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Synthesis of protective Mo–Si–B coatings in molten salts and their oxidation behavior in an air–water mixture

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Abstract

The formation of various phases during boronizing of silicided molybdenum substrates ($MoSi_2/Mo$) was investigated. Boronizing treatments were conducted in molten salts under an inert gas atmosphere in the 700–1000 °C temperature range for 3–7 h. Depending on the process type (non-current or electrochemical) and molten salt temperature, the formation of different boride phases (MoB, Mo_2B_5, MoB_2, MoB_4) was observed. At the same time, substantial oxidation of the bulk molybdenum disilicide phase ($MoSi_2$) to the Mo_5Si_3 phase was observed in non-current boronizing. The oxidation resistance of the coatings was investigated by the weight change in an air–water (2.3 vol.%) mixture at a temperature of 500 °C for a period up to 700 h. Results indicated that a two-phase microstructure consisting of the $MoSi_2$ matrix phase with 12–15 wt.% of the MoB_4 phase greatly improved the oxidation resistance of the molybdenum substrates. The weight gain rate observed was $6.5 \cdot 10^{-4}$ mg/cm^2 h.

Keywords: Electrochemical deposition; $MoSi_2$; Molten salts; Molybdenum; Boronizing; Oxidation resistance

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1. Introduction

Refractory metals can be used as a substrate material for deposition of catalytic coatings as well as structural material for microreactor fabrication due to their high melting points, good corrosion resistances, and relatively low thermal expansion coefficients. Molybdenum was chosen in previous work [1–4] as a substrate material due to its high thermal conductivity to facilitate rapid heat removal from the reaction zone to the environment. However, above 350 °C in the presence of oxygen, molybdenum oxidizes to the thermodynamically most stable oxide, orthorhombic MoO_3 [5]. The oxidation kinetics shows parabolic weight gain, which is limited by oxygen diffusion through the MoO_3 scale at temperatures up to 500 °C, and a linear weight loss due to the evaporation of MoO_3 above 650 °C [6,7]. On the contrary, Mo intermetallic compounds display an attractive combination of physical and mechanical properties, including high thermal conductivity and melting point, low density, and good oxidation or corrosion resistance. This has led to their utilization in many non-structural applications, but success in microstructural applications has been limited [8]. Therefore, an approach for the development of intermetallic materials is to utilize, where appropriate, their intrinsic high-temperature oxidation resistance through application as coatings on less oxidation-resistant (micro-) structural materials. In particular, in fossil fuel reformers and catalytic burners, where excellent oxidation resistance and moderate creep-strength are critical material requirements, the application of such materials is of a large interest. Because water vapor is present as a major product of the combustion of hydrocarbon fuels, these materials must have long-term durability in a water–oxygen environment.

Parthasarathy et al. [9] proposed a method for enhancing the oxidation resistance of molybdenum substrates by depositing silicon on the surface of the substrate followed by heating in vacuum to 850 °C [9]. As a result, an outer layer of $MoSi_2$ is formed. Synthesis in molten salts is another widely used technique for the production of various protective coatings to be

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applied as thermal barriers and wear- and corrosion-resistant surface layers. A thin protective $MoSi_2$ layer can also be obtained in molten salt baths [7,10]. The oxidation kinetics of the $MoSi_2$ phase is one of a parabolic weight gain below 450 °C [11], when simultaneous oxidation of molybdenum and silicon happens without evaporation of the produced scales causing breakdown of the protective layer (pesting) and the formation of cracks [12]. After an induction period, the mass gain increases linearly due to the development of cracks [7,11]. The Mo_5Si_3 phase has also a very poor oxidation resistance at 800–1300 °C, with pesting occurring below 800 °C. Boron doping reduces oxidation significantly by forming a low viscosity scale with oxygen diffusion as rate-limiting step [13]. The Mo_5Si_3 phase has a significant thermal expansion anisotropy (TEA) with the coefficient of thermal expansion (CTE) of the *c*-axis (α_c) more than twice that of the *a*-axis (α_a) [14,15], which limits its application as protective coatings.

The more recent works are focused on Mo–Si–B intermetallics with a high Mo content. The improved oxidation behavior of Mo–Si–B intermetallics is due to the formation of a borosilicate layer, which has a lower viscosity than pure silica scales [16]. The isothermal mass loss rate decreases with an increase of the scale viscosity of the Mo–Si–B alloys. The oxidation kinetics can be divided the into the transient and steady state oxidation stages [17]. During the transient oxidation, the surface is intensively oxidized, and molybdenum trioxide (MoO_3) rapidly volatilizes. As a result, a rapid mass loss occurs and a borosilicate scale is left on the surface. When the whole surface is covered by a borosilicate scale, the oxidation rate decreases, switching to steady state oxidation.

Unfortunately, many of the Mo–Si–B multiphase alloys have a poor oxidation resistance in the range of 500–800 °C due to the competing oxide formation of the molybdenum oxides and the silicate scales [18]. The oxidation kinetics on several systems Mo_5SiB_2 (T2 phase)–Mo_3Si [19], $Mo_5Si_3B_x$ (T1 phase)–$MoSi_2$–MoB [20], and boron doped Mo_5Si_3 [21], dramatically increase in the 650–760 °C range where weight loss is observed. Below and above this critical range, the oxidation rate is moderate [21,22]. It is mainly controlled by the diffusion of oxygen through a borosilicate layer and, therefore, depends much on the phase composition of this layer [23]. MoO_2 oxide-scale formation was observed on Mo–Si–B alloys in dry air above 1000 °C [24]. Water vapors accelerate the growth of the multiphase Mo and MoO_2 interlayers in the Mo–Si–B alloys compared to dry air [25]. All of the intermetallics in the Mo–Si–B system (Mo_5SiB_2, $MoSi_2$, MoB and Mo_3Si) have moderate coefficients of thermal expansion values ranging from $6.0 \cdot 10^{-6}$ K^{-1} for Mo_5SiB_2, to nearly $14 \cdot 10^{-6}$ K^{-1} for the *c*-axis of Mo_5Si_3B and show an approximate linear thermal expansion behavior from room temperature up to 1000 °C [14,26].

Several techniques were developed to deposit the Mo–Si–B coatings on different substrates. A multiphase Mo–Si–B alloy coating was deposited on a Mo–ZrC substrate by a low pressure plasma spraying method [27], on a steel substrate by high-velocity oxy-fuel spraying [28,29]. A B-doped Mo_5Si_3 layer was deposited on a niobium substrate by spark plasma sintering and low-pressure plasma spraying [30]. A $MoSi_2$ substrate was also previously boronized by a molten salt process at 1000 °C for 3 h [31,32]. The authors reported that oxidation of the $MoSi_2$ phase to Mo_5Si_3 takes place with simultaneous formation of the Mo_2B_5 phase. The thickness of the boronized layer was 10–20 mm [32]. Although these alloys have improved oxidation resistance, as compared to either molybdenum metal, or to the $MoSi_2$ phase, they are still not appropriate for use in microstructured applications either due to a relatively large thickness of the protective layers or due to formation of thick scales, which can change the geometry of the channels. Therefore, new compositions of protective coatings have to be found that provide sufficient or superior protection even at a thickness of few microns.

In previous work we have studied the electrochemical and diffusional synthesis (non-current transfer) of thin (5–40 μm) protective coatings of molybdenum silicides and borides in molten salts in the temperature range of 850–1050 °C and their oxidation resistance in an air–water mixture. The objective of the present work is to study the low temperature oxidative stability of different Mo–Si–B composites produced by siliciding of Mo sheets followed by boronizing of the $MoSi_2$ phase in ionic melts. Boronizing is a process by which active boron atoms diffuse into the surface of the substrate metal in order to produce a layer of borides. Mo–Si–B alloys having several different compositions will be synthesized as protective coatings on a Mo substrate in ionic melts. The thermodynamic description of the Mo–Si–B system has recently been reported [33]. However, coatings have usually properties quite different from bulk materials of the same composition, due to a strong influence of the substrate on their thermodynamic properties. Therefore, thermodynamic data cannot be directly transferred from a bulk composition to the coatings and the phase composition has to be determined experimentally. Finally, the oxidation behavior of the coatings will be measured at 500 °C in flowing air containing 2.3 vol.% water. Structural/microstructural characterization of the surface and cross-section of the oxidized alloys will be conducted to assess the scale thickness and to investigate the formation of an interlayer between the scale and the underlying molybdenum.

2. Experimental

Molybdenum sheets (99.99+ wt.% Mo) of 10 mm long, 8 mm width, with a thickness of 100 μm were used in this study.

2.1. Synthesis of $MoSi_2$

Siliciding of molybdenum substrates was carried out in a melt consisting of NaCl, KCl, K_2SiF_6, NaF, and Si (10 wt.%). NaCl and KCl (Prolabo, 99.5 wt.%) were dehydrated by continuous and progressive heating just above the melting point under a gaseous HCl atmosphere in quartz ampoules. Excess HCl was removed from the melt by argon. Sodium fluoride (Aldrich, 99.5 wt.%) was purified by double melt recrystallization: NaF was dried in a glassy carbon crucible (SU-2000) at 400–500 °C under vacuum, then heated by 50 °C above the