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Influence of minor Fe addition on the oxidation performance of Mo–Si–B alloys

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Multiphase Mo–Si–B alloys composed of Mo, Mo_3Si and Mo_5SiB_2 phases offer excellent high-temperature mechanical properties with the ability to resist oxidation via production of a borosilica surface layer. In the current study the effects of Fe addition were examined on the oxidation performance of Mo–2Si–1B and Mo–3Si–1B (wt.%) alloys. The analysis of the results indicated that the Fe addition limits the initial oxidation stage appreciably, primarily by enhancing the fluidity of the borosilica.

Keywords: Mo–Si–B alloys; Refractory alloys; Amorphous oxides; Oxidation; Silica glass

Mo-rich Mo–Si–B alloys are attractive for high-temperature structural applications, with strength levels well above that of pure Mo while offering some oxidation protection through the formation of a protective borosilica glass layer [1–5]. Most structural Mo–Si–B alloys have compositions in the Mo(ss)–Mo_3Si(A15)–Mo_5SiB_2(T_2) three-phase region. Oxidation protection is achieved by the initial oxidation of Mo to volatile MoO_3, accompanied by the oxidation of Si and B at the substrate surface. The borosilica produced by this process acts as a barrier to further oxidation by lowering the activity of oxygen (p_{O_2}) and slowing transport to the substrate [6].

The oxidation resistance developed in Mo–Si–B alloys is related to the effect of B (as B_2O_3) in the silica that develops upon oxidation exposure [7]. Pure SiO_2 produced by molybdenum silicides is highly viscous at temperatures below 1400 °C [8]. However, the addition of B_2O_3 decreases the viscosity of silica [9] to enhance coverage of the surface [10]. Accordingly, the B/Si ratio and relative amount of B and Si are design parameters to minimize mass loss and substrate recession during oxidation.

Previous work has shown that minor additions (0.01–2.0 wt.%) of transition metals (Fe, Ni, Co, Cu) enhance the oxidation performance of Mo-rich Mo–Si–B alloys by significantly reducing mass loss during transient oxidation at sufficiently high temperatures (1100–1370 °C) [11]. The mechanism accounting for the improvement in oxidation resistance is unclear and is the motivation for this study.

The alloys used in the current study were prepared from elemental components of at least 99.9% purity obtained from Alfa Aesar. Six 20 g ingots were produced, consisting of three Mo–2Si–1B and three Mo–3Si–1B (wt.%) alloys: a base alloy and two alloys with Fe additions of 0.05 wt.% (low addition) and 1.35 wt.% (high addition) substituted for Mo. Each ingot was synthesized by arc melting in a gettered inert argon atmosphere after repeated evacuation. Ingots were cut along their length into 2 mm thick slices. The slices were polished to 1 μm using standard metallographic processes. Scanning electron microscopy (SEM) observations indicated Mo dendrites averaged 40 μm in length and 15 μm in width, which corresponds approximately to the coarsest microstructure scale size examined in [10]. Slices near the center of each ingot were selected for sample production to ensure similar microstructure size scales. Quantitative oxidation rates were determined in a Netzsch 409CD thermogravimetric analyzer under simulated air consisting of 20% oxygen and 80% argon, with a total flow rate of 100 ml min^{-1} at 1100 °C for times ranging from 3 to 10 h. Additional samples were oxidized in ambient air at 1100 °C for 1 and 5 h, and used for the identification of crystalline oxide particles by X-ray diffraction (XRD).

Thermogravimetric analysis (TGA) results of the Mo–2Si–1B base composition and corresponding Fe

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addition alloys oxidized for 6 h at 1100 °C are shown in Figure 1. Compared to the base alloy, significant improvements in oxidation performance were demonstrated even by the low 0.05 wt.% Fe addition samples, showing a 33% mean reduction in mass loss during transient oxidation. Samples from the 1.35 wt.% Fe addition alloy demonstrated further improvement in oxidation performance, with a mass loss reduction of 75% vs. the base composition. Moreover, for the Mo–3Si–1B–0.05Fe alloy, the mass loss after a 6 h exposure at 1100 °C was saturated at 60 mg cm^{-2}, which is essentially the same as that reported by Woodard et al. [11] for a Mo–3Si–1B–0.3Fe alloy after 500 h at 1093 °C. Since similar improved oxidation performance was observed for the Mo–3Si–1B composition alloys, the discussion is focused on the analysis of Mo–2Si–1B sample behavior.

Plan view SEM images of the base and 1.35 wt.% Fe addition samples analyzed in Figure 1(a) are shown in Figure 1(b) and (c), respectively. The benefit of Fe addition for sample retention is indicated by the maintenance of the original sample size and shape in Figure 1(b) compared to the undoped sample in Figure 1(c). Inspection of Figure 1(b) shows a 48% reduction in area due to significant oxidation and volatilization of Mo in the base alloy, while Figure 1(c) shows no noticeable dimensional change and good retention of edges and overall shape of the Fe-doped alloy. The viscous borosilica produced in the base alloy necessitates local glass production for protective coverage since it cannot easily flow to unprotected areas. In Mo(ss) regions, MoO_3 production will continue until the Mo(ss) is consumed and the A15/T_2 matrix is exposed, which yields a mass loss whose magnitude is highly dependent on the micro-

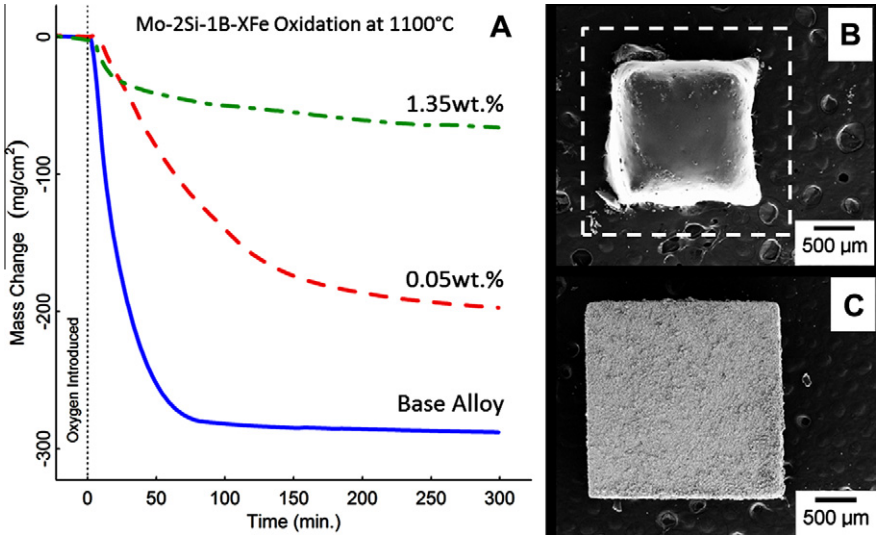

Figure 1. (A) TGA results for Mo–2Si–1B base and Fe addition alloys oxidized in simulated air for 6 h at 1100 °C with plan view SEM images of typical (B) base and (C) high Fe addition samples after oxidation. Dashed white lines outline the original sample dimensions in (B).

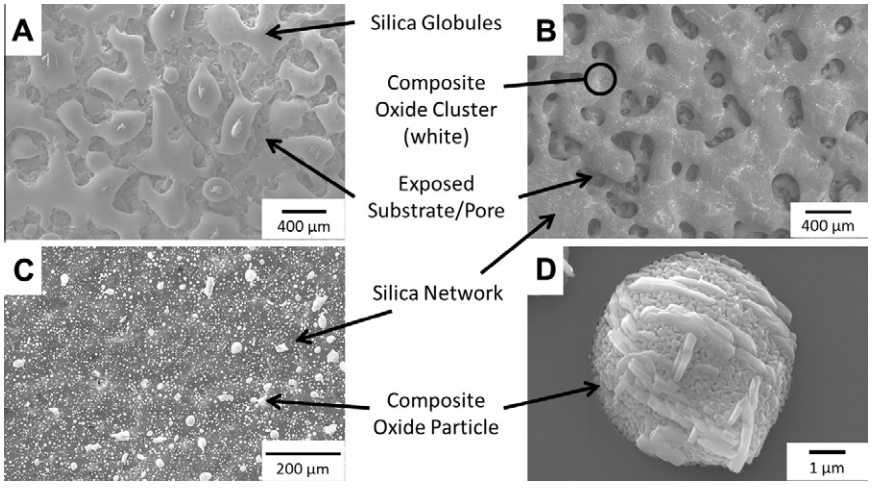

Figure 2. Plan view SEM images of Mo–2Si–1B alloys oxidized in ambient air for 1 min at 1100 °C for (A) the base alloy, (B) the low addition Mo–2Si–1B–0.05Fe alloy and (C) the high addition Mo–2Si–1B–1.35Fe alloy. An enlarged view of an individual $Fe_2(MoO_4)_3/MoO_2$ composite oxide particle in the high Fe addition sample is given in (D).