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Molten salt synthesis of mullite whiskers on the surface of SiC ceramics

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ABSTRACT

Mullite whiskers coating on the surface of SiC ceramics was fabricated by chemical reactions between the SiC ceramic substrate and molten salts ($Al_2(SO_4)_3 + Na_2SO_4$), which greatly improved the oxidation resistance of the porous SiC ceramic. Scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, Fourier transform-infrared spectroscopy and high resolution transmission electron microscopy were employed to characterize the structural morphology and phase compositions of the modified porous SiC. The results show that the surface of SiC ceramic was covered by dense mullite whiskers with nanometer-sized (100–300 nm) diameters and micrometer-sized (10–20 μm) lengths. The molten salts chemical reactions were firstly proposed and demonstrated by thermo gravimetric (TG) analyzer coupled with mass spectrometry (MS) and fourier transform infrared spectrometry (FTIR).

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1. Introduction

Silicon carbide (SiC) is a kind of strong covalent bond compound, and it has been used as structural and functional components due to its excellent overall physical, chemical and mechanical performances [1–4]. The oxidation behavior of SiC ceramic has been investigated for many years because of its great potential for high-temperature applications [5]. Bulk SiC ceramic exhibits good oxidation resistance for formation of a protective surface scale of SiO_2. One of methods to further improve the oxidation resistance of SiC at high temperature is achieved by adding a protective oxide coating on the ceramic substrate. Mullite has attracted considerable interest as a protective coating for Si-based ceramics (SiC and Si_3N_4) because of its low coefficient of thermal expansion (CTE) and chemical compatibility with them [6–8]. In particular, the mullite with CTE of $4.4–5.6 \times 10^{-6}$ °C^{-1} can exactly match the SiC ceramic with CTE of $4.3–5.4 \times 10^{-6}$ °C^{-1} [9]. Presently, several techniques have been applied to fabricate a mullite coating on the surface of SiC substrate, including chemical vapor deposition (CVD) [10–13], plasma spraying [14–16], sol–gel [17,18], hydrothermal electrophoretic deposition [9,19], and pulsed laser deposition (PLD) [20,21]. Moreover, the mullite coating as a barrier for oxygen diffusion can improve the oxidation resistance of SiC ceramic [16,17]. However, the preparation processes of mullite coatings obtained by these methods are somewhat expensive or complex. Thus, to develop new approaches to form the mullite coating on the SiC surface still remains a challenge.

In this paper, we firstly fabricate a mullite whisker coating on the dense or porous SiC ceramic substrate by chemical reactions between the SiC and molten salts ($Al_2(SO_4)_3 + Na_2SO_4$), and then the chemical reaction process and related oxidation resistance performances were investigated experimentally.

2. Experimental procedure

The porous and dense SiC substrates (Xi'an powder Co., Ltd., 60% open porosity for the porous SiC), aluminum sulfate ($Al_2(SO_4)_3$, AR, Xi'an chemical reagent Co.) and sodium sulfate (Na_2SO_4, AR, Xi'an chemical reagent Co.,) were used as raw materials in the present study. The $Al_2(SO_4)_3$, Na_2SO_4 and rectangular SiC substrate were weighed accurately according to a ratio of 9:10:1 in wt.%. The mixed powder ($Al_2(SO_4)_3 + Na_2SO_4$) was grinded in a ceramic mortar for 30 min. The porous or dense SiC ceramic sample was placed in the bottom of alumina boat and covered by the mixed powder after grinding, and then slowly heated to 900 °C for holding 60 min and cooled down to room temperature in a maffle furnace under air atmosphere. Subsequently, the samples were boiled in distilled water to remove the unreacted sulfate. Finally, the modified SiC substrate with a white coating was obtained after further drying.

Crystalline phase and morphologies of the samples were examined by using X-ray diffractometer (XRD, D/MAX-RA) and scanning electronic microscope (SEM, S-4800) coupled with energy dispersive spectrometer (EDS, INCA-350) or high resolution transmission electron microscopy (HRTEM, JEOL-2100F), respectively. The fourier transform infrared spectrum (FTIR) was recorded with an infrared spectrometer (AVATAR 360) in the wavenumber range of 4000–400 cm^{-1}. The isothermal oxidation tests were carried out in an electrical furnace at 1400 °C in static air. All the samples were weighted carefully by an electronic balance before the oxidation test and the heating rate is about 10 °C/min. After the respective holding time, each set of samples were directly put out from the furnace and cooled down to room temperature. Then, the samples were immediately weighted. The mean

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weight loss rates and their deviations of the modified and unmodified SiC ceramics were obtained by the arithmetical average and standard deviation analysis of 2–4 samples, respectively.

In order to investigate the chemical reaction process, a SiC powder (Xi'an chemical reagent Co. Ltd., average particle size of 20 μm) was used as the reactant for mixing with the mixed powder ($Al_2(SO_4)_3 + Na_2SO_4$). Then, the resulting powder mixture ($SiC + Al_2(SO_4)_3 + Na_2SO_4$) was measured by thermo gravimetric analyzer (TG) coupled with mass spectrometry (MS) and fourier transform infrared spectrometry. The thermo gravimetric-differential scanning calorimetry (TG-DSC) was performed on a thermal analyzer (STA 409C, Netzsch), and the resulting gases were introduced to an infrared spectrometer (Nicolet 5700, Thermo Electron Scientific Instruments Corp.) and a mass spectrometry (MS403C, Thermo Electron Scientific Instruments Corp.) to carry out specific absorbance peak checking and molecular mass investigation, respectively. The temperature of connection pipe and sample pond was 185 °C, and the TG was performed in an Ar flow rate of 40 ml min^{-1} at a heating rate of 10 °C min^{-1} from room temperature to 1200 °C.

3. Results and discussion

3.1. XRD analysis

The XRD pattern of the modified porous SiC is shown in Fig. 1. It can be seen that the modified porous SiC is mainly composed of SiC and mullite ($3Al_2O_3{\cdot}2SiO_2$), and the intensity of mullite is weaker than that of SiC. Mullite phase was formed through chemical reactions between porous SiC substrate and molten salts ($Al_2(SO_4)_3 + Na_2SO_4$).

3.2. FT-IR analysis

Fig. 2 presents the FTIR spectrum of the modified porous SiC substrate. The peak at 835 cm^{-1} in the FT-IR spectrum is characteristic of the transverse optical phonon (TOP) vibration in SiC [22], and the centered peak at 1159 cm^{-1} is attributed to the Si–O–Si stretching vibration of SiO_4, however, the centered peaks at 549 cm^{-1} and 437 cm^{-1} are attributed to the vibration of tetrahedrally and octahedrally coordination Al—O bonds [23].

3.3. Microstructure characterization

A needle-like whisker coating is formed on the dense SiC substrate as shown in Fig. 3a and b, and the corresponding EDS spectrum (Fig. 1b, inset) indicates that the surface layer is composed of Al, Si and O and a thin transition layer forms at the coating/substrate interface, showing the adhersion of coating and substrate is produced by chemical bonding. The whiskers present nanometer-sized (100–300 nm) diameters and micrometer-sized (10–20 μm) lengths. Fig. 3c and d displays the fracture surface of the modified porous SiC substrate after the molten salts treatment, indicating the whisker layer also forms and covers on the surfaces of the porous SiC ceramic (here the surfaces involve the outer surface of the porous ceramic substrate and the inner surface of its pores). In addition, the modified porous SiC substrate can inherit well the porous structure, only the pore sizes are changed, which can contribute to realize some integrated functions of the whisker coating and the porous SiC substrate.

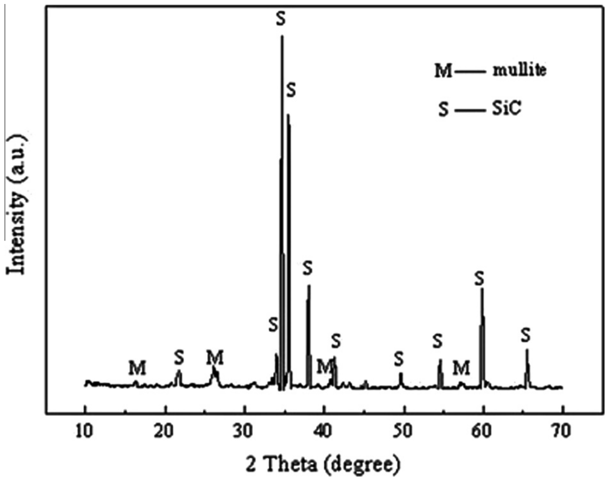

Fig. 1. XRD pattern of the modified porous SiC.

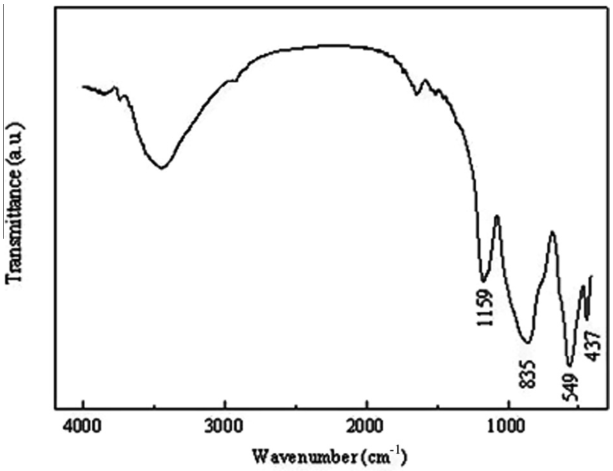

Fig. 2. FTIR spectrum of the modified porous SiC.

Fig. 4a and b shows the HRTEM images of the whiskers (scraped from the dense SiC substrate), the corresponding SEAD pattern from whiskers in Fig. 4(a) can be index to orthorhombic structure and the average crystal lattice spacing (0.539 nm) is consistent with the (1 1 0) crystal plane of mullite. Therefore, the whiskers covered on the surfaces of modified SiC substrates are determined as mullite.

3.4. Anti-oxidation property

Fig. 5 shows the isothermal oxidation curves of unmodified and modified porous SiC ceramics at 1400 °C for 1–20 h. Both the weight gain rates of unmodified and modified porous SiC ceramics increase with the oxidation time prolonging, and the weight gain rate climbs rapidly before holding 5 h and then becomes relatively slow. As expected, the weight gain rate of the modified porous SiC ceramic is far lower than that of unmodified porous SiC ceramics, and the rate of decrease of oxidation weight gain rate (i.e. $W_u - W_m)/W_u \times 100\%$, where W_u and W_m are the oxidation weight gain rate of unmodified and modified porous SiC ceramics, respectively) falls from 77.40% to 12.49%, indicating that the mullite whisker coating greatly improves the oxidation resistance of the porous SiC substrate and that the improvement level somewhat descends with the holding time prolonging.

3.5. TG–DSC–FTIR–MS coupling analysis and chemical reaction process

In order to investigate the formation of mullite, the TG–DSC–MS–FTIR system was employed to analyze the chemical reaction process. Fig. 6a shows the TG–DSC curves of the powder mixture ($SiC + Al_2(SO_4)_3 + Na_2SO_4$). It can be seen that the weight loss mainly takes place in the following three ranges. The first low weight loss ($\sim$4.2%) can be attributed to the dissociation of absorbed water at 154 °C and crystal water at 215–247 °C. The second one occurs between 630–900 °C and some complex endothermic and exothermic peaks appear on the DSC curve simultaneously, which are mainly originated from the low eutectic point (646 °C) of Na_2SO_4–$Al_2(SO_4)_3$ system [24], the decomposition of $Al_2(SO_4)_3$ [25] and some chemical reactions that were not re-

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