Abstract

The effect of Zr (2 *at*.%) or Fe (0.5 or 1 *at*.%) addition at the expense of Mo and moist environment on the isothermal oxidation behavior of $Mo_{76}Si_{14}B_{10}$ or $Mo_{79.5}Si_{12}B_{8.5}$ intermetallic alloys processed by either arc-melting or spark plasma sintering, have been investigated at temperatures in the range of 700–1300 °C. All the alloy microstructures have exhibited the presence of α-Mo, Mo_3Si and Mo_5SiB_2, with 7–8 vol.% SiO_2 being also observed in the spark plasma sintered (SPS) alloys. The Zr-containing SPS alloys have additionally shown 5 vol% ZrO_2. The grain-sizes in SPS alloys being finer by an order of magnitude has led to higher hardness than those of arc-melted (AM) alloys. The mass loss is found to be unabated up to 24 h at 700 °C in dry air, whereas in the range of 800–1300 °C, the initial mass-loss caused by vaporization of MoO_3 is followed by a steady-state regime of negligible mass change. Reduced mass-loss is observed in Zr or Fe containing alloys due to the consumption of volatile MoO_3 in forming non-volatile $Zr(MoO_4)_2$ or $Fe_2(MoO_4)_3$, respectively, lower volume fraction of □-Mo and microstructural refinement, all of which together has enhanced the kinetics of protective B_2O_3–SiO_2 scale formation. Strengthening of glass network by dissolved Zr or Fe ions by reducing non-bridging oxygen anions is believed to have increased stability of the glassy scale. During exposure at 700 or 800 °C in dry or moist air, the SPS alloys with finer microstructure have exhibited poorer resistance to oxidation, as the SiO_2 rich protective scale is unable to form due to slower kinetics of Si diffusion at these temperatures. However, the SPS alloys exposed in dry or moist air at temperatures □ 1000 °C have been found to be superior due to the faster kinetics of protective scale formation. In moist air too, Zr addition is found to be beneficial because $ZrSiO_4$ formation at □ 1000 °C retards the devitrification of SiO_2-rich glass. Formation of $Zr(MoO_4)_2$ and $ZrSiO_4$ is also desirable for lowering the stress generation by phase transformation of ZrO_2. The hardness of sub-scale region in arc-melted or SPS alloy is decreased by 4–10% compared to that of the unoxidized alloy.

The mass loss during exposure at 700–800 °C in moist air is reduced by 2 orders of magnitude compared to that in dry air due to the formation of protective $Si(OH)_4$ gel as the outer layer of oxide scale. Based on residual area fraction measurements too, the oxidation resistance of the Fe-less and Fe-containing alloys in moist air is found to be superior to that in dry air at 700–800 °C, whereas this trend is reversed on exposure at higher temperatures. In the temperature range of 1000–1300 °C, Fe addition is found to be particularly helpful because of the reduced vaporization of MoO_3 due to the formation of $Fe_2(MoO_4)_3$, enhanced kinetics of protective scale formation facilitated by refinement of microstructure, increased fluidity, and stabilization of borosilicate glass. The bulk hardness of the AM Si14Fe1 is reduced only by 6.7% upon oxidation at 1300 °C in both dry and moist air.

Keywords: Intermetallics (silicides); Mo–Si–B (Zr/Fe) alloys; alloying, arc-melting; spark plasma sintering; microstructure; x-ray diffraction; hardness; isothermal oxidation; oxide scale, scanning electron microscopy, transmission electron microscopy; moist air; residual alloy fraction.