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Oxidation resistance of a La–Mo–Si–O–C coating prepared by Supersonic Atmosphere Plasma Spraying on the surface of SiC-coated C/C composites

Xiaohong Shi *, Changcong Wang, Hongjiao Lin, Caixia Huo, Xiuxiu Jin, Guoge Shi, Kaiyuan Dong

State Key Laboratory of Solidification Processing, Carbon/carbon Composites Research Center Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

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ABSTRACT

To prevent the oxidation of carbon/carbon (C/C) composites at high temperature, a La–Mo–Si–O–C coating was prepared on the surface of a porous SiC-coated C/C composites by Supersonic Atmosphere Plasma Spraying method. The surface microstructure, interface construction and high temperature oxidation behavior of the prepared coated C/C composites were investigated. Results show that the La–Mo–Si–O–C coating has a significant anti-oxidation property that could protect C/C composites for 85 h at 1773 K in air environment. La acted as the penetration enhancer could accelerate the sintering of Mo–Si–O–C ceramic coating and increase the penetrating capacity of the coating components into SiC coating. After oxidation, the as-prepared coating was dense with free-cracks and glass phases La_2O_3, La_2SiO_5, SiO_2, with low oxygen permeability. The glass phases were formed on the surface of coating, and could effectively obstruct the diffusion of oxygen into the inner of coating.

1. Introduction

As excellent mechanical properties and thermal shock resistance, carbon/carbon(C/C) composites are attractive materials for applications of high temperature structural components in the field of aerospace [1]. But C/C composites would been oxidized above 653 K in oxygen-containing atmosphere [2,3]. Studies have shown that 1% of mass loss with oxidation of C/C composites, and 10% of strength will be decreased [4], which limits their extensive applications in oxygen-containing atmosphere. Therefore, oxidation protection is the key to the C/C composites for widely application [5,6]. Multi-layer coatings are efficient method to protect C/C composites from oxidation at high temperature [7]. Because of the good physical and chemical compatibility, SiC was widely used as the bonding layer between C/C composites and outer layers [8,9]. Besides, $MoSi_2$ has received considerable attention as a material for high-temperature applications due to its high melting point of 2303 K, moderate density of 6.24 g/cm^3, high modulus of 440 GPA [10,11], as well as excellent resistance to oxidation (up to 1973 K) [12]. Numerous coatings containing $MoSi_2$ present good oxidation protective ability for C/C composites, such as Mo—Si [13–14], $MoSi_2$–Si [15–18], $MoSi_2$–SiC [19–23]. But with the growth of oxidation time, more and more defects generated in the Mo—Si coating, which lead to protection failure of the C/C composites [13].

Rare earth and rare earth compounds (RE) can be added to refine the grains, because the recrystallization preferentially at the grains boundary of powder particles was promoted by the rare earth during sintering occurs [23,24]. The recrystallization phases move on both sides of the internal particles, after that the particles merge, and the pores between the particles shrink or even disappear [25,26]. Rare earth compounds (RE), LaB_6, Which has unique characteristics of high hardness, high melting point, low density, low thermal expansion coefficient and good chemical stability [26,27]. The addition of LaB_6 can accelerate the sintered of $MoSi_2$ ceramic coating and improve the penetration of the coating composition [23,27]. Thus, the LaB_6 was selected as penetration enhancers to improve the coating compactness, which could increase the high-temperature oxidation resistance of the $MoSi_2$-based ceramic coating.

To date, a number of coating techniques, such as slurry [28], chemical vapor deposition [22] and pack cementation [29], have been used to obtain $MoSi_2$-based coatings. However, these techniques have their own limitations. Firstly, the $MoSi_2$-based coatings prepared by pack cementation need to spread with a long time at high temperature, and the sample size is restricted at the same time. The fundamental characteristic of C/C composites is changed by chemical reaction at high temperature. Besides, the change range of coating composition is limited by chemical vapor deposition, and the thickness of prepared coating is so thinner that the oxidation resistance is feeble with a loose structure [30]. Supersonic Atmosphere Plasma Spraying (SAPS) with plasma temperature in the region of 10,000 K and in jet velocities of up to 600 m/s is a novel method to prepare coating [30,31]. The SAPS has the advantages

* Corresponding author.
E-mail address: npusxh@nwpu.edu.cn (X. Shi).

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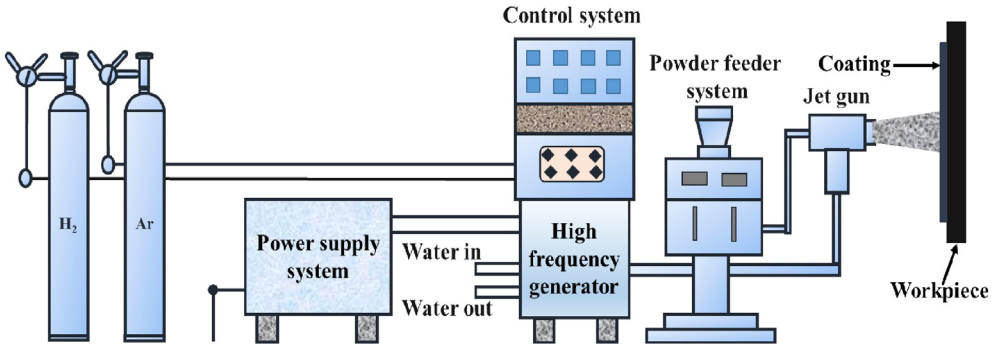

Fig. 1. The diagram of SAPS equipment.

of low base material deformation, and the change range of coating composition become broaden and the thickness of the prepared coating could be artificial controlled. In conclusion, the preparation of the oxidation protective coating by SAPS shows a bright prospect.

In present work, a novel kind of La–Mo–Si–O–C coating was prepared by SAPS for SiC-coated C/C composites. To alleviate the mismatch of thermal expansion coefficient between outer coating and C/C composites, the SiC internal coating was first prepared by pack cementation for C/C composites. The phase composition, microstructures and oxidation resistance property of the La–Mo–Si–O–C coating have been studied.

2. Experimental

2.1. Coating preparation

In this experiment, small specimens (10 mm × 10 mm × 10 mm) used as substrates were cut from the bulk 2D C/C composites material with a density of 1.65–1.72 g/cm^3. The preparation process of C/C composites is described as follows: 2.5D needle punched carbon fiber fabrics (0.45 g/cm^3, Yixing Tianniao High Technology Co., Ltd., Jiangsu, China) were chosen as the reinforcement for the porous C/C preforms. The fabrics were densified by pyrolytic carbon through thermal gradient chemical vapor infiltration (TCVI). The final density of the porous preforms was about 1.6–1.8 g/cm^3. During TCVI process, the natural gas was used as carbon source and nitrogen was used as carrier gas. The deposition temperature was about 900 °C–1200 °C and the deposition time was about 100 h. The specimens were hand-polished with 80, 200 and 600 grit SiC papers orderly, then cleaned with distilled ethanol and dried at 353 K for 4 h in the Constant Temperature Drying Ovens. The SiC inner layer was prepared by pack cementation and the details have been reported elsewhere [32]. The La–Mo–Si–O–C multi-phase coating was prepared by SAPS. The SAPS was conducted with the following powders composition: 30–50 wt.% Si, 30–40 wt.% $MoSi_2$, 10–20 wt.% C and 4–8 wt.% LaB_6. Before spraying process, the mixture particles were agglomerated by spray dryer to ensure flow ability of particles when transported from powder feeder to injector. The spraying powders were obtained by agglomerating the slurry, which was composed of distilled water (40–50 wt.%), polymeric binder (1–5 wt.% PVA), and mixture particles (40–50 wt.%).

The diagram of SAPS equipment is shown in Fig. 1, the spraying system consists of plasma torch, powder feeder, gas supply, water-cooling circulator, control unit with PC interface and power supply unit [33]. The spraying parameter for producing the La–Mo–Si–O–C coating was carried out with the current of 420 A and the voltage of 130 V. The samples were perpendicular to plasma arc and held by fixtures. The distance between the tip of injector and top of samples was 100 mm. The injector (internal diameter 5.5 mm) was moved by robot. The flow rate of the carried gas (Ar) and second gas (H_2) was 78 L/min and 2.1 L/min, respectively. The feedstock rate of the mixture powder was 4.0 r/min.

The coating forming process by SAPS contains four stages (Fig. 2). The first stage is particles flight, it can be described as the spraying powders are heated and accelerated to form the molten particles. Through accelerated flight, the molten particles are collided with the matrix. After collision, particles begin to become deformed and spreading slowly on the surface of the matrix. After a certain time, molten particles gradually covered substrate surface and cooling to form coating.

2.2. Characterization

The isothermal oxidation test was carried out at 1773 K with air in an electrical furnace. The specimens were put into the 1773 K electrical furnace and maintained at that temperature for some time, after which they were taken out of the electrical furnace and cooled for weighed. Then the specimens were put directly into the furnace again for the

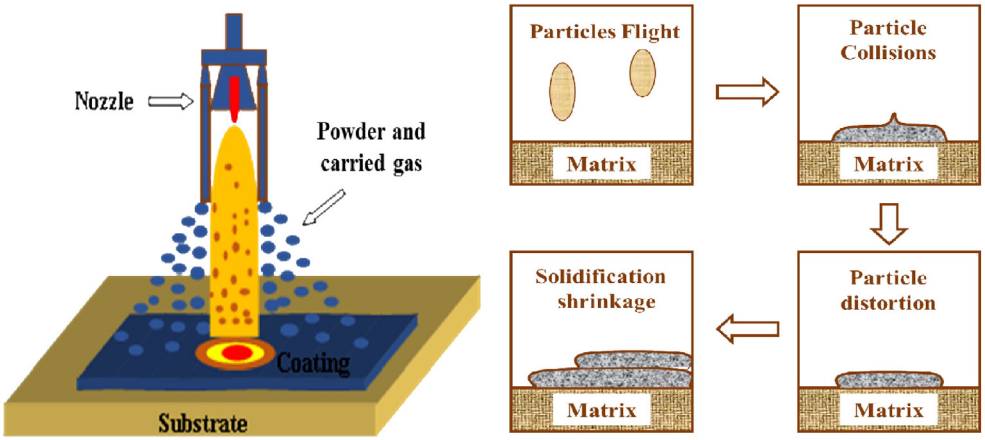

Fig. 2. The schematic diagram of SAPS processing coating.