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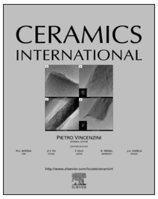

Molten salt synthesis of a SiC coating on graphite flakes for application in refractory castables

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ABSTRACT

A silicon carbide coating was formed on the surface of graphite flakes by reaction of molten Si with carbon at 1100–1300 °C in a 95%KCl-5%NaF molten salt under Ar atmosphere. The effect of temperature and Si/graphite ratio in the initial mixture on the quality and the amount of SiC were investigated by XRD and SEM/EDS analyses. Also, the water wettability, oxidation resistance and zeta potential of un-coated and coated graphite were examined by TGA analysis and sedimentation test. The results show the amount of coating to increase in the coated flakes with increasing temperature and Si/graphite ratio. The SiC coating improves water wettability of graphite and acts as a protective layer to enhance oxidation resistance. The zeta potential of coated graphite was also increased which indicated a better dispersion in water based systems. These improvements in both the water dispersivity and oxidation resistance of SiC coated graphite would make it as promising candidate raw materials for application in C-containing refractory castables.

1. Introduction

Graphite is a unique raw material used in refractory industries because of many advantages such as non-wettability by molten metal/slag, high thermal conductivity, low thermal expansion coefficient, and thermal shock resistance [1,2]. Since the first successful development of carbon-containing refractories – so-called Oxide-Graphite Refractory Bricks (OGRBs) – the processing, microstructures and properties of these refractory products have been successively improved, and the service life of industrial furnaces has been substantially extended [3]. Recently, studies have investigated more will continue to investigate the development of Oxide-Graphite Refractory Castables (OGRCs) worldwide owing to their quicker and cheaper installation and certain superior properties [4,5]. Despite the significant R&D work performed, the incorporation of sufficient levels of carbon and graphite to an OGRC system still remains a great challenge owing to several technical difficulties, particularly the low water wettability and poorly homogenized dispersion of carbon and graphite materials in castable systems [6]. This drawback results in unsuitable castable flow ability and considerable need for higher water content, which greatly increases the porosity after heating and results in lower mechanical properties and corrosion resistance [7,8]. Therefore, coating of graphite flakes as main raw materials for application in C-containing refractory castables has been a challenge in recent decades. Aiming to provide a solution to these problems, various techniques and methodologies have been investigated, including the use of surfactant dispersants [9], incorporation of micro-pellets [10] and coating techniques [11–13] to improve the wettability and dispersion of carbon and graphite flakes in a refractory body and increase their oxidation resistance. These techniques alleviate the problems to a certain extent, but various drawbacks remain.

In the case of coating techniques, the graphite flake surface is coated with oxide and non-oxide components that have high water wettability and high dispersion properties. Oxide coatings are mainly prepared by the sol-gel method, but chemical vapour deposition (CVD) and carbothermal reduction have also been used to coat SiC, TiC and other components on the surface of carbon/graphite particles. Zhang et al. [14] used the sol-gel technique to form Al_2O_3/SiO_2 coating on the surface of graphite to improve water wettability and oxidation resistance. Yilmaz et al. [15] and Saberi et al. [16] also reported the coating of boehmitic alumina and $MgAl_2O_4$ spinel on the surface of graphite flakes by the sol-gel method, respectively. Ono et al. [17] developed SiC crystals on graphite particles via a mechanical impact treatment. However, the SiC fine grains were very loose and discontinuously adhered onto the graphite surfaces; thus easily disintegrating during mixing.

Some studies have attempted to use pitch, a by-product of

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petroleum distillation, as a coating on the surface of graphite flakes by melting at low temperatures (<200 °C) such that the coating is easy and cheap. However, pitch has only slightly better water wettability than graphite and is environmental unfriendly owing to the formation of carcinogenic fumes during decomposition [14]. Despite the disadvantages of the methods summarized above, the findings obtained so far have one important clue: the key issue with the coating technique depends on how to economically prepare high-quality (uniform, sufficiently thick and strongly bonded) coatings on a graphite surface [18]. In response to this, a low-temperature and low-cost technique with a simple technological background–so-called molten salt synthesis (MSS)—has recently been developed to synthesise some complex oxide powders and carbide materials [19,20]. MSS is an electrochemical synthesis method that has good advantages for refractory powder synthesis and provides wide possibilities for coating production by in situ phase formation [21,22].

The present work aims to prepare a SiC coating on graphite flakes by reacting graphite with Si metal powder in molten salts, which serve as a solvent medium to accelerate the reaction kinetics by enhancing reactant diffusion. The effect of synthesis temperature and raw material ratio on the coating quality was investigated, and the coated graphite properties were evaluated.

2. Experimental

2.1. Raw materials and sample preparation

Graphite flakes (purity 95%, flake size: 150–300 μm, China), Si metal powder (purity $>99\%$, 10 μm, Sigma-Aldrich) were used as main starting materials. The salts used were potassium chloride (KCl) and sodium fluoride (NaF) (purity $>99\%$, Sigma-Aldrich), that predried in an oven for 5 h at 110 °C before adding to mixture of main raw materials. The molar ratio of Si to graphite (Si/G) were taken as 1/2, 1/4, 1/6, 1/8 and the weight ratio of dried KCl to NaF as 95/5. Mixed salt combined with approximate amount of graphite and Si powders was ball-milled and placed in a zirconia crucible with a lid and fired for 6 h at 1100–1300 °C under Ar atmosphere in a tube furnace. After cooling to room temperature, the reacted mass was washed with hot distilled water and filtered by repeating several times to remove the residual salt completely. The remained coated graphite flakes were oven-dried 1 day at 110 °C and then characterized.

2.2. Sample characterization

Phase evolution of reacted samples was evaluated by powder X-ray diffraction (XRD, Philips, X′Pert Pro, PANanalytical). Spectra was recorded at 30 MA and 40 KV, using Ni-filtered Cu$_{k\alpha}$ radiation. Microstructural analysis was carried out using a scanning electron microscope (SEM, TESCAN-LMU/VEGA), along with an energy-dispersive spectroscope (EDS). To elucidate the oxidation resistance of as-received and coated graphite flakes, thermo gravimetric analysis (TGA) were performed at temperature up to 1200 °C with heating rate of 10 °C/min in air by a simultaneous thermal analyzer (TGA/SDTA 851e, mettler). The zeta potential of uncoated and coated graphite was determined by a zeta potential analyzer (Zeta-sizer 3000, HAS, Molvern). The powders and distilled water were prepared into a 1% w/w suspension, and then the suspension was subjected to the test for its zeta potential. To evaluate water-wettability and dispersivity of graphite flakes after coating, a sedimentation test was employed. 1 gr of uncoated and coated graphite were introduced into water and agitated violently for 1 min. The wetting behaviour were then observed after setting time for 5 min then suspension pictures were taken by ordinary camera.

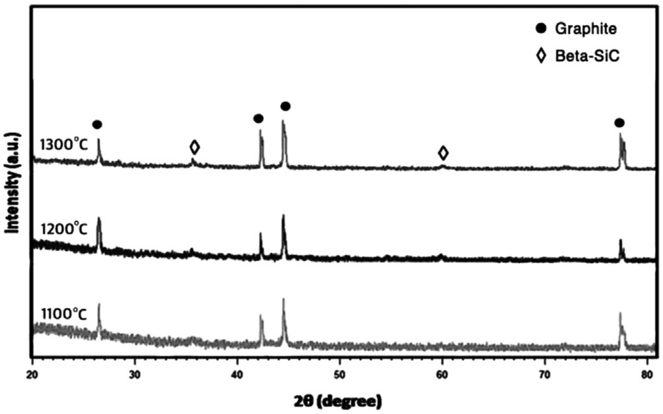

Fig. 1. XRD pattern of samples with molar ratio of Si/graphite = 1/8 fired for 6 h at different temperatures.

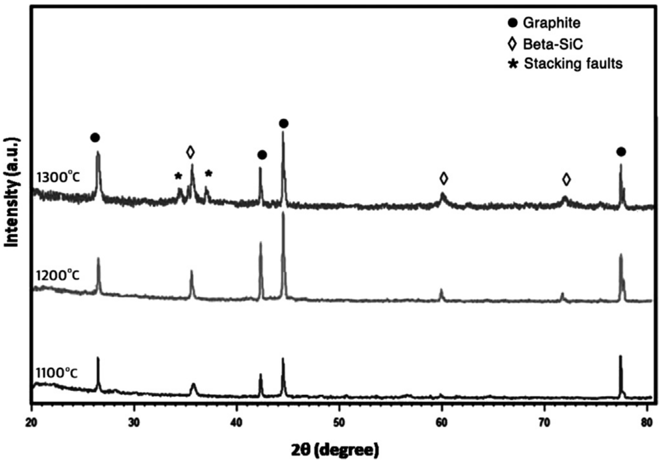

Fig. 2. XRD pattern of samples with molar ratio of Si/graphite = 1/2fired for 6 h at different temperatures.

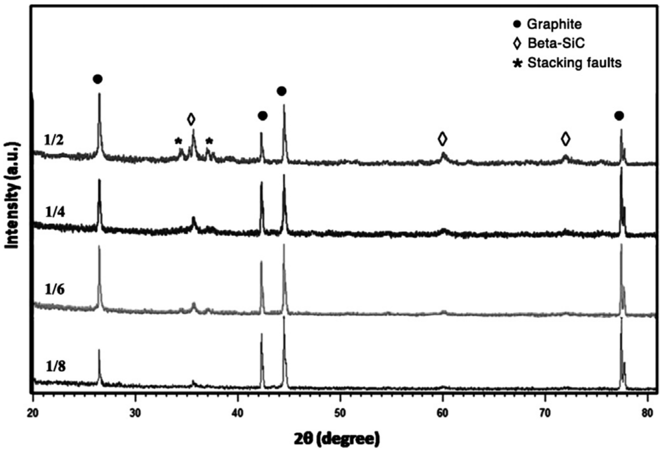

Fig. 3. XRD pattern of samples with different molar ratio of Si/graphite fired for 6 h at 1300 °C.

3. Results and discussion

3.1. The influences of firing temperature and Si/G ratio on SiC coating synthesis

Fig. 1 reveals the XRD pattern of a sample with a Si/G:1/8 ratio fired in molten salt media at 1100–1300 °C for 6 h. Fig. 1 shows