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Comparison of solid state and sol–gel derived calcium aluminate coated graphite and characterization of prepared refractory composite

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Abstract

This paper entails an extended investigation on sol–gel thin film of calcium aluminate ($CaAl_2O_4$) over graphite flakes that improved their oxidation resistance and water wettability. The commercial preparation of calcium aluminate has been compared with the sol–gel synthesis by differential thermal analysis (DTA) and X-ray diffraction (XRD) to assess the feasibility of the latter for coating preparation. Poorly crystalline nanostructured Ca-doped γ-Al_2O_3 is considered to be an important intermediate for this preparation. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of the calcined gel have been carried out to ascertain its composition. Quantitative chemical analysis of sol gel derived calcium aluminate was also estimated. Atomic force microscopy (AFM) has been conducted to ensure the evolution of hydrophilic nanosized cementitious phases on graphite. Zeta potential values of coated and uncoated graphites with increasing pH have also been determined to distinguish between their compatibility in a refractory castable matrix. Improved physical properties of that high alumina castable containing coated graphite, e.g. apparent porosity (AP), bulk density (BD), cold crushing strength (CCS) have been measured to evaluate the refractory quality. The reasons for its better performance are explored by taking further insight on the microstructural analyses of the fired castable (1500 °C) soaked for an extended period.

Keywords: A. Sol–gel processes; B. Electron microscopy; D. Graphite; $CaAl_2O_4$; E. Refractory castables

1. Introduction

Several attempts are going on to develop carbon containing monolithic castables and ensure their successful performance in steel plants [1–3] .The most important factor during preparation of this refractory is to make the carbon wettable with minimum water that could disperse and result in a dense structure in due course. The second important factor is to hold that carbon in that structure for a longer period. In the carbon–oxygen system, many condensed phases and gas species are generated, namely C(s), CO_2(s,l), O_2(l,g), CO(g), CO_2(g), etc. [4]. As such the oxidizing atmosphere of furnaces leads to substantial loss of carbon present in the refractories. It is possible to incorporate carbon in different refractory linings in the form of coke, carbon black and graphite. Among these solids, flaky graphite has been chosen in our previous work [5–8], due to its crystalline nature, superior bulk density, overall stability and other advantages. Viscosity of liquid binders and impregnating agents (e.g. resin, tar, pitch) should be carefully monitored for installation of castables; nevertheless, these have been utilized in refractories as carbonaceous materials since decades [9,10]. These two are excluded from our investigation to avoid the liberation of hazardous pyrolysis products. Many fruitful efforts have already been reported for improving the water wettability and thermal stability of graphite [11–13]. We adopted a modified sol gel route for surface treatment of graphite by spinel and mullite thin films [5–8]. It assured stabilization of graphite and substantially overcame the two impediments mentioned above. The chemical treatment of graphite with sol–gel derived calcium aluminate, in this regard, has been studied in our recent communication [14]. It is well documented that the wet chemical synthesis of calcium aluminate results in high surface area, controlled chemical composition, homogeneous distribution of the constituents and relatively low temperature requirement [15–19]. The use of calcium aluminate cement in refractory applications still dominates its other applications and

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it is compatible to both high alumina and basic castables. The other reasons for developing calcium aluminate coated graphite have been explained in that previous communication with a brief description of its synthesis and characterization. This paper includes further insight on that work and an extended investigation on the characteristics and performance of a high alumina castable containing that coated graphite. In this regard a comparison between the traditional solid state preparation and sol–gel processing of calcium aluminate has also been highlighted to emphasize here the relevance of the latter.

2. Experimental

Synthesis of calcium aluminate precursor by sol–gel route has been discussed in our earlier work along with the preparation of coated graphite by that precursor [14]. The sol–gel process employed here is quite easy-to-use involving a hybrid set of precursors e.g. aluminium-sec-butoxide and hydrated calcium nitrate. Propanol, acetylacetone, deionised water, acetic and nitric acids were the other important chemicals for sol preparation involving less expensive equipments. Supplied graphite (97% carbon) was slowly mixed to the binary sol, dried, sieved and calcined (600 °C) to prepare calcium aluminate coated graphite for incorporation in a monolithic refractory composite. A parallel attempt has been done here to derive calcium aluminate as followed conventionally in cement industries. However unlike bauxite and limestone, we used purer and finer grades of these materials. For this purpose, LR grade calcium carbonate powder (assay >98.5%, Merck) and reactive alumina ($Al_2O_3 > 99.5\%$, specific surface area 4.6 m^2/g, INDAL) were thoroughly mixed in a slurry form, dried and milled again, keeping the mole ratio of (1:1) to maintain ($CaO:Al_2O_3$) stoichiometry. The DTA and XRD of this mix were compared with that obtained for sol–gel derived calcium aluminate powder. XRD patterns of the main precursor gel, namely boehmite (γ-AlOOH) calcined at 300 and 500 °C, had also been studied to understand the evolution of nano crystalline γ-Al_2O_3 as performed earlier in a similar work [20]. The XRD phase evolution of dried and heat-treated calcium aluminate gels were also investigated within a broad temperature spectrum, namely, 110, 600, 750, 930, 1100 and 1400 °C. The SEM (with EDS) of this gel calcined at 930 °C and 1400 °C were also carried out to confirm the composition of the cementitious phases in those micrographs. The quantitative chemical analysis of sol–gel calcium aluminate powder (1400 °C) was estimated to substantiate the EDS results. AFM of coated graphite was analysed to verify the existence of hydrophilic nanodimensional calcium aluminate enriched phases over graphite flakes.

As these coated graphites have been incorporated to refractory castable slurry [14], the comparison of changes in zeta potentials between coated and uncoated graphites was also studied with respect to the variation of pH. The monolithic castable composite containing graphite (5.0%) was a low cement (4.0%) formulation with white fused alumina aggregates (72%). The matrix part (28%) contained microsilica, spinel ($MgAl_2O_4$), reactive alumina, aluminium powder, sodium hexa-metaphosphate including the cement fines with graphite. Its fabrication and heat treatment (110 °C, 900 °C and 1500 °C) had been outlined in our previous articles [5–8]. C^+ and C^- codes were used respectively for castables containing coated and uncoated graphites. Determination of AP, CCS, BD values of heat treated castables has been conducted in accordance with ASTM C133-94, C133-97 and C20-00 specifications. Micrographs of C^+ castables fired at 1500 °C (with 5 h soaking) were thoroughly examined finally with respective EDS reports at several points to explain its better performance.

Chemical analysis of cement composition was done quantitatively by rapid estimation (by oxalic–tartaric–citric acid mixture) together with the conventional EDTA method, taking cement solution in concentrated HCl [21]. Zeta potential vs. pH plots were taken by the Malvern Zetasizer Nanoseries instrument (Model ZEN 2600) using deionised water, HCl and NH_4OH in proper dilution (HACH SENSION model). DTA traces of both the precursors was carried out in a Shimadzu instrument (DT-40 model) in air at a rate of 10 °C/min. XRD patterns were obtained from ‘Philips Analytical Instrument’, PANalytical (XPERT-PRO) model with Ni-filtered CuKα radiation. SEM/EDS experiment was conducted with Hitachi S-3400N and JEOL JSM 5200 models. For AFM analysis, the NANOSCOPE(R)IIIa (Version 5.3, 2005, Veeco instruments Limited) model was employed with a scan rate 1.2 Hz and scan range 1 mm by tapping mode operation. Differential thermogravimetry (DTG) of as-received graphite was done in NETZSCH STA 449 C (model) at a rate of 10 °C/min in air.

3. Results and discussion

Fig. 1 shows the comparison of DTA plots (up to 1000 °C) between sol–gel routed calcium aluminate gel and that of solid state precursor mix required to prepare calcium aluminate. For solid state preparation it is known that calcium carbonate decomposes at around 900 °C; however depending on the type and quantity of impurities present, surface area, morphology,

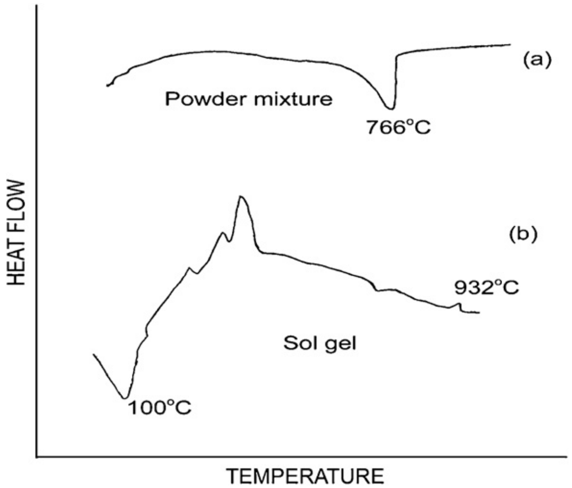

Fig. 1. DTA of (a) Al_2O_3—$CaCO_3$ powder mix and (b) sol gel derived calcium aluminate powder.