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Preparation and characterization of SiO_2 thin film and SiC nanofibers to improve of graphite oxidation resistance

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ABSTRACT

In this study, a multiphase coating was prepared on a graphite substrate by a two-step technique to improve oxidation resistance of graphite. The first step was to prepare a functionally graded SiC layer by a pack cementation process and the second step was to obtain a nano SiC and SiO_2 thin film coating by a slurry painting technique. The microstructure and the surface chemistry of the coating were characterized by X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. The spectral deconvolution was conducted using CasaXPS software based on Gaussian-Lorentzian function. The isothermal oxidation test of the coated samples was performed at 1773 K for 10 h. A 500 μm thick graded C–SiC layer was observed at the graphite-coating interface. An amorphous SiO_2 thin film and SiC nanofibers with the diameter in the range of 30–75 nm were formed on the coatings. The SiC nanofibers can efficiently improve oxidation resistance of graphite.

1. Introduction

Carbon and graphite materials are widely used for high temperature applications due to the retention of their mechanical and thermal properties. However, the oxidation of graphite above 773 K in air cannot meet the demand of the practical application requirement, especially for high-temperature causing a drop in their strength and other mechanical properties. Furthermore, with the increase in oxidation temperature, the rate of graphite chemical reaction with oxygen, as well as the extent of oxidation, is strongly increased. Therefore, more efforts need to be made to improve the ablation resistance of graphite in the oxidizing atmosphere [1–3]. It is well known that the SiC ceramic coating is an efficient solution for protecting the graphite at high temperature, since it can significantly prevent the oxygen diffusion into the graphite by producing a protective SiC layer. In addition, the glassy SiO_2 film formed on the surface of the coating could efficiently avoid the oxygen diffusion into the graphite. On the other hand, the mismatch of thermal expansion coefficient between graphite and the SiC coating commonly lead to cracking of SiC coating, facilitating the oxygen diffusion to graphite substrate and the failure of the coating [4–6].

One of the approaches employed to solve this problem is the application of nanostructured coatings, since it has been confirmed that nanostructured SiC coatings can reinforce the interlayer bonding at the interface, consequently serve an important role in the retardation of microcracks and the enhancement of the oxidation resistance by improving toughness [7,8]. Mei [9] indicated that for SiC whisker contents of 5 and 15 wt.%, the SiC_w–C/SiC composite work of fracture increased up to 209.8% and 179.0%, respectively from the whisker-free case. Also Xie [10] showed that the fracture toughness of laminated SiC_w/SiC ceramics with a volume fraction of 30% and 40% of SiC whiskers were 7.09 and 8.02 $MPa\,m^{1/2}$, respectively. The application of SiC nanoparticles has been studied by researchers. By adding SiC nanoparticles to a pack cementation mixture for the synthesis of a protecting coating, Li [8] and Jafari [11] indicated that SiC nanoparticles can increase the toughness and decrease the stress on SiC ceramic coating, thus improving the protective ability of the coating against oxidation. Chu [12] also prepared a multi-layer SiC and SiC nanowire coating on a carbon-carbon composite using the hybrid chemical vapor deposition (CVD). They verified that the nanowires in the coating could efficiently suppress the cracking of the coating by various toughening mechanisms including nanowire pullout, nanowire bridging, microcrack deflection and the good interaction between nanowire/matrix interfaces [12]. In this study, a multiphase protective coating including of SiO_2 thin film, nanoSiC and functionally graded SiC was developed on a graphite substrate by the pack cementation and slurry painting methods. The oxidation resistance of the coated samples was investigated at 1773 K. The

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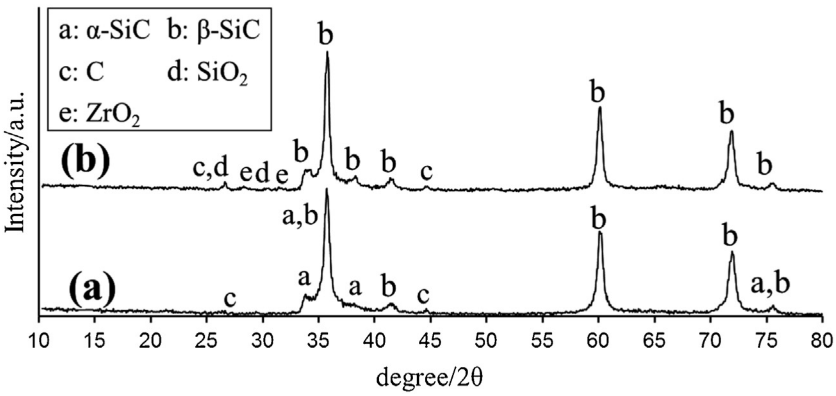

Fig. 1. XRD patterns of: (a) the first step coating, (b) the second step coating.

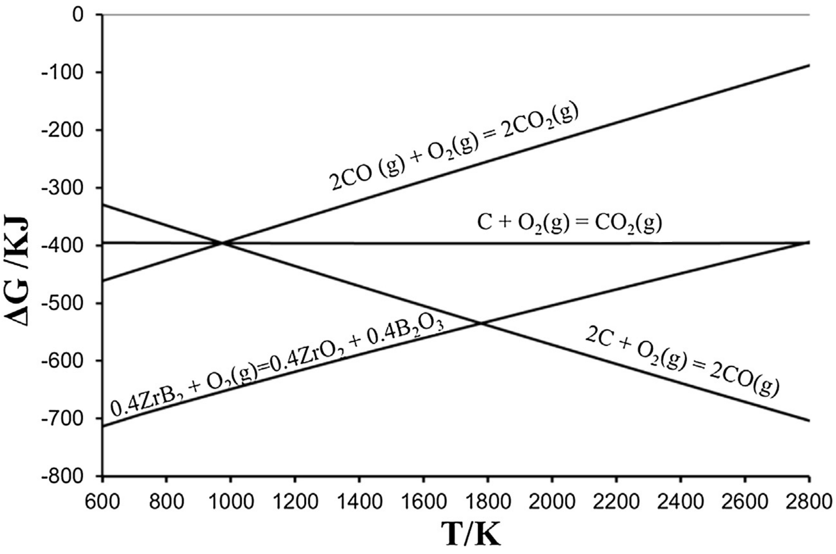

Fig. 2. The variations of Gibbs free energy with temperature for ZrB_2 and C reactions with oxygen at 0.1 MPa.

surface chemistry of the coating was described by X-ray photoelectron spectroscopy (XPS).

2. Experimental procedures

2.1. Preparation of the coatings

The specimens, with a dimension of 10mm × 10mm × 10 mm were cut from a graphite with an apparent density of 2.07 g/cm^3, a bulk density of 1.77 g/cm^3, an apparent porosity of 14.56% and a flexural strength of 49.51 MPa. After being hand-abraded using 400 and 800 grit SiC paper, these specimens were cleaned with distilled ethanol and dried at 383 K for 2 h. The first step coating was formed on the surface of graphite by pack cementation technique with a powder mixture composed of 50 wt.% Si (400 mesh, Panadyne) 40 wt.% α-SiC (α-SiC, 800 mesh, Goodfellow), and 10 wt.% α-Al_2O_3 (800 mesh, Panadyne). The Al_2O_3 was added into the pack powders in order to increase the rate of diffusing reaction [13]. The graphite samples were embedded in the powder mixture and placed in a graphite crucible, and were then heat-treated at 1873 K for 2 h in an argon protective atmosphere to form the first step SiC coating. The second step coating was prepared by painting a slurry mixture comprising of 30 wt.% ZrB_2 (800 mesh, H.C.Starck), 40 wt.% xylene and 30 wt.% polycarbosilane (PCS, Suzhou CeraFil Ceramic Fiber) with a molecular weight of 1000–1500 g/mol and a melting point of 448–493 K on the surface of the first step coated substrates and then dried at 383 K for 24 h. The samples were wrapped in a parchment paper on which the silicon-silica gel mixture of 1:1 ratio was painted and then heat-treated at 1873 K for 2 h in an argon atmosphere to form the second step coating. In order to fill the pores obtained by the slurry painting method, the coated samples were immersed in tetraethoxysilane (TEOS, $(C_2H_5O)_4Si$, Merck) solution for 3 h, and then dried at 383 K for 2 h [14].

2.2. Characterization

The isothermal oxidation test of the coated samples was performed at 1773 K in an electrical furnace in a static air atmosphere. The cumulative weight changes of the coated samples after oxidation were measured by a precision balance and recorded as a function of time. An X-ray diffractometer (XRD, Philips, PW1730) equipped with a copper X-ray source was used for the phase analysis of the coatings. A scanning electron microscope (SEM, Tescan, VegaIII) operating at 30 KV and equipped with energy dispersive X-ray analysis (EDS), secondary electrons detector (SE) and back scattered electrons detector (BSE) were employed for the characterization of the coating morphologies. The surface chemistry of the coating was characterized by X-ray photoelectron spectroscopy (XPS, Bestec) at an operating pressure of less than 10^{-7} Pa. The coating was irradiated with Al (Kα) X-ray (1486.6 eV). The sampling depth for XPS can be estimated at around 10.8 nm. The sampling depth is defined as three times the inelastic mean free

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