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ScienceDirect

Ceramics International 40 (2014) 1481–1488

CERAMICS INTERNATIONAL

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Synthesis of silicon carbide whiskers using reactive graphite as template

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Received 15 June 2013; received in revised form 5 July 2013; accepted 5 July 2013
Available online 11 July 2013

Abstract

Silicon carbide whiskers have been synthesized by using reactive graphite as a template. Natural graphite flake was firstly activated using chemical oxidation and thermal oxidation methods. After that, the reactive graphite sources were mixed with silicon powder and heated in the coke bed at 1200 and 1400 °C. The structural evolution of graphite and morphologies of SiC whiskers were studied with the aids of XRD, SEM, TEM and EDS techniques. The results showed that natural graphite flake can be activated into reactive graphite such as oxidized graphite and expanded graphite with much more defects using thermal and chemical oxidation methods. The expanded graphite with a great deal of defects has higher reactivity than natural graphite flake and oxidized graphite and accelerates the formation of long and thick SiC whiskers. It is proposed that the vapor–solid mechanism is predominant for the growth of β-SiC whiskers in this system. During heating-up, Si or SiO vapors meet with the activated carbon atoms on graphite substrate to form SiC nucleus. Then these vapors continually deposit on the SiC nucleus following the SiC whiskers which grow along the ⟨111⟩ direction.

Keywords: Silicon carbide; Graphite flake; Expanded graphite

1. Introduction

In the past decades, much attention has been paid to silicon carbide (SiC) whiskers due to their excellent properties, such as high hardness, good flexibility, high thermal conductivity, high thermal stability and large band gap [1–3]. Consequently, they are widely used to fabricate structural and functional composites for extremely harsh environment [4,5]. Nowadays, various synthesis methods have been explored to produce β-SiC whiskers, including chemical vapor deposition using silicon precursor [6–8], carbon template of carbon nanotubes to β-SiC whiskers [9,10], thermal evaporation [11,12], carbothermal reduction [13], etc. Generally, the growth mechanisms of SiC whiskers are involved in vapor–solid (VS) and vapor–liquid–solid (VLS) mechanisms [14–17]. As for VS mechanism, Si-containing vapors such as Si (g) or SiO (g) react with CO (g) or C (s) to form SiC nucleus and the whiskers or nanowires grow along the directions of the least stable plane. In the VLS mechanism, once SiC nucleus formed, the metal droplets on the nucleus absorb Si (g) and SiO (g) gaseous species and the SiC whiskers precipitate from supersaturated liquid at the liquid–solid interface. Based on the mechanisms mentioned above, carbon source is very important in the process of preparing SiC whiskers. Until now, carbon nanotubes, carbon black, carbon fiber and phenolic resin, etc., were used to synthesize SiC whiskers [18–21]. The carbon source usually operates as reductant and substrate for the formation of SiC whiskers. Chen et al. [22] synthesized SiC nanowires on the substrate of polyacrylonitrile carbon fiber by evaporating silicon and proposed that Si-containing vapors are easily absorbed at points of flaws and react with the active carbon atoms quickly. Also, activated carbon was selected as carbon source to prepare SiC whiskers by many researchers [23–26]. However, most work focused on the morphologies of SiC whiskers, so it is still indistinct how the carbon sources impact on the growth of SiC whiskers. In our previous work, SiC whiskers preferentially appeared on the edge of graphite flake in Al_2O_3–C refractories, whereas silicon carbide granules grew in this system when using carbon black as carbon source [27]. It seems that the formation

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http://dx.doi.org/10.1016/j.ceramint.2013.07.032

of SiC whiskers was strongly dependent on the structure of graphite flake and related to the defects such as fractured C═C bonds at the edge of graphite, which are called as activated carbon atoms. So it was supposed that graphite flake acts as template and these defects existing on graphite can react with SiO (g) or Si (g) in order to nucleate SiC whiskers.

The objective of this work is to further elucidate the growth mechanism of SiC whiskers and to develop a novel method to synthesize SiC whiskers using reactive graphite as template. Natural graphite flake was firstly activated using thermal oxidation and chemical oxidation methods to prepare reactive graphite sources such as oxidized graphite and expanded graphite with much more defects than natural graphite flake. Then these kinds of graphite were mixed with silicon powder and heated in coke bed at 1200 and 1400 °C to prepare SiC whiskers based on the activated graphite templates.

2. Experimental

2.1. Preparation of the activated graphite

Two approaches have been used to activate graphite flake. To prepare the oxidized graphite, natural graphite flake (100 mesh, 97.58 wt% fixed carbon, China) was heat-treated in a sealed heat-resistant steel (cubiform reactor, 100 mm × 110 mm × 250 mm) at 1000 °C for 3 h. To prepare the expanded graphite, the same graphite flake was chemically oxidized by the Hummers method [28] and then exfoliated in a microwave oven for 20 s.

2.2. Fabrication of specimens

Three kinds of specimens were prepared by mixing silicon powder (45 μm, 98.47 wt% Si, Anyang Yuhong Metallurgy & Refractory Co., Ltd., China) with graphite flake, oxidized graphite and expanded graphite. The C/Si weight ratios of all specimens were 2:1. These mixtures were then cold pressed into cylindrical specimens with 20 mm in diameter and 20 mm in height at 30 MPa. The specimens containing graphite flake, oxidized graphite and expanded graphite were designated as GF, OG and EG, respectively.

All batches of specimens were placed inside a corundum sagger with a cover, which was filled with carbon black powder. Finally, the whole sagger was placed into an electrical furnace and heated from room temperature to 1200 °C and 1400 °C with a heating rate of 5 °C/min and a holding time of 3 h before cooling to room temperature.

2.3. Characterization and measurement methods

Thermogravimetry–differential scanning calorimetry (TG–DSC, STA499, NETZSCH, Germany) was employed to evaluate the reactivity and to calculate the non-isothermal oxidation kinetics of graphite flake, oxidized graphite and expanded graphite. Meanwhile, the Raman spectra of carbon sources were obtained with a high-resolution, dispersive Raman spectrometer system (Horiba-Jobin Yvon LabRam HR) equipped with a confocal microscope (Olympus BX-30) and a notch filter (532 nm). The phase compositions and microstructure of the specimens were analyzed by X-ray diffraction (XRD, X'Pert Pro, Philips, Netherlands), a scanning electron microscope (SEM, Quanta 400, FEI Company, USA) equipped with an energy dispersive X-ray spectroscope (EDS, Noran 623M-3SUT, Thermo Electron Corporation, Japan) and a high-resolution transmission electron microscope (HR-TEM, Model JEM-2010, JEOL, Japan).

3. Results and discussion

3.1. The structural characterization and reactivity of graphite

Fig. 1 shows the SEM micrographs of three kinds of graphite. It can be clearly seen that the natural graphite flake possesses relatively smooth basal planes and a few multilayer terraced edges with length of dozens of micrometers (Fig. 1a). Whereas, after thermal oxidation, much more multilayer terraced edges were observed on the surfaces of the oxidized graphite (Fig. 1b). It can be clearly seen that much more C═C bonds were broken on the basal planes. Interestingly, the expanded graphite showed a loose and worm-like structure, in which the basal layers were opened thoroughly to form large amount of pores.

Raman spectroscopy has been widely used to identify disorder of sp^2-network in different carbon sources [29–33]. The Raman signature at about 1585 cm^{-1} is known as the first-order of G band, which is the only feature in highly ordered crystalline graphite (e.g. HOPG, Highly Oriented Pyrolitic Graphite). The first-order of D band (D for disorder)

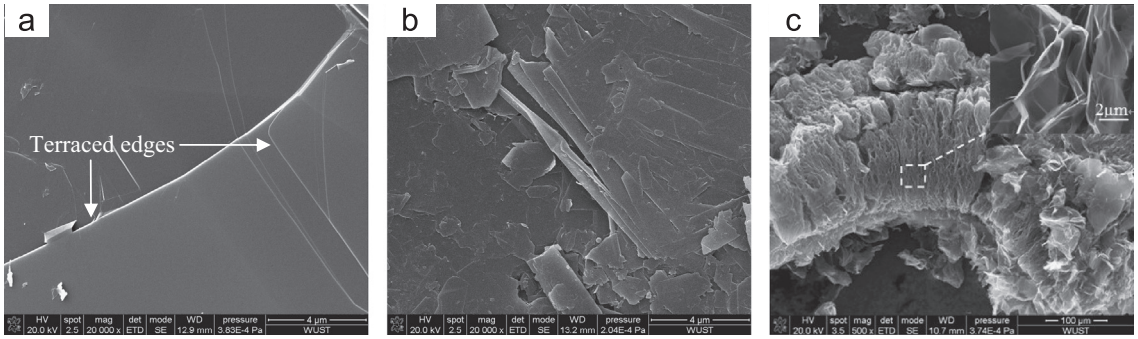

Fig. 1. SEM micrographs of (a) natural graphite flake, (b) oxidized graphite and (c) expanded graphite.