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Catalyst-free hybridization of silicon carbide whiskers and expanded graphite by vapor deposition method

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Abstract

A simple approach was developed to hybridize silicon carbide (SiC) whiskers on graphitic layers in expanded graphite (EG) by silicon vapor deposition without catalyst. The synthesis of EG/SiC composite was carried out above 1000 °C in an enclosed crucible where the EG was placed above the silicon powders. The vapor–solid (VS) mechanism is the predominant one for the growth of SiC whiskers. Namely, Si (g) vapor derived from silicon powder at high temperatures deposits on the active carbon atoms locating at the edge and layer of EG to form the SiC nuclei. Subsequently, SiC whiskers grow up with a continuous deposition of Si (g) vapor on the SiC nuclei. The partial pressure of Si (g) vapor is favored with the increasing firing temperature, which promotes the growth and coarsening of SiC whiskers on EG.

Keywords: Expanded graphite; Silicon carbide whiskers; Hybridization; Vapor–solid (VS); Vapor deposition

1. Introduction

Expanded graphite (EG) is a vermicular-shaped carbon source with many pores and composed of parallel graphene nanosheets, which possess high elastic modulus and tensile strength [1–3]. It is usually applied as reinforcement in ceramics or polymer materials to enhance their mechanical properties [4–9]. Just like carbon fiber and graphene, the smooth surface of EG nanosheets could influence the reinforcement effect in the composites because of low cohesive force between EG and matrix of materials [10]. To improve the interfacial properties, one way is to modify the surface roughness of above mentioned carbon sources by hybridization of one-dimensional nano phases on them. Fan et al. [11] reported the growth of carbon nanotubes (CNTs) on the surface of carbon fiber by chemical vapor deposition with Fe, Co and Ni as catalysts. Lee et al. [12] fabricated CNT-graphene hybrid film on the graphene substrate and it shows excellent stretchability and flexibility.

Besides CNTs, SiC whisker also could be applied to improve the interfacial characteristics of carbon sources if SiC whiskers grow up on the surface of carbon sources. In the past decades, many efforts have been spent to the synthesis of pure SiC whiskers. Usually, the growth of SiC whiskers is involved in vapor–liquid–solid (VLS) or vapor–solid (VS) mechanism [13–16]. The formation of SiC whiskers depends on the carbon structure, in which the defects like as the fractured C═C bonds are the active sites for the nucleary and growth of SiC whiskers [17]. Therefore, SiC whiskers were usually reported to grow on the surface of amorphous carbon sources, such as phenolic resin [18], amorphous activated carbon powder [19,20], polycarbosilane [21] and so on. On the other side, it is difficult to synthesize silicon carbide (SiC) whiskers on the surface of the graphite and graphene owing to their highly graphitization contents with less active fractured C═C bonds. As a consequence, metal-catalytic and molten salt synthesis methods are applied to synthesize SiC whiskers on the surface of these carbon sources. Wang et al. [22] synthesized silicon carbide nanowires on graphene sheets by firing a mixture of Si powders and commercial graphene sheets with Fe catalyst addition. Ding et al. [23] reported that SiC nanowires are grown on the surface

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of graphite by reacting with silicon powders in NaF–NaCl based salt at 1150–1400 °C in the argon atmosphere. In our previous work [24], silicon carbide whiskers were synthesized by using reactive graphite, e.g. oxidized graphite and expanded graphite as the templates in the coke bed. Compared to natural flake graphite, the reactive graphite has a lot of defects in the crystal structure, which can play the role of active sites for the subsequent nucleary and growth of SiC whiskers.

In the present paper, different to the methods mentioned above, EG/SiC whisker composite will be fabricated in the nitrogen atmosphere without applying catalyst. Due to the application of nitrogen atmosphere, the Si (g) vapor is the only silicon-containing gaseous phase, which avoids the formation of SiO (g) vapor and the growth of cristobalite in carbon bed atmosphere [24]. The EG/SiC whisker composite not only possesses vermicular-shaped morphology of EG, but also the nano structure of silicon carbide whiskers. It is proposed that the EG/SiC composite reinforced by SiC whiskers can not only enhance the strength of EG, but also offer excellent wear resistance and anti-washout properties. Also, the interfacial structure between SiC and EG is characterized by SEM and TEM. Finally, the growth mechanism of SiC whiskers is discussed in details.

2. Experimental

The EG used in these experiments was prepared by exfoliating commercial expandable graphite (50 mesh, 98% C, Shangdong, China) in microwave oven (MM721AAU-PW, Midea, 700 w, China) for 20 s. The experimental setup contains a graphite crucible with lid as depicted in Fig. 1. The silicon powder (< 45 μm, 98.47 wt% Si, China) and EG was placed in the crucible and was separated by a graphite interlayer with many holes. Before the test, the pressure in the furnace was pumped down to −0.1 MPa. The flowing nitrogen gas (60 ml/min, 99.99% purity) was filled into the furnace until the pressure in furnace was 0.101325 MPa and kept persistently in whole process to avoid the oxidation. The furnace was heated to 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C, respectively, at a heating rate of 5 °C/min with a holding time of 3 h. Following it a natural cooling down to the room temperature was allowed.

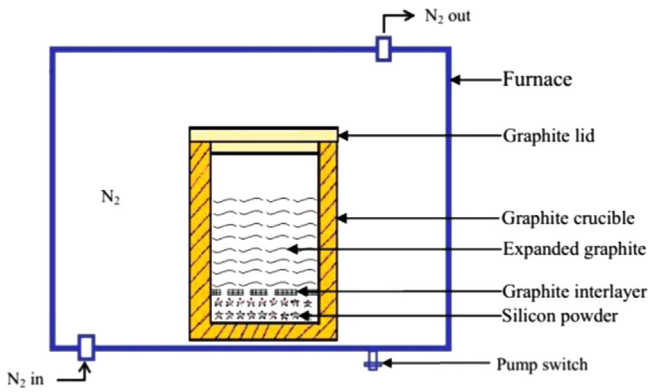

Fig. 1. Schematic diagram of the experimental setup.

The phase compositions of all the products were examined by X-ray diffraction (XRD, X'Pert Pro, Philips, Netherlands; using Ni filtered, Cu Ka radiation at a scanning speed of 2 °/min and a temperature of 289 K (16 °C)). The microstructure of all the products was analyzed by a field emission scanning electron microscope (FESEM, Nova 400 NanoSEM, FEI Company, USA) equipped with a energy dispersive X-ray spectroscope (EDS, INCA IE 350 PentaFET X-3, Oxford, UK) and a high resolution transmission electron microscope (HR-TEM, Model JEM-2010 UHR, JEOL, Japan).

3. Results and discussion

3.1. Phase composition

XRD patterns in Fig. 2 show the phase evolution of the specimens fired at different temperatures. It is obvious that the as-received specimen was made of graphite phase. With thermal treatment at high temperatures among 1000 °C and 1400 °C, additional β-SiC phase was observed. The peaks around $2\theta = 35.61°$, 41.41°, 60.01° and 71.81° corresponded to (111), (200), (220) and (311) planes of cubic SiC [25,26], respectively. Moreover, the relative diffraction peaks of β-SiC to the graphite increases with respect to temperatures, which indicates the large amount of β-SiC formed at 1400 °C.

3.2. Microstructure characteristic and evolution

As mentioned above, the EG was prepared by a microwave method using commercial expandable graphite, in which some functional groups, e.g. hydroxyl and carboxyl, are intercalated into graphite layers. During the microwave treatment, the expansion of graphite along the C axial direction occurs due to the formation of large amounts of gaseous species (carbon dioxide, water vapor, etc.) from the functional groups (hydroxyl, carboxyl and so on). A typical morphology consisting of porous and vermicular structure is presented in Fig. 3a. The magnification image reveals that among the nanosheets many interconnected pores exist in nano and microscale (Fig. 3b).

Fig. 4 shows the SEM micrographs of the specimens fired from 1000 °C to 1200 °C. For the specimen fired at 1000 °C, some whiskers (identified as β-SiC ceramic phases by XRD

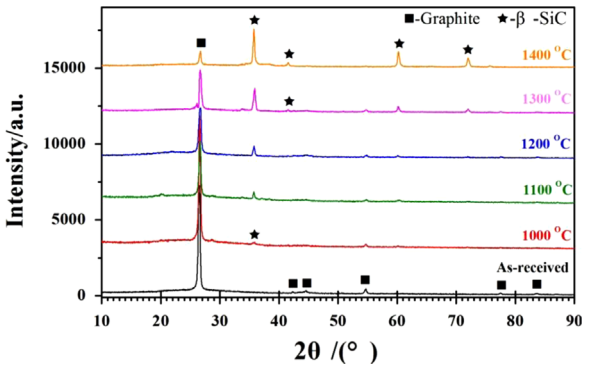

Fig. 2. XRD patterns of all the products fired from 1000 °C to 1400 °C.