



# In depth studies on cementitious nanocoatings on graphite for its contribution in corrosion resistance of alumina based refractory composite

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**Abstract:** Some newer insights had been reported in this paper on synthesis and application of calcium aluminate coated graphite in alumina–carbon refractory castables. The course of evolution of  $\text{AlO}_4$  (tetrahedral) and  $\text{AlO}_6$  (octahedral) units in the nanocoating was investigated by XRD (X-ray diffraction), Raman spectroscopy and FTIR (Fourier transformed infrared spectroscopy) studies. An extended research on the resemblance and disparity between sol–gel and conventional refractory cements were also explored. FESEM (Field Emission Scanning Electron Microscopy), XRD of coated and uncoated graphites had been revisited with a special study on ESEM (environmental scanning electron microscopy) of those two. The hydrophilic thin film containing Ca-doped  $\gamma\text{-Al}_2\text{O}_3$  phases rendered a decisive influence on graphite retention in castable matrix. A comparison between pore size distribution and thermogravimetric analysis (TGA) of two fired castable refractories advocated the superiority of the one containing coated graphite. Determination of corrosion and penetration indices by the static slag corrosion test, supplemented with microstructural studies, confirmed that the less porous castable containing coated graphites excelled again in the harsh environment.

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## 1. Introduction

Industrialization and urbanization are rapidly growing throughout the world, particularly in the developing countries. Almost half of all materials used in this regard are concrete. Steel and cement, in this context, have become the main stakeholders that provide the wherewithal for developing a prospective industrial world. Refractory ceramic materials are intended whenever a process involves heat treatment or exposure to high temperature e.g. that required for iron, steel and cement making. Monolithic refractory castables have been increasingly demanded in last few decades due to their several advantages over shaped refractory bricks [1]. As a consequence, unshaped refractories are now being developed rapidly and regarded unequivocally as complex multicomponent composite materials, which include oxide or non-oxide ceramics, metallic powders, carbon in several forms

along with different kinds of organic binder and deflocculants. Refractory Industries sometimes considered as more traditional and untidy areas; as such time has come now to develop newer and sophisticated refractory materials to bring the refractory technology in a fascinating way to the consumers and researchers.

The matrix part of the composite array of this refractory castable includes superfine materials, which may go down nowadays to nanometric size. Refinement of refractory technology, based on such nanoscale materials are currently employed in several areas of iron, steel and cement industries. Different physicochemical properties of refractories are strongly dependent on its microstructures. Incorporation of nano-materials in the matrix part results in the desired phase-assembly in the microstructure leading to interesting properties of the refractory e.g. strength, density, resistance to thermal shock, corrosion etc. Recent literatures clarify how introduction of nanoscale materials in refractory composite enhances the surface energy, controls the rate of chemical reaction and modifies the surface and interfaces of bulk

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structures [2–5]. Selective application of nanodimensional materials thus firmly stands as a prerequisite for obtaining user friendly refractory ceramics. One such elegant route to prepare these nano-materials at a mild condition is the sol–gel process. New generation castables containing silica, alumina sols and /or nano powders (carbon black etc) have been well reported [6–11]. The ceramic–carbon refractories are appreciated since decades owing to high thermal conductivity, low thermal expansion and non-wetting behavior of graphite. Incorporating carbon (e.g., graphite) in refractories has, therefore, always been a common practice to achieve higher resistance to slag attack and spalling of the lining. Iron and steel production in fact, emits a lot of CO<sub>2</sub> annually and associated with a large quantity of energy. Low CO<sub>2</sub> steel making is thus desired in recent time that involves a lesser quantity of carbon in steel making. The pitfalls of using graphites in castable, however, are their low water-wettability and poor oxidation resistance which result in more water consumption with a less homogeneous and porous refractory. Several ingenious methods are therefore being attempted to address all these requirements and materialize graphite retention in refractories for longer duration at extreme environments [12–14].

In order to alleviate the problems of as-received graphite a thin hydrophilic nanostructured selective coating of oxide ceramic on graphite surface has been applied. It was accomplished by a cost-competent sol–gel process that sustained graphite in castable composite at aggressive atmosphere. Sol–gel method enables to prepare the coating at a low temperature. When assisted with ultrasonication and heat treatment, partly exfoliated graphite platelets with intermittent graphite oxide formation are quite likely. In our maiden effort it has been reported that surface treatment of graphite by inorganic sol–gel routed precursors was found to be quite promising for application in refractory castables [15–23]. However our persistent research on this area recently revealed that some special facets of this material are yet to be unfolded. Thus, the present contribution revisits our work on these new generation cementitious nanocoatings with a primary focus on two objectives.

Firstly, a fundamental work has been explored on identifying the substructures associated with the coating evolution and correlating this to the mechanism of formation of selective ceramic thin film over graphite. The second important part is the in depth studies on slag resistance parameters involved for evaluating the performance of refractory castables containing coated graphite in comparison with the same prepared by as-received graphites.

## 2. Experimental

The synthesis of calcium aluminate precursor sol has been discussed elsewhere [19–23]. Aluminum-sec-butoxide, hydrated calcium nitrate, deionised water, propanol, acetyl acetone, acetic acid were the main ingredients to prepare this sol. In order to make a compromise between the cost factor and the coating quality, one ingredient of the sol has been selected

from the alkoxide origin and other from the cheaper inorganic origin. The wet chemical processing of binary ceramic oxide materials, especially by sol–gel route, has always been appreciated due to several process advantages. The hydrolysis and condensation reactions of alkoxide with water–propanol mixture at > 85 °C with continuous stirring at pH~3.0 followed their own course in presence of acetic and nitric acids to result in a polymeric boehmite sol [16,18]. Finally diluted calcium nitrate solution was drop wise and slowly added to it with continued stirring to yield the stable precursor sol having (1:1) mole ratio between CaO and Al<sub>2</sub>O<sub>3</sub>. Natural flaky graphite with 97% fixed carbon and surface area 1.82 m<sup>2</sup>/gm has been utilized for this work. The preparation of sol gel coating on to this refractory grade graphite flake involving magnetic stirring, ultrasonication, ageing and controlled heating up to 600 °C had also been elucidated in our previous publications. The solid content of the coating on graphite surface was kept only 1.7 mass% to avoid chipping off of the substrate during refractory application. The difference in characteristics between coated (code: CA-C) and uncoated (code: GR2) graphites had been studied by FESEM, ESEM and XRD experiments. FESEM study (with EDS) was performed in JEOL JSM 6700 F instrument to distinguish between the elemental composition at several coated and uncoated regions of surface-treated graphite. ESEM microstructural studies had been conducted using low vacuum mode (in presence of water) in an instrument Quanta FEG 250 with chamber pressure kept at 600 Pa. Information about crystallite sizes of two graphite fines from a powder diffractogram was obtained by fitting (002) reflections at ~26.5° with *Pseudo-Voigt profile* function to determine the integral breadth and the peak shape, followed by *Williamson-Hall plot* in 2θ space. The instrumental influence on the peak shape was corrected with a cerium oxide standard. Line profile analysis was done using *Highscore Plus software* (Panalytical).

The FTIR of calcium aluminate gel calcined at progressively higher temperatures (600, 750, 1100, 1200 °C) has been conducted to understand the bond status with the thermal evolution of crystalline phases of calcium aluminate and other constituents. It was done by KBr pellet method using a Perkin Elmer model. The prime objective of the cementitious sol–gel coating applied to graphite was incorporating it to a refractory batch having low cement formulation. Owing to this a comparative study between this sol–gel derived calcium aluminate powder (calcined at 1400 °C) and refractory grade high alumina cement (Al<sub>2</sub>O<sub>3</sub>=70 mass% approx) has also been done. In this regard, XRD and FTIR studies between these two cement fines has been performed. XRD phase analyses were obtained by a PANalytical (XPRT-PRO) instrument with Ni-filtered Cu-Kα radiation. Raman spectroscopy study of the calcined (930 °C) calcium aluminate gel powder was carried with the excitation wavelength 488 nm by the instrument ‘Microramanspectrometer’ (50 ×).

The refractory castables preparation has also been elaborately discussed in our previous contributions [15–17]. It was a low cement (4.0 mass%) batch containing white fused alumina(WFA) aggregates (72.0%) in several size fractions, e.g. –6+16,

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