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Effects of HfC nanowire amount on the microstructure and ablation resistance of CVD-HfC coating

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ABSTRACT

To improve the ablation resistance of HfC coating for carbon/carbon (C/C) composites, various fractions of HfC nanowires were incorporated into the HfC coating by chemical vapor deposition (CVD). Effects of HfC nanowire amount on the microstructure and ablation resistance of the CVD-HfC coating were investigated. Results indicated that the HfC nanowire layer became thicker and denser with the deposition time extending. HfC nanowires could inhibit the formation of cracks and interlaminar gaps in the HfC coating. With the increase of HfC nanowire amount, the HfC coating became thicker, while its porosity and roughness firstly decreased and then increased. Ablation tests indicated that the incorporation of HfC nanowires could effectively improve the ablation resistance of the HfC coating, which could be ascribed to the decreasing surface temperature of the coated samples and the effective alleviation of cracking and delamination of the coating during ablation. The HfC coating with HfC nanowires deposited for 1 h exhibited better ablation resistance owing to its compact microstructure, and its mass and linear ablation rates were only 0.41 mg/s and − 1.53 μm/s after ablation for 120 s.

1. Introduction

The oxidation sensitivity is considered as the main challenge for the practical applications of carbon/carbon (C/C) composites in the field of high-temperature thermal structural components [1–3]. The oxidation and ablation of C/C composites will result in the rapid deterioration of their mechanical properties and reliability [4,5]. Ceramic coating is an effective method to solve this problem [6–9]. Refractory metal carbides (HfC, ZrC, TaC, etc.) are promising ablation resistant materials owing to their high melting point, high strength, good oxidation resistance and so on [9–12]. HfC has many excellent high-temperature properties, such as highest melting point (3959 °C), high temperature phase stability, low vapor pressure, good oxidation and ablation resistance and so on [12–14]. Moreover, the melting point of its oxidation product (HfO_2) is 2810 °C, higher than that of ZrO_2 (2677 °C) and Ta_2O_5 (1800 °C) [14]. Therefore, HfC is considered to be an ideal candidate for ablation resistant coatings. Up to date, several different methods have been used to prepare HfC coatings, such as chemical vapor deposition (CVD) [12,14,15], supersonic atmospheric plasma spraying (SAPS) [16], reactive melt infiltration [17] and reactive magnetron sputtering [18]. Among these methods, CVD has attracted much attention because it is a low-cost and convenient technique, which is easy to design and control coating composition and microstructure [19]. Therefore, in the present work, CVD is selected to prepare HfC coating.

The coefficient of thermal expansion (CTE) mismatch between HfC coating (6.7×10^{-6} °C^{-1}) and C/C substrate (1.0×10^{-6} °C^{-1}) and the phase transformation of HfO_2 during cooling process may result in the cracking and delamination of the coating. In order to solve this problem, nanowires have been introduced into the HfC coating as reinforcements. Chu [20] and Li [21] prepared SiC nanowire-reinforced HfC coatings, results showed that the SiC nanowires improved the mechanical performance and ablation resistance of the HfC coating. However, the ablation resistance of SiC nanowires is not very impressive due to the low melting point of SiC and quick volatilization of its oxide (SiO_2) above 2000 °C. Because of the higher melting point of HfC and HfO_2, HfC nanowires are expected to be a better reinforcement in ceramic coatings at high temperatures. Our previous research proved that HfC nanowires could improve the toughness, thermal shock resistance and ablation resistance of the ceramic coatings [22–24]. Moreover, owing to the good physical and chemical compatibility between HfC nanowires and HfC coating, HfC nanowires are more suitable for HfC ablation resistant coating than SiC nanowires applying above 2000 °C. For fiber-reinforced composites, the factors of fiber shape, aspect ratio and volume fraction have a great influence on the microstructure and mechanical properties of the composites [25,26]. So, the morphology and amount of HfC nanowires will also influence the

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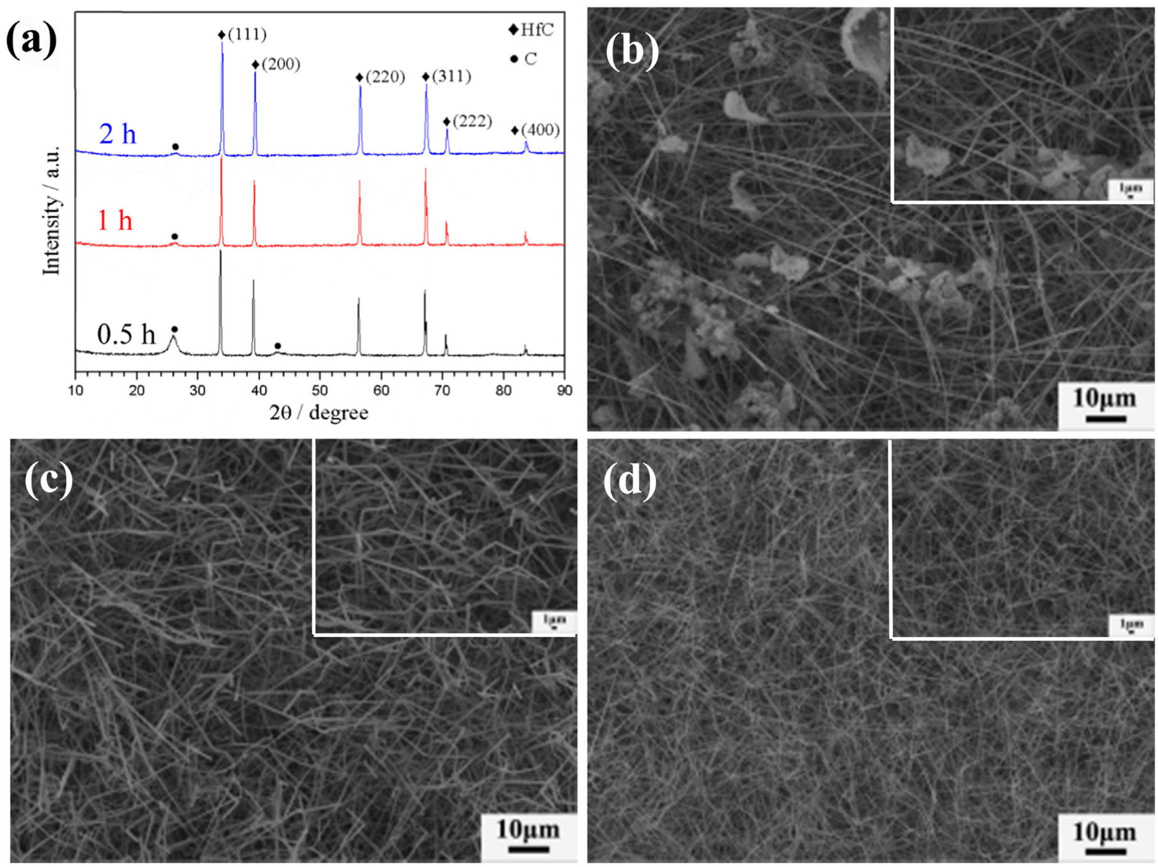

Fig. 1. XRD patterns (a) and surface secondary electron SEM images of the synthesized HfC nanowires on C/C substrate at different deposition time: (b) 0.5 h; (c) 1 h; (d) 2 h.

microstructure and ablation resistance of the HfC coating. Up to now, limited researches have been reported about the HfC nanowire-reinforced HfC coating, especially the influence of HfC nanowires amount on the microstructure and ablation resistance of the HfC coating.

In this work, HfC coatings with different amount of HfC nanowires were synthesized on C/C substrates by two-step CVD. Firstly, HfC nanowires were prepared on C/C substrates by CVD for different deposition time. Then, HfC coatings were deposited on the HfC nanowire porous layers by the second step of CVD to fill the nanowire porous layer. So, HfC coatings reinforced by different amount of HfC nanowires were obtained. Influence of the HfC nanowire amount on the microstructure and ablation resistance of the HfC coating was investigated.

2. Experimental procedure

2.1. Preparation of the HfC coatings with different amount of HfC nanowires

C/C composites (1.65 g/cm^3) were used as the substrates, which were prepared by isothermal chemical vapor infiltration. The bulk C/C substrates were cut into small specimens (10 × 10 × 10 mm^3 for morphology characterization, φ30 × 10 mm^3 for ablation test), polished by SiC paper, ultrasonically cleaned with distilled water and then dried at 80 °C.

HfC nanowires were synthesized on C/C substrates by catalyst-assisted CVD in a vertical tube furnace. $Ni(NO_3)_2$ particles acting as catalyst were covered on C/C specimens by soaking method before deposition process. $HfCl_4$ powders (purity: 99.9%) and CH_4 gas (purity: 99.99%) were used as hafnium source and carbon source, respectively. H_2 and Ar gas acted as reducing gas and diluting gas, respectively. C/C specimens hung by a thin molybdenum wire were placed in the deposition chamber of the furnace. Sufficient $HfCl_4$ powders were put into an alumina crucible and then placed in the volatilization chamber of the furnace. After vacuum treatment, the furnace was heated up to 1100 °C in H_2 and Ar atmosphere. When the furnace reached the pre-set temperature, CH_4 gas was immediately injected into the furnace. During deposition, the flow rates of CH_4, H_2 and Ar were 200, 2000 and 1000 ml/min, respectively. The pressure in the furnace was 10–15 KPa. To obtain HfC nanowires with different morphology and amount, the deposition time was 0.5, 1 and 2 h, respectively. After the deposition process, the furnace was naturally cooled to room temperature.

HfC coating was prepared on C/C specimens by the second step of CVD. No catalyst was used in this step. The preparation process of HfC coating was similar with that of the HfC nanowires. During preparing HfC coating, the deposition temperature, pressure and time were 1300–1500 °C, 5–10 KPa and 4 h, respectively. The gas flow rates of CH_4, H_2 and Ar were 300, 1500 and 1500 ml/min, respectively. To simplify, the HfC-coated C/C samples without HfC nanowires were denoted as S0, and the HfC-coated C/C samples with HfC nanowires deposited for different time (0.5, 1 and 2 h) were denoted as S1, S2 and S3, respectively.

2.2. Ablation resistance test of the HfC coatings

Ablation resistance of the HfC coatings was tested under oxyacetylene torch with a heat flux of 2400 kW/m^2 [27]. The pressure of O_2 and