CONCEPTS FOR SMART PROTECTIVE HIGH-TEMPERATURE COATINGS

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INTRODUCTION

The need for high-temperature environmental resistance is a critical material barrier to the operation of fossil systems with the improved energy efficiency and emissions goals of the U.S. Department of Energy's Office of Fossil Energy. All fossil fuel-derived processes contain reactive species and high-temperature degradation arising from reactions of solids with gases and condensible products often limits performance or materials lifetimes such that efficiency, emission, and/or economic targets or requirements are not realized. Therefore, historically, the development of materials for fossil-fuel combustion and conversion systems has been closely linked to corrosion studies of alloys and ceramics in appropriate environments. This project is somewhat different; it focuses on the feasibility of new routes to controlling the critical chemical and mechanical phenomena that collectively form the basis for environmental protection in relevant fossil environments by exploring compositional and microstructural manipulations and cooperative phenomena that have not necessarily been examined in any detail to date. This can hopefully lead to concepts for "smart" coatings or materials that have the ability to sense and respond appropriately to a particular set or series of environmental conditions in order to provide high-temperature corrosion protection.

The strategies being explored involve cooperative or in-place oxidation or sulfidation reactions of multiphase alloys.[1,2] The first material systems to be evaluated involve silicides as there is some evidence that such materials have enhanced resistance in oxidizing-sulfidizing and sulfidizing environments and in air/oxygen at very high temperatures.[3] In this regard, molybdenum silicides may prove to be of particular interest. Molybdenum is known to sulfidize fairly slowly[4] and there has been recent progress in developing Mo-Si-B systems with improved oxidation resistance at high and intermediate temperatures.[5-11] Consequently, the high-temperature oxidation and sulfidation behaviors of multiphase Mo-Si-B alloys with different compositions and phase morphologies have been, and are being, studied.[12,13]

DISCUSSION OF CURRENT ACTIVITIES

Results from cyclic oxidation exposures of three-phase Mo-Si-B alloys have been reported previously.[8,12,13] There was a clear differentiation in oxidation behavior among the different compositions and phase assemblages at 1200°C. The multiphase alloys, α-Mo-Mo_5SiB_2-Mo_3Si, Mo_5Si_3(-B)-Mo_5SiB_2-

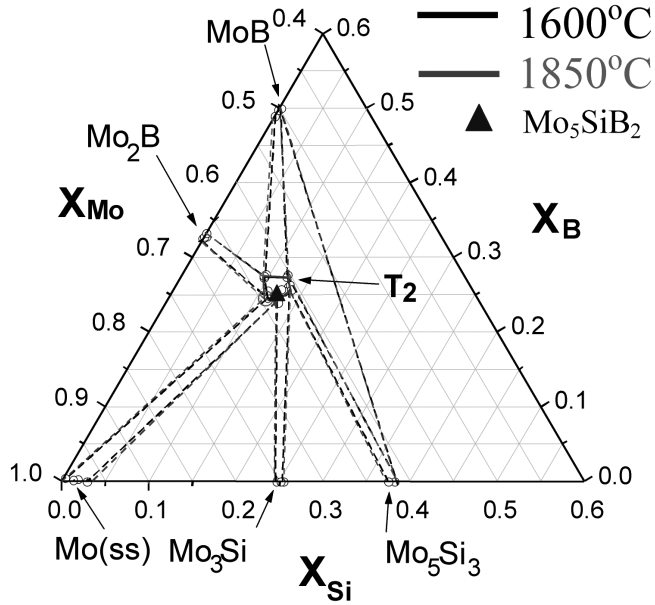

Fig.1. Partial Mo-Si-B phase diagram. Axes are in at.%.

Mo_3Si, and Mo_5Si_3(-B)-MoB-$MoSi_2$ (see Fig. 1), showed substantially better cyclic oxidation resistance than the single-phase Mo_5Si_3(-B) compositions. The results for the specimens with α-Mo suggested a multistage mechanism in which the Mo is rapidly removed by formation of volatile MoO_3 and the resulting near-surface enrichment in silicon and boron facilitates the formation of a protective borosilicate or silica layer that grows laterally to seal the remaining Mo-rich areas of the alloy from the environment.[13] Following Gesmundo and Gleeson,[1] this process would be categorized as a cooperative oxidation phenomenon.

The sulfidation resistance of α-Mo-Mo_5SiB_2-Mo_3Si alloys was evaluated by isothermally exposing specimens to an H_2-H_2S-H_2O-Ar gas mixture at 800°C for 100-150 h. At this temperature, the gas composition yielded a p_{S_2} of ~10^{-6} atm and a p_{O_2} of ~10^{-22} atm. This environment represents severe coal gasification conditions, but has been used previously to evaluate the corrosion of the most sulfidation-resistant alloys.[14,15] Furthermore, calculations based on equilibrium thermodynamics predict that Mo-Si alloys should form SiO_2 and MoS_2 under these conditions (Fig.2). Gravimetric results are shown in Fig. 3, which also includes typical data for a very sulfidation-resistant alloy, Fe_3Al,[14,16] another alumina-former (FeCrAl), and a model austenitic stainless steel (based on the nominal Cr and Ni concentrations of type 310). The different α-Mo-Mo_5SiB_2-Mo_3Si specimens (same Mo concentration, 34 vol%, but differing coarseness of the microstructure) showed similar gravimetric behavior representative of very good sulfidation resistance.

Because only thin corrosion products were observed on the α-Mo-Mo_5SiB_2-Mo_3Si (Fig. 4) after the exposures under oxidizing-sulfidizing conditions, x-ray diffraction (XRD) could not definitively determine their compositions. However, there was some XRD evidence that sulfides had formed. Typically, the Mo_3Si+T2 phase mixture was observed to be in relief above the α-Mo phase. This could be due to the formation of volatile MoO_3, but, as shown in Fig. 2, this is not expected under the present exposure conditions. Alternatively, there could be preferential spallation of the product that forms on the α-Mo phase (most likely MoS_2, see Fig. 2). A remnant of scale formed on the α-Mo phase was observed.

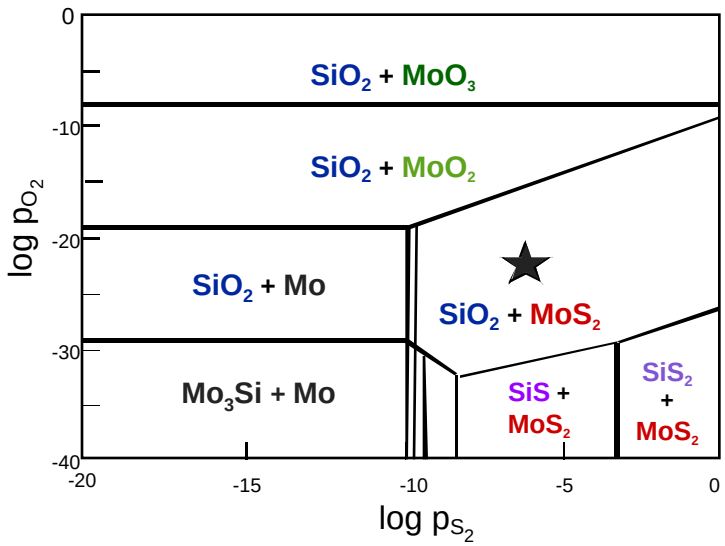

Fig. 2. Calculated product stability diagram for Mo-Si as a function of the partial pressures of oxygen and sulfur. The star represents partial pressures of H_2-H_2S-H_2O-Ar gas mixture used for oxidation-sulfidation exposures at 800°C.

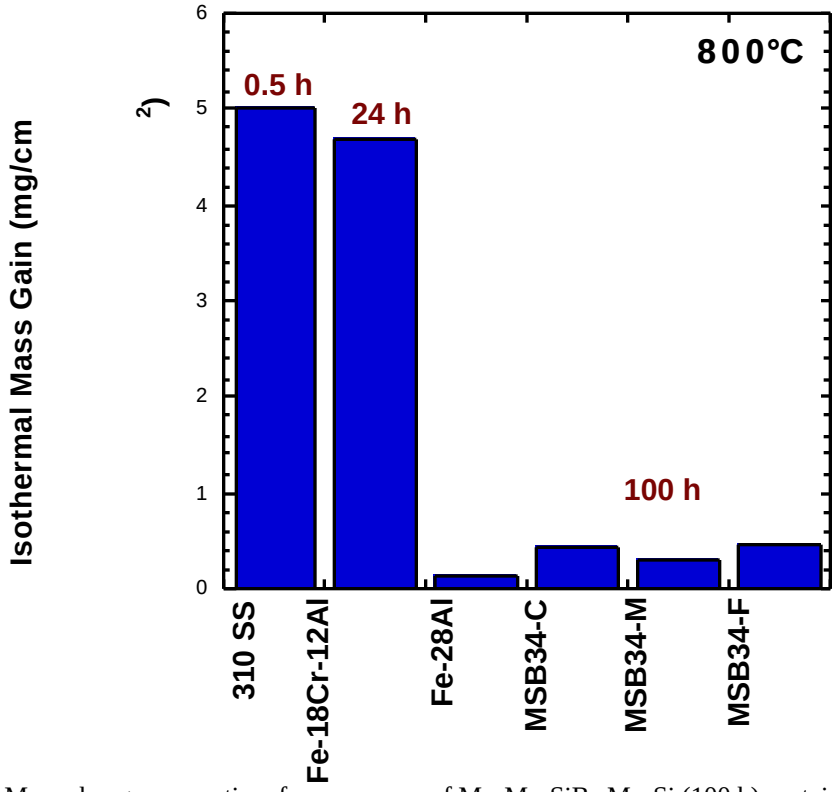

Fig. 3. Mass change versus time for exposures of Mo-Mo_5SiB_2-Mo_3Si (100 h), a stainless steel model alloy (Fe-27%Cr-19%Ni, 0.5 h), and a FeCrAl alloy (24 h) to H_2-H_2S-H_2O-Ar at 800°C. C,M, and F refer to coarse, medium, and fine phase dispersions. Concentrations are in at.%.

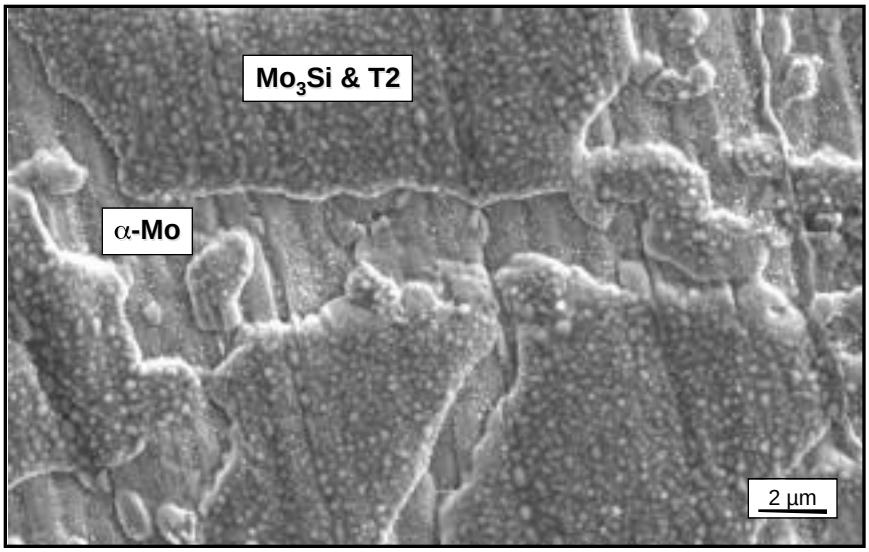

Fig. 4. Scanning electron micrograph of the surface of a specimen of α-Mo-Mo_5SiB_2-Mo_3Si after exposure to H_2-H_2S-H_2O-Ar at 800°C for 150h.

This is shown in Fig. 5, which also reveals that one part of this layer is in the process of spalling. As these products are thin and can easily reform on the α-Mo phase, such spallation may not be an important issue, but will need to be investigated in more detail.

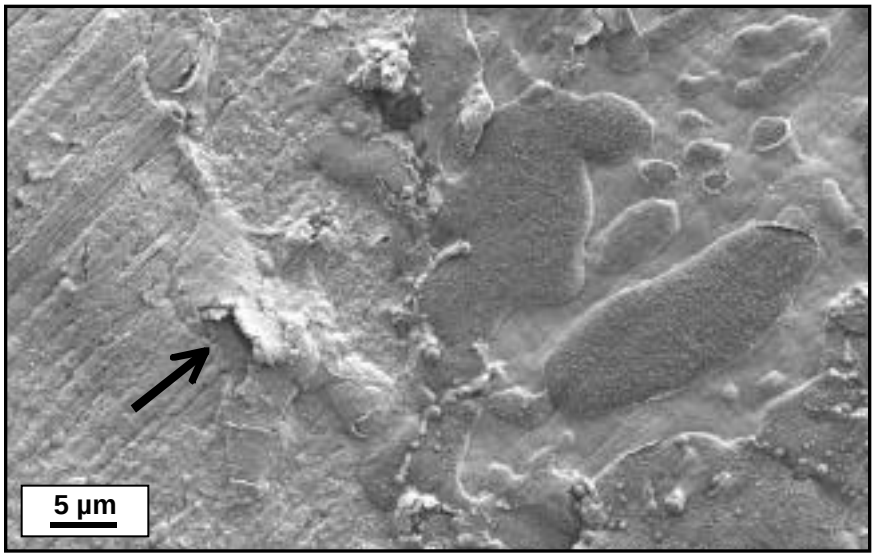

Fig. 5. Scanning electron micrograph of the surface of a specimen of α-Mo-Mo_5SiB_2-Mo_3Si after exposure to H_2-H_2S-H_2O-Ar at 800°C for 100h. Arrow indicates site of spalling of scale formed on α-Mo phase

As shown in Figs. 4 and 5, the various phases in the α-Mo-Mo_5SiB_2-Mo_3Si alloy appeared to react with the environment independently of each other. These observations suggest that, under the current exposure conditions, this alloy exhibits the "in-place" (or "independent") mode of multiphase oxidation.[1] This is in contrast to the cooperative process observed for purely oxidizing conditions at higher temperatures (see above). For in-place reactions, it is expected that the coarseness of the phase distribution should not have a major effect on corrosion behavior and this is what is observed in the gravimetric results under

oxidizing-sulfidizing conditions: there is no significant difference in mass change among those specimens with fine, medium, and coarse phase dispersions (Fig. 3).

Future work will include detailed cross sectional analyses of the sulfidized specimens as well as exposures of other variants of the base α-Mo-Mo_5SiB_2-Mo_3Si phase field. Also, oxidation exposures at 800°C will be conducted so as to directly compare behavior at 800°C under oxidizing and oxidizing-sulfidizing conditions. The knowledge gained about the different modes of reaction in different environments will be used to help explore further phase-size and composition manipulations in the Mo-Si-B system in order to evaluate the possibilities of developing such alloys as smart protective coatings. A similar approach will be used with the Ti-Al-Cr system.

Smart protective coatings may provide one of the breakthrough areas to overcome materials barriers imposed by the requirements of advanced fossil energy systems. To this end, multiphase molybdenum silicides with boron are being examined as the first material system for evaluating smart coating concepts for high-temperature corrosion resistance in fossil environments. The present work confirmed that Mo-rich, B-containing silicides can have good high-temperature sulfidation resistance.

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