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Ceramics International 40 (2014) 4407–4414

CERAMICS INTERNATIONAL

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Significant improvement of refractoriness of Al_2O_3–C castables containing calcium aluminate nano-coatings on graphite

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Received 1 August 2013; received in revised form 26 August 2013; accepted 26 August 2013
Available online 5 September 2013

Abstract

The performance of alumina-carbon castables containing graphite flakes coated by nanosized Ca-doped γ-Al_2O_3 phases has been investigated in terms of refractoriness under load (RUL) and oxidation resistance tests. The coating characteristics and its beneficial effects in castable matrix have been conceived by water-wettability test, differential scanning calorimetry and some physical characteristics. In this regard, a schematic representation of coated graphite has been proposed to elucidate its sustainability in the refractory mass. The comparative gain in performance of the refractory has also been ascertained by scanning electron microscope (SEM) and X-ray diffraction (XRD) studies of the castable matrix. The sol–gel coating overcomes the pitfalls of including uncoated graphites in castables and should be explored for commercial utilization.

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Keywords: B. X-ray methods; D. Al_2O_3, Carbon; E. Refractories; Nano-coatings

1. Introduction

The fast pace of technological advancement has urged for the demand of more robust and stringent property specifications for refractories and monoliths. It provides longer campaign life in ladles, converters, blast furnace hearth, incinerators, boilers, rotary kiln sintering zone, etc. Various castable systems e.g. Al_2O_3, SiO_2, MgO, Al_2O_3–MgO, Al_2O_3–SiC, Al_2O_3–$MgAl_2O_4$ etc have gained popularity but carbon containing and nano-bonded castables are the latest substitutes for both ferrous and non-ferrous industries [1,2].

Carbon in the form of natural graphite or from pitch, resin, carbon black and coke can be present to the extent of 4–30 wt% in castable and refractory systems. Incorporation of carbon in the form of liquid binders like tar, resin and pitch has been known since decades [3]. But due to liberation of hazardous pyrolysis products, choice of solid form of carbon is nowadays more intended. Graphites are, however, much appreciated owing to their chemical, mechanical, thermal stability and other appreciable characteristics. Flaky graphite possesses some drawbacks if its content is increased. Increase in carbon content leads to risk of higher carbon pick up from castable affecting the quality of steel. Also chances of deformation of steel vessel exist due to increased shell temperature as a result of higher thermal conductivity of carbon [4]. Thus to reduce the energy consumption per unit of steel produced, an optimum carbon content is to be selected.

Though graphite offers several advantages to the castable matrix, its main limitations are low water-wettability and poor oxidation resistance. The main challenge is to disperse flaky graphite in a water-based castable batch with minimum casting water so as to obtain a dense structure after firing. A secondary problem of atmospheric pollution arises due to emission of carbon monoxide (CO) and/or carbon dioxide (CO_2) gases because of prevailing oxidizing atmosphere at the application site. Surface modification of graphite has thus been adopted by many researchers with a desire to reduce water content of batch and minimize rate of emission of carbonaceous products by environmentally benign manner [5–7]. The use of novel forms of carbon materials e.g. carbon nanotubes, graphene platelets and nanosheets in refractory ceramics recently opened up newer possibilities for carbon containing refractories [8–13].

Various scientists have tried to modify the surface with different types of coatings though each one has its own distinct merits and demerits [14–16]. Sol–gel methods, in this regard,

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http://dx.doi.org/10.1016/j.ceramint.2013.08.112

had been and are still being practiced, stemming from its operational simplicity, moderate reaction parameters and reproducible coating quality. However, only a handful of reports are available that takes the full advantage of this method [17–19].

In spite of cost factor, sol–gel based coatings with binary oxides has been dealt with by some researchers. Selective thin coating, prepared by a hybrid set of precursors and applied over flaky graphite can make a balance between cost factor and coating quality [20,21]. In other words, an optimization between utilization of inherent graphitic properties as well as a stronger linkage of graphite with composite matrix can be realized.

Calcium aluminate based coatings, in this context, needs further exploration. Calcium aluminate cement, a crucial hydraulic material to bind aggregate and matrix in conventional, low and ultra-low cement castables has its own merits. Development of calcium aluminate forming bond over the hydrophobic graphitic surface has been investigated in detail in our previous publications [22,23]. The nanostructured Ca-doped γ-Al_2O_3 phases possessing Lewis acidic characteristics are sporadically distributed over graphite flake thereby improving its hydrophilicity. Heat treatment of this graphite under oxidizing conditions (at controlled pH) leads to development of some graphite oxide regions containing hydrophilic functional groups like carboxylic (–COOH), hydroxyl (–OH) etc. Zeta-potential test confirmed that it rendered better miscibility of castable matrix fines with minimum quantity of water. Raman spectroscopy studies revealed that partial exfoliation of graphite helped in the development of sp^2 hybridized small sheets of graphene-like regions [24]. These were responsible for better intercalation of Ca-ions and boehmitic nano-crystallites in between the sheets. It provided better connectivity of hydrophilic Lewis acidic sites with the adjacent aromatic ring structure via the functional groups present on surfaces and edges. The nanostructured phases of Ca-doped γ-Al_2O_3 also improved the surface area and intimately bonded the graphene sheets through the defects, fine pores and cleavages present. As a result graphite is well retained within the alumina based castable batch via better bonding of the matrix with the coating constituents.

Flaky graphites (both coated and uncoated) to the extent of 5.0% has been incorporated in a high alumina castable batch in this work. A comparison between the physical properties, thermal shock resistance and slag resistance of above mentioned castables had already been reported in our last papers [7,22–24]. However it is worth discussing the other refractory characteristics in detail to extrapolate the possibility of including increasing amount of coated graphites in refractories. The present investigation entails the mechanism of dramatic improvement of refractoriness, e.g. RUL and oxidation resistance by incorporation of only 5.0% of coated graphite. The matrix part of monolithic mass containing the surface-modified graphite has been separately characterized. The role of partially formed cross-linked nanoplatelets of graphite oxide in the refractory matrix, in this context, has been emphasized. In addition, the coating characteristics and phase evolution in castable have also been studied in depth to substantiate the refractory performance.

2. Experimental

Refractory grade natural flaky graphite having 97% fixed carbon and surface area 1.82 m^2/gm has been selected for this investigation. The sol–gel synthesis of calcium aluminate and preparation of that coating on graphite flakes had been discussed elsewhere in detail [22,23]. Stoichiometric calcium nitrate and aluminum-sec-butoxide were the chief ingredients to prepare calcium aluminate precursor. Thermal analysis study of graphite has always been considered as an important parameter, especially for its refractory applications [25]. To allow a quantitative measure of the enthalpy changes as a function of temperature, differential scanning calorimetry (DSC) test of coated and uncoated graphites have been conducted. This experiment was carried out up to 1600 °C from room temperature with a heating rate of 10 K/min (in air), using a NETZSCH instrument (Model Jupiter F3). Water-wettability of as-received and calcium aluminate-coated graphites has been compared by a method reported by Yoshimatsu et al. [26]. The quantity of floated graphites at the water surface and sediment volume of at the bottom was qualitatively estimated by taking photo snaps.

The main objective of the present work is to retain graphite in the castable matrix for a longer duration at elevated temperatures. In this regard, an investigation on the probable mechanism of bonding of graphite in castable matrix was attempted. A pictorial representation of nanosized calcium-doped gamma alumina coatings on graphite platelets has therefore been proposed. This schematic model has been utilized later to explain the outstanding performance of the castable containing this graphite.

The effects of incorporation of 5.0 mass% of coated and uncoated graphite separately to a low cement (4.0%) high alumina castable had been studied in this work. The composition of refractory batches and preparation of castable cubes (25.4 mm^3) and cylinders (50 mm diam, 50 mm height) had been the same as published in our previous contributions [7,22–24]. White fused alumina particles (72.0%) in several fractions comprised of the aggregate part of the castable. Apart from graphite and cement fines, the matrix part included aluminum powder (0.5%), microfine alumina (10.0%), microsilica (0.5%) and 8.0% commercial alumina-rich preformed $MgAl_2O_4$ spinel fines (with Al_2O_3=78%). C+ and C− codes were used as usual for castables containing respectively coated and uncoated graphites. All such samples were cured at humid condition (24 h), followed by air drying (24 h) and oven drying at 110 °C (72 h). The dried castables were then heat-treated at 900 °C, 1200 °C, and 1500 °C with 2 h of soaking at each temperature.

The present contribution focuses mainly on two important properties of castables which had not been reported before. These are refractoriness under load (RUL) and oxidation resistance tests compared between C+ and C− castables. Apparent porosity (AP), cold crushing strength (CCS), bulk density (BD) and XRD reports had also been furnished as supporting information. XRD phase analysis of the C+ castable samples heat-treated at 110 °C and 1200 °C were performed using a PANalytical (XPERT-PRO) Instrument with Ni-filtrated CuKα radiation at 40 kV/20 mA. The AP, BD and CCS of all

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