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Fabrication of a SiC/Si/$MoSi_2$ multi-coating on graphite materials by a two-step technique

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Abstract

A SiC/Si/$MoSi_2$ multi-coating for graphite materials was prepared by a two-step technique. SiC whisker reinforcement coating was produced by pyrolysis of hydrogen silicone oil (H-PSO) at 1600 °C, and then the dense coating was formed by embedding with the powder mixture of Si, graphite and $MoSi_2$ at 1600 °C in argon atmosphere. The microstructure, thickness, phase and oxidation resistance of the coating were investigated. Research results showed that, the phase of multi-coating was composed of SiC, Si and $MoSi_2$. The thickness of the coating was about 300 μm. In addition, the coating combined with matrix well, and surface was continuous and dense. The oxidation pretreatment experiment was carried out in the static air at 1400 °C for 4 h before thermal failure tests and the specimens had 0.045% weight gain. Subsequent thermal failure tests showed that, the SiC/Si/$MoSi_2$ multi-coating had excellent anti-oxidation property, which could protect graphite materials from oxidation at 1000 °C in air for 12 h and the corresponding weight loss was below 1 wt%. Based on the surface morphology changes, oxidation pretreatment experiment and thermal failure tests enhanced densification of multi-coating and the coating had a certain self-healing ability.

Keywords: Multi-coating; Oxidation resistance; Graphite materials

1. Introduction

Due to excellent high-temperature performance, graphite materials were widely used in many industries [1]. But the deadly problem for the application of these materials lay in their quick oxidation at high temperature in the presence of oxygen, which seriously affected the performance and service life of graphite materials [2,3]. SiC ceramic had a series of advantages for use in coating due to its excellent oxidation resistance, chemical stability and corrosion resistance [4,5]. There was good chemistry compatibility between SiC and graphite, and interface reaction happened almost impossibly. The smaller difference of thermal expansion coefficient was beneficial to get good gradient transition layer formed in the interface of coating and matrix, so SiC was the ideal coating materials to improve oxidation resistance and wear ability of graphite materials [6]. Up to now, many methods had been reported to coat SiC on carbon material surfaces, such as pack cementation technique [7,8], slurry-sintering [9,10], chemical vapor decomposition (CVD) [11,12], pyrolysis of organic compounds [13–15] and so on. However, these methods that aim to get excellent coatings were mostly complicated and high cost. Preparing SiC coating by Si-infiltrating [16] was considered as the most promising method. Only when the infiltration rate of liquid Si was higher than the chemical reaction rate, the dense SiC coating could be formed [17,18]. However, bigger infiltration rate required higher temperature, which made the cost of production increase. In addition, over infiltration of Si would lead to corrosion of matrix. Consequently, we introduced SiC whisker coating before formation of final coating by a low-cost technique, aiming to reduce production temperature and protect the matrix against over corrosion in the premise of the coating's performance.

In this investigation, we prepared a SiC/Si/$MoSi_2$ multi-coating by a cheaper and easier technique. For a start, we produced a SiC whisker reinforcement coating on the graphite matrix by pyrolysis and siliconization of low-cost hydrogen silicone oil (H-PSO), and then the dense coating was formed by

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embedding with the powder mixture of Si, graphite and $MoSi_2$ at 1600 °C in argon atmosphere. We investigated the microstructure, thickness, phase composition and oxidation resistance of SiC coating, and we found that the multi-coating had excellent anti-oxidation property.

2. Experimental

2.1. Preparation of the SiC whisker coating

The graphite named G347 (Shandong Weiji carbon technology Co. Ltd., Jinan, China) was used as carbon matrix in this work. The physical parameters were listed in Table 1. Small graphite matrixes of 10 mm × 10 mm × 10 mm size were hand-polished, cleaned and dried. The H-PSO (CH_3–$(SiO)_n$–Si–H, Hydrogen content: 0.1%–1.6%, Guobang Chemical Co. Ltd., Jinan, China) was main Si-containing organic impregnation solution, and divinyl benzene (DVB) ($C_6H_4(CH{=}CH_2)_2$, Sigma–Aldrich, USA) in certain proportion was crosslinker. In the preparation, platonic chloride ethanol solution as catalyst was added into impregnation solution to promote cross-linking. Pt element was approximately 10 ppm in 100 ml impregnation solution. First, the impregnation solution was mixed about 30 min. Second, dipping treatment was carried out under a pressure of 0.5 MPa and subsequently crosslinked at 120 °C for 6 h [19]. Finally, the SiC whisker reinforcement coating was prepared on the surface of graphite matrix by pyrolysis of H-PSO at 1600 °C for 2 h in an argon protective atmosphere with the flux of 150 ml/min.

2.2. Preparation of the final multi-coating

The specimens after first step were embedded in the mixture powder composed of Si, graphite and $MoSi_2$. In this work, the ratio of the Si, graphite and $MoSi_2$ powder was set at 9:2:1 wt% based on the results of previously different power proportion tests. All the powders with the granularities of 300 meshes were analytically pure and were mixed by a dry powder blender for 30 min. The heat treatment was carried out at 1600 °C for 2 h in argon atmosphere with the heating and cooling rate of 4 °C/min, and the flow rate was 150 ml/min.

2.3. Microstructure and phase composition of the SiC/Si/$MoSi_2$ multi-coating

The surface and cross-section morphology images of the coating were analyzed by scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS) and X-ray diffraction (XRD) with CuKα radiation (λ = 0.154056 nm) was used to determine the crystalline phases of the coating.

2.4. Thermal failure tests of the SiC/Si/$MoSi_2$ multi-coating

The oxidation pretreatment experiment was carried out in a corundum tube furnace in static air flowing freely at 1400 °C for 4 h before thermal failure tests and the weight change was recorded. The thermal failure tests were carried out in box furnace at 1000 °C for 2 h in the presence of air. Six cycles for each specimen were carried out. The weight loss ($\Delta\omega\%$) was calculated by Eq. (1) to measure anti-oxidation property.

$$\Delta\omega\% = \frac{(m_0 - m_1)}{m_0} \times 100\% \quad (1)$$

where m_0 was the weight of the specimens before oxidation and m_1 was the weight after oxidation. After the thermal failure tests, the surface of the coatings was also observed by SEM to investigate transformation.

3. Results and discussion

3.1. Microstructure and phase analysis of the SiC whisker coating

From Fig. 1a and b, it could be seen that SiC whiskers coated the surface of matrix randomly. SiC whisker in the coating was generally several micrometers in length and different in diameter with straight or irregular morphology. Fig. 1c revealed that SiC whisker coating was generally 100 μm in thickness.

Fig. 2 showed the XRD pattern of the SiC whisker coating. All of the strong intensity peaks could be indexed to the β-SiC structure (JCPSD file: 65-0360), indicating that the β-SiC whisker was synthesized on the surface of the graphite matrix after pyrolysis of H-PSO. The low intensity peak marked with SF at 33.6° indicated the presence of stacking fault. These stacking faults were generally thought to originate from thermal stress during the growth process of β-SiC whisker [20,21]. Besides β-SiC, the weak peaks of carbon were detected, which suggested there were a certain amount of spaces in SiC whisker coating.

The formation of SiC whiskers was governed by the vapor–solid mechanism. During pyrolysis of H-PSO, the cleavage of CH_3–Si was initiated by Si–H bonds [22] and dehydrogenation of Si–H bonds occured simultaneously, which achieved H-PSO transitions from organic to inorganic. SiC was generated above 1200 °C gradually, accompanying with vapor SiO and CO as following reaction [23].

$$Si - O - C \rightarrow SiO_2 + SiC + SiO\uparrow + CO\uparrow \quad (2)$$

Thermodynamic calculations demonstrated that SiC whiskers were prone to form when the P_{SiO}/P_{CO} ratio was higher than 1 [24–26]. In addition, the pore size and its distribution of the matrix were also very important parameters for microstructure

Table 1
Basic physical parameters of the G347.

Materials	Young modulus (GPa)	Mechanical strength (MPa)	Shore hardness (–)	Thermal conductivity (W/mK)	Open porosity (%)
G347	10.8	49.0	58	116	15.4

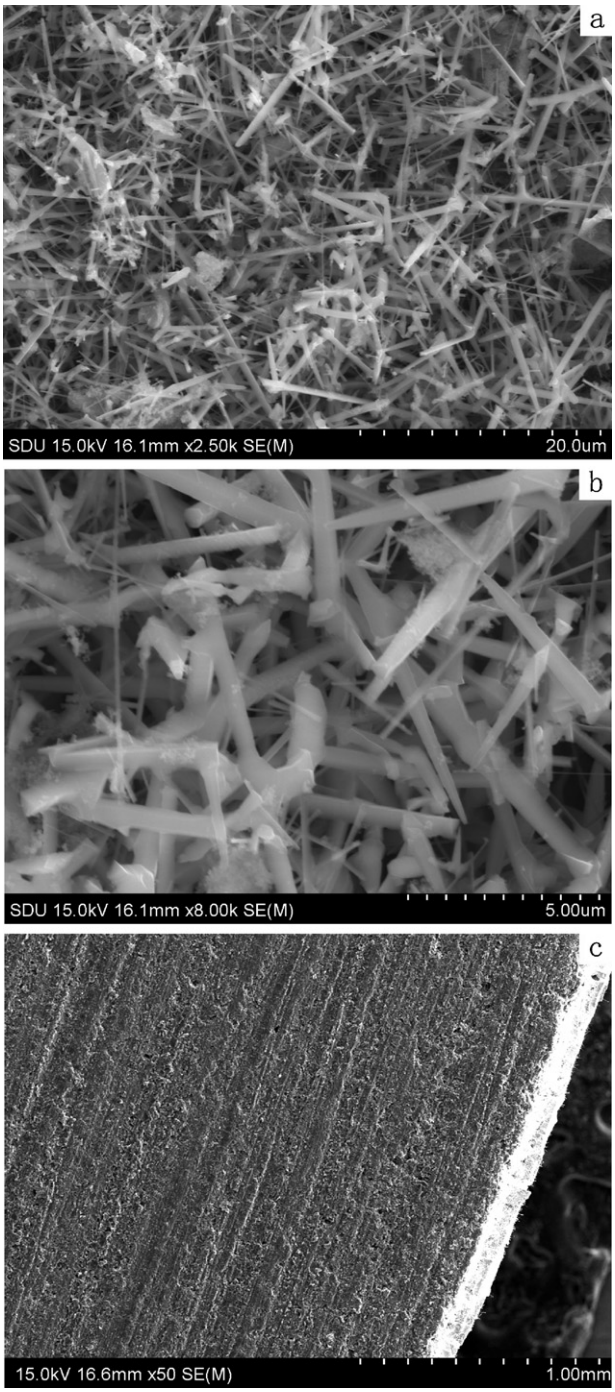

Fig. 1. Morphology images of the SiC whisker coating.

and thickness of SiC whisker reinforcement coating. It was confirmed in the latter experiments, and a detailed analysis on this point would be given in a special paper.

3.2. Microstructure and phase analysis of the SiC/Si/$MoSi_2$ multi-coating

Fig. 3a depicted the surface morphology of the final multi-coating, suggesting that the coating was relatively continuous and dense. Fig. 3b was the cross-section morphology image, where no obvious cracks and holes in the coating were

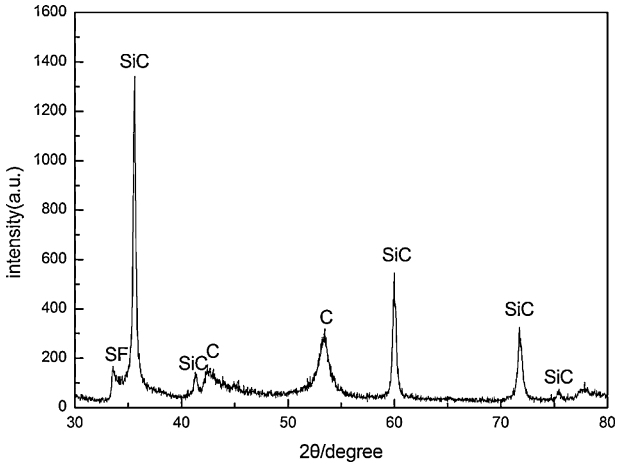

Fig. 2. X-ray pattern of the SiC whisker coating.

observed. The thickness of the coating was about 300 μm. In addition, it was difficult to find a clear boundary between the coating and matrix, which indicated the coating combined with matrix well. On the basis of the above results, a perfectly dense coating that had good compatibility with matrix had been prepared. Combined with the analysis for SiC whisker coating, we could deduce that it might be the new born SiC grains sealed the pores of SiC whisker coating and formed the final dense

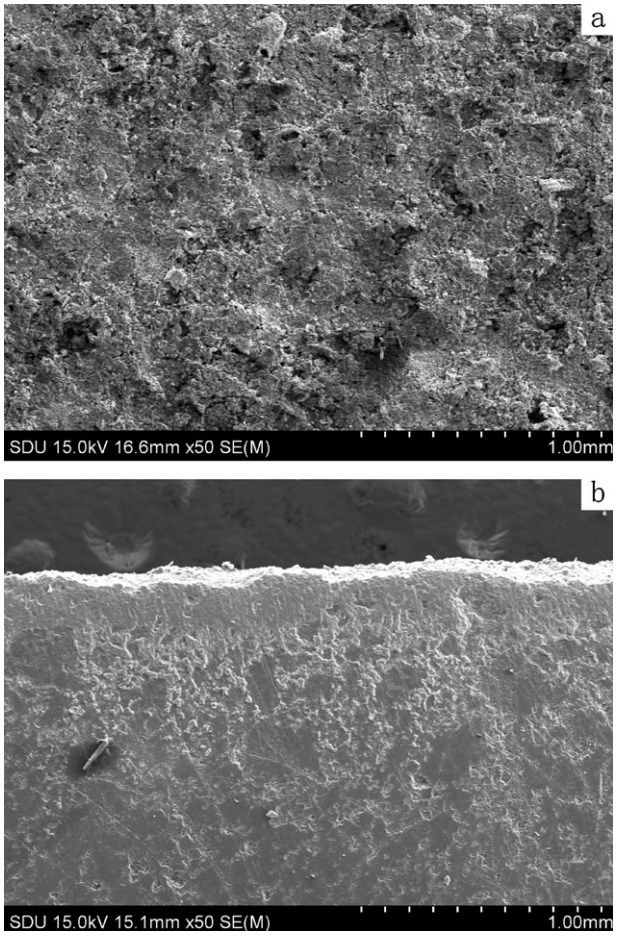

Fig. 3. Morphology images of the SiC/Si/$MoSi_2$ multi-coating.

coating. Some studies showed that introduction of SiC whisker could promote the stress transmission, reduced stress destruction caused by thermal expansion differences, inhibited over infiltration of molten Si effectively and protected the matrix well.

From Fig. 4, we could see that besides β-SiC (JCPSD file: 29-1129), new strong peaks of Si (JCPSD file: 27-1402) and weak peaks of $MoSi_2$ (JCPSD file: 65-2645) also appeared in X-ray pattern of the final multi-coating, indicating that the surface phase of the coating was composed of β-SiC, Si and $MoSi_2$. Peaks of Si and $MoSi_2$ appeared in the X-ray pattern, suggesting the two following aspects: On the one hand, some $MoSi_2$ succeeded in getting into the multi-coating and it was beneficial to improve the oxidation resistance [27]. On the other hand, a part of Si failed to react with carbon during sintering process. The reasons could be contributed to the sedimentation of silicon steam after high-heat treatment. The intensification of the β-SiC peaks in Fig. 4 indicated concentration of the coating obtained after the second high-heat treatment. When the temperature reached the melting point of Si, molten Si infiltrated SiC whisker coating with $MoSi_2$ particles and filled pores of the SiC whisker coating. During sintering process, liquid Si not only reacted with embedding-carbon, but also infiltrated through SiC whisker coating to react with matrix-carbon to form new SiC grains simultaneously. As was well known, the chemical reaction rate of Si and C was a function of temperature. When the sintering temperature was 1600 °C or below, the infiltration rate was bigger than the chemical reaction rate of liquid Si [28], where the SiC whisker coating acted as big diffusion barrier against over infiltration of liquid Si. Moreover, along with liquid Si infiltrated through SiC whisker coating that $MoSi_2$ was successfully mixed into the final multi-coating, where the SiC whisker coating acted as injection molded frame. The new SiC grains and molten Si with $MoSi_2$ particles filled the frame. The existence of SiC whisker coating reduced processing temperature and protected the matrix well simultaneously in the premise of the coating's performance.

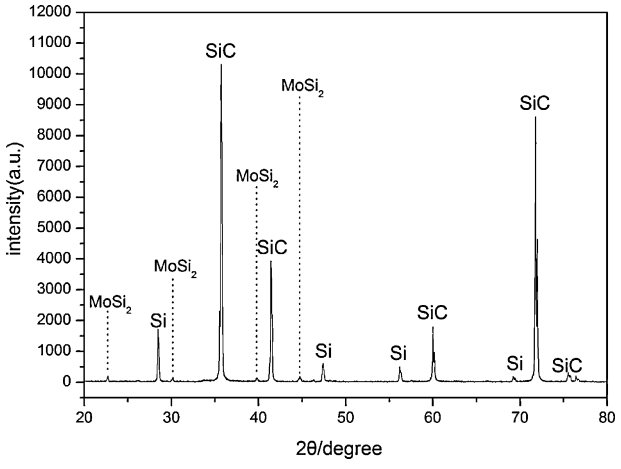

Fig. 4. X-ray pattern of the SiC/Si/$MoSi_2$ multi-coating.

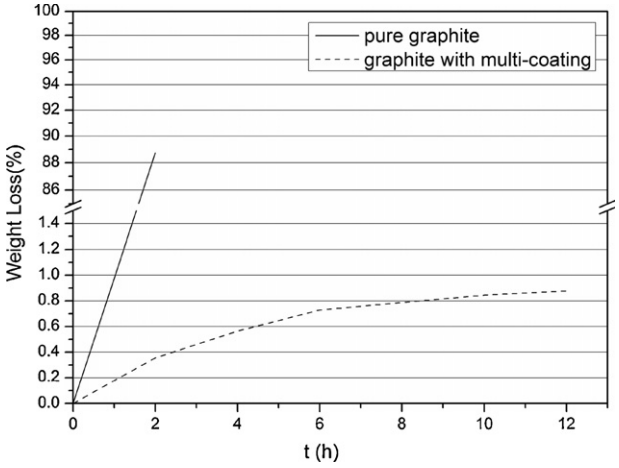

Fig. 5. Weight loss of the coated graphite specimens after thermal failure tests.

3.3. Thermal failure tests of the multi-coating

The result of oxidation pretreatment experiment showed that the weight did not fall to be added instead, and the mass gain was 0.045 wt%. This was probably caused by the oxidation of the multi-coating at higher temperature. The weight change of specimens could be attributed to the reactions as the following [29,30]:

$$SiC(s) + O_2(g) = SiO_2(s) \quad (3)$$

$$MoSi_2(s) + 7/2O_2(g) = 2SiO_2(s) + MoO_3(g) \quad (4)$$

$$Si(s) + O_2(g) = SiO_2(s) \quad (5)$$

The SiO_2 generated from oxidation reaction of coating component could effectively self-seal the defects of the coating surface during oxidation pretreatment experiment, which showed a certain self-healing ability and improved the quality of coating, and investigations below would provide additional support for it.

The multi-coating was proved to have excellent oxidation resistance. The weight loss after thermal failure tests was showed in Fig. 5. It could be seen that the weight loss was not only small (which did not exceed 1 wt% after six cycles oxidation), but also slowed down after three cycles. Whereas, 88.75 wt% of the graphite was burnt off in air at 1000 °C for 2 h. The excellent anti-oxidation property of the multi-coating might result from its dense structure of the coating. Fig. 6 showed morphology images of the SiC/Si/$MoSi_2$ multi-coating after thermal failure tests. We could see that the entire surface was smoother and denser compared with that of Fig. 3a. From Fig. 6b, no penetration cracks or holes in cross-section of the coating were observed; moreover we could not see obviously oxidation sign of matrix, which was in accordance with the result of thermal failure tests.

Fig. 7 was X-ray pattern of the SiC/Si/$MoSi_2$ multi-coatings before and after thermal failure tests. The peaks of SiO_2 (JCPSD file: 39-1425) appeared here, which confirmed occurrence of reactions (Eqs. (3–5)). During thermal failure tests, besides formation of SiO_2, the following reactions would

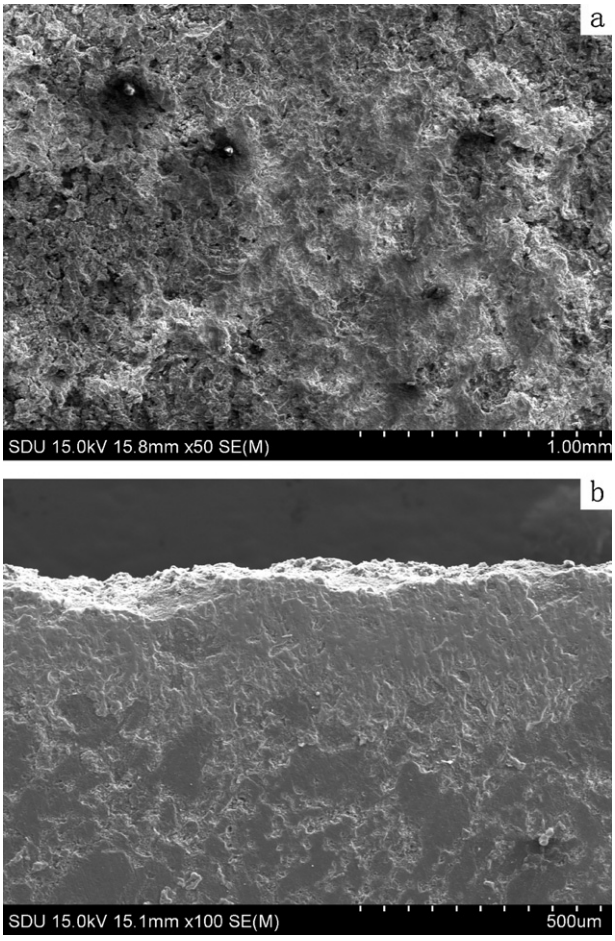

Fig. 6. Morphology images of the SiC/Si/$MoSi_2$ multi-coating after thermal failure tests.

occur:

$$SiC(s) + 2SiO_2(s) \rightleftharpoons 3SiO(g) + CO(g) \quad (6)$$

$$C(s) + O_2(g) = CO_2(g) \quad (7)$$

From Fig. 7, it could be seen that intensities of the peaks at 41.4°, 60.0°, 71.8° correspond to (2 0 0), (2 2 0), (3 1 1)

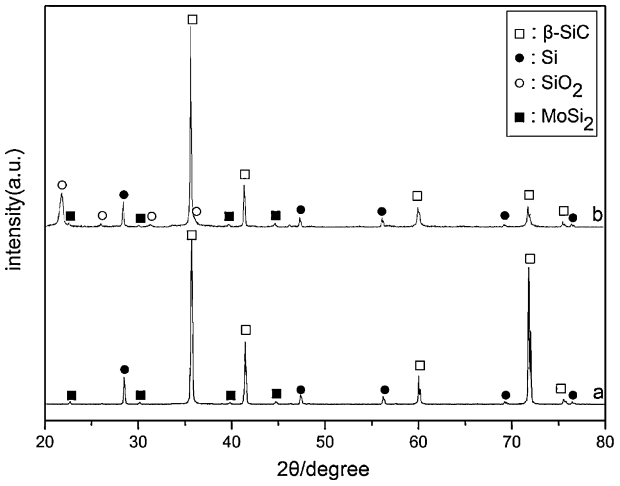

Fig. 7. X-ray pattern of the SiC/Si/$MoSi_2$ multi-coating.

reflection of β-SiC were weaken obviously, especially the peak (3 1 1). It suggested that the SiC grains formed along these crystal growth directions were instable and took part in reaction (3). What was more, reaction (6) came with it. The positive reaction of Eq. (6) resulted in partial loss of gas SiO and CO, showing weight loss of specimens. Nevertheless, reverse reaction of Eq. (6) occured in cooling after each cycle thermal failure test. The new SiC and SiO_2 sedimentated on the coating surface and formed SiC/SiO_2 eutectic solid, which could promote the densification of coating and strengthen the grain boundaries. The result of EDS showed that a certain amount of oxygen existed in the coating after thermal failure test, which confirmed the existence of SiC/SiO_2 eutectic solid, too. The main growth direction of the new born SiC was (1 1 1), which could be verified by the obvious strengthening of the corresponding peak (1 1 1) at 35.6°. In the process of thermal failure tests, the oxygen diffused through the micropore of coating to the inner structure as reaction (7) showed. The oxidation rate of this material was controlled by micro-porous diffusion [31]. Surface density rose with prolonged oxidation time, and the increasingly denser coating on the surface reduced oxidation channel, which represented that weight loss slowed down after three cycles. On the basis of the above analysis, it could be concluded that the coating by the two-step technique had excellent resistance against oxidation and a certain self-seal ability.

4. Conclusions

In this work, a continuous and dense SiC/Si/$MoSi_2$ multi-coating for the graphite materials was prepared by a cheaper and easier technique. The existence of SiC whisker coating simplified the preparation methods and protected the matrix well in the premise of the coating's performance. In addition, the technique to prepare SiC whisker coating was simple and low-cost. Research results showed that the multi-coating had excellent resistance against oxidation and had a certain self-healing ability. The weight loss did not exceed 1% after six cycles thermal failure test.

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