

# Improving the quality of nanocrystalline $\text{MgAl}_2\text{O}_4$ spinel coating on graphite by a prior oxidation treatment on the graphite surface

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## Abstract

This paper aims to report the effect of surface oxidation treatment on graphite flakes and its effect on the improvement of  $\text{MgAl}_2\text{O}_4$  spinel coating developed by sol–gel citrate process. The graphite surface was oxidized by hydrogen peroxide and the coating was subsequently applied. The coating structure, water-wettability and oxidation resistance of coated samples were taken as criteria to evaluate the coating integrity. It was clarified that the oxidation treatment developed hydrophilic functional groups on graphite surface. This helped the formation of an even and smooth  $\text{MgAl}_2\text{O}_4$  spinel coating texture on graphite flakes. The water-wettability and oxidation resistance were also found to be improved significantly compared to non-treated samples. The results were supported by thermogravimetric analysis, contact angle and zeta-potential measurements.

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## 1. Introduction

Since 1970, oxide-carbon shaped refractories have been widely used in iron and steel industries due to the excellent thermal conductivity and low slag/molten-wettability of graphite.<sup>1,2</sup> However, low water-wettability of graphite as a result of the presence of few hydrophilic functional groups on its surface, as well as its low oxidation resistance have restricted development and application of graphite-containing refractory castables.<sup>3,4</sup>

Modifying the surface properties of graphite by coating techniques is considered an effective way to tackle these problems.<sup>5</sup> First attempts focused on using pitch (coal tar) as coating. Pitch offers a low melting point (<80 °C) and price, but its insufficient water-wettability and the evaporation of toxic vapours during decomposition have limited its broader usage.<sup>6</sup> Ono and Ono<sup>7</sup> improved the water-wettability of graphite particles by depositing very fine silicon carbide particles on the graphite surface via a high-speed impact milling technique. However, weak bond-

ing between SiC particles and the graphite surface caused the coating to lose its efficiency during the castable preparation.

Later, because of the excellent water-wettability of oxides as well as considerable progress in sol–gel techniques, oxide coatings based on alkoxides were introduced. Different coating materials have been studied, e.g.  $\text{Al}_2\text{O}_3$  by Kawabata et al.<sup>8</sup>,  $\text{TiO}_2$  by Yu et al.<sup>9</sup>, and  $\text{ZrO}_2$  by Sunwoo et al.<sup>10</sup>. Recent attempts by Zhang and Lee<sup>11</sup> have improved the water-wettability of graphite by coating its surface with hydrophilic oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3/\text{SiO}_2$ .

All these techniques effectively improved the water-wettability and oxidation resistance of graphite. However, the need for expensive raw materials has limited their use by the refractory industries. In addition, due to the hydrophobic nature of graphite, there are only few sites onto which molecules of sol can be adsorbed on the graphite surface so that after the forced hydrolysis reaction, uncoated regions remain on the graphite surface.<sup>10</sup> To solve this problem two different approaches have been used. (1) Mixing graphite particles in a pre-hydrolyzed sol (gel).<sup>8</sup> (2) Addition of a polymeric compound like polyvinyl alcohol (PVA) to promote molecule adsorption on the graphite surface.<sup>10</sup> Agglomeration of particles and an inhomogeneous distribution of the second phase on the graphite surface are the

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main disadvantages of the first approach. The second approach suffers from crack formation at the of graphite/coating interface during burn out of PVA.<sup>12</sup>

Recently, the authors have developed a convenient and cheap procedure to coat graphite surface with nanocrystalline  $MgAl_2O_4$  spinel synthesized via sol–gel citrate technique.<sup>13</sup> In the current study, to enhance the quality of  $MgAl_2O_4$  spinel coating on graphite surface and subsequently improve the water-wettability and the oxidation resistance of coated graphite, the intrinsic hydrophobic properties of natural flaky graphite were changed by surface oxidizing before coating.

## 2. Experimental

### 2.1. Raw materials

Chinese natural flaky graphite (purity >96 wt.%,  $SiO_2$  content in ash >83 wt.%, and particle size <220  $\mu m$ ) was used as the graphite source. Magnesium nitrate ( $Mg(NO_3)_2 \cdot 6H_2O$ ), aluminum nitrate ( $Al(NO_3)_3 \cdot 9H_2O$ ), citric acid ( $C_6H_8O_7 \cdot H_2O$ ), and ammonia solution ( $NH_4OH$ , 0.2 M) were used as starting materials to synthesis  $MgAl_2O_4$  spinel. Also hydrogen peroxide ( $H_2O_2$ , 30%) and nitric acid ( $HNO_3$ , 65%) were utilized as oxidizing agents.

### 2.2. Oxidation treatment of graphite surface

Graphite surfaces were oxidized according to Kunii's technique<sup>14</sup> as follows: 100 g graphite was added to a beaker containing 200 ml hydrogen peroxide. The solution pH was adjusted to 1 by adding nitric acid. The suspension was stirred for 72 h at 50 °C and then passed through a filter paper to separate the solid portion. The surface-oxidized graphite (GO) was washed three times with a dilute solution of nitric acid (2% solution in water) and then dried at 60 °C in an electric oven.

Decomposition of hydrogen peroxide is accompanied with oxygen release. The released oxygen is adsorbed on the graphite

surface and reacts with it. The reaction changes hydrophobic functional groups such as  $-CH\equiv$ ,  $-CH_2=$ ,  $-CH_3-$ , and  $-C=O$  into hydrophilic groups like  $-OH$ , and  $-COOH$ . Surface defects and impurities in the graphite have a catalytic effect on the reaction. These hydrophilic functional groups are responsible for improved graphite water-wettability. The hydrophilic functional groups are stable below 126.85–176.85 °C and at higher temperatures convert to CO and  $CO_2$ .<sup>15–18</sup> Surface oxidation treatment can also form a new phase so-called graphite oxide on the graphite surface; porous structure and ion exchange ability are its main characteristics.<sup>19</sup>

### 2.3. Preparation of $MgAl_2O_4$ spinel coating

Initially, spinel sol was prepared by adding stoichiometric molar ratio of magnesium nitrate (1.804 g) and aluminum nitrate (2.64 g) in 200 ml distilled water. Citric acid with a molar ratio of  $C_6H_8O_7/NO_3^- = 0.5$  was added to the solution according to sol–gel citrate technique.<sup>20</sup> The solution was agitated using a magnetic stirrer at room temperature for 1 h. The pH of the solution was adjusted to 6 by drop-wise addition of ammonia. Then 50 g of either as-received graphite (G) or surface-oxidized graphite were introduced into the prepared sol to get 2 wt.%  $MgAl_2O_4$  spinel as coating on its surface. The mixtures of graphite and the sol was stirred by a mixer for 2 h and concurrently heated by a hot plate to 120 °C and kept at this temperature for 3 h. The mixture was dried in an oven at 180 °C for 3 h and then the dried mixtures were heat treated at 450 °C for 1 h in air, calcined at 900 °C for 2 h in argon atmosphere and finally cooled naturally in this condition.

### 2.4. Characterization techniques

FTIR spectra were recorded in the range 600–4000  $cm^{-1}$  by a Bruker FTIR spectrophotometer (vertex-70), using the KBr pellet technique, powder/KBr weight ratio was 1/500.

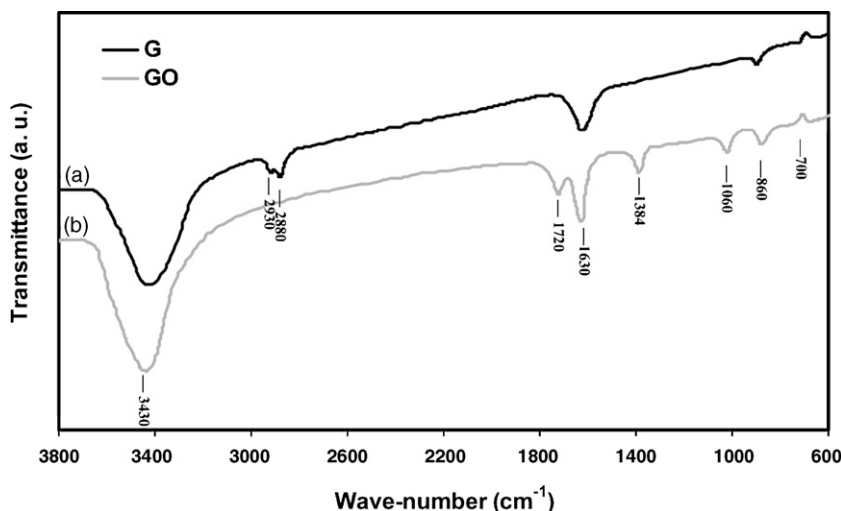


Fig. 1. FTIR spectra of (a) as-received graphite (G) and (b) surface-oxidized graphite (GO).

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