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Formation mechanism and oxidation behavior of $MoSi_2$−SiC protective coating prepared by chemical vapor infiltration/reaction

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Abstract: In order to protect C/C composites from oxidation, SiC−$MoSi_2$ composite coating was synthesized by chemical vapor infiltration /reaction (CVI/CVR) technology. A porous Mo layer was prefabricated on SiC coated C/C composites, and then $MoSi_2$ and SiC were subsequently prepared in a CVI /CVR process using methyltrichlorosilane (MTS) as precursor. The deposition and reaction mechanism of the $MoSi_2$−SiC composite coating was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The oxidation behavior of SiC−$MoSi_2$ coated specimens was tested. The results show that the porous Mo layer can be densified with SiC phase decomposed from MTS, and transformed into SiC−$MoSi_2$ by reacting with MTS as well. A dense composite coating was prepared with optimized deposition parameters. The coated specimen exhibits a good oxidation resistance with a little mass loss of 1.25% after oxidation at 1500 °C for 80 h.

Key words: $MoSi_2$−SiC coating; deposition temperature; initial partial pressure of MTS; oxidation resistance

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1 Introduction

In the past decades, carbon/carbon (C/C) composites have been paid much attention for their illustrious properties such as light weight, high toughness and modulus above 2000 °C, good thermal shock resistance, and low coefficient of thermal expansion (CTE) [1,2]. However, the poor oxidation resistance of C/C composites has seriously hindered their development in the field of high temperature [2]. To improve the anti-oxidation performance of C/C composites, a protective coating is applied to the surface of C/C composites [3,4].

$MoSi_2$ is known as a potential candidate for protective coating material due to its outstanding performance in resistance to oxidation and corrosion up to 1800 °C [5]. But there are several detrimental habits of $MoSi_2$ coating including the low ductility at ambient temperature, the pest oxidation in the intermediate temperature range, the poor strength at high temperature and CTE mismatch between $MoSi_2$ coating (8×10^{-6} °C^{-1}) and C/C substrate (1×10^{-6} °C^{-1}) [6,7]. To remedy the above drawbacks of pure $MoSi_2$, introducing a second phase (in the form of particles, fibers or whiskers) to prepare a composite coating is one of the most effective methods. SiC has been considered an appropriate second phase material because of its thermodynamical and chemical stability with $MoSi_2$, lower CTE (4.5×10^{-6} °C^{-1}), and good oxidation resistance [8,9].

Although many studies have been carried out about the fabrication of $MoSi_2$−SiC composites [10,11], there was just a little research about producing $MoSi_2$−SiC composite coating. YOON et al [12,13] fabricated a $MoSi_2$−SiC nanocomposite coating by carbonizing and then siliconizing the Mo substrate in a chemical vapor deposition (CVD) process. ZENG et al [8] fabricated a $MoSi_2$−SiC composite coating by pack cementation, which could well protect C/C composites from oxidation up to 1600 °C [8]. WANG et al [14] fabricated a SiC_n−$MoSi_2$ coating on C/C composite surface by hydrothermal electrophoretic deposition process.

As an extension of CVD, chemical vapor infiltration (CVI) can uniformly densify a porous preform at low temperatures by infiltrating and depositing coatings within the porous preform [15,16]. Meanwhile, the in

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situ formation of the second phase in a matrix can generate a stable interface between them, and improve the thermodynamical and chemical stability of composites [17,18]. Combining the above technologies, chemical vapor infiltration /reaction (CVI /CVR) was employed to synthesize a $MoSi_2$−SiC composite coating to protect C/C composites from oxidation in this work.

A porous Mo layer was preformed on the SiC coated C/C composites by a slurry method, and then $MoSi_2$−SiC composite coating was prepared with the deposition of SiC and the simultaneous reaction with Mo during CVI /CVR process using methyltrichlorosilane (MTS) as precursor. The deposition temperature and initial partial pressure of MTS were investigated and optimized. The isothermal oxidation resistance of the as-coated samples at 1500 °C was explored.

2 Experimental

2D-C/C composites, as substrate materials, were cut into small specimens with dimensions of 10 mm×10 mm×10 mm. The small specimens were hand-polished with 400 grit SiC sandpaper and cleaned with ethanol. The cleaned specimens were lastly dried in a oven at 90 °C before the next step.

A Mo slurry made up of Mo powders and adhesive phenolic resin was brushed on the surface of specimens. The obtained specimens were treated in a vacuum environment at 1000 °C for 2 h. The thickness of the porous Mo layer was dependent on the viscosity of the slurry and brush times. The vacuum heat treatment was carried out in an electric furnace.

CVI /CVR process, using methyltrichlorosilane (MTS, CH_3SiCl_3) /hydrogen (H_2) as reactant species, was also performed in the electric furnace. The specimens were hung inside the reaction chamber with Mo wires. The liquid MTS precursor was transported into the reaction chamber using a bubbling method with a carrier gas of H_2. The mass flow of MTS was manipulated by the flow rate of carrier H_2. The flow rate of the dilute H_2 was fixed at 1200 mL/min, and the flow rate of dilute Ar was 300 mL/min. The deposition temperature, time and pressure were in the range of 1100−1250 °C, 5−10 h and 5−10 kPa, respectively.

The isothermal oxidation test was performed in the electrical furnace in air. An inner SiC coating was pre-coated on the specimens by pack cementation method [19], and then an outer $MoSi_2$−SiC composite coating was prepared through a CVI /CVR process. During the oxidation test, the coated specimens were firstly put in the furnace at 1500 °C and endured for a certain time. After that they were got out of the furnace immediately and then cooled down quickly to room temperature. The mass change of the specimens was examined with an electronic balance (sensitivity: 0.1 mg). When the specimens were put into the furnace again, another oxidation cycle was begun. Therefore, the thermal shock performance of the specimens was evaluated during the isothermal oxidation test.

The crystal structure and morphology of the $MoSi_2$−SiC composite coating before and after oxidation were analyzed by X-ray diffraction (XRD, X'Pert Pro MPD) and scanning electron microscopy (SEM, Tescan VEGA TS5136XM), respectively.

3 Results and discussion

3.1 Characteristics of porous Mo layer

Figure 1 shows the phase composition (Fig. 1(a)) and the SEM image (Fig. 1(b)) of the pre-coated Mo layer after vacuum heat treatment. It can be seen that the layer consists of pure Mo phase in Fig. 1(a), and the Mo particles are connected with each other to form a porous structure with uniform distribution of pores shown in Fig. 1(b).

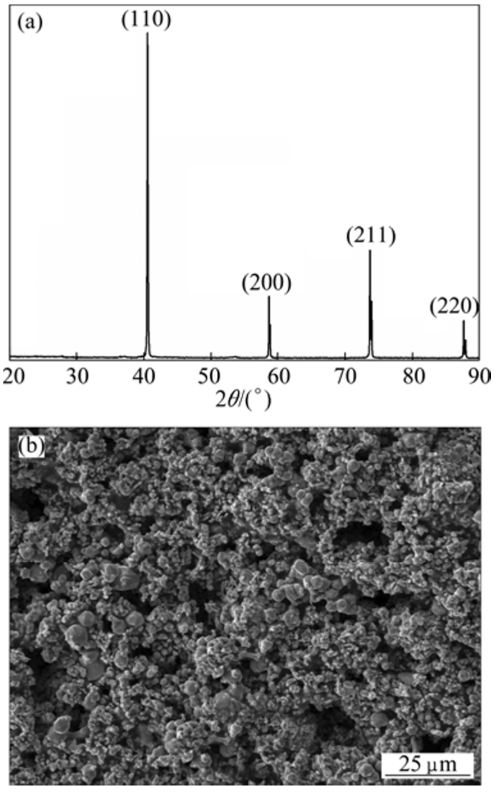

Fig. 1 XRD spectrum (a) and SEM image (b) of surface of coated samples

However, the pore geometry is irregular and a wide pore size distribution is ranging from 5 to 25 μm, which resulted from the unhomogeneity of the Mo powders and the phenolic resin adhesive in the brushing process. During the vacuum heat treatment, the phenolic resin combining the Mo powders pyrolyzed and released