

Oxidation Behavior of Oxide Particle Spray-deposited Mo-Si-B Alloys

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Abstract The effect of spray deposition of oxide particles on oxidation behaviors of as-cast Mo-14.2Si-9.6B (at%) alloys at 1200°C up to for 100 hrs has been investigated. Various oxide powders are utilized to make coatings by spray deposition, including SiO₂, TiO₂, ZrO₂, HfO₂ and La₂O₃. It is demonstrated that the oxidation resistance of the cast Mo-Si-B alloy can be significantly improved by coating with those oxide particles. The growth of the oxide layer is reduced for the oxide particle coated Mo-Si-B alloy. Especially, for the alloy with ZrO₂ coating, the thickness of oxide layer becomes only one fifth of that of uncoated alloys when exposed to in air for 100 hrs. The reduction of oxide scale growth of the cast Mo-Si-B alloy due to oxide particle coatings are discussed in terms of the change of viscosity of glassy oxide phases that form during oxidation at high temperature.

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Key words: spray deposition, oxidation resistance, Mo-Si-B alloy

1. Introduction

High demands for higher service temperature of aircraft engines have led to search alternative materials replacing Ni-based superalloys. Among the developed high temperature materials, intermetallics such as aluminides and silicides have been received attention for their high melting points and thermal stability[1]. Especially, Mo based silicides exhibit excellent materials properties at high temperature together with the inherent high melting temperature[2]. While the nature of molybdenum silicides shows high thermal stability, the brittleness of the materials has limited structural applications. The discovery of Mo-Si-B ternary system has provided a resolution for the inherent brittleness of molybdenum silicides by formation of a stable two phase composite, i.e. ductile Mo (solid solution) and Mo₅SiB₂ (called as T₂ phase) [3].

The stable in-situ composite that can be produced by a casting process at an inert atmosphere exhibits a ductile phase toughening mechanism upon applied loading at high

temperature. The phase equilibrium between Mo and T₂ phase is shown in Fig. 1[4]. The two phase mixture (Mo and T₂ phase) exhibits high tensile strength (~ 1 GPa) with a fair amount of elongation at 1400°C, which can be an excellent potential materials for replacing Ni-based superalloys[3-5]. However, the inherent

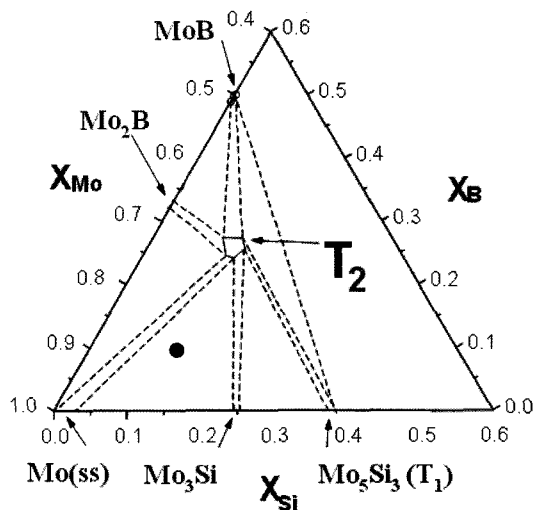


Fig. 1. Isothermal phase diagram of the Mo-Si-B ternary system. The marked point stands for the nominal composition.

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fatal oxidation behavior of the Mo-Si-B alloys still requires further study in order to select the materials for structural parts at high temperature[4,5]. It has been documented that a fatal pesting process, which forms MoO_3 and evaporates at low temperature, leads to decomposition of Mo alloys and raised concern for practical application[6]. Moreover, the formation of low viscosity of the exterior SiO_2 - B_2O_3 oxide scale during oxidation exposure limits a high temperature application. It has been reported that the low viscosity of the SiO_2 - B_2O_3 oxide scale (high B/Si ratio) can accelerate oxidation process, while a low B/Si ratio in the alloy system provides a synthesis of high viscosity SiO_2 - B_2O_3 oxide scale during oxidation[7-9]. However, when the alloy is composed of a extremely low B/Si ratio, a ductile phase toughening mechanism may not be achieved due to the low amount of T_2 phase. In order to increase the viscosity of SiO_2 - B_2O_3 oxide scale, ternary phase mixture Mo (ss) + T_2 + Mo_3Si that allows increased silicon content in the SiO_2 - B_2O_3 oxide has been practiced and showed that the three phase mixture does also show an excellent mechanical behavior at high temperature.

In this perspective, a strategic alloy and coating design is needed in order to maintain a ductile phase toughening mechanism and to protect the alloy surface from oxidation. In order to enhance the oxidation resistance, several coating processes have been performed such as pack cementation, which modifies the B/Si ratio at the alloy surface, and a controlled B/Si ratio can bias the viscosity of the protective oxide scale[10]. Previous results show that the pack cementation process works for protection of the alloy, while there are still an unresolved issue of an initial period of the oxidation process that includes evaporation of MoO_3 [8].

In this regard, strategic surface coatings that allow evaporation of MoO_3 at the initial oxidation period, and protective surface coatings during oxidation process are needed for the practical application of the Mo-Si-B alloy system.

For the present study, a spray deposition process using a compressed air has been selected for coating the Mo (ss) + T_2 + Mo_3Si three phase alloys, since the spray deposition process possesses (1) easy accessibility, (2) economically favorable, (3) low coating layer density before heating that allows evaporation of MoO_3 during the initial period of oxidation, (4) the coating layer density becomes higher upon exposure at high temperature (i.e., sintering process). In order to evaluate the extents of oxidation, the thickness of the oxide scale formation has been measured that reflects the oxygen diffusion during the exposure in air atmosphere. Cross sectional observations of the as-cast Mo (ss) + T_2 + Mo_3Si alloy and oxide layer coated Mo (ss) + T_2 + Mo_3Si alloy were compared at 1200°C and the effect of the oxide coatings on the oxide scale layer formation has been investigated during high temperature exposure in air.

2. Experimental procedure

30 grams of ternary alloy ingots with a composition of Mo-14.2Si-9.6B (at%) were prepared by arc-melting in a Ti-gettered Ar atmosphere and sliced into 3 mm thick discs. Each sliced piece was polished with SiC paper and ultrasonically cleaned. For producing oxide layer coatings, spray deposition process has been adopted using compressed air. The schematic illustration of the spray deposition process is shown in Fig. 2. Oxide powders (SiO_2 , ZrO_2 , HfO_2 , TiO_2 , and La_2O_3) were mixed with ethanol in a cup holder that attached on the spray gun. Then, compressed air was attached to the

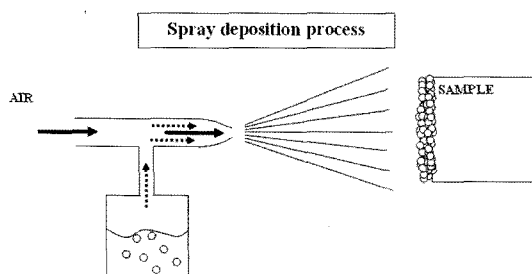


Fig. 2. Schematic figure of the spray deposition process.

spray gun, so that when the compressed air is open to the gun, (1) the compressed air carries the oxide powders with ethanol towards the substrate, and (2) the Mo-Si-B alloy can be coated with the oxide powder with ethanol. The powder deposited substrates were left in a drying oven for about 1 hour so that the ethanol can be evaporated. For oxidation tests, the specimen was placed in an alumina boat and inserted into a furnace initially set at 1000 or 1200°C in air. After the samples are reached the designated exposure time, they

were pulled out of the furnace promptly and cooled in air. All of the oxidation tests have been practiced in this manner.

Following oxidation tests, the samples were cut in perpendicular to the interface with a diamond saw. The cross sections were examined by SEM (Scanning Electron Microscopy (JEOL 6100)) with BSE (Back Scattered Electron) imaging. XRD (X-ray Diffraction (STOE X-ray Diffraction System)) was used for identification of crystal structures and synthesized phases. Phase compositions were determined by EPMA (Electron Probe Micro Analysis (CAMECA SX51)).

3. Results and discussion

The cross section of the as-cast Mo-Si-B alloy exposed at 1000°C is shown in Fig. 3. The oxide scale was identified in a following sequence: $\text{SiO}_2\text{-B}_2\text{O}_3$ layer, MoO_2 , oxide affected zone, and substrate, in which the MoO_2 layer

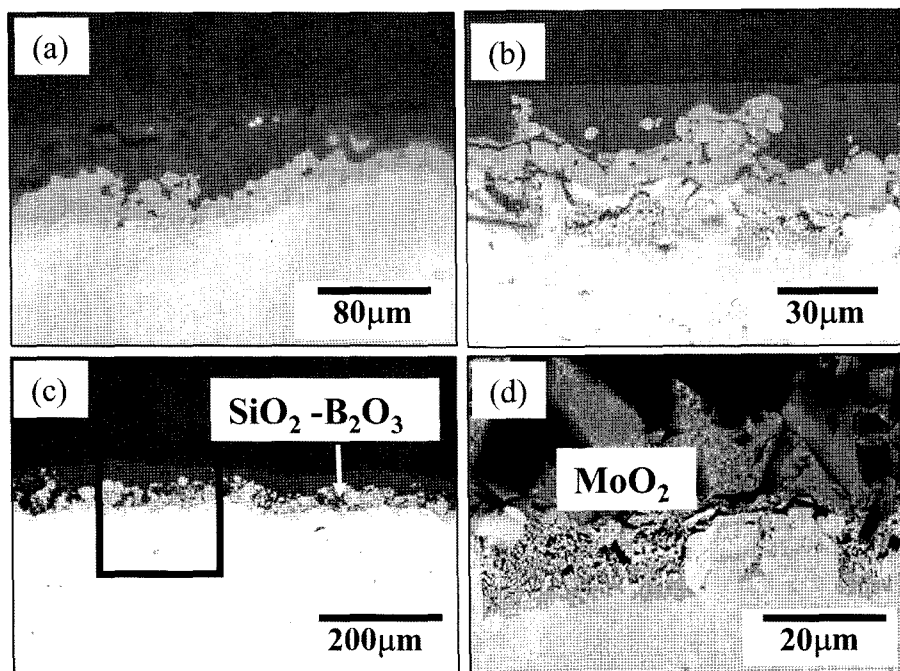


Fig. 3. SEM back scattered image of the Mo-14.2Si-9.6B alloy exposed at 1000°C in Air for (a) 25 hr, (b) 50 hr, and (c) 100 hr. (d) is enlargement of the marked area in (c).

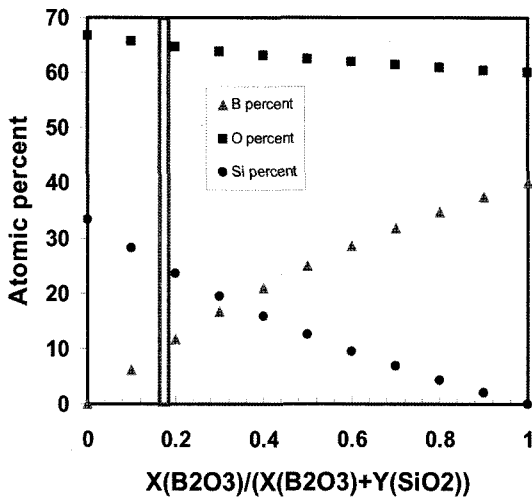


Fig. 4. Mole fraction of B_2O_3 of the exterior oxide scale synthesized during oxidation.

was developed as an irregular shape. The layer thickness became larger when the oxidation time was increased. The B/Si ratio of the EPMA measurements of the exterior SiO_2 - B_2O_3 layer was about 0.4 and the amount of oxygen was about 65.8 at%. When the composition was transformed into a mole fraction of SiO_2 - B_2O_3 , the B_2O_3 mole fraction was estimated as about 0.2 mole percent (Fig. 4), indicating that the exterior oxide scale is composed of mainly SiO_2 . When the growth of the scale was measured with respect to the oxidation exposure time, the thickness of the total growth layer was identified as a parabolic growth, implying that the scale formation is governed by inward diffusion of oxygen as shown in Fig. 5.

In order to examine the growth behavior of the Mo alloy at higher temperature, the as-cast Mo-Si-B alloy was exposed at $1200^\circ C$, and the cross section is shown in Fig. 6. The layer sequence was very similar to the specimen exposed at $1000^\circ C$. The morphology of the oxide layer was developed in an irregular manner, indicating that the viscosity of the SiO_2 - B_2O_3 layer is lowered at $1200^\circ C$. At the same

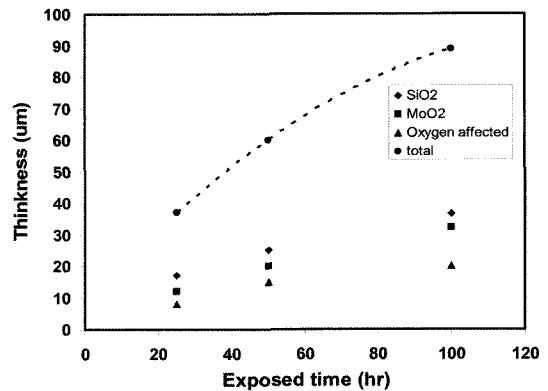


Fig. 5. Oxidation thickness vs. exposed time for the Mo-14.2Si-9.6B alloy exposed at $1000^\circ C$.

time, the SiO_2 - B_2O_3 layer was also found beneath the MoO_2 layer. It is probable that since the viscosity of the SiO_2 - B_2O_3 layer is extremely low, the liquid-like oxide scale penetrates through MoO_2 layer and precipitates between MoO_2 and the oxygen affected area, as shown in Fig. 6(d). This also indicates that the low viscosity of the oxide scale is a serious problem for the practical application of the alloy, and surface coatings are needed.

In order to examine the growth behavior of the oxide scale, the thicknesses of the oxide scale were examined with exposure time. The relationship between oxide layer thickness and exposure time is shown in Fig. 7. The growth of the oxide layer thickness was increased, when the exposure time was increased. Also, it is specially noted that the growth of the oxide scale was accelerated, when the exposure time is reached 100 hr. This implies that the oxide scale growth is almost following a linear growth manner, that usually observed in an initial stage of new phase growth at the interface during annealing (i.e., interface controlled growth)[11]. It is probable that the basic mechanism for the accelerated growth is due to the low viscosity of the exterior SiO_2 - B_2O_3 layer, which can enhance the diffusion rates

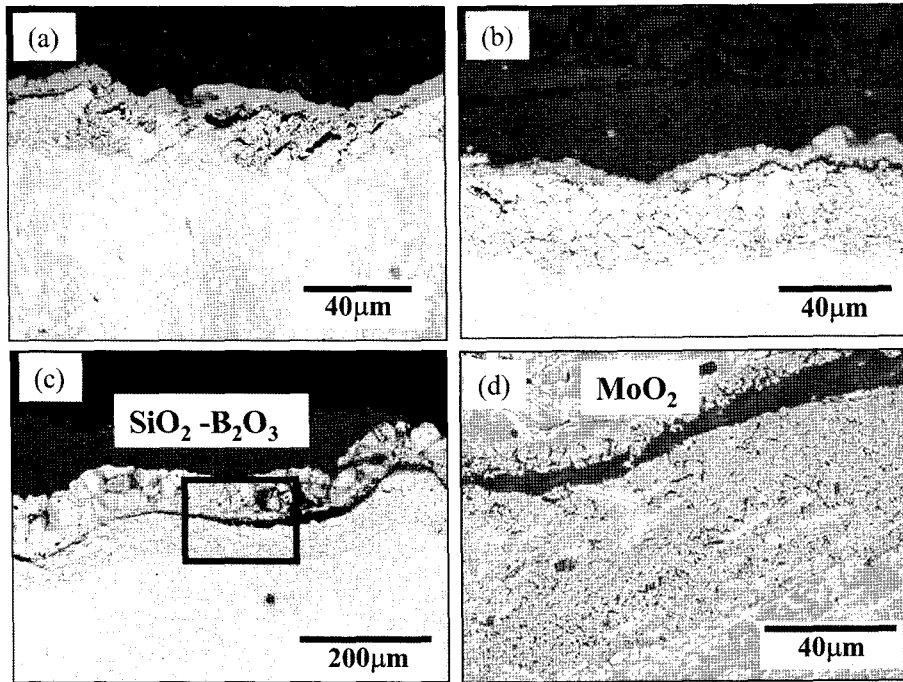


Fig. 6. SEM back scattered image of the Mo-14.2Si-9.6B alloy exposed at 1200°C in Air for (a) 10 hr, (b) 50 hr, and (c) 100 hr. (d) is enlargement of the marked area in (c).

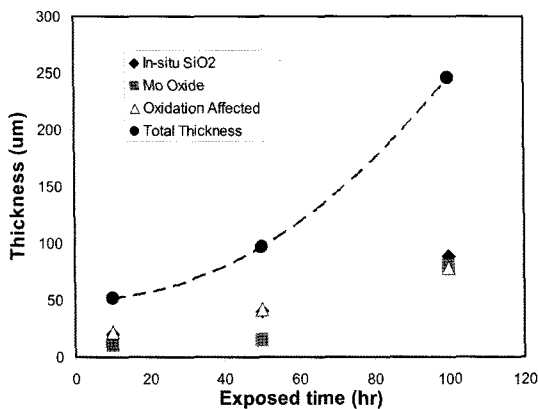


Fig. 7. Oxidation thickness vs. exposed time for the Mo-14.2Si-9.6B alloy exposed at 1200°C.

during oxidation exposure. Since the formation of the low viscous SiO₂-B₂O₃ layer can be a main factor for the enormous growth of the oxide scale, surface coatings may do work for preventing the oxygen diffusion towards the oxide scale.

SEM BSE image of the oxide layer deposited

specimen is shown in Fig. 8. It is clear that the coating layers were tightly bonded on top of the SiO₂-B₂O₃ layer after oxidation exposure. The oxide layers were formed in a similar manner to the uncoated specimen, indicating that the same oxidation mechanism worked regardless of coating. Also, when the produced oxide morphology was compared depending on each powder coated specimen, the morphology was similar to ceramic powder coated specimens (i.e., SiO₂, TiO₂, HfO₂, La₂O₃, ZrO₂ powders). The thicknesses of the powder coating layer were not strictly controlled due to the nature of the spray deposition. The oxide layer thickness upon the species of the oxide powder is shown in Fig. 9. It is clear that when spray deposition was applied to the alloy surface, the total oxide layer was decreased, indicating that the oxidation resistance was increased when the deposition was applied. It is probable that the sintering effect of the ceramic powder together with tight

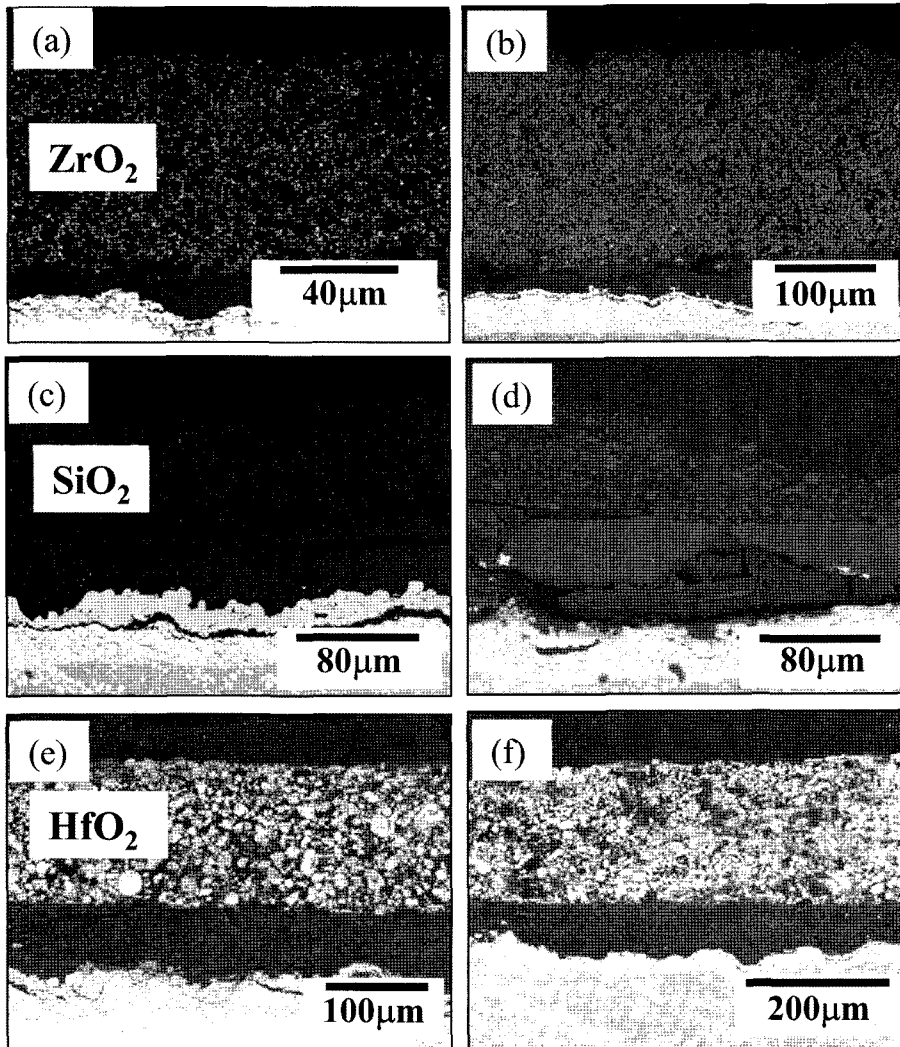


Fig. 8. Powder spray coated Mo-B-Si Alloys exposed at 1200°C in Air.

bonding between the ceramic coating layer and substrate prevents oxygen diffusion towards the $\text{SiO}_2\text{-B}_2\text{O}_3$ scale during high temperature exposure. It should be mentioned that if the ceramic powder coating layer was not tightly bonded with the substrate, oxygen would penetrate through the coating layer and the thickness should be same as uncoated specimen. Also, it is probable that the viscous $\text{SiO}_2\text{-B}_2\text{O}_3$ scale may work for bonding of the powder with the substrate.

The total thickness of the produced oxide

layer was smallest for the ZrO_2 powder coated specimen. The oxygen diffusivity of ZrO_2 was reported as about 10^{-11} (m^2/sec), while that of TiO_2 was documented as about 10^{-17} m^2/sec at 1273 K [12], implying that the oxidation resistance of the specimen deposited by TiO_2 should be the best among the examined powders. However, the oxide layer thickness was similar for ZrO_2 or TiO_2 deposited specimen. This observations show that the oxygen diffusivity is not the only factor that affects the oxidation process of the spray deposited specimen. Further study is

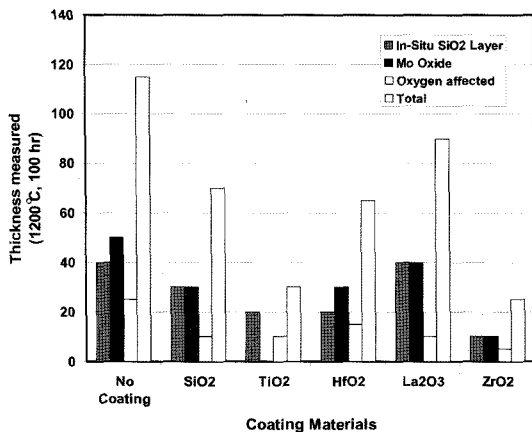


Fig. 9. Comparison of the layer thicknesses of the oxidized alloy.

underway in order to identify the further evidence for controlling oxidation process. At the present stage, it is clear that when the Mo-Si-B alloy is spray deposited by ZrO₂ powder, the oxidation resistance is increased by a factor of five, which is a large effect for enhancement of the oxidation resistance in terms of the of the simplicity and economic consideration.

4. Conclusion

In the present research, the microstructural evolution during oxidation exposure was investigated for various oxide powder spray deposited and uncoated Mo-14.2Si-9.6B (at%) alloy. The major conclusions can be summarized as follows:

1. The growth of the oxidation scale of the uncoated Mo-14.2Si-9.6B (at%) alloy followed a parabolic manner, indicating diffusional growth governs during oxidation exposure at 1000°C. However, when the uncoated alloy was exposed at 1200°C, the growth behavior of oxide scales followed almost a linear growth manner, implying that the growth is accelerated by the low viscous oxide scale.

2. The oxide particle spray deposition was

successfully made on the Mo-14.2Si-9.6B (at%) alloy, and the spray coated particles were not detached from the surface during oxidation exposure. It is mainly considered that the in-situ formed and viscous SiO₂-B₂O₃ scale may work for bonding of the powder with the substrate.

3. When the oxide spray deposited Mo-Si-B alloy was exposed at 1200°C, the thicknesses of the oxide scale were reduced compared with uncoated specimen. The oxidation resistance, reflected by the oxide scale thickness, was enhanced by a factor of five for the ZrO₂ oxide powder coated Mo-14.2Si-9.6B (at%) alloy. It appears that the spray deposition process is an effective routine for protecting Mo-Si-B alloy

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