COATING STRATEGIES TO IMPROVE THE OXIDATION RESISTANCE OF BCC-MO-BASED MO-SI-B ALLOYS

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ABSTRACT

Bcc-Mo-based Mo-Si-B alloys have promising high temperature mechanical properties. In particular, the bcc-Mo+T2(Mo_5SiB_2)-based alloys have excellent resistance to fracture, with toughness values approaching 20 MPa·m^{½} for a continuous α-Mo matrix material. However, a fundamental limitation of these alloys is their poor oxidation resistance at temperatures envisioned for Vision 21 goals. On the other hand, the oxidation resistance of T1 ($Mo_5Si_3B_x$)-based alloys is exceptional, and a consensus is emerging to protect the bcc-Mo-based alloys with an oxidation resistant coating such as the T1-based alloy. The present work explored coating strategies to protect the bcc-Mo+T2 (Mo_5SiB_2)-based alloys to develop potentially oxidation resistant alloys. Two different coating processes were investigated. First, the T1-based alloy was plasma-sprayed onto Mo substrates to determine the feasibility of protecting the bcc-Mo+T2(Mo_5SiB_2)-based alloys. This work showed that air plasma spraying leads to excessive loss of Si, shifting the overall phase assemblage of the coating to a T1+T2 composition. The microstructural evolution of the coating upon annealing was studied. The second coating strategy involved siliconizing the surface of the bcc-Mo based alloy by the halide activated pack-cementation (HAPC) process. This vapor-phase process deposits Si onto the surface of the alloy, which reacts at the deposition temperature of 900°C to form a conformal layer of $MoSi_2$. The microstructure and oxidation resistance of the coating were investigated as a function of HAPC processing parameters.

INTRODUCTION

Molybdenum borosilicides are being investigated by researchers in both government and industry in the United States for use in high temperature applications. In the Mo-Si-B system, compositions based on the T1 phase, $Mo_5Si_3B_x$, have excellent oxidation resistance and creep strength [1, 2]. However, these alloys also have low fracture toughness, and the thermal expansion anisotropy of the T1 phase make these alloys susceptible to thermal stress induced microcracking [3]. These deficiencies in mechanical behavior can be improved by moving towards the Mo-rich portion of the system. Alloys which incorporate the bcc-Mo phase have dramatically improved fracture toughness, but they present a challenge in achieving oxidation resistance on par with $Mo_5Si_3B_x$–based alloys. The oxidation resistant phase of these alloys is the T2 phase (Mo_5SiB_2), and its high boron content renders a borosilicate glass with a viscosity much lower than that formed on the T1 phase. This enables excessive volatility of MoO_3 through the scale, contributing to unacceptable metal recession rates above about 1300°C [4].

Other recent works have explored microstructurally designing a bcc-Mo containing composite to balance both oxidation resistance and adequate mechanical behavior [5].

An emerging consensus is to protect the bcc-Mo-based alloys with an oxidation resistant coating such as the T1-based alloy. One technique to produce such a coated component is to plasma spray the T1-coating onto a bcc-Mo-based substrate. Spraying of the T1-based composition has been investigated recently [6,7], and those results indicated that reasonable coating densities can be achieved without excessive loss of Si and B due to evaporation during spray transit time. Another technique for developing an oxidation resistant coating is to deposit a silicon-rich coating onto the surface of the component. The halide activated pack cementation (HAPC) process is a technique which has been successfully deposit $MoSi_2$ onto a a two-phase T2/Mo(ss) alloy [8,9]. Although the steady-state oxidation rate of the coated alloy was nearly equal to $MoSi_2$ for up to 50 hours at 1300°-1500°C, the $MoSi_2$ layer partially transformed to the T1 phase, and the long term effect of this microstructural change on oxidation resistance of the coating was not investigated. The present work investigates feasibility of using both plasma spraying and the HAPC process to form oxidation resistant coatings on the bcc-Mo-based alloys.

EXPERIMENTAL PROCEDURE

PLASMA SPRAYING

Two alloy compositions were investigated as coatings for plasma spraying: an oxidation resistant alloy having the phase assemblage T1-MoB-$MoSi_2$ (Alloy 1) and a mechanically tough alloy having the phase assemblage Mo-T2-Mo_3Si (Alloy 3). Details on the synthesis and properties of these two alloys have been previously discussed [10]. Because of the difficulty with fabricating large samples of Alloy 3 suitable for plasma spraying, Mo sheet was used as a surrogate substrate on which to plasma spray Alloy 1 and Alloy 3. Both alloys were sprayed onto Mo foil of nominal thickness 0.5 mm to enable a simultaneous comparison of the oxidation behavior of both alloys. Mo foil coupons about 2 x 2 inches were grit blasted, then plasma sprayed. The standoff distance for spraying was 100 mm, and the substrate was air cooled from the backside through holes in the support plate. Spraying was performed using a 200 mm/sec raster at a 2.5 mm pitch. Alloy 1 was sprayed on one face, then the coupon was reversed and Alloy 3 was sprayed on the other side. Five coupons were prepared, with 10 layers of Alloy 3 sprayed and 10-20 layers of Alloy 1 being sprayed on each substrate.

Inconsistent layer thickness was noted on the Alloy 1 coating due to poor feeding of the powder into the gun. Unbalanced residual stresses were present in the coupons as warpage was noted in each tile. In order to relieve these residual stresses, and also to promote chemical and thermodynamic equilibrium of the sprayed coatings, the tiles were annealed at 1800°C in flowing argon. Previous work has shown that this promotes complete re-crystallization of plasma sprayed Alloy 1, but no previous work is available regarding sprayed and annealed Alloy 3.

HALIDE ACTIVATED PACK CEMENTATION

Alloy 3 pellets were prepared for HAPC coating using a powder metallurgical process, and more details on the processing of these pellets can be found elsewhere [10]. This process involved

sintering powders of composition Mo-4.3Si-1.1B (at%) with a particle size < 20 μm in an argon atmosphere at 1800°C for 2 hours. The pellets were then cut into coupons of nominal surface area 1 cm^2, polished to 0.05 μm alumina abrasive, and ultrasonically cleaned in ethanol. The halide-activated pack cementation process [11] was used to deposit silicon or to co-deposit both silicon and boron onto the pellet. The coupons were embedded in two powder mixtures (wt%): $Si:NaF:Al_2O_3$ = 10:2:88 or $Si:B:NaF:Al_2O_3$ = 9:1:2:88. The substrate coupon was packed in the powder in an alumina crucible closed by an alumina lid using alumina-based cement. The crucible was loaded into a quartz tube and high purity argon was flowed for two hours to purge ambient air. The packs were then heated under flowing argon to 900°C and held for 16 hours.

CHARACTERIZATION

Both the plasma sprayed tiles and the HAPC coated substrates were examined by X-ray diffraction (XRD, Scintag XDS 2000, Cupertino, CA) to identify the phases formed, and both the surface and cross-section were examined by scanning electron microscopy using backscattered electron imaging (SEM/BSE, JEOL, JSM 6100, Peabody, MA) with energy dispersive spectroscopy (EDS, Oxford Instruments, Valley, CA). For oxidation testing, the coated substrates were first oxidized in air at 1100°C to form a protective glassy scale. For the plasma sprayed tiles, this step resulted in the complete oxidation of the plasma sprayed Alloy 3 coating and the underlying Mo foil, leaving an intact Alloy 1 plasma-sprayed coating. The samples were then heated to 1600°C in ambient air. For quantitative measurement, the oxidation coupons were suspended from a sapphire wire in a vertical tube thermo-gravimetric analyzer using an electrobalance sensitive to 0.01 mg (Cahn-2000, Cahn Instruments, Inc., Cerritos, CA). The surface and cross-section of the oxidized samples were analyzed similarly as the coated samples.

RESULTS AND DISCUSSION

PLASMA SPRAYING

XRD analysis of the unannealed and 2 hour annealed Alloy 1 coating revealed some interesting changes. The pre-anneal pattern indicated that a large degree of chemical inhomogeneity as Mo, MoB, T1, T2, and $MoSi_2$ were present. However, the post anneal pattern indicated that the overall phase assemblage had enriched in Mo, shifting to a T1+T2 structure. Pre and post anneal XRD analysis of the Alloy 3 coating also revealed interesting changes. The pre-anneal pattern indicated that the coating pattern was dominated by the Mo phase, but this is similar to the condition of the as-received powder prior to plasma spraying. However, after annealing the coating appears to be predominantly the bcc-Mo phase as no other measurable peaks were present in the pattern. It must noted that these results only indicate the condition of the near surface of the coatings, and so the coating cross-sections were investigated by SEM to better characterize the final phase assemblage of the annealed coatings.

SEM investigations confirmed the findings of the XRD analysis. The Alloy 1 coating was much thicker than the Alloy 3 coating, with thicknesses of about 1000 μm and 500 μm, respectively. Figure 1 shows the 2 hour annealed Alloy 1 coating was relatively dense, with porosity decreasing throughout the coating from the substrate to the surface. Large and irregular pores were found closer to the substrate, with much finer micron sized pores uniformly distributed

throughout the coating. Figure 2 shows that the non-equilibrium structure of the unannealed coating, while Figure 3 shows that the 2 hour annealed coating was composed of a T2 matrix with T1 distributed throughout the entire coating. The surface of the coating became porous after annealing, forming a continuous, 10 μm thick T2 layer, due primarily to the loss of Si in the low oxygen partial pressure atmosphere. A 10 μm thick interlayer of T2+Mo_3Si formed between the coating and the Mo substrate, as shown in Figure 4, and this is expected from literature work on diffusion in the Mo-Si-B system [12]. Extended annealing for 100 hours at 1800°C exaggerated both of these reactions. Figure 5 shows that only a thin layer of the original coating (which contains the T1 phase) remains unreacted, with Si loss due to surface evaporation leading to complete metallization of the surface. Interestingly, the phase evolution between the coating and atmosphere roughly mimicked that between the coating and the Mo substrate. An exclusive T2 layer formed adjacent to the Mo layer with an expanded Mo_3Si + T2 interlayer, shown previously in Figure 4, adjacent to the original coating.

Figure 6 shows that the Alloy 3 coating, being much thinner and more porous than the Alloy 1 coating, was dominated by very large and irregular pores exceeding 50 μm in size. The matrix phase of the coating was bcc-Mo (from XRD analysis) containing measurable Si in solution (3.5 at% by EDS). There was a minor amount of finely distributed T2 phase. No distinct interface was evident between the Mo substrate and the Alloy 3 coating, indicating that annealing promoted formation of an intimate bond between the Mo-phase components of the coating and the substrate.

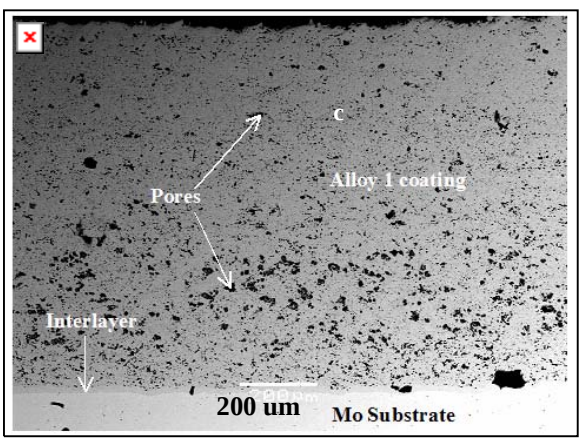

Figure 1: BSE image of cross-section of plasma-sprayed Alloy 1 coating after annealing at 1800°C for 2 hours in argon.

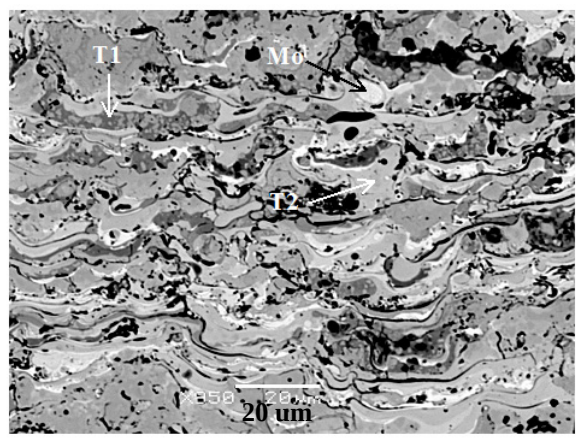

Figure 2: BSE image of cross-section of as-sprayed Alloy 1 coating showing inhomogeneous phase formation.

HALIDE ACTIVATED PACK CEMENTATION

Figures 7 and 8 show the cross-section of the coating formed on Alloy 1 coupon from the Si pack. A uniform coating layer with a thickness of about 8 μm formed on the substrate. EDS and XRD analysis confirmed that the coating was $MoSi_2$. Although the edges of the coupon were rounded prior to HAPC, the $MoSi_2$ layer still cracked in that area. Figure 9 shows that the $MoSi_2$ coating grain size ranged from several microns to about 30 microns.

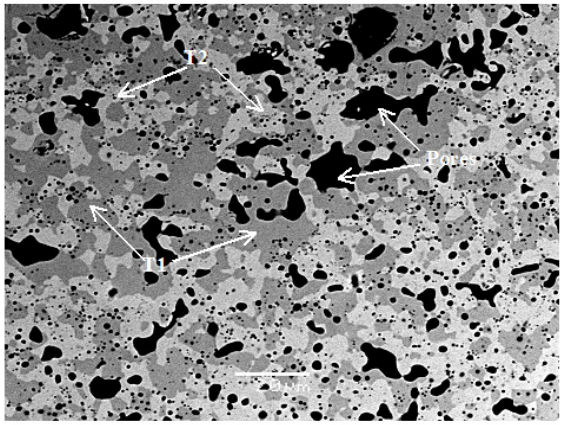

Figure 3: BSE image of area C in Figure 1 showing T1 + T2 phase assemblage after annealing at 1800°C for 2 hours in argon.

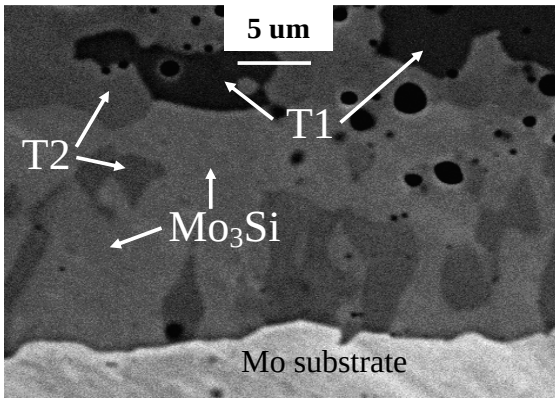

Figure 4: Reaction layer between Mo substrate and plasma sprayed Alloy 1 coating after annealing at 1800°C for 2 hours in argon.

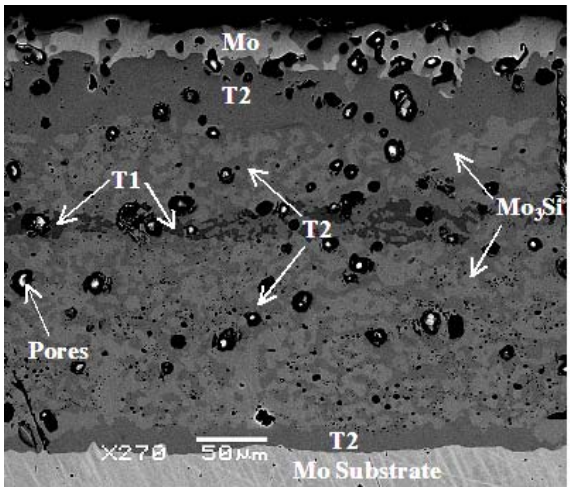

Figure 5: BSE image of cross-section of plasma-sprayed Alloy 1 coating after annealing at 1800°C for 100 hours in argon.

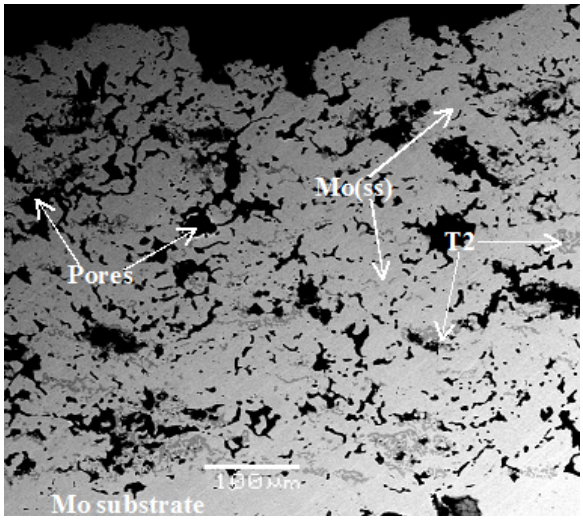

Figure 6: BSE image of cross-section of plasma-sprayed Alloy 3 coating after annealing at 1800°C for 2 hours in argon.

While some pores are visible on the surface of the $MoSi_2$ coating, these pores are believed to be coated. Area 1 of Figure 10 shows a pore that impinged the surface and was uniformly coated with $MoSi_2$, indicating the conformal nature of the HAPC process. Area 2 of Figure 10 shows a region where the $MoSi_2$ coating spalled from the surface, and together with the coating cracking at the coupon edges, this suggests that the coating may not form a suitable oxidation barrier.

Figure 11 shows the cross-section microstructure of the coating formed on Alloy 1 coupons from the B+Si pack. A mixed phase coating with a thickness of about 10 µm formed on the coupon,

with the main phase (dark grey region) in the coating verified as $MoSi_2$ by combined XRD and EDS analysis. The bright grey region was not identified from the XRD analysis, although EDS analysis suggested a Mo-rich phase such as MoB.

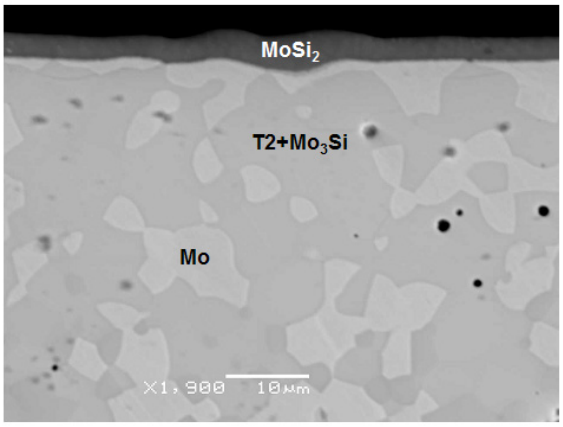

Figure 7: BSE image of cross-section of coating formed on Alloy 3 in the Si pack mixture at 900°C for 16 hours in argon.

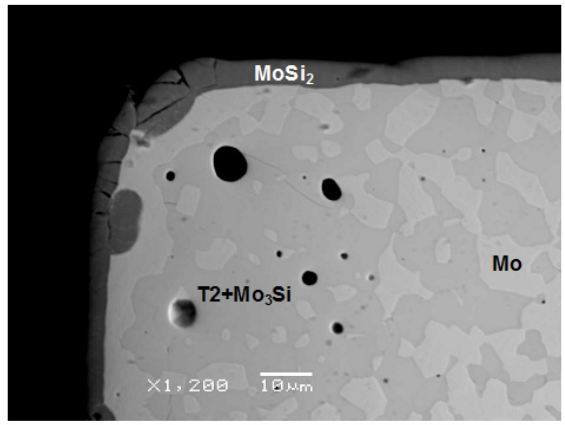

Figure 8: BSE image of cross-section of coating formed at the substrate corner in the Si pack mixture at 900°C for 16 hours in argon.

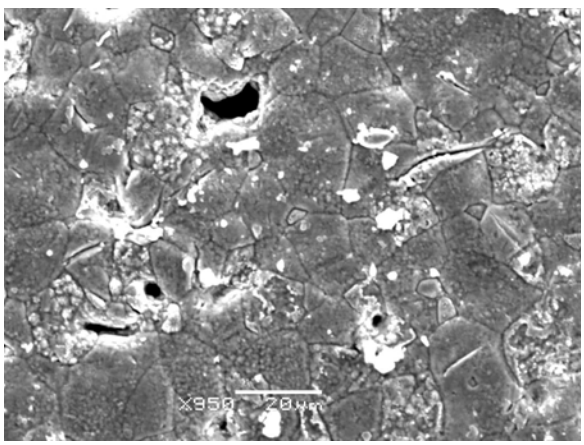

Figure 9: Surface morphology of the coating formed on Alloy 3 in the Si pack mixture at 900°C for 16 hours in argon.

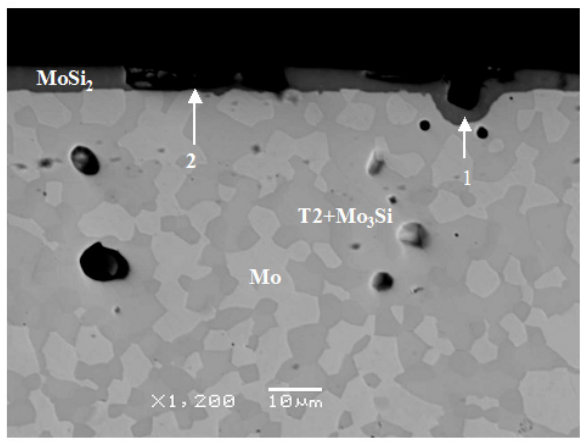

Figure 10: Coating formed on Alloy 3 in the Si pack. Area 1 shows a conformally coated pore, while Area 2 shows coating surface spallation.

OXIDATION TESTING

The plasma-sprayed tile was first pre-oxidized at 1100°C for 1 hour in ambient air. The Alloy 3 coating, which is essentially pure bcc-Mo, and the Mo substrate were completely oxidized, leaving an intact Alloy 1 plasma-sprayed coating. The coating was then oxidized for 500 hours in flowing air at 1600°C, and the plot of mass change is shown in Figure 12. The parabolic rate constant, kp, was comparable to monolithic Alloy 1, indicating that the plasma spray process does not have a detrimental effect on the intrinsic oxidation resistance of Alloy 1. Figure 13 shows that a continuous glassy scale formed on the oxidized coating, and that a region of silicon depletion is suggested since a continuous layer of T2 formed adjacent to the glassy scale.

Oxidation testing of HAPC coated Alloy 3 verified the incomplete coverage of the coating. The Alloy 3 substrate was rapidly oxidized as it was nearly consumed after 50 hours at 1600°C in air.

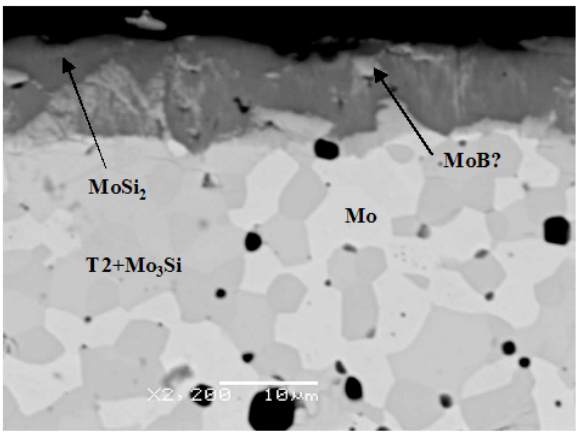

Figure 11: BSE image of cross-section of coating formed on Alloy 3 in the Si+B pack mixture at 900°C for 16 hours in argon.

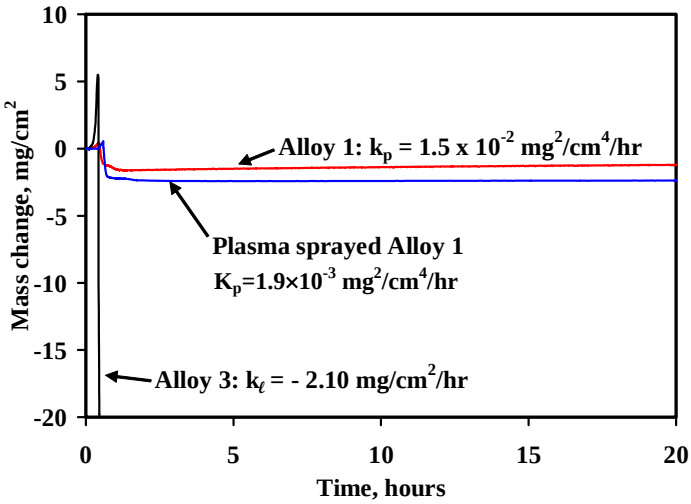

Figure 12: Plot comparing the mass change of plasma-sprayed Alloy 1 to monolithic Alloy 1 and Alloy 3 at 1600°C in air.

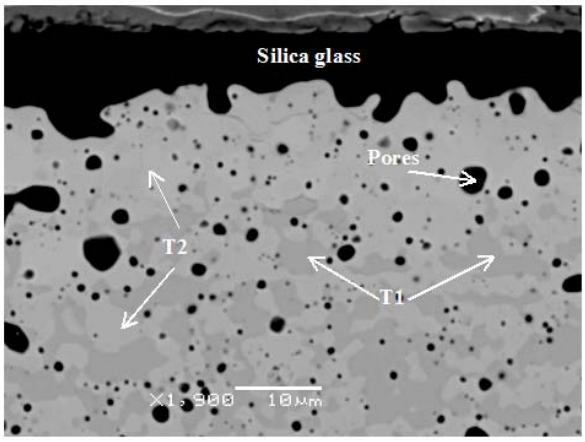

Figure 13: BSE image of cross-section of scale formed on plasma-sprayed Alloy 1 after 100 hours at 1600°C in air.

CONCLUSIONS

Air plasma spraying of Alloy 1 led to the loss of Si and B, but this was not detrimental to the oxidation resistance of the sprayed Alloy 1 coating. A protective glassy scale formed on the coating with a parabolic rate constant similar to monolithic Alloy 1 at 1600°C in air. However, air plasma spraying of Alloy 3 led to severe loss of Si and B, with the coating shifting to almost pure bcc-Mo. This contributed to the rapid oxidation of the coating at 1100°C, while monolithic Alloy 3 which contains T2 and Mo_3Si is expected to form a protective glassy scale [10]. Low pressure plasma spraying will be essential in order to maintain the stoichiometry of the Alloy 3

coating. Conformal $MoSi_2$ coatings were deposited onto Alloy 3 using the HAPC process. However, localized spalling of the coating led to incomplete coverage, and this resulted in the loss of protective behavior of the coating. Process modification to produce thicker coatings and to eliminate spalling is needed in order to validate the protective nature of HAPC coatings.

ACKNOWLEDGEMENTS

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