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A comparative study of $MoSi_2$ coatings manufactured by atmospheric and vacuum plasma spray processes

Xiaoai Fei [a,b], Yaran Niu [a,b], Heng Ji [a,b], Liping Huang [a,b], Xuebin Zheng [a,b,*]

[a] Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, China
[b] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

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Abstract

In this work, $MoSi_2$ coatings were manufactured by atmospheric plasma spraying (APS) and vacuum plasma spraying (VPS) technologies, respectively. Phase composition and microstructure of the coatings were characterized by X-ray diffraction and scanning electron microscopy. Microhardness, void and oxygen content of the coatings were also determined. Oxidation behavior of the coatings at high temperature was examined. The results showed that the surface of VPS-$MoSi_2$ coating was dense and homogeneous. However, there were many microcracks formed on the surface of APS-$MoSi_2$ coating. The VPS-$MoSi_2$ coating also had lower void and oxygen contents, higher Vickers hardness compared with those of APS-$MoSi_2$ coating. Besides, oxidation resistance of the VPS-$MoSi_2$ coating was better than that of APS-$MoSi_2$ at 1500 °C.
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Keywords: Plasma spray; $MoSi_2$ coatings; Microstructure; Oxidation behavior

1. Introduction

$MoSi_2$ has been extensively studied during the last three decades for its rather low density, high electrical conductivity and enhanced oxidation resistance at high temperatures, even in harsh environments [1]. It has been widely used as heating elements operating at high temperatures, such as gas turbine engines, missile nozzles, diesel engine grow plugs, among other applications [2]. One of its main applications is oxidation resistant coatings [3]. The protection against rapid oxidation is accomplished by the formation of a thin, coherent and adherent SiO_2 layer on the surface of $MoSi_2$, thereby retarding oxygen diffusion to the substrate [4].

Many techniques have been suggested to deposit $MoSi_2$ coatings, such as chemical vapor deposition [5], pack siliconizing [6], vacuum sintering [7], solid surface reaction [8], pulsed laser ablation and deposition (PLAD) [9], among the main considered processes. Among the various coating manufacturing methods, plasma spraying is considered to be a versatile technology. Plasma spray technology enables the processing of a broad variety of coating materials, including refractory materials. It can be a suitable way for protective coatings manufacturing, because of its ability to cover large surfaces with thick coatings at high deposition rate and relatively low operating cost than most of the other coating deposition techniques [10].

Both atmospheric (APS) and vacuum plasma spraying (VPS) technologies use the energy of a high velocity Ar–H_2 or Ar–He hot plasma jets to melt and accelerate feedstock particles onto a pre-treated substrate surface to form coatings [11]. However, there are some differences between them. In case of APS technology, the process is carried out in air environment. Therefore, the feedstock particles would interact with air engulfed in the plasma flow, which may limit the choice of the spray material since reaction products such as oxides or secondary phases could be built into the coatings. The APS applications are normally related to wear and corrosion protection, which are often based on oxide and carbide ceramic materials. But APS technology has some issues with metal and oxygen sensitive coating materials processing such as $MoSi_2$ and B_4C. [12]. For VPS system, the coating deposition process takes place in inert atmosphere in a closed chamber with

* Corresponding author at: Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, China.
Tel.: +86 21 52411050; fax: +86 21 52413903.
E-mail addresses: xiaoaif@yahoo.cn (X. Fei), xbzheng@mail.sic.ac.cn (X. Zheng).

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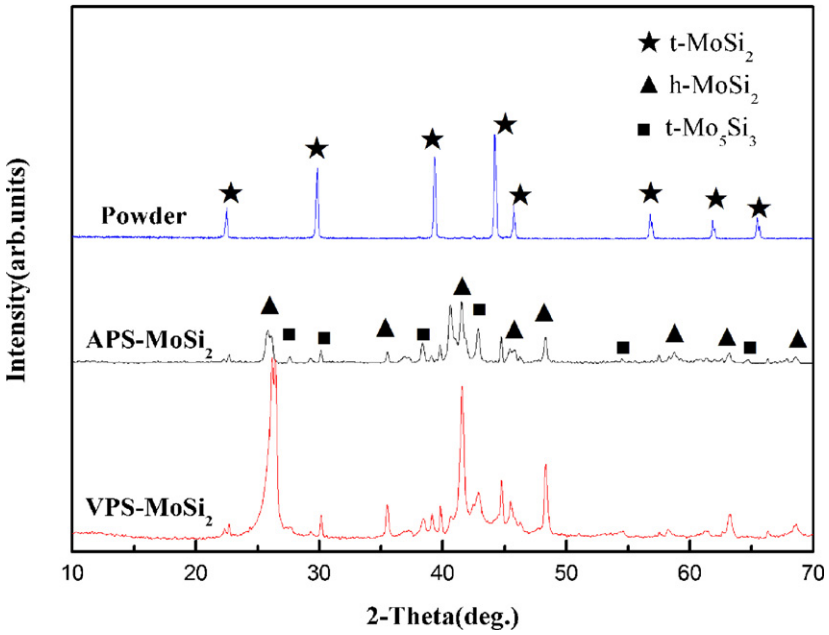

Fig. 1. XRD patterns of feedstock powders and as-sprayed APS-$MoSi_2$ and VPS-$MoSi_2$ coatings.

reduced pressure. The chamber is firstly pumped to pressures lower than 10 Pa and then filled with inert argon gas at about 5000–40,000 Pa. In order to tailor the working chamber pressure, efficient pump systems have to be implemented to remove steadily injected plasma gases. The limited reaction between melted particles and environment gases allows avoiding the formation of subproducts and the resulting coatings exhibit lower oxygen content as well as lower void content due to higher particles momentum upon impact [13,14].

Although several plasma sprayed silicide coatings were manufactured in previous studies [3,15], very few reports were focused on comparison of oxidation resistance of atmospheric and vacuum plasma sprayed $MoSi_2$ coatings. In this work, the microstructure and oxidation resistance behavior between APS-$MoSi_2$ and VPS-$MoSi_2$ coatings were investigated. Phase composition and microstructure of coatings were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Some other characteristics, including microhardness, void content and oxygen content of coatings were determined. The oxidation behavior of the two types of $MoSi_2$ coatings was assessed at 1500 °C.

2. Experimental

2.1. Materials and preparation

Commercial $MoSi_2$ (Zhengzhou Chida Tungsten & Molybdenum Products Co., Ltd., Zhengzhou, China) feedstock powders with the medium size d_{50} of 17.6 μm were chosen as feedstock. The powders are made of tetragonal $MoSi_2$ (Fig. 1). The coatings deposition was carried out by a plasma spray system (A-2000, Sulzer Metco, Wohlen, Switzerland) equipped with a F4-MB torch for APS and a F4-VB torch for VPS processes, respectively. Argon and hydrogen were used as the plasma forming gases. The optimized spray operating parameters are summarized in Table 1. The powders were preheated at 60 °C for 20 min. C/C composite material with a specific mass of 1.8 g/cm^3 and thermal conductivity of 20 W/m K was used as a substrate. It was grit-blasted to the waviness Wt of 1.92 μm, average roughness Ra of 2.05 μm and maximum peak-to-valley height Rt of 7.62 μm, and then cleaned with ethanol prior to the spraying process. The powders were also simultaneously sprayed onto a polished carbon steel substrate (average roughness Ra of 1.93 μm). Caused by the smooth surface and the different thermal coefficients of expansion the coatings were peeled off easily from the substrate.

2.2. Coating composition and microstructure characterization protocols

Crystalline phases of feedstock powders and coatings were analyzed by X-ray diffraction (XRD, RAX-10, Rigaku, Japan) operating with Cu Kα (λ = 1.5406 nm) radiation. The scan

Table 1
Atmospheric and vacuum plasma spray operating parameters of $MoSi_2$ coatings.

Parameters	APS	VPS
Power (kW)	35	35
Gas Ar (slpm)	42	42
Gas H_2 (slpm)	10	10
Spray distance (mm)	150	300
Carrier gas Ar (slpm)	4	4
Powder feed rate (g/min)	14	14
Surrounding atmosphere pressure (Pa)	$\sim 10^5$	10^4
Anode nozzle diameter at exit (mm)	6	6
Plasma mass enthalpy (J/kg)	8×10^6	8×10^6
Torch scanning velocity (m/s)	1.2	1.2
Scanning step (mm/pass)	4	4
Substrate average temperature during deposition (°C)	<350	<350

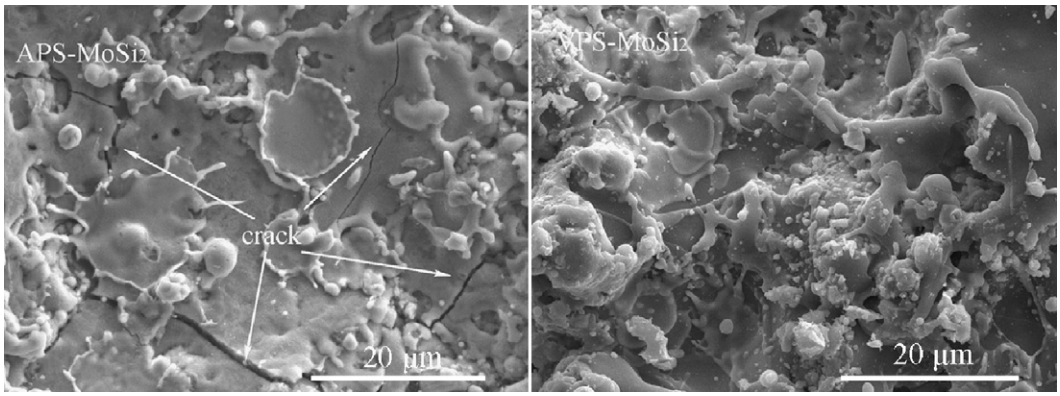

Fig. 2. Surface morphologies of as-sprayed APS-$MoSi_2$ (left) and VPS-$MoSi_2$ (right) coatings.

ranges from 10° to 70°, with step size of 0.02° and counting time of 1 s at each step. The surface and cross-section morphologies of coatings were investigated by field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan). The composition of coatings was estimated by energy dispersive spectrometer (EDS, INCA ENERGY, UK). Vickers hardness measurements were conducted on polished cross-section of the coatings using a microhardness instrument (HX-100, Shanghai Second Optical Instrument Factory, China) under loading weight of 1.96 N and dwell time of 15 s. The depicted values represent an average of twenty point measurements randomly located along the cross-section. The void content of as-sprayed coatings was measured on polished cross-sections (resolution: 270 PPI) by image analysis (IMAGE, National Institute of Health, Springfield, MD, USA). Ten measurements were carried out for each sample. Surface roughness was measured by HOMMEL WERKE (T8000-C, Wave, Germany). The oxygen content in the coatings was detected by nitrogen/oxygen analyzer (TC600, Leco, USA).

2.3. Oxidation behavior characterization

Freestanding coatings were cut into small buttons of 7 mm in diameter and 1 mm thick for the oxidation test. The surfaces were mechanically polished with surface average roughness Ra of 0.38 μm using corundum sand of F60 grade at a blasting angle nearly 90° for about 20 s and blasting distance 120 mm, and then cleaned ultrasonically. The specimens were placed in an alumina crucible in a box type furnace and were oxidized at 1500 °C in ambient air at atmospheric pressure up to 50 h. The samples were furnace-heated and cooled with the rate of 5 °C/min. The mass change of each sample was measured with an electronic balance (sensitivity: 10^{-4} g). Weight changes/surface areas of the samples were then calculated.

3. Results and discussion

3.1. Phase composition and microstructure of as-sprayed coatings

The XRD patterns (Fig. 1) show that both the as-sprayed APS-$MoSi_2$ and VPS-$MoSi_2$ coatings are composed of $MoSi_2$ tetragonal and hexagonal phases and Mo_5Si_3 tetragonal phase. Phase compositions of both coatings were changed compared with the feedstock $MoSi_2$ powders. A fraction of the tetragonal $MoSi_2$ was converted to hexagonal phase due to high cooling rate of the deposited molten particles (about 10^6 K/s). The high temperature hexagonal $MoSi_2$ phase was kept as main phase in the coatings [16]. The existence of Mo_5Si_3 phase is very likely due to oxidation of the $MoSi_2$ according to Eq. (1).

$$5MoSi_{2(s)} + 7O_{2(g)} \rightarrow Mo_5Si_{3(s)} + 7SiO_{2(s)} \quad (1)$$

It is worth noticing that the ratio of the intensity of Mo_5Si_3/$MoSi_2$ in APS-$MoSi_2$ coating was higher than that in VPS-

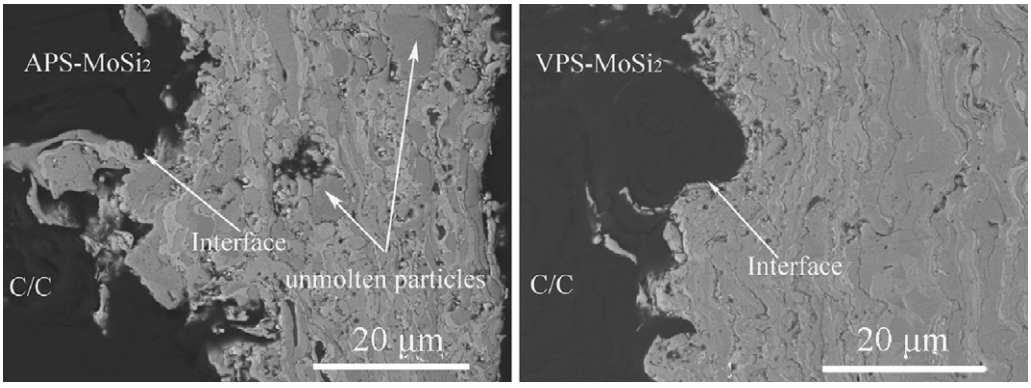

Fig. 3. Cross-section morphologies of as-sprayed APS-$MoSi_2$ (left) and VPS-$MoSi_2$ (right) coatings.

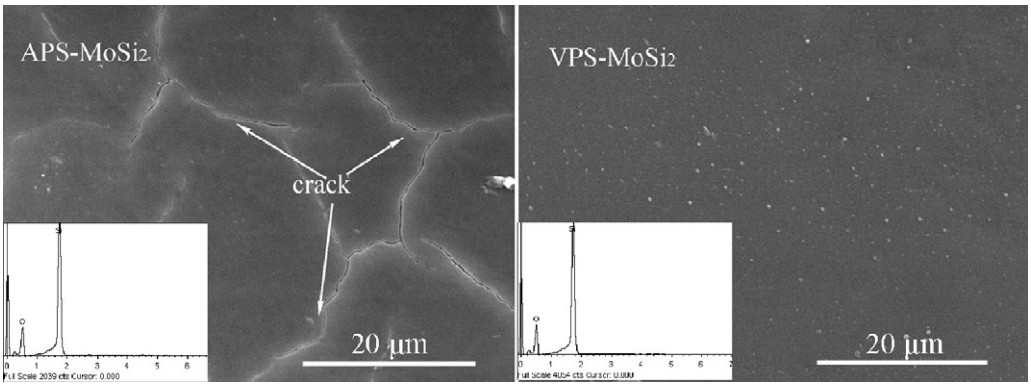

Fig. 4. Surface morphologies of APS-$MoSi_2$ (left) and VPS-$MoSi_2$ (right) coatings heated at 1500 °C for 50 h.

$MoSi_2$ coating, indicating that more $MoSi_2$ were oxidized during APS process. Due to the residue of O_2 in the large chamber and in plasma gases, small amounts of Mo_5Si_3 were also detected in VPS-$MoSi_2$ coatings.

Surface morphologies of as-sprayed APS-$MoSi_2$ and VPS-$MoSi_2$ coatings are depicted in Fig. 2. Well-flattened lamellar along with some spherical features were observed on the surfaces of both of the coatings, which exhibit typical morphologies of plasma sprayed coatings. However, the surface of APS-$MoSi_2$ coating contains some microcracks, which are supposed to be caused by the internal residual stresses during the spraying process [14]. Besides, the coefficients of thermal expansion (CTE) of the tetragonal Mo_5Si_3 is highly anisotropic, and thermal expansion anisotropy is undesirable since it gives rise to microcrack [17]. In comparison, no obvious microcracks were found for VPS-$MoSi_2$ coating. The VPS system limited the oxidation of $MoSi_2$ and little amount Mo_5Si_3 was embedded in the coatings.

Polished cross-section morphologies of the as-sprayed coatings (Fig. 3) allow observing coating structures and their interface with substrates. Structure of the APS-$MoSi_2$ coating appeared non-compact, and the particles seemed distributed unevenly with numerous unmolten particles, whereas the VPS-$MoSi_2$ coating exhibited a dense and homogeneous structure, and the lamellar morphology was much clearly revealed. It was worth noticing that neither interfacial delamination nor void was found at substrate/coating interfaces for both considered manufacturing routes.

Some coating characteristics are displayed in Table 2. Void content in APS-$MoSi_2$ coating was $12 \pm 2\%$, while it was only $5 \pm 1\%$ in VPS-$MoSi_2$ coating as determined by image analysis. The low void content plays very likely a role in decreasing the void network connectivity, therefore increasing the oxidation resistance of coatings. Oxygen contents of APS-$MoSi_2$ and VPS-$MoSi_2$ coating were 0.86 wt.% and 0.25 wt.%, respectively. The oxygen content of VPS-$MoSi_2$ coating was significantly lower than that of APS-$MoSi_2$ coating owing to the intrinsic characteristics of VPS technology. Vickers hardness of VPS-$MoSi_2$ coating was 6.85 GPa, while the one of APS-$MoSi_2$ coating was 4.06 GPa. The higher microhardness of VPS-$MoSi_2$ coating can be explained by its lower void content, higher inter-splat cohesion and fewer defects because of less oxidation [18].

3.2. Oxidation resistance of coatings

Both the freestanding APS-$MoSi_2$ and VPS-$MoSi_2$ coatings were oxidized at 1500 °C to evaluate their oxidation resistance behavior. After oxidized for 50 h, mass gains of the VPS-$MoSi_2$ and APS-$MoSi_2$ coatings were increased by 1.46 mg/cm^2 and 1.68 mg/cm^2, respectively. The VPS-$MoSi_2$ coatings exhibited a lower mass gain in comparison with the APS-$MoSi_2$ coating. Fig. 4 illustrates the surface morphologies of APS-$MoSi_2$ and VPS-$MoSi_2$ coatings oxidized at 1500 °C for 50 h. It can be seen that both the coatings had smooth surfaces, which was proved to be composed of SiO_2 by EDS. However, some microcracks appeared on the surface of oxidized APS-$MoSi_2$ coating (about 10 μm to be compared to about 20 μm). Corresponding polished cross-section pictures (Fig. 5) revealed that the oxide layer of VPS-$MoSi_2$ coating was thinner than that of APS-$MoSi_2$ coating, which indicated it had a better oxidation resistance [19]. At the same time, it was found that for APS-$MoSi_2$ coating, the formed microcracks penetrated into, or even through the SiO_2 film, as illustrated in Fig. 5 (left).

In previous studies, the oxidation resistance of atmospheric plasma sprayed WSi_2 (very similar of $MoSi_2$) was unsatisfactory owing to their high void contents [15]. They suggested one possible means of creating a denser coating would be vacuum plasma spraying. Apart from the denser coatings obtainable with the VPS process, this homogeneous coating structure may have a positive effect on the formation of a continuous dense SiO_2 layer. And Tiwari et al. [3] reported also that the oxidation resistance of the vacuum plasma sprayed $MoSi_2$ matrix was very good under cyclic and isothermal conditions. Oxygen is reported to have a very low diffusion coefficient in SiO_2 films. The dense glassy SiO_2 can retard transportation of oxygen,

Table 2
Some characteristics of the as-sprayed coatings.

Coatings	Void content (%)	O content (wt.%)	Microhardness (GPa)
APS-$MoSi_2$	12 ± 2	0.86	4.06
VPS-$MoSi_2$	5 ± 1	0.25	6.85

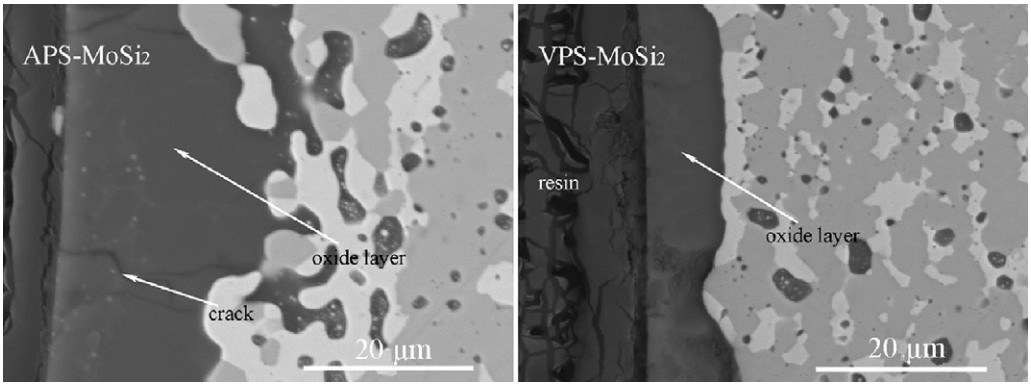

Fig. 5. Cross-section morphologies of APS-$MoSi_2$ (left) and VPS-$MoSi_2$ (right) coatings heated at 1500 °C for 50 h.

therefore provide a good oxidation resistance [6]. However, microcracks in the SiO_2 might not be self-sealed completely because that the fluidity of SiO_2 glass is poor below 1700 K [20]. Oxygen can hence diffuse through the formed microcracks and directly react with attack internal substrate. In our present work, the cracks on the surface of APS-$MoSi_2$ coating accelerated oxygen transport to substrate diffusion and aggravated the oxidation process, leading therefore to a comparatively worse oxidation resistant property compared with VPS-$MoSi_2$ coating [21,22].

4. Conclusion

$MoSi_2$ coatings were manufactured by atmospheric and vacuum plasma spray processes, respectively. The as-sprayed VPS-$MoSi_2$ coating exhibited a dense and homogeneous microstructure. However, there were many microcracks formed on the surface of APS-$MoSi_2$ coating. Besides, the VPS-$MoSi_2$ had lower void and oxygen contents, higher Vickers hardness in comparison with those of APS-$MoSi_2$ coating. Glassy SiO_2 films formed on both APS-$MoSi_2$ and VPS-$MoSi_2$ coatings after oxidation test. Due to the absence of microcracks in the SiO_2 film, the oxidation resistant property of VPS-$MoSi_2$ coating was better than that of APS-$MoSi_2$ coating at 1500 °C.

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