International Journal of Refractory Metals & Hard Materials 71 (2018) 246–254

Contents lists available at ScienceDirect

International Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

High temperature environmental resistant Mo-Si-B based coatings

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ARTICLE INFO

Keywords:
Mo alloys
Environmental coatings
Oxidation
Water vapor
CMAS
Hot corrosion

ABSTRACT

For high temperature applications nickel base superalloys with aluminide coatings are reaching the service limit. Alternate materials such as refractory metal silicide alloys can extend high temperature capability, but the silica surfaces require coatings for enhanced environmental resistance. We present a review of an effective strategy to achieve the environmental resistance through the use of an integrated Mo-Si-B based coating that is applied by a co-deposition of Si and B by pack cementation. During oxidation of the (Si + B)-pack alloys, the initial $MoSi_2$ outer layer is consumed by formation of the Mo_5Si_3 (T_1) phase and the development of the underlying Mo_5SiB_2, T_2 borosilicide and/or MoB boride phase layer. The T_1 phase with B has excellent oxidation resistance and the loss of Si to the substrate is blocked by the underlying diffusion barrier (T_2). Any damage to the outer T_1 layer can be recovered from the T_2 + MoB layer to yield a self-healing characteristic. The Mo-Si-B based coating on Mo based alloys exhibits robust performance up to at least 1700 °C not only to high temperature oxidation, but also to water vapor and corrosive deposit attack. Some of the applications are discussed for use of the coating strategy on ceramic materials.

In the search for high temperature materials with capabilities beyond the limit of current Ni base superalloys the choices of alternative materials are limited by numerous performance criteria [1]. One empirical guideline, the Johnson relation, would require that the melting temperature, T_m be above 2500 °C [2]. Another issue is creep, the slow deformation of a material subjected to stress. Lower creep rates translate into higher maximum operating temperatures and creep rates tend to be lower for materials with higher T_m. There are only a limited number of ceramics, intermetallic compounds, and refractory metals that keep their strength at high temperatures and satisfy this initial T_m criterion. As single components, the ceramic and intermetallic phases, which have good oxidation resistance and low density, suffer from severe embrittlement problems and flaw sensitivity at low temperatures that make them unacceptably prone to failure. Composite design strategies have addressed some of the limitations, and silicon carbide matrix composites are being considered for temperatures up to 1200 °C [3]. Of the refractory metals, Mo and Nb form alloys that satisfy many of the requirements for engine applications, but they suffer from a severe drawback of poor oxidation resistance. The oxide layer that forms on Nb, Nb_2O_5, does not offer protection from further oxidation, and Mo forms an oxide, MoO_3, that is volatile above about 700 °C [4]. However, silicon- containing alloys (silicides) of these metals show some oxidation resistance. The route forward for Mo and Nb alloys borrows from lessons learned in the development of nickel superalloys along with some assistance from computational studies [5,6]. One key aspect is that the many design requirements can be satisfied with a multiphase microstructure. In the Mo base alloys, whose typical composition includes boron (Mo containing 9 at.% Si and 7 at.% B, or Mo-9Si-7B), silicide (Mo_3Si or Mo_5Si_3, called T_1) and borosilicide (Mo_5SiB_2 called T_2) phases are also present [7]. During oxidation, after a transient period when the volatilization of MoO_3 enriches the surface in B and Si, a borosilicate surface layer develops that is protective to about 1300 °C [8,9]. For the Nb base alloys, the chemistry is more complex and includes other transition metals, such as Cr, Ti and Hf [10,11]. The oxidation behavior is also more complex [10]. While both the Mo and Nb silicide alloys show high strength at high temperature, the oxide that develops on these alloys yields an alloy recession rate that is too high for the 250 μm/100 h. value for the desired lifetime [12].

One effective strategy to address an enhanced resistance to environmental attack in high- strength materials is the application of oxidation-resistant coatings. While this strategy is attractive, the successful implementation of protective coatings over the entire operating temperature range requires the satisfaction of other requirements involving thermodynamic and mechanical compatibility between the coating and the alloy substrate and the robust stability of the coating in order to maintain the integrity of the environmental protection. For the development of a coating design, the first step is to identify the key compositional and kinetic factors controlling the oxidation response. In the current work this has been accomplished by analyzing the oxidation products and the reaction pathway as a basis for applying a novel kinetic biasing strategy to control the coating phase structure and sequencing and enhance the oxidation resistance. The approach for

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https://doi.org/10.1016/j.ijrmhm.2017.11.033
Received 23 October 2017; Accepted 24 November 2017

refractory metals is reviewed for pure Mo and Mo-Si-B alloys to identify the key components of the coating design and the extension to ceramic materials such as SiC/C composites.

1. Experimental

Ingots of Mo-rich alloys with compositions of Mo-3Si-1B (wt%) [Mo-8.9Si-7.1B (at.%)] and (Mo-14.2Si-9.6B at.%) were prepared by repeated arc-melting in a Ti-gettered Ar atmosphere. Coating of the alloy slices was applied by a pack cementation process involving co-deposition of B and Si. Briefly, the pack cementation process involves the elevated temperature deposition of Si or Si + B, carried by a volatile metal-halide vapor species to the substrate embedded in a mixed powder pack containing powder of the deposition element, a halide salt activator, and an inert filler [13]. The detailed procedure of pack-cementation process is well-defined elsewhere [14,15]. The powder mixture composed of 70 wt% Al_2O_3, 25 wt% total of Si and B powder and 5 wt% NaF was loaded in an alumina crucible together by sealing with an Al_2O_3 slurry bond. The prepared crucible was annealed at 900 °C for 48 h in an Ar atmosphere. Following pack cementation coating the samples were annealed at 1300 °C for up to 10 h (i.e. conditioned) in order to establish the coating structure. For oxidation testing, the alloys were annealed in air between 700 and 1700 °C. Microstructural evaluation was performed by both optical and scanning electron microscopy (SEM) using either secondary or backscattered electron (BSE) imaging modes. Composition measurements were obtained by electron probe microanalysis (EPMA). Thermogravimetric analysis (TGA) was conducted in a Netzsch 409 instrument in an environment where O_2 was introduced at 20 mL/min to determine the in-situ weight loss.

SiC-C samples consisted of bi-directional carbon fibers contained within a SiC matrix with an external coating of ~50 μm SiC for added oxidation resistance. The SiC-C composites necessarily have an ambient SiO_2 layer present due to the external SiC coating, though as-received SiC-C composites are referred to as uncoated samples in this work.

2. Results

2.1. Mo silicides

For Mo-rich Mo-Si-B alloys the phase equilibria has been established as shown in Fig. 1 where the ternary intermetallic Mo_5SiB_2 (T_2) phase is a key constituent in the multiphase equilibria [7] along with the Mo and Mo_3Si phases. During initial contact with oxygen at elevated temperatures, Mo-Si-B alloys experience a transient oxidation stage characterized by rapid mass loss due to volatilization of MoO_3. After some time, the borosilica originating from the Mo_5SiB_2 and Mo_3Si phases extends to cover the sample surface, thereby reducing the inward oxygen diffusion. Further, it was also found that none of the alloys were passivated at lower temperatures, and all suffered from catastrophic oxidation between 700 °C and 800 °C. For example, bubbles were observed in the Mo-11Si-11B alloy scale at 800 °C, indicating that oxidation of molybdenum was occurring and that the MoO_3 bubbles were moving through the scale [16].

While there are several factors influencing the oxidation resistance that have been identified, it is clear that the B to Si ratio of the alloy is the dominant factor that controls the constitution, the viscosity and oxygen diffusivity [17] of the in-situ SiO_2-B_2O_3 passive layer upon oxidation. It is generally understood that lowering the B to Si ratio in the scale by means of increasing the silicon content in the Mo-Si-B alloys yields an increase in the high temperature oxidation resistance due to the formation of the passive SiO_2 rich layer. However, this response must be balanced by the result that excessive Si content will impact the oxidation resistant at low temperatures (i.e. 650–750 °C) since the formation of a protective SiO_2 layer in this temperature region is slow compared to the loss of Mo by the formation and volatilization of MoO_3 [18]. Thus, coating designs are necessary to provide for enhanced oxidation protection.

In order to provide a baseline for comparison, the development of oxide layer formation was analyzed in the uncoated alloy substrate. A Mo-14.2Si-9.6B (at.%) (B/Si = 2/3) ternary alloy was selected based upon prior reports that alloys with B/Si ≤ 1 exhibited a superior oxidation resistance. The Back Scattered Electron (BSE) image of an as-cast Mo-14.2Si-9.6B (at.%) sample and location of the nominal composition on the ternary isotherm at 1600°C are shown in Fig. 2a and b. The as-cast microstructure is based on the Mo(ss) + T_2 two-phase eutectic and a fine three-phase eutectic structure that shows no noticeable modification after annealing at 1300 °C for 100 h in an Ar atmosphere. The amorphous layer was determined from EPMA measurements to contain mostly SiO_2 with about 10 at.% B (or 17 mol% of B_2O_3) and in the MoO_2 layer the solubility of boron and silicon is negligible. From the layered product structure, the kinetic sequence involved in oxidation can be depicted in terms of the diffusion pathway [19] that is represented in Fig. 2c. The phase sequence in Fig. 2 indicates that the borosilica layer is connected to MoO_2 behind the initial pole between oxygen and the substrate composition [20]. An examination of the pathway reveals that the composition of the borosilica layer directs the initial phase development and influences the composition of the final product phases. For example, the formation of MoO_2 rather than MoO_3 confirms that the coating does restrict oxygen transport since it reduces

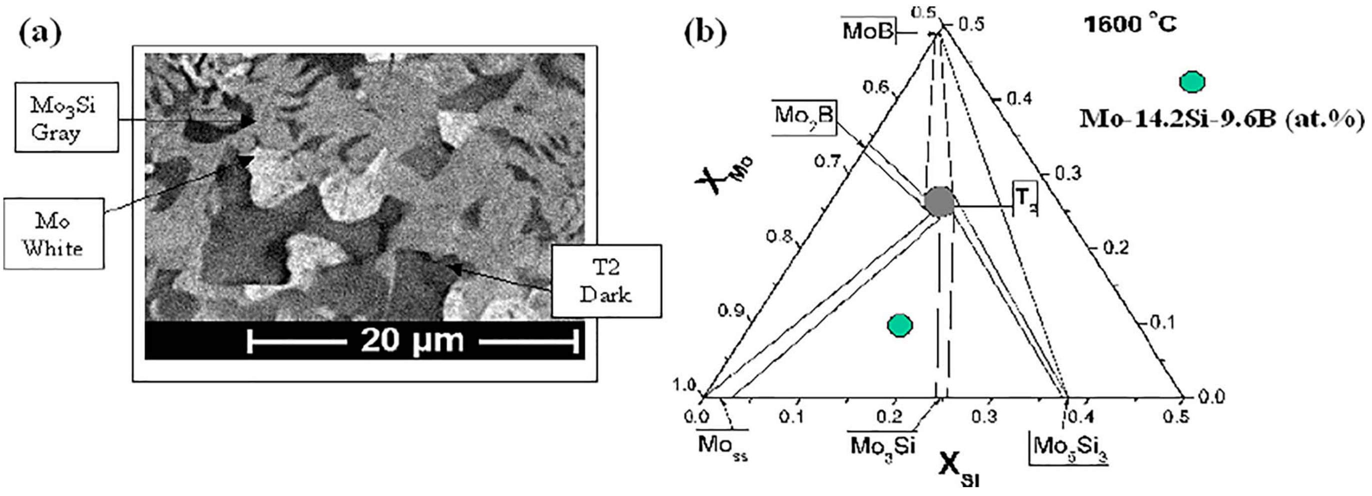

Fig. 1. a) BSE image of Mo-14.2Si-9.6B (at.%). b) Isothermal section of Mo-Si-B phase diagram [7] at 1600 °C with the Mo-14.2Si-9.6B composition marked as a triangle.