

Short communication

Dense $\text{ZrB}_2\text{--MoSi}_2$ composite coating fabricated by low pressure plasma spray (LPPS)Yaran Niu^{a,*}, Hongyan Wang^b, Hong Li^b, Xuebin Zheng^{a,*}, Chuanxian Ding^a^aKey Laboratory of Inorganic Coating Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China^bResearch Center of Composite Materials, Shanghai University, Shanghai 200072, China

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Abstract

Low pressure plasma spray was applied to fabricate $\text{ZrB}_2\text{--MoSi}_2$ composite coatings. Their microstructure and oxidation behavior were characterized and compared with those of the $\text{ZrB}_2\text{--SiC}$ coatings. The $\text{ZrB}_2\text{--MoSi}_2$ coating displayed compact and lamellar microstructure with porosity lower than 5%, where MoSi_2 phase was uniformly distributed in the ZrB_2 matrix. $\text{ZrB}_2\text{--30 vol\% MoSi}_2$ coating exhibited much better oxidation-resistance at high temperature compared to the $\text{ZrB}_2\text{--30 vol\% SiC}$ coating. It is thought that the fine distribution of sufficient MoSi_2 in the matrix and dense microstructure of the $\text{ZrB}_2\text{--MoSi}_2$ coating contributed to its excellent high temperature oxidation-resistance.

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1. Introduction

Ultra-high-temperature ceramics (UHTCs), having extremely high melting points, are expected to be potential candidates as thermal protective materials for hypersonic aerospace vehicles and reusable atmospheric re-entry vehicles [1,2]. Zirconium diboride (ZrB_2) based composites, which are representative among UHTCs, possess a unique set of material properties, including unusually high thermal conductivity, good thermal shock resistance and modest thermal expansion coefficients. However, the difficulty in processing and unsatisfactory mechanical properties of UHTCs ceramics limits their further application [3]. The combination of structural and surface demands like, outstanding strength and high oxidation-resistance can often only be met economically via coatings. The application of UHTC protective coatings on the surface of lightweight fiber reinforced composites, such as C/SiC and C/C, is an effective way to resolve the application problems at high temperatures exceeding 1400 °C.

Plasma spray is a versatile and efficient technique to fabricate various coatings on surfaces with different sizes and shapes. It is widely applied in diverse industries, including medical, automotive and aerospace fields [4,5]. Moreover, plasma spray deposition is a new technique for fabrication of near-net-shape components [6,7]. Tului et al. [8,9] have done some work on the fabrication of $\text{ZrB}_2\text{--SiC}$ composite coatings using controlled atmosphere plasma spray (CAPS) at low pressure (400 mbar) and high pressure (2000 mbar), respectively. They found that substantial loss of SiC due to thermal decomposition during deposition could be inhibited to some extent under high pressure of inert gas. However, complete inhibition of the SiC loss during deposition remains a great challenge, which could not be effectively controlled. This would directly influence the uniformity and reproducibility of microstructure of the coatings and thus causing potential risk in the practical usage.

MoSi_2 has excellent oxidation-resistant property at high temperature, no matter as bulk or coating materials, for the development of a protective silica-based surface layer [10,11]. It has also been added to the ZrB_2 -based bulk material and resultantly led to improved oxidation-resistant property of the composite ceramics [12,13]. MoSi_2 coatings fabricated by low pressure plasma spray (LPPS) also showed a dense microstructure

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and excellent oxidation-resistance at high temperature [14]. However, to the best of our knowledge, no studies have been done so far on plasma sprayed ZrB_2 – MoSi_2 composite coatings.

In this work, the LPPS technique was applied to fabricate ZrB_2 -based composite coatings and MoSi_2 was selected as the secondary enhancing phase. The coating was produced at a pressure ranging from 50 to 400 mbar, which shows lower technical effort and expense compared to HPPS (pressure of 1000–4000 mbar). The main purpose of this work is to investigate the microstructure and high temperature oxidation-resistant property of ZrB_2 – MoSi_2 composite coatings. At the same time, ZrB_2 – SiC coatings having the same percent of additive (SiC) was also fabricated using the similar parameters for comparison.

2. Experimental processes

Commercially available ZrB_2 powders with a particle size ranging from 5 to 40 μm and MoSi_2 powders with a particle size in range of 10–50 μm were chosen as feedstocks. The mixed ZrB_2 – MoSi_2 powders with composition of 70 vol% ZrB_2 and 30 vol% MoSi_2 were ball-milled in absolute ethanol for 6 h to ensure complete blending of the two components, followed by drying and sieving. A common carbon material, graphite, was used in this study as a substrate. The graphite substrates were grit blasted using corundum sand and then cleaned in 100% ethanol by ultrasonication.

The coatings were deposited using a Metco A-2000 low pressure plasma spray equipment (Sulzer Metco F4-VB type gun, Switzerland). The Twin-System (Plasma-Technick, Switzerland) was applied for powder feeding. The deposition parameters of coatings are listed as follows: a mixture of argon (36 slpm) and hydrogen (12 slpm) were used as plasma forming gases. The feeding rate of powders was about 26 g min^{-1} using argon as the carrier gas. The plasma power input was 42 kW and the spraying distance was 300 mm under a pressure of 100 mbar. For comparison, ZrB_2 coating reinforced by 30 vol% SiC and pure ZrB_2 coating were also prepared. Free-standing specimens with a thickness about 0.6–0.8 mm were deposited on the graphite substrates and peeled off for property characterization.

The phase compositions of the powders and coatings were examined by X-ray diffraction (XRD, RAX-10 X-ray diffractometer, Rigaku, Japan) operating with $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation. The morphologies of the coatings were observed by field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan). Energy-dispersive X-ray spectroscopy (EDX) attached to SEM equipment was applied to analyze the chemical compositions and element distribution of the coatings. The average void contents of the coatings were determined by five cross-section images using an image software (Leica Qwin, Germany). For evaluating the high temperature oxidation behaviors of the coatings, the specimens were placed in a box type furnace in ambient air at 1500°C for different duration time with a heating rate of 5°C/min and followed by natural furnace cooling to room temperature.

3. Results and discussion

Fig. 1 presents the XRD patterns of the as-received powders and as-sprayed composite coatings. It can be seen that the phase of SiC could not be detected in the ZrB_2 – SiC coating, indicating serious decomposition of SiC during the deposition process (Fig. 1a). For the ZrB_2 – MoSi_2 coating, both ZrB_2 and MoSi_2 can be observed. It is noted that the tetragonal MoSi_2 in the composite powders disappeared and was replaced by hexagonal MoSi_2 and tetragonal Mo_5Si_3 phases. The formation of hexagonal MoSi_2 was due to the high cooling rate of the deposited molten particles (near 10^6 K/s for metals) [15]. The existence of Mo_5Si_3 phase is supposed to result from the oxidation of MoSi_2 by the residue air in the chamber during the deposition process [14].

The cross-section morphologies and element mappings of the two kinds of ZrB_2 -based coatings are presented in Fig. 2. The ZrB_2 – MoSi_2 coating exhibits compact microstructure compared to the ZrB_2 – SiC coating. The porosities of ZrB_2 – MoSi_2 and ZrB_2 – SiC coating measured by SEM images are

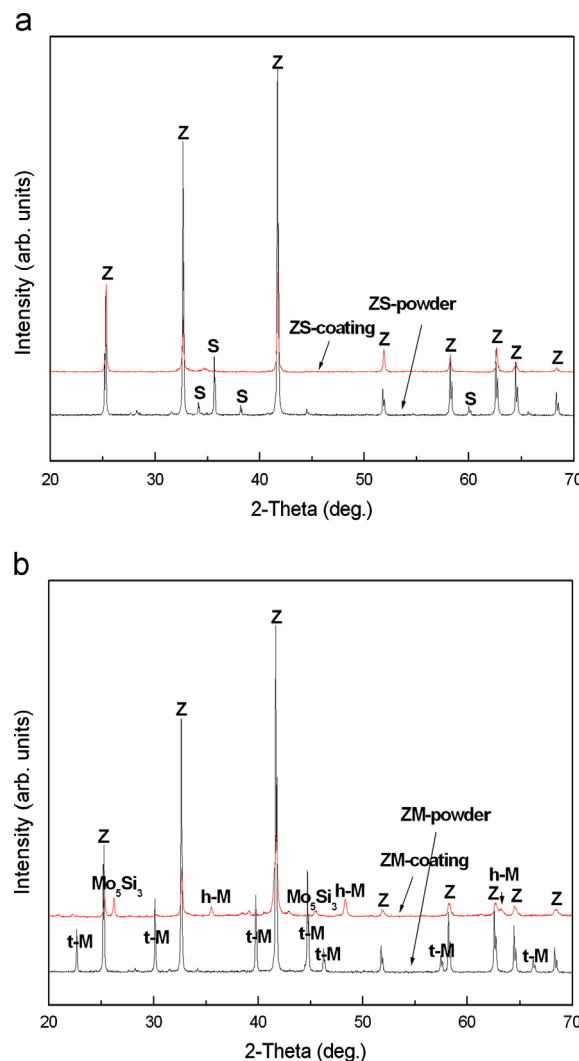


Fig. 1. XRD patterns of as-sprayed powders and coatings of ZrB_2 – SiC (a) and ZrB_2 – MoSi_2 (b).

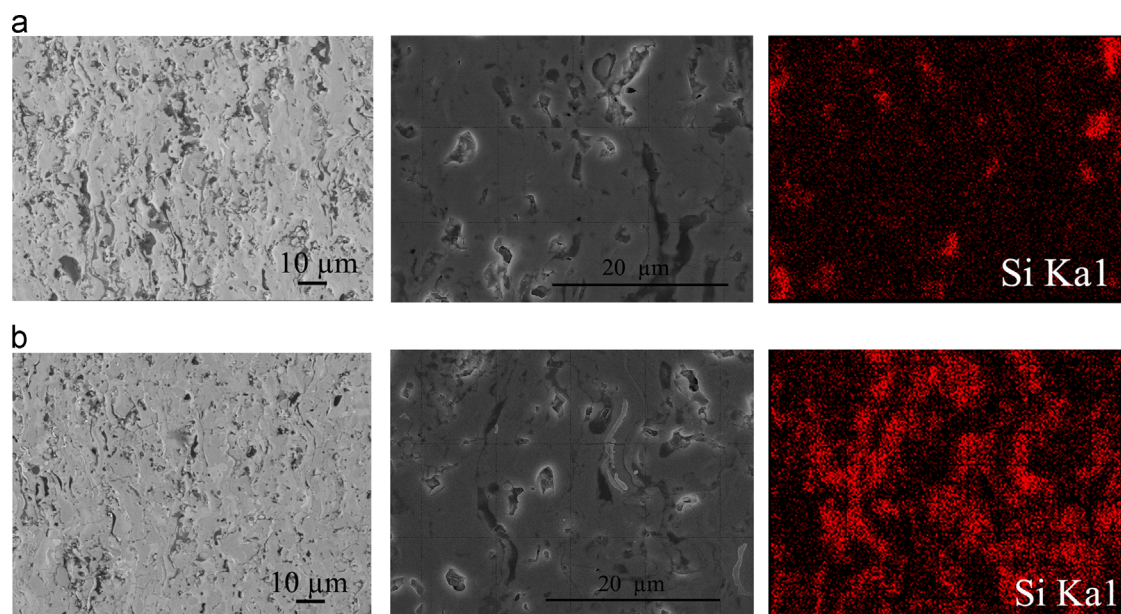


Fig. 2. Cross-sectional micrographs and element mappings of ZrB₂-SiC (a) and ZrB₂-MoSi₂ (b) coatings.

about 3% and 9%, respectively. The result of element mapping reveals that the amount of SiC in the sprayed coating was limited and its distribution was not uniform (Fig. 2a). By contrast, MoSi₂ uniformly distributed in the ZrB₂-MoSi₂ coating (Fig. 2b). The melting point of MoSi₂ is much lower (about 2030 °C) than that of ZrB₂ (about 3040 °C). It is worth noticing that MoSi₂ exhibits plastic deformation at high temperature, which is good for the deformation, spreading and adhering of semi-melted or un-melted particles [16]. These characters would improve the density of the composite coating and release the residual stresses accumulated during the deposition process. The decrease of defects (pores and micro-cracks) in the coatings would be good for improving the oxidation-resistant and mechanical properties of the coating.

The high temperature oxidation behaviors of the ZrB₂-30 vol% SiC and ZrB₂-30 vol% MoSi₂ coatings were evaluated at 1500 °C in air for different duration time. The pure ZrB₂ coating was also checked for comparison at the same time. Mass change as a function of time for the three kinds of coatings is shown in Fig. 3. For both ZrB₂-MoSi₂ and ZrB₂-SiC coatings, a significant mass gain was observed within 1 h from the starting of oxidation. The mass gain of the ZrB₂-MoSi₂ coating was maintained throughout the test. However, the mass gain of ZrB₂-SiC coating was maintained within the first 6 h and turned into mass loss after then. The curve of ZrB₂-SiC coating after 10 h was similar to that of the pure ZrB₂ coating, suggesting the coating had been totally oxidized.

The surface morphologies of the ZrB₂-MoSi₂ and ZrB₂-SiC coatings after the heat-treatment for 6 h are illustrated in Fig. 4a and 4b, respectively. There were many voids with a size of several micrometers formed on the surface of the treated ZrB₂-SiC coating. However, the surface of the treated ZrB₂-MoSi₂ coating was dense and smooth, which was confirmed to be mainly composed of silicon oxide by EDS, which is not presented.

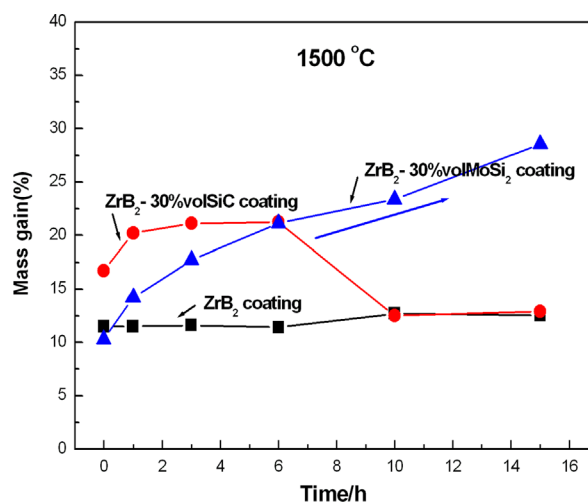
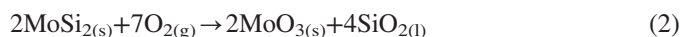


Fig. 3. Mass change as a function of time at 1500 °C in air for the ZrB₂-SiC and ZrB₂-MoSi₂ coatings.

During the long term exposure to air at high temperature, there were some chemical reactions taking place in the coatings, including:



The reactions during oxidation of the ZrB₂-SiC coating includes reaction formula (1), (3) and (4) while the oxidation of the ZrB₂-MoSi₂ coating is according to reaction formula (2)–(4) [13,17]. It has been proved by many researchers that the formed

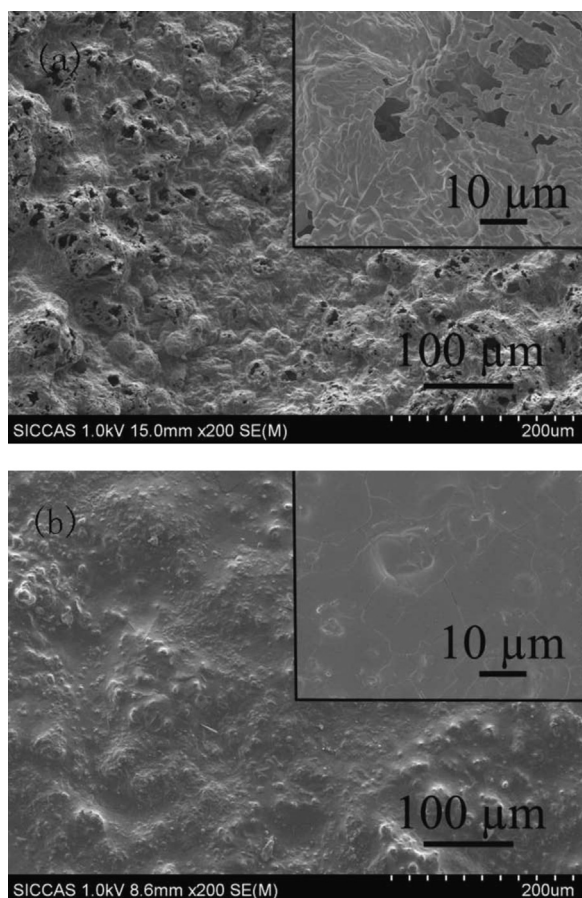


Fig. 4. Surface morphologies of the composite coatings oxidized for 6 h at 1500 °C: (a) ZrB₂-SiC coating and (b) ZrB₂-MoSi₂ coating.

silicon oxide, which is continuous on the surface of the ceramic composites, could separate the exterior environment and underlying material and inhibit inward diffusion of oxygen. This is the reason why the introduction of second phase particles, such as MoSi₂ and SiC, could significantly improve the oxidation-resistant performance of ZrB₂-based composites [13,18]. The amount of silicon oxide is dependent on the content of original silicon-containing phase. For the ZrB₂-SiC coating, the amount of SiC inside the coating is limited, which is confirmed by the results of element mapping (Fig. 2a). Therefore, the formed silicon oxide could not effectively protect the underlying coating. The vapor pressure of formed gaseous B₂O₃ increased with extending the holding time until it burst out of the oxide layer by creating voids. Then the silicon oxide layer was broken down, which led to the further oxidation of the ZrB₂-SiC coating. In addition, the non-uniform distribution of SiC in ZrB₂ matrix could also speed-up the out-of-service time of the ZrB₂-SiC coating. By contrast, the amount of MoSi₂ in the ZrB₂-MoSi₂ coating was enough and its distribution in the composite coating was uniform, which produced sufficient and homogenous silicon oxide on the surface of the composite coating. And this inhibited the penetration of oxygen and thus avoiding the formation and overflow of gaseous B₂O₃. Therefore, the mass of ZrB₂-MoSi₂ coating kept increasing throughout the oxidation test.

4. Conclusions

ZrB₂-MoSi₂ and ZrB₂-SiC composite coatings were fabricated by low pressure plasma spray with mechanically mixed powders. It was found that dense ZrB₂-MoSi₂ coating having a lamellar microstructure with porosity of 3% was fabricated. The amount of SiC in the ZrB₂-SiC coating was limited and the porosity of the coating was high (9%). The oxidation tests at 1500 °C in air showed that the oxidation behaviors of the composite coatings significantly depended on the content and distribution of the second phase. The mass loss of the ZrB₂-SiC coating took place after 6 h exposure. While the mass gain of the ZrB₂-MoSi₂ coating maintained within the test time of 16 h, indicating its excellent oxidation-resistance. The controllable quantity of MoSi₂ and dense uniform microstructure of the ZrB₂-MoSi₂ coating contributed to its good oxidation-resistant property at high temperature.

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