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High-temperature diffusion behavior of ZrC in C matrix and its promotion on graphitization

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Abstract: C/C composite material is widely used in aerospace field and others, however, it is easy to be oxidized at high temperature. In order to improve the oxidation resistance, ZrC is introduced as an oxidation inhibitor used in matrix modification of C/C composite material. Flat plate samples of ZrC/C composite materials were prepared by hot-pressing sintering. The degree of graphitization increases with rising sintering temperature, and layer structure of carbon matrix is observed clearly in the sample treated at 2273 K. Diffusion behavior of Zr in C matrix at high temperature is studied, which can be generally expressed as $D=3.382\times10^{-11}\exp[2.029\times10^{5}/(RT)]$. The diffusion of Zr in C matrix leads to the over-saturation of C in the micro area and the oversaturated C precipitates as graphite. This continuous process promotes the transformation of carbon to graphite.

Key words: ZrC; carbon material; diffusion; graphitization

1 Introduction

Carbon materials (graphite, carbon/carbon composites) are considered to be promising light-weight, high temperature-resistant structural materials [1,2], which are widely used in the advanced technology fields of aeronautic and aerospace due to the excellent electrical conductivity, thermal conductivity, low thermal expansion coefficient, and high-temperature strength retention [3,4]. However, the carbon materials are easily oxidized in the high-temperature and oxidized environment, which leads to poorer performance and limited application. To improve the anti-oxidation property of carbon materials, the generally accepted method is the use of oxidation resistant coating [5,6] or matrix modification [7−9]. ZrC not only has higher melting point (>3000 °C) and better compatibility with carbon, but also the oxide itself has enough high melting point and relatively low vapor pressure. It has been confirmed that the ablative rate of ZrC-modified C/C composite is decreased obviously as compared with that of original material, which results in the enhanced ablation resistance of the C/C composite [10−12]. Moreover, it is also discovered that ZrC could catalyze and induce graphitization at high temperatures [13,14].

The graphitization degree is one of the most important structural parameters for carbon materials. After high temperature graphitization treatment, the microstructure of carbon materials could be improved to obtain high electrical conductibility, heat conductivity and mechanical property [15−17]. Nowadays, few efforts were taken on the effect of ZrC modified carbon materials on the microstructure, and the mechanism of the ZrC catalytic graphitization was rarely investigated. In this work, flat plate sample of ZrC/C composite material was successfully prepared, and the diffusion kinetic behavior of Zr in C at high temperature was studied. Furthermore, the mechanism of ZrC promotion on graphitization of carbon was also discussed.

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2 Experimental

2.1 Synthesis of ZrC modified carbon material

Flat plate sample of ZrC modified carbon material was prepared by the hot-pressing sintering method. In a typical synthesis, ZrC powder was compressed into a wafer (d=10 mm, h=3 mm) at around 300 MPa, and then the ZrC wafer was embedded in the active carbon and sintered at 1600 °C for 4 h at a heating rate of 5 °C/min with the protection of high purity argon. After that, the ZrC wafer was transferred into a graphite mould. To avoid contamination, a layer of carbon paper was adhered to the inner wall of the graphite mould and a small amount of carbon powder was added to it in advance. Then, the graphite mould was placed in a hot-pressing sintering furnace with an axial pressure of 30 MPa. Finally, the graphite mould was first calcined to 473 K at a heating rate of 5 K/min, maintained at that temperature for 180 min, followed by a second calcination at a heating rate of 10 K/min up to 2073, 2173 and 2273 K, respectively (holding time, 180 min), and then it was naturally cooled to room temperature. It was noted that the high purity argon was used as the protective atmosphere in the whole sintering process.

2.2 Characterization

The fracture micro-morphology of the flat plate sample of ZrC modified carbon composite was observed on a field emission scanning electron microscope (FESEM, JSM−6700F). Line scanning and spot sampling of fracture section were determined using energy dispersive spectrometry (EDS) equipped on FESEM.

3 Results and discussion

3.1 Microstructure of flat plate sample

Figure 1 shows the SEM images of C matrix layers, ZrC layers and their interface layers of fracture section of flat plate samples treated at different temperatures. From Figs. 1(b, e, h), it can be seen that with increasing of the heat treatment temperature, the layer structures could be observed in the C matrix, especially that treated at 2273 K, indicating that the graphitization degree of the C matrix could increase with the rise of heat treatment temperature. However, no significant changes are discovered in the ZrC layers as temperature is increased in Figs. 1(c, f, g). In addition, the ZrC flat plates are bonded tightly to C matrix in the diffusion interface layers, as shown in Figs. 1(a, d, g).

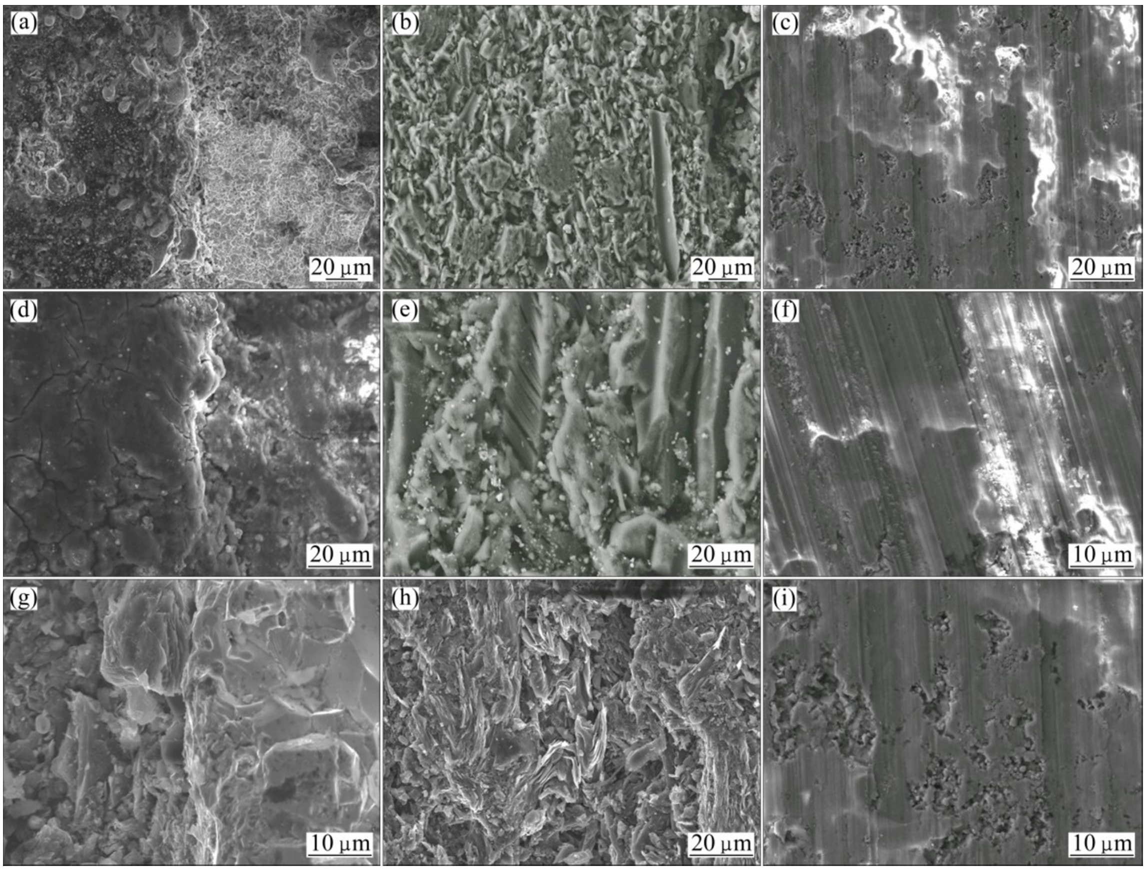

Fig. 1 Microstructures of ZrC/C samples sintered at high temperatures: (a, d, g) Interface layers treated at 2073, 2173 and 2273 K, respectively; (b, e, h) C matrix layers treated at 2073, 2173 and 2273 K, respectively; (c, f, i) ZrC layers treated at 2073, 2173 and 2273 K, respectively