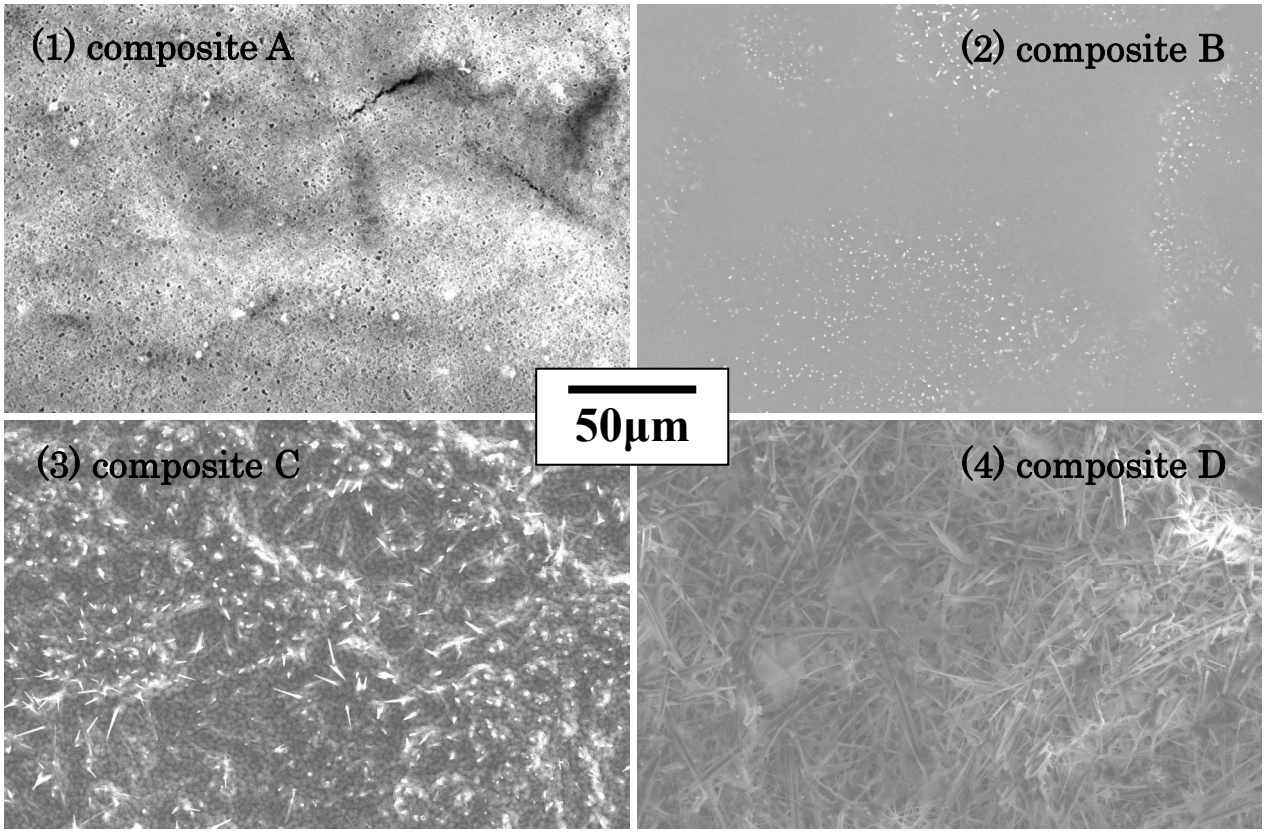

Fig. 2. SEM micrographs of the surface morphology of composite A, B, C and D oxidized at 1273 K for 86.4 ks in an atmosphere of Ar-20%O_2.

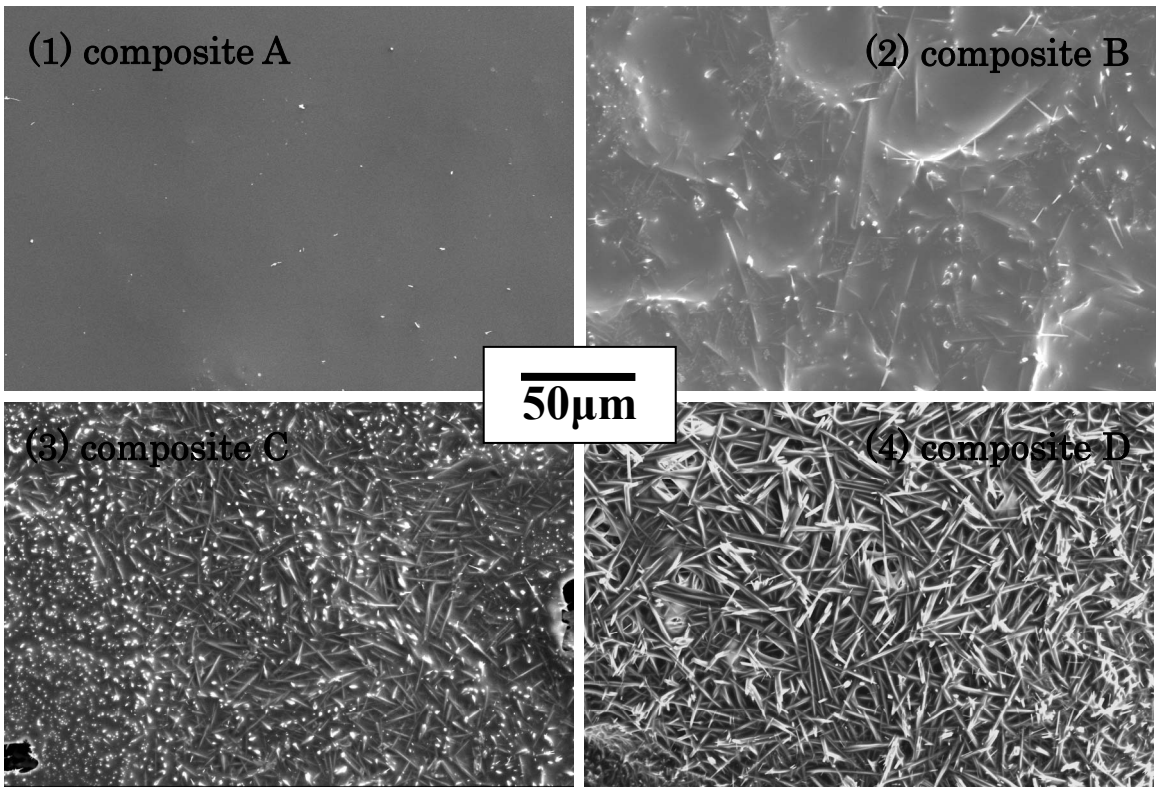

Fig. 3. SEM micrographs of the surface morphology of composite A, B, C and D oxidized at 1473 K for 86.4 ks in an atmosphere of Ar-20%O_2.

Table 2 Compositions of scales formed on the Al added Mo/Mo_5SiB_2 *in-situ* composites at 1273 and 1473 K (mol %).

		1273 K						1473 K				
		Mo	Si	B	O	Al		Mo	Si	B	O	Al
1Al	1	2.42	23.35	1.26	71.43	1.54	1	0.005	28.46	3.76	66.75	1.02
	2	1.53	28.73	2.6	66.05	1.09	2	0.007	29.17	2.12	67.09	1.61
	3	2.43	31.91	1.01	63.3	1.35	3	0.22	19.12	4.13	64.95	11.58
		Mo	Si	B	O	Al		Mo	Si	B	O	Al
3Al	1	0.34	28.34	3.02	63.44	4.86	1	0.06	22.91	4.44	64.25	8.34
	2	1.74	16.68	12.01	66.89	2.68	2	0.06	23.06	2.7	65.58	8.6
	3	0.72	26.63	2.42	64.84	5.39	3	0.03	17.25	5.35	64.12	13.25
		Mo	Si	B	O	Al		Mo	Si	B	O	Al
5Al	1	0.32	16.37	26.12	54.16	3.03	1	0.006	18.03	4.59	62.42	14.95
	2	0.61	25.99	4.7	62.43	6.27	2	0.005	18.22	6.51	60.34	14.92
	3	0.13	8.52	38.01	51.24	2.1	3	0.22	16.72	0	59.44	23.62

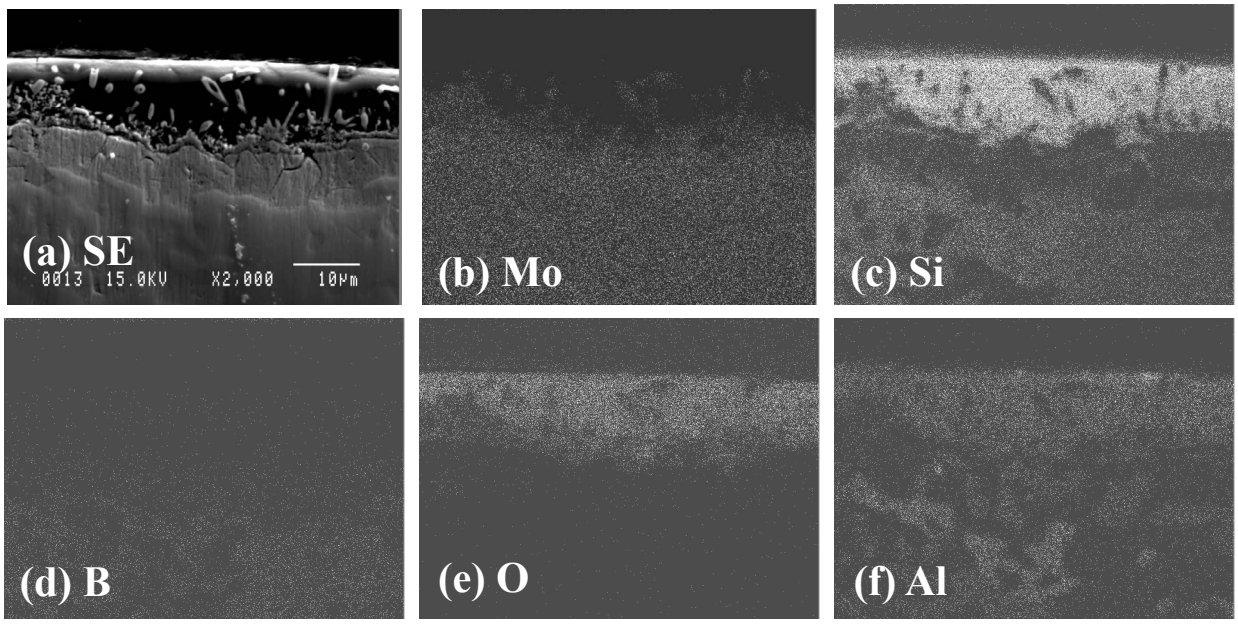

Fig. 4. (a) Scanning electron micrograph image of cross-section microstructure of composite 2 oxidized at 1273 K for 86.4 ks in an Ar-20%O_2 atmosphere. (b)-(f) Element mapping images by EPMA at the same location of (a). (b) Mo, (c) Si, (d) B, (e) O and (f) Al.

Therefore, the formation of crystalline Al-Si oxide complexes is enhanced with increasing Al concentration and oxidation temperature.

To characterize oxide scales formed on the composites, the cross-section of composite B oxidized for 86.4 ks at 1273 K, corresponding to figure 2 (2), was observed by SEM and analyzed by EPMA. Figure 4 shows a scanning electron micrograph (figure 4(a)) and element maps of Mo, Si, B, O, and Al (figure 4(b)-(f)) at the scale/substrate interface. From the scanning electron micrograph, the formation of a dense oxide scale on the substrate is observed. From the element maps, it is found that the top of the oxide layer consists of Si, O, and Al. The above results indicate that the protective scale is composed of Ai-Si complex oxides such as Al_2SiO_5. In the case of 5mol%Al, $Al_6Si_2O_{13}$ is also detected in the oxide scale. Inclusions of Mo oxides are also observed in the oxide side just around the scale/substrate interface (see in figure 4 (b)-(f)). Furthermore, a Si and B

depletion zone is observed under the Al-Si complex oxide scale. These results suggested that the selective oxidation of Si and B caused the formation of the depletion zone.

Conclusions

In the present work, the oxidation behavior of ternary Mo/Mo_5SiB_2 *in-situ* composite and quaternary Al added Mo/Mo_5SiB_2 *in-situ* composites were investigated. The following results were obtained.

1. Al added Mo/Mo_5SiB_2 *in-situ* composites show good oxidation resistance in the temperature range from 1073 to 1573 K. Al addition is effective in suppressing the initial mass loss. The oxidation resistances of Al added Mo/Mo_5SiB_2 *in-situ* composites are almost similar irrespective of Al concentration.
2. In Al added Mo/Mo_5SiB_2 *in-situ* composites, the crystalline Al-Si oxide complexes are formed on the top of the protective scale. As the Al concentration in the substrate increases, the amount of needle-like Al-Si complex oxides in the scale increases.

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