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Molten salt synthesis and characterization of SiC coated carbon black particles for refractory castable applications

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Abstract

Silicon carbide (SiC) coatings were prepared on carbon black (CB) particles after 6 h at 1100 °C by a molten salt synthesis (MSS) technique. By controlling the Si to CB ratio (Si/C) in the initial batch mixture, the SiC coating thickness could be readily tailored to meet practical requirements in real castable systems. True densities of CB particles after SiC coating increased with Si/C. The zeta potential values indicated that their dispersivity was improved evidently over a wide range of pH. At a given shear rate, the apparent viscosity of a water suspension containing SiC-coated CB was significantly lower than that of a water suspension containing as-received uncoated CB, indicating the improved flowability of SiC-coated CB in water. The improvements in both the water-dispersivity and flowability of SiC coated CB particles would make them a promising candidate carbon material for future castable applications.

Keywords: SiC coating; Carbon black; Molten salt synthesis; Water-wettability; Carbon-containing castable

1. Introduction

Thanks to carbon's high thermal conductivity, low thermal expansion coefficient and non-wettability by slag, carbon-containing refractory bricks (CCRBs) show much better physicochemical properties and performance than their carbon-free oxide-based counterparts. During the past three decades, CCRBs have been extensively and successfully applied to line important steel-making furnaces such as converters and ladles and to make functional devices for steel flow control (such as nozzles, stoppers and sliding gates).[1–3] On the other hand, compared to CCRBs, only limited success has been made in the development and application of carbon-containing refractory castables. Despite the significant R&D work carried out, incorporation of sufficient levels of carbon to a castable system still remains a great challenge, due to several technical difficulties, in particular, the poor water-wettability/dispersivity of carbon materials.[4]

Aiming to provide solutions to these problems, several techniques and methodologies have been attempted, including use of surfactants, incorporation of micro-pellets and coating techniques. They alleviate the problems to a certain extent, but still suffer from various drawbacks.[4]

In the case of coating technique, an oxide or carbide coating having better water-wettability was prepared on a carbon raw material. A sol–gel technique was used mainly to form oxide coatings.[5–8] However, it suffered from several drawbacks, including difficulties in making thick enough coatings and weak coating-substrate bonding and thus poor coating abrasion resistance on mixing. The techniques used to form carbide coatings (e.g. SiC) on a carbon material were more complex and expensive. Ono et al.[9] tried to prepare a SiC coating on graphite *via* a mechanical impact treatment. However, the SiC fine grains were only loosely adsorbed onto the graphite surfaces, so the resultant coatings were discontinuous and easily disintegrated or dislodged on mixing. Despite these disadvantages, the findings obtained so far have given one important clue, i.e., the key issue with the coating technique depends on how to economically

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prepare high quality (uniform, thick enough, and strongly bonded) coatings on carbon materials.

In response to this, a low temperature and relatively low cost molten salt synthesis (MSS) technique has been developed recently by the authors[10–13] and used to make high quality carbide coatings (such as TiC and SiC) on various carbon substrates (e.g., graphite flakes and carbon blacks (CB)). The authors' results have revealed that as-prepared carbide-coated carbon materials exhibited much better water-wettability/dispersivity as well as improved rheological performance, compared to their uncoated counterparts. Consequently, it could be expected that the water demand for castable placement in the case of using coated carbon would be significantly reduced. In this paper, the results from the work on SiC coated CB will be presented and discussed.

2. Experimental

2.1. Raw materials and sample preparation

CB (N990, 100–700 nm, 280 nm in average, Cancarb Ltd., Canada) and silicon (Si) powder (~44 µm, 99% pure, Sigma–Aldrich) were used as the main starting materials. Salts used were sodium chloride (NaCl) and sodium fluoride (NaF) (99 + % pure, Sigma–Aldrich).

Si and CB powders pre-mixed in a molar ratio (Si/C) of 1/12–1/2 were ultrasonically dispersed in isopropyl alcohol (IPA) for 2 h. After evaporation removal of IPA in an oven, the dry mix obtained was ball milled with a single NaCl salt or a NaCl–NaF binary salt containing 1.25, 2.5, 5 or 20 wt% NaF. The powder mixture was then placed in a graphite crucible with a lid and fired in a tube furnace under Ar protection to 900–1200 °C and held for 6 h.

After firing and cooling to room temperature, the solidified mass was washed repeatedly with distilled water to remove any residual salt, and then dried in an oven for further characterization. To assist verifying their core–shell structure (i.e., the coating formation), as-prepared particles were heated to 600 °C for 60 min in air to oxidise their carbon cores. In addition, to examine the effect of NaF on the dissolution of Si in the salt and assist understanding the MSS mechanism, Si powder was fired alone at 1100 °C for 6 h in a single NaCl, a single NaF or a binary salt containing 5 wt% NaF, and their morphology changes before and after firing were examined using the techniques described below (Section 2.2).

2.2. Sample characterization

Phase identification in the resultant powder samples was performed by powder X-ray diffraction (XRD) analysis (Siemens D500 reflection diffractometer). ICCD cards used were SiC (29-1129) and Si (27-1402). Spectra were recorded at 30 mA and 40 kV using Ni-filtered Cu Ka radiation ($k = 1.54178$ Å). The scan rate (2θ) was 2°/min with a step size of 0.05°. Morphologies and microstructures were observed by using a field emission gun scanning electron microscope (SEM) and a transmission electron microscope (TEM) (Philips EM420T), along with an energy-dispersive spectroscope (EDS) and selected area electron diffraction (SAED). A high resolution TEM (HRTEM, JEOL 2010F microscope) was also employed for lattice-resolved imaging so as to identify the atomic structure of SiC shells.

True densities of as-received uncoated CB and as-prepared SiC coated CB after ultrasonic dispersion were determined using a Helium Pycnometer (AccuPyc II 1340, Micromeritics Instruments). Zeta potential values were measured using a ZetaProbe Analyzer (Colloidal Dynamics Pty Ltd., USA) based on the multi-frequency electroacoustic principle. In this case, uncoated CB and SiC coated CB were ultrasonically dispersed respectively in distilled water for 2 h to form 2 wt% water suspensions. 1 mol/L HCl and KOH solutions were used for the pH titration. A strain-controlled rheometer (TA instruments AR 2000, USA) was used to investigate the rheological behavior of a water suspension containing 25 wt% of solid particles at room temperature (20 °C, pH 10). A flat plate geometry with 60 mm diameter was used for steady rate sweep ranging from 10^{-2} to 500 s^{-1}.

3. Results and discussion

3.1. Effects of temperature and NaF on the molten salt synthesis

Fig. 1 shows phase evolution in mixtures of Si and CB (with the molar ratio of 1/8) (referred to as the 1/8 mixture hereafter) after 6 h firing in molten salt containing 20 wt% NaF, at various temperatures. At 900 °C no SiC was formed and only unreacted carbon (indicated by the broad peak) and Si remained, whereas at 1000 °C SiC started to appear and Si peaks concurrently decreased. On increasing the temperature to 1100 °C, Si disappeared and only SiC was seen along with unreacted carbon. On further increasing the temperature to 1200 °C, no further phase changes were seen, though the peaks of SiC became slightly sharper, indicating its enhanced crystallinity or increased size.

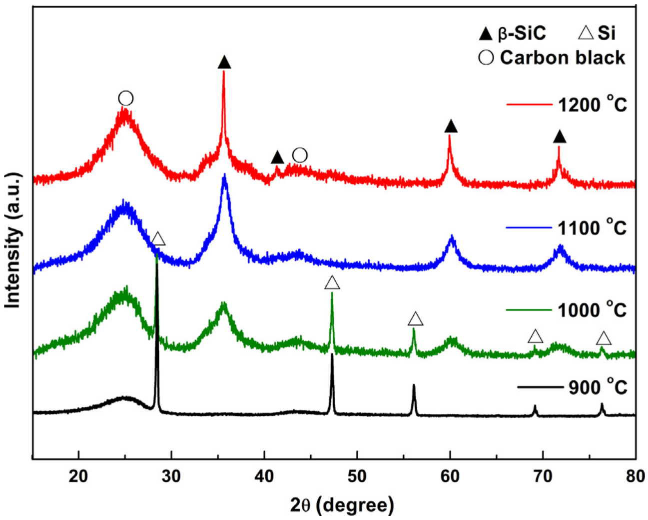

Fig. 1. XRD patterns of the product of firing mixtures of Si and CB (in the molar ratio of 1/8) for 6 h in a binary salt containing 20 wt% NaF at 900, 1000, 1100, and 1200 °C.