

Improving the quality of nanocrystalline MgAl_2O_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 MgAl_2O_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 MgAl_2O_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.^{1,2} 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.^{3,4}

Modifying the surface properties of graphite by coating techniques is considered an effective way to tackle these problems.⁵ 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.⁶ Ono and Ono⁷ 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. Al_2O_3 by Kawabata et al.⁸, TiO_2 by Yu et al.⁹, and ZrO_2 by Sunwoo et al.¹⁰. Recent attempts by Zhang and Lee¹¹ have improved the water-wettability of graphite by coating its surface with hydrophilic oxides such as SiO_2 , Al_2O_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.¹⁰ To solve this problem two different approaches have been used. (1) Mixing graphite particles in a pre-hydrolyzed sol (gel).⁸ (2) Addition of a polymeric compound like polyvinyl alcohol (PVA) to promote molecule adsorption on the graphite surface.¹⁰ 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.¹²

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.¹³ 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 μm) 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 technique¹⁴ 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 .^{15–18} 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.¹⁹

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.²⁰ 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.

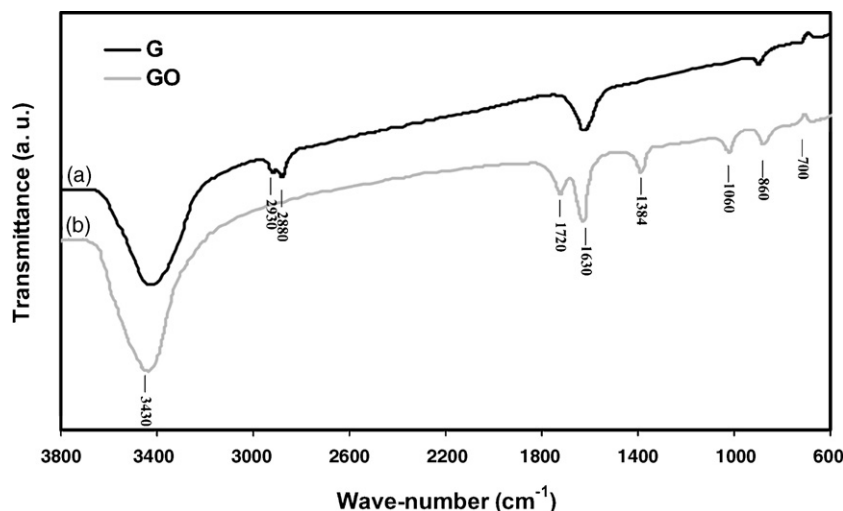


Fig. 1. FTIR spectra of (a) as-received graphite (G) and (b) surface-oxidized graphite (GO).

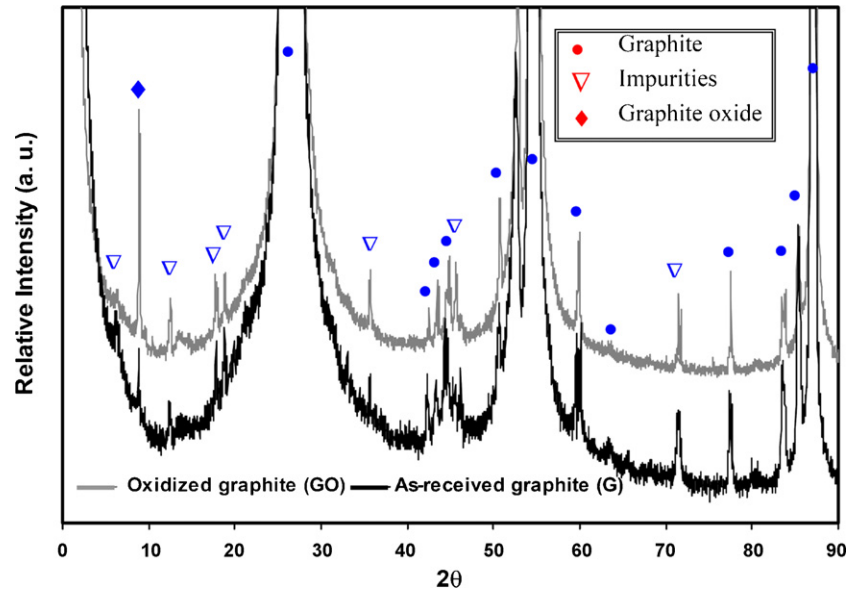


Fig. 2. XRD patterns of G and GO.

The phase compositions of samples were studied using an X-ray diffractometer (PW-3040) with Cu K α radiation (scan rate = $0.001^\circ \text{ min}^{-1}$, scan step = 2 s). JCPDS cards used for identification were graphite (08-0415) and MgAl $_2$ O $_4$ spinel (21-1152).

A field emission gun scanning electron microscope (FEG-SEM, LEO 1530, Zeiss Co., Germany) equipped with energy dispersive spectroscopy (EDS) analyzer was used for microstructural observations. Electrokinetic behaviour of dispersed powder in water was investigated by an ultrasound spectrometer (DT-1200, Dispersion technology Co., USA).

Water-wettability of samples was examined quantitatively by two different techniques. According to the first technique after Yu et al.⁹, 5 g of the as-received and the coated graphites were put into a graduated cylinder containing 100 ml distilled water. After 30 min the floating ratio (FR) was calculated by the following equation:

$$\text{FR}(\%) = \frac{\text{weight of floating graphite}}{\text{total weight of graphite}} \times 100 \quad (1)$$

Decreasing floating ratio reveals improvement of the water-wettability of graphite.⁹ In the second method, the water-wettability of samples was directly estimated by observation of the contact angle of a de-ionized water drop (2 μl) laid on the surface of the samples. After 3 s, water contact angle on the surface of each sample was measured with an OCHA 230 contact angle meter (Dataphysics GmbH, Germany) equipped with a CDD camera (90 images per second). Before measuring contact angles, flake graphite powder was pressed using one directional hydraulic press into a cylindrical mould (diameter = 13 mm and pressure = 450 MPa). The oxidation behaviour of samples was studied by thermogravimetry analysis technique (Netzsch STA-449C, heating rate = $10^\circ\text{C}/\text{min}$, rate of air flow = 40 ml/min).

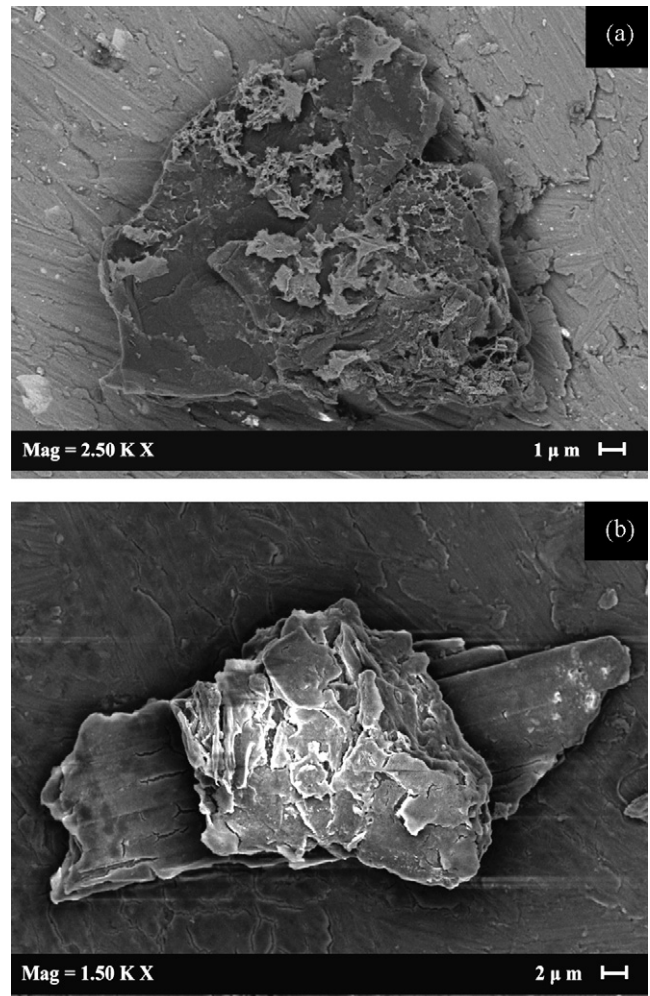


Fig. 3. Back scattered electron image of GS (a) and GOS (b).

3. Results and discussion

3.1. Characterization of oxidized graphite surface

Formation of hydrophilic functional groups on the surface of oxidized graphite has been analyzed using IR-spectroscopy.

FTIR spectra of as-received and surface-oxidized graphite are depicted in Fig. 1(a and b). A broad band in the range of $3200\text{--}3500\text{ cm}^{-1}$ and also a small band in the range of $700\text{--}850\text{ cm}^{-1}$ which respectively can be associated with the presence of Si–O–Si bands, from the presence of SiO_2 as impurity of natural graphite, and free hydroxyl groups

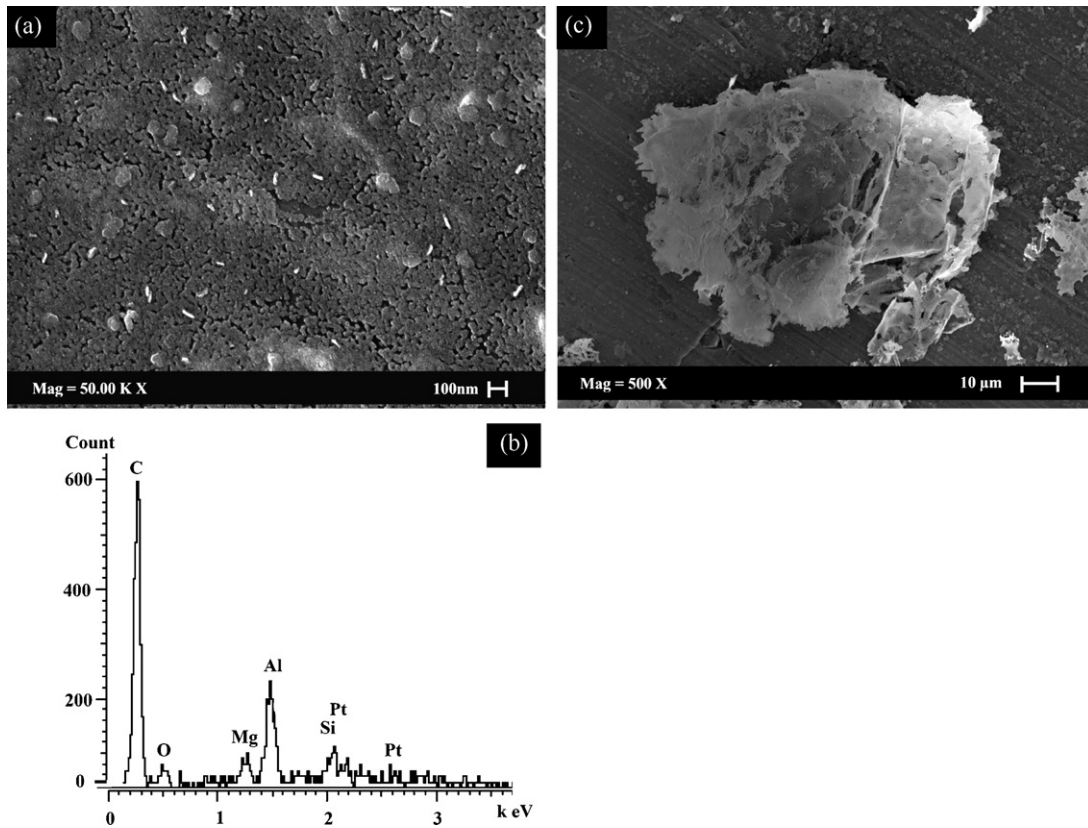


Fig. 4. (a) The microstructure of MgAl_2O_4 spinel coating on GOS, (b) EDS analysis of coating and (c) SEM micrograph of the relicts of the MgAl_2O_4 spinel coating after GOS was oxidized in air at 900°C for 2 h.

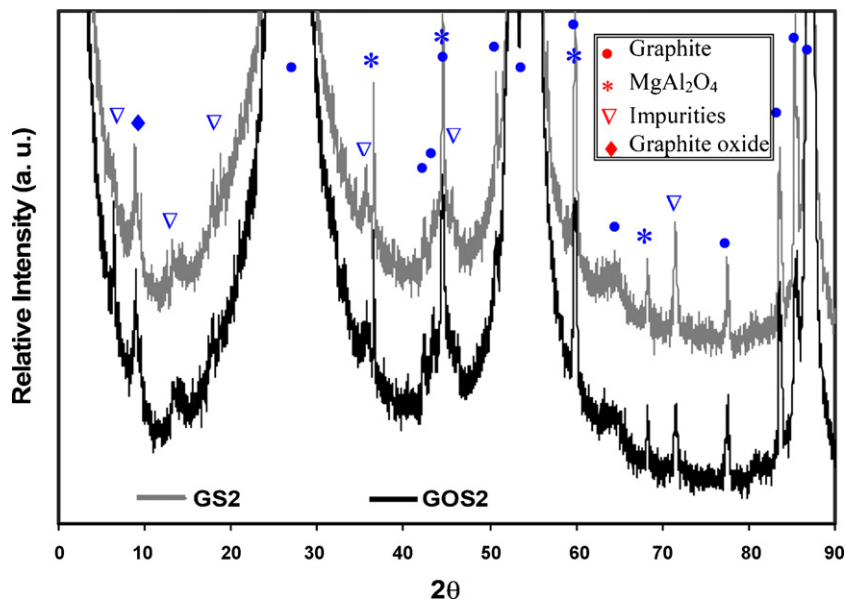


Fig. 5. XRD patterns of MgAl_2O_4 spinel-coated graphite flakes (GS: spinel-coated G; GOS: spinel-coated GO).

are common in the IR-spectra of G and GO.^{21,22} The C–H band at 2800–2900 cm⁻¹ shows the presence of hydrophobic functional groups on the surface of as-received graphite. The major bands in the surface-oxidized graphite are carboxyl groups at 1720 cm⁻¹, C=C bands at 1630 cm⁻¹, NO₃ groups at 1384 cm⁻¹, and C–O bands at 1060 cm⁻¹ (Fig. 1b). These bands are in agreement with published data.^{21,22}

Fig. 2 shows XRD of as-received and surface-oxidized graphite. Consistent with the results of Titelman et al.¹⁷, in addition to the main graphite peaks and some small peaks related to inorganic impurities in the graphite, a sharp peak attributed to graphite oxide is seen around $2\theta = 8.85^\circ$. It appears likely that the released oxygen and hydrogen from decomposition of H₂O₂ intercalate between the atomic structures of graphite and change the distance between planes in its atomic lattice. The interesting point is the presence of this peak in the as-received graphite, however, its intensity in the surface-oxidized sample is much higher.

3.2. Characterization of MgAl₂O₄ spinel coating

In Fig. 3 the as-received graphite coated with MgAl₂O₄ spinel (GS) and surface-oxidized graphite coated with MgAl₂O₄ spinel (GOS) sample surfaces are compared in term of coating integrity. As seen (Fig. 3a), in GS surface the coating has not been shaped in monolithic form and shows the island type structure. The GOS (Fig. 3b) however demonstrates an even and smooth texture without significant disintegration. These observations indicate that primary oxidation treatment was significantly influential.

Fig. 4a illustrates secondary electron image of surface-oxidized graphite coated with MgAl₂O₄ spinel at higher magnification. It reveals the graphite surface have been coated with nanostructured MgAl₂O₄ spinel (Fig. 4b). The relict of GOS after oxidizing of GOS in air at 900 °C for 2 h, also con-

firms that MgAl₂O₄ spinel coating could cover the most part of graphite surface (Fig. 4c).

Fig. 5 displays XRD patterns of as-received graphite coated with MgAl₂O₄ spinel and surface-oxidized graphite coated with MgAl₂O₄ spinel. Beside the peaks attributed to graphite and its impurities, the main peaks of MgAl₂O₄ spinel are present. Decreased intensity of the peak assigned to graphite oxide ($2\theta = 8.85^\circ$) in comparison with that in the XRD pattern of GO (Fig. 2) shows decomposition of graphite oxide at higher temperature. The main impurities were clarified in XRD pattern of oxidized graphite to be cristobalite, potassium aluminum silicate, sodium silicate, and potassium silicate.¹³

The influence of prior surface oxidation treatment on the water-wettability and oxidation resistance of graphite as a function of MgAl₂O₄ spinel coating quality on graphite surfaces was investigated. Electrokinetic behaviour (zeta-potential–pH curves) for MgAl₂O₄ spinel powder synthesized at 900 °C via sol–gel citrate technique, as-received graphite, surface-oxidized graphite, as-received graphite coated with MgAl₂O₄ spinel, and surface-oxidized graphite coated with MgAl₂O₄ spinel are illustrated in Fig. 6. Due to the presence of few ionic surface groups on the surface of as-received graphite, this sample has the lowest zeta-potential. Below pH 10, before isoelectric point (IEP), the surface-oxidized graphite shows higher zeta-potential compared to the as-received graphite. In spite of disintegration of hydrophilic functional groups at higher temperatures, the surface-oxidized graphite coated with MgAl₂O₄ spinel had higher zeta-potential than the as-received graphite coated with same amount of spinel coated. However, the IEP of GOS is close to the IEP of synthesized spinel than GS. These data suggest GOS will have better dispersibility in aqueous media.

The water-wettability of samples was also examined by measuring the water-contact angle on the surface of pressed graphite tablets. It was recognized that the surface oxidation treatment has a dramatic effect on the water-wettability of graphite. The

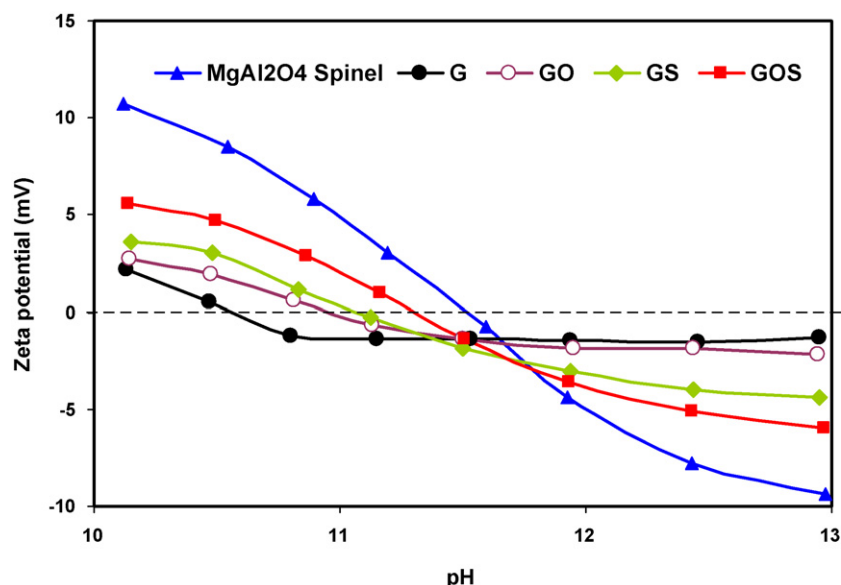


Fig. 6. ζ -pH curves of MgAl₂O₄ spinel synthesized at 900 °C, G, GO, GS, and GOS in 0.01 M KCl solution (solid portion of suspension: 6 wt.% and particle size <80 μm).

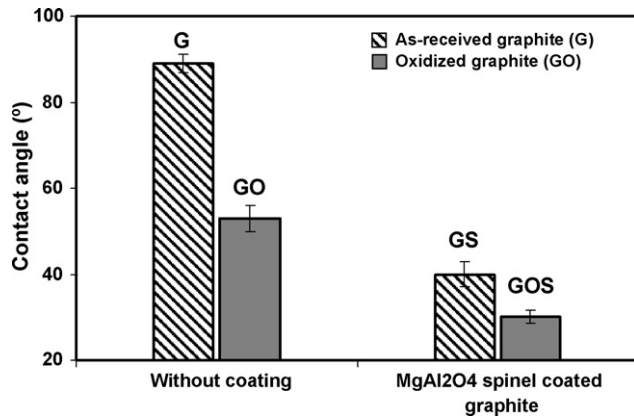


Fig. 7. Contact angles of G, GO, GS, and GOS.

water-contact angle of as-received graphite is 88° in comparison, the contact angle of surface-oxidized graphite has decreased to 52° (Fig. 7). Both MgAl₂O₄ spinel-coated samples, GS and GOS, exhibit a further substantial decrease in contact angle.

Fig. 8 illustrates FR values for as-received, surface oxidized, and coated graphites. Due to the presence of a few hydrophilic functional groups on the graphite surface, natural flaky graphite cannot be wetted by water. In spite of the low water-wettability of as-received graphite, more than 80 wt.% of surface-oxidized graphite could be wetted by water revealing that surface oxidizing treatment improves the water-wettability of graphite. The best results were achieved with GOS.

The oxidation behaviour of different samples was compared using TG (thermogravimetry) in flowing air (Fig. 9). Despite significant changes in surface characteristic of surface oxidized sample created by hydrogen peroxide, the oxidation behaviour of GO did not show any difference to primary G sample. It shows that the initial surface oxidation treatment has not created defects which could lower the activation energy for graphite oxidation. On the other hand, initiate oxidation temperature of spinel-coated samples (GS and GOS) exhibits a shift to higher temperatures in comparison with as-received graphite. This reveals that MgAl₂O₄ spinel coating has a protective effect in the oxidation of graphite.

The results demonstrated that the prior surface oxidation has a significant effect on improving the water-wettability, the coating quality, and the oxidation behaviour of MgAl₂O₄ spinel-coated

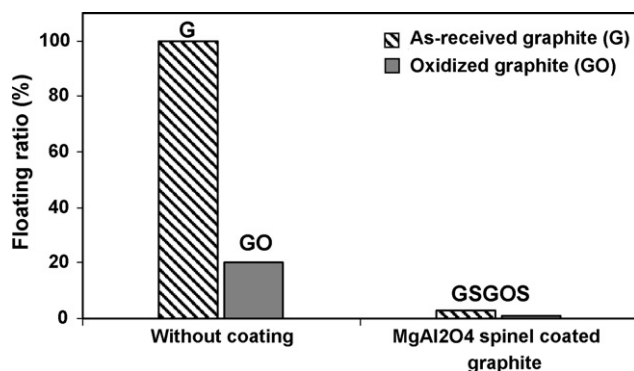


Fig. 8. FR values of G, GO, GS, and GOS.

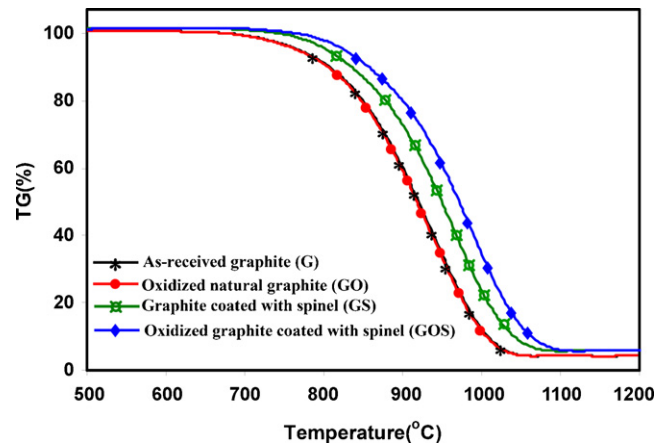


Fig. 9. TG analysis of G, GO, GS, and GOS (dry air flow: 40 ml/min).

graphite. The enhancement of coating quality can be explained by the presence of hydrophilic functional groups as well as graphite oxide on the graphite surface which resulted in a noticeable increase in available sites for ions (Al³⁺ and Mg²⁺) to attach to the graphite surface.

4. Conclusions

To improve the quality of MgAl₂O₄ spinel coatings on graphite surfaces, the surface of natural graphite flakes was oxidized by hydrogen peroxide and its influence on enhancement of the water-wettability and oxidation resistance of nanocrystalline MgAl₂O₄ spinel-coated graphite was investigated. FTIR showed formation of hydrophilic functional groups on the surface of oxidized graphite. In addition to the formation of hydrophilic functional groups on graphite surface, hydrogen peroxide could react with the graphite surface. It seems the liberated oxygen and hydrogen from decomposition of hydrogen peroxide could react with graphite and form graphite oxide phase on the surface of graphite. In spite of disintegration of the induced hydrophilic functional groups and graphite oxide phase after heat treatment, the hydrophilic groups on the surface of oxidized graphite along with the porous structure of graphite oxide provide sufficient sites to adsorb ionic ingredients of sol on graphite surface and improve the quality of MgAl₂O₄ spinel coating on graphite surface. On the other hand, thermal analysis results revealed that surface oxidation of graphite has not had any negative effect on the oxidation resistance of graphite. Microstructural observations showed that a nanostructured spinel coating could virtually cover the surface of graphite flakes. The results of contact angle and zeta-potential measurements as well as thermogravimetry analysis confirmed that the prior surface oxidation treatment has a significant effect on the water-wettability and the oxidation resistance of MgAl₂O₄ spinel-coated graphite.

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