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Preparation and oxidation resistance of SiC-coated graphite powders via microwave-assisted molten salt synthesis

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ABSTRACT

Silicon carbide (SiC)-coated graphite composite powders was synthesized at 1423 K by a microwave-assisted molten salt synthesis, using graphite flakes and silicon powders as raw materials. The phase composition, morphology and microstructure of the coated graphite were characterized by X-ray diffraction, field emission scanning electron microscopy and high resolution transmission electron microscopy. The results showed that the formation temperature of SiC coating which consisted of lots of nanofibers with hundreds nanometers in length and several tens in diameter was reduced for about 150 K compared with conventional molten salts method. The water wettability and oxidation resistance of as-prepared coated graphite were greatly enhanced owing to the existence of SiC coating. The apparent oxidation activation energy of the coated graphite was 168.3 kJ/mol, which was higher than that 157.4 kJ/mol for raw graphite.

1. Introduction

Thanks to the low thermal expansion coefficient and non-wettability to metal slags of graphite flake, the thermal shock resistance and corrosion resistance of carbon-containing refractory can be significantly enhanced. Even though carbon-containing refractories were widely applied in the field of steelmaking [1–3], however, the uniformly distribution of graphite flake in refractory castables is still a challenge due to the hydrophobic nature of graphite.

Great efforts have been paid to enhance the dispersibility of graphite flake in castables. The first common approach was modification of the surface feature of graphite flake by certain amphiprotic surfactant that contained both non-polar and polar functional groups. Generally, the non-polar group had strong affinity with non-aqueous liquid, while the polar group tended to bond with polar liquid. As a result, the graphite flakes (non-polar) modified by the surfactant tended to be dispersed more uniformly in refractory castables [4–8]. However, even though this approach was of convenience and low cost, the surfactants was found to play negative effects on the rheological performance of the resultant castables [1]. Another approach was to coat the graphite flakes by hydrophilic oxides such as Al_2O_3 [9], SiO_2 [10], $MgAl_2O_4$ [11], TiO_2 [12], and ZrO_2 [13] by sol-gel method [14–18]; and this approach was verified to be capable of improving both the water wettability and oxidation resistance of graphite. Nevertheless, it is noted that the processing procedure of the method was complex and the cost of raw materials high, which indeed limited its application field. Forming a carbide coating on the surface of graphite flakes was the thirdly choice to modify the graphite. For example, SiC and TiC-coated graphite was both prepared by directly heating the mixture of graphite and Si powders at 1773 K under a protective atmosphere in previously published papers [1,19–23]. Even though all the results revealed that the water wettability and oxidation resistance of graphite flake were improved. Nevertheless, relatively high temperatures were normally required in the methods, and thus caused high energy consumption.

In this work, a facile microwave-assisted molten salts synthesis was developed for low-temperature preparation of SiC-coated graphite composite powders. Moreover, the influences of various processing conditions including processing temperature and the molar ratio of graphite to silicon on the morphology as well as water wettability and oxidation resistance of the coated graphite were analyzed.

2. Experimental

2.1. Raw materials and sample preparation

Silicon powders (purity ≥ 99%, ~10 μm, Sinopharm Chemical

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Reagent Co., Ltd., China) and graphite flakes (purity ≥ 99%, ~100 μm, Dongguang Xiangyang Graphite Fabricating Plant, China) were used as the starting materials. Sodium chloride (NaCl) and sodium fluoride (NaF) (AR, Sinopharm Chemical Reagent Co., Ltd., China) were adopted as the salt medium.

The graphite/Si molar ratios were respectively set to be 1/1, 3/1, 5/1, 7/1 and 9/1. The weight ratio of NaCl to NaF was fixed to be 20/1, and the weight ratio of salts to graphite and Si was 2/1. The mixtures of graphite flakes, Si powder and salt after ball-milling treatment were contained by alumina crucibles with a lid, and then fired at 1373–1473 K for 2 h under an argon atmosphere in a microwave heating furnace (HAMiLab-V3000, SYNO THERM, China). After cooling down to room temperature, the powder mixtures were repeatedly washed with hot deionized water until salt was completely eliminated. Finally, the resultant powders were dried up at 383 K for 24 h to obtain the SiC-coated graphite composite powders.

Al_2O_3-C based castable containing 5.0 wt% SiC-coated (denoted as CG sample) and uncoated (denoted as G sample) graphites were fabricated to investigate the effects of the coated graphite on the performance of carbon containing castables. These two kinds of graphites were incorporated separately into the same castable batch containing 69.0 wt% white fused alumina aggregates and 31.0 wt% matrix. The ingredients of the castables were listed in Table 1. The samples were heating treated at 1473 K and 1773 K for 2 h under air atmosphere, respectively.

2.2. Characterization

The phase composition of sample was characterized by X-ray diffractometer (XRD, Philips X'Pert PRO with Cu K_α radiation, the Netherlands) at 40 mA and 40 kV using Cu K_α ($\lambda = 0.1542$ nm). The morphologies and microstructures were observed by a field-emission scanning electron microscope (FE-SEM, Nova400NanoSEM, the Netherlands, 15 kV) equipped with an X-ray energy dispersive spectroscopy (EDS, Oxford, UK). A high resolution transmission electron microscope (TEM, JEM-2100U HRSTEM, Japan, 200 kV) was employed to identify the crystal structure of SiC. The zeta potentials of samples were measured by a zeta potential analyzer (Zetasizer Nano ZSP, Molvern, UK). A sedimentation test was employed to evaluate the dispersivity of modified graphite. 0.2 g of raw graphite and modified graphite were respectively added into water and agitated for 2 min, and the dispersivity behavior was evaluated based on the sedimentation volume of the products via the images of a digital camera. TG-DSC (Netzsch STA 449C, Germany) analysis was performed to investigate the oxidation resistance of samples with heating rate of 5–20 K/min. The apparent porosity of the castable samples was performed by using Archimedes method, and the cold crushing strength was measured using a compression testing machine at ambient temperature.

Table 1
Composition of Al_2O_3-C based castables.

Constituents	Graphite series, wt% (G sample)	Coated graphite series, wt% (CG sample)
White fused alumina	69	69
Microfine active alumina	10	10
Fused spinel	10	10
Uncoated graphite	5	–
SiC-coated graphite	–	5
Calcium aluminate cement	5	5
Microsilica	0.5	0.5
Aluminium powder	0.5	0.5
Dispersant	0.1	0.1

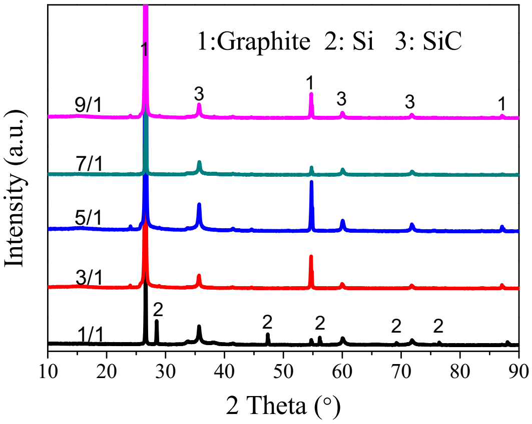

Fig. 1. XRD pattern of samples fired at 1423 K for 2 h respectively with graphite/Si molar ratio of 1/1, 3/1, 5/1, 7/1 and 9/1.

3. Results and discussion

3.1. The effects of C/Si molar ratio and firing temperature on the SiC coating

Fig. 1 presents the XRD patterns of samples fired at 1423 K for 2 h respectively with graphite/Si molar ratio of 1/1, 3/1, 5/1, 7/1 and 9/1. The diffraction peaks of all the samples were assigned to graphite (ICDD card No. 26-1076), SiC (ICDD card No. 74-2307) and Si (ICDD card No. 89-5012). As the graphite/Si molar ratio was 1/1, the diffraction peaks locating at 35.7°, 60.0°, and 71.8° were respectively indexed to the (111), (220) and (311) planes of 3C-SiC phase. In addition, the diffraction peaks of residual Si were also observed, revealing the expected synthetic reaction had not been completed. On increasing the graphite/Si molar ratio to 3/1, the diffraction peaks of Si disappeared, and only the diffraction peaks of graphite and SiC existed in the spectrum, indicating that the raw Si was completely converted into SiC. On further increasing the graphite/Si molar ratio to 5/1, 7/1 and 9/1, no obvious changes in the phase composition were found, suggesting that the optimal graphite/Si molar ratio was 3/1 in present paper.

Fig. 2 shows the XRD patterns of the samples with graphite/Si molar ratio of 3/1 fired for 2 h at 1373–1473 K. At 1373 K, the main crystal phases of final product were graphite, Si and SiC, indicating the occurrence of the formation of SiC. On increasing temperature to 1423–1473 K, the main phases in the sample evolved to graphite and SiC, and no silicon could be detected, suggesting that the optimal reaction temperature of present work was 1423 K; and the content of SiC phase was about 5 wt% according to the Rietveld refinement of XRD

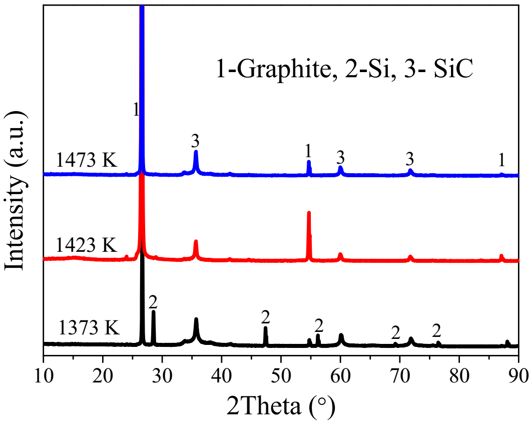

Fig. 2. XRD pattern of sample with graphite/Si molar ratio of 3/1 fired at 1373–1473 K for 2 h.