



A crack-free SiC nanowire-toughened Si-Mo-W-C coating prepared on graphite materials for enhancing the oxidation resistance

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ABSTRACT

To protect the graphite materials against oxidation at high-temperature, a SiC nanowire-toughened Si-Mo-W-C coating was prepared through a two-step technique. First, a porous structure of SiC nanowires was synthesized by a simplified chemical vapor deposition. Afterward, the treated specimen was coated with Si-Mo-W-C ceramics by the pack cementation. The microstructure, phase composition and oxidation resistance of the coating were analyzed in detail. It was found that a dense and crack-free nanowire-toughened Si-Mo-W-C coating was formed. The coating toughened with SiC nanowires could protect graphite at 1500 °C for 30 h with weight loss of 1.43%. After oxidation, there is still no any crack in the coating. It was inferred that the multiphase composition of the coating along with the toughening effects of the SiC nanowires can lead to a crack-free coating together, and then a good anti-oxidation performance was obtained.

1. Introduction

Graphite materials have been widely applied in nuclear industry, aerospace and other fields due to their well-thermal conductivity, low coefficient of thermal expansion (CTE), thermal shock resistance, chemical stability and so on [1–3]. But, the carbon materials only can be used under 450 °C in the presence of oxygen or used in the oxygen-free environment because of the serious reaction between oxygen and carbon at high temperature. The oxidation problem can seriously restrict its potential applications in oxygen-containing atmosphere [4,5]. Therefore, a reliable protection system to protect the graphite from oxygen attack is crucial for its high-temperature uses.

Applying surface coating on the graphite has been confirmed to be an effective method to improve its oxidation resistance [6]. In recent decades, the anti-oxidation coatings for carbon materials have been widely researched and some significant breakthroughs have been made about solving the oxidation issue of carbon materials, especially for carbon/carbon (C/C) composites. Silicon carbide (SiC) was accepted as the coating material at the very early stage, and so far, it has been the most commonly used one [7,8]. This is because that SiC has many advantages as an anti-oxidative coating material for carbon-based composites. First, the reaction between SiC and oxygen can generate sufficient SiO₂ with the low oxygen permeability and viscous flow at

high temperature [9], which is the basis of the anti-oxidation and gives the coating good self-sealing performance. Moreover, for the pack cementation method, SiC transition layer can be obtained as a result of the deep infiltration of silicon into carbon substrate and the reaction between silicon and carbon at above 1410 °C. The transition layer helps to enhance the interface adhesion strength between the coating and substrate. Third, the CTE gap between SiC and carbon materials is much smaller, compared with most of other ceramic materials with an excellent oxidation resistance. In recent years, the multi-phase coating has been designed through combining various silicon-based ceramics or ultra-high temperature ceramics (UHTCs) with SiC, such as SiC-ZrB₂ [10], SiC-Si-MoSi₂ [11] etc. The multi-phase coating is an effective approach to obtain protection for a longer time or a higher temperature application.

However, during oxidation cycles, the penetrating cracks will inevitably develop in the ceramic coating due to CTE mismatch between the carbon substrate and the coating materials. These cracks can provide some paths through which oxygen can migrate to the underlying substrate and oxidize it. Efforts have been made to minimize the effect of the CTE mismatch, such as preparing a multi-layer coating [12,13] or a toughened coating [14–16]. SiC nanowire-toughened ceramic coating is a good method for addressing the issue of inherent brittleness of the ceramic coating and reducing the size of cracks. Huang et al. [17] have

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studied the effect of incorporating SiC nanowires in mullite/SiC protective coating for C/C composites. The results showed that the thermal shock and oxidation resistance of the coating could be greatly improved by introducing SiC nanowires. However, the relevant researches are mostly based on C/C composites and there is few work focusing on graphite.

Herein, a two-step technique was used to construct a SiC nanowire-toughened Si-Mo-W-C coating for the graphite materials. Firstly, a porous structure of SiC nanowires was prepared on the graphite through a simplified chemical vapor deposition (CVD) method. Afterward, the treated specimen was coated with Si-Mo-W-C ceramics by the pack cementation. The microstructure, phase composition and anti-oxidation performance of the coating were investigated, as well as the toughening mechanism of SiC nanowires in the coating.

2. Experimental

Graphite substrates with dimension of 10 mm × 10 mm × 5 mm were cut from a bulk piece of graphite with density of 1.85 g/cm³ (Shandong Weiji carbon technology Co. Ltd., Jinan, China). All specimens were hand-polished with SiC papers (200 and 500 grit), then cleaned ultrasonically with ethanol and dried in an oven at 100 °C for 2 h.

Fig. 1 displays the diagram of preparing SiC nanowire-toughened Si-Mo-W-C coating on the graphite. The porous structure of SiC nanowires was prepared on the graphite through a simplified CVD. The cured products of hydrogen silicone oil (H-PSO) and divinylbenzene (DVB) were used as the air supply. The details of the reaction process and mechanism were reported in our previous works [18,19]. The outer Si-Mo-W-C coating on the graphite substrate with SiC nanowires was prepared by a pack cementation technique. The powder mixture for the second step was composed of 10–20 wt% Si, 55–75 wt% C, 5–15 wt% W, 5–15 wt% Mo and 5 wt% Al₂O₃. The as-prepared samples were embedded in the powder mixture in a graphite crucible and then heat treated at 2000–2200 °C for 2 h in argon.

The isothermal oxidation test was carried out at 1500 °C in static air to investigate the oxidation behavior of the coated samples. During the oxidation test, the samples were put into a muffle furnace and heated to 1500 °C at a rate of 8 °C/min and then kept a certain time at 1500 °C. After that, the samples were taken out from the furnace when the furnace was cooled down to room temperature at the same rate. The mass loss of the samples was measured by an electronic balance with sensitivity of ± 0.1 mg. This oxidation process was repeated several times. Cumulative weight loss of the oxidized samples was calculated and reported as a function of oxidation time. The weight loss (w%) was calculated by Eq. (1) to measure the anti-oxidation property.

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

where m_0 and m_1 are the weight of samples before and after oxidation, respectively.

The crystalline structure of the samples was analyzed by X-ray diffraction (XRD, Rigaku D/max-c, 4°/min). The morphology of the SiC nanowires and the outer coating was characterized by scanning electron microscopy (SEM, Hitachi SU-70) equipped with energy dispersive spectroscopy (EDS). High-resolution transmission electron microscopy (HRTEM) was employed to investigate the interior structure of the SiC nanowires. In addition, the surface profile showing the surface

roughness of the coating was measured by a contour elite 3D optical microscope (Bruker Contour GT-I).

3. Results and discussion

Fig. 2(a) displays XRD pattern of the as-obtained graphite coated with a layer of SiC nanowires. Three characteristic peaks of β -SiC can be indexed as a cubic structure with $a = b = c = 0.4359$ nm (PDF No. 29-1129). A minor shoulder peak at around 33.8° marked with “SF” is ascribed to the stacking faults of nanowires [20,21], which is related to the preparation technique. In view of the porous network consisting of β -SiC nanowires, which can be revealed by Fig. 3, all diffraction peaks of carbon from the graphite substrate also appeared distinctly. XRD pattern of the as-obtained coating reinforced by SiC nanowires is displayed in Fig. 2(b). The phase composition of the coating prepared by the pack cementation technique from Si, C, W and Mo powders can be analyzed. Results show that there are mainly three phases in the coating, that is, SiC, WSi₂ and MoSi₂. In addition, it is possible that W₂C and Mo₂C can be generated due to the reaction of C with Mo and W during the cementation process at 2000–2200 °C. It also can be found that all the peaks of the characteristic diffraction are very sharp, suggesting a good crystallization of the grains in the coating. The melting point of some components of the cementation powders, such as individual elements C, W and Mo, is essentially higher than applied temperature during the cementation process. Thus, the particles of these components could form grains and contribute to the sharp peaks on the XRD pattern. At high temperature, the molten Si and Al₂O₃ in the original mixed powders could penetrate into the porous nanowire layer, carrying other metal powders simultaneously, to promote the formation of a dense coating.

Fig. 3 shows the typical SEM and TEM images about the morphology of SiC nanowires on the graphite. The randomly oriented nanowires with large length to diameter ratio uniformly cover the entire substrate, forming a network structure. From TEM images, the straight crystal of the nanowires with a diameter in the range of 80–500 nm can be confirmed. It also can be observed from Fig. 3(c–d), that the surface morphology of the SiC nanowires is rugged, having an obvious amorphous shell.

Fig. 4(a–d) exhibit the surface backscattered electron images of the as-obtained Si-Mo-W-C coating and EDS analysis of the corresponding spot. Obviously, the gray parts and white parts are evenly distributed, indicating that the phase compositions of the coating are homogeneous. From EDS spectrum lines, the gray parts (spot 1) are mainly composed of Si and C, representing the SiC particles. While the white platelets (spot 2) contain the Si, C, Mo and W. Combined with XRD pattern, it can be inferred that the white platelets are a mixture of SiC, WSi₂ and MoSi₂. It can be seen that the WSi₂ and MoSi₂ did not form separate grains and the SiC grains were embedded in them. It is because that W and Mo have close electronic structure and their corresponding metal silicides possess the similar chemical property. In the formation of the Si-Mo-W-C coating, the WSi₂ and MoSi₂ tend to attach to each other. This result is consistent with the work by Zhang et al. [22]. It is hard to distinguish MoSi₂ and WSi₂ phases. In addition, the areas of the white and gray platelets can roughly reveal that the total content of WSi₂ and MoSi₂ is approximate to that of SiC. The plenty of interfaces between the different phases can relax the thermal stress, contributing to the decrease of cracks in the coating [23]. Fig. 4(e) shows the backscattered electron image and element line scan along the cross-section of the Si-Mo-W-C coated graphite. As the same with the surface images, the well dispersed gray and white platelets on the cross-section also indicate the homogeneity of phase distribution in the thickness direction. During the pack cementation, W and Mo particles can easily infiltrate into the SiC nanowire layer due to the flowing liquid Si and Al₂O₃ [23,24]. Moreover, the coating has an average thickness of about 150 μ m.

Fig. 5 displays the surface and cross-section morphology of the Si-Mo-W-C coating. From SEM of the surface image, it is clear that the



Fig. 1. Diagram of preparing SiC nanowire-toughened Si-Mo-W-C coating on the graphite.

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