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Development of $MgAl_2O_4$ spinel coating on graphite surface to improve its water-wettability and oxidation resistance

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Abstract

Low water-wettability and oxidation resistance of graphite have limited its application in carbon containing refractory castables. The aims of this study are the improvement of water-wettability and the oxidation resistance of natural flaky graphite by applying an oxide coating on its surface. To develop the coating, magnesium aluminate spinel sol was formulated via a citrate–nitrate route and graphite powder was then added to the sol. The mixture was heat treated in appropriate temperature and atmosphere to get the polycrystalline $MgAl_2O_4$ coating on graphite particles surface. The microstructure of coating was studied by X-ray diffractometer, SEM and TEM. The water-wettability was evaluated by measuring the water drop contact angle and plotting the zeta potential vs. pH. The results showed the development of a stable nanocrystalline $MgAl_2O_4$ spinel coating which improved the water-wettability and oxidation resistance of graphite significantly. Also, characterization of the coating is explained with emphasis on its application importance.

Keywords: B. Surface; D. Carbon; E. Refractories; Spinels; Water-wettability

1. Introduction

The excellent thermal conductivity and low slag-wettability of graphite have caused graphite is used frequently in shaped refractories. Unfortunately low water-wettability and poor oxidation resistance of graphite have limited its application in castable refractories [1,2].

Some attempts were made to find a solution: Zhou and Rigaud [3,4] have used graphite in micropellet and briquette forms to decrease the interaction between the surface of graphite and water. Due to the enhancement in graphite size, from micron to millimeter scale, the main drawback of this approach is inhomogeneous distribution of graphite in castable. Zhang and Lee [5] have coated graphite with hydrophilic oxides such as SiO_2 or Al_2O_3/SiO_2 via sol–gel technique. Although they could effectively improve the water-wettability and the oxidation resistance of graphite, using of expensive raw materials has limited their attempts in refractory industry. The others have also coated the graphite with TiO_2, ZrO_2, and mullite or developed hydrophobic functional groups on the graphite surface [6–11]. However, finding a proper solution for the difficulties results in addition to graphite in refractory castables is still a big challenge for the manufacturers.

In the current study, due to the excellent chemical resistance and refractoriness of $MgAl_2O_4$ spinel at higher temperatures, natural flaky graphite was coated with different amount of $MgAl_2O_4$ spinel and its effect on the water-wettability and the oxidation resistance of graphite was investigated.

2. Experimental procedure

Chinese natural flaky graphite (purity > 96 wt.%, SiO_2 content in ash > 83 wt.%, 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, 30%) all analytic grade were used as starting materials to synthesis $MgAl_2O_4$ spinel.

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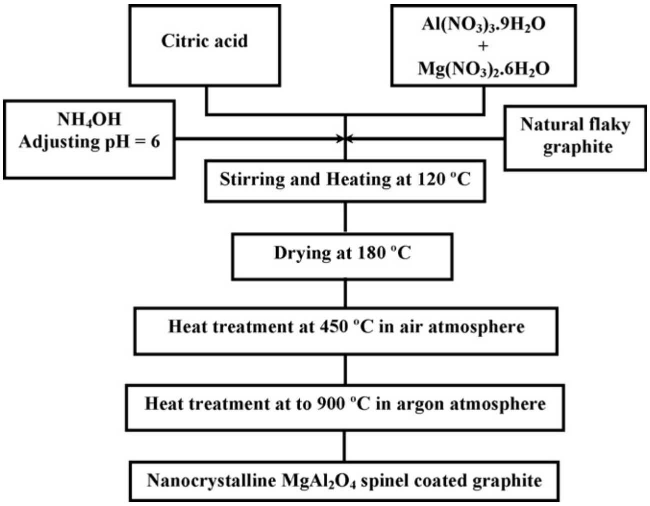

Fig. 1. Flowchart of preparation of $MgAl_2O_4$ spinel coated graphite particles.

The flowchart of coating procedure is demonstrated in Fig. 1. Details of $MgAl_2O_4$ spinel synthesis via citrate–nitrate route were discussed in the previous article [12]. In summary, stoichiometric molar ratio of magnesium and aluminum nitrate [$MgO/Al_2O_3 = 1$] were added in distilled water. Then citric acid with molar ratio [$C_6H_8O_7/NO_3^- = 0.5$] was added to the solution. The solution was agitated using a magnetic stirrer at room temperature for 1 h. The pH of the solution was adjusted to 6 by adding ammonia drop-wisely. As-received graphite was introduced in the prepared sol in order to get different amount of $MgAl_2O_4$ spinel (0.5, 1, 1.5, and 2 wt.%) as coating on the graphite 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.

Differential scanning calorimetry and thermogravimetric analysis (DSC + TG) of natural flaky graphite were carried out with a Netzsch STA-449C with a heating rate of 10 °C/min in static air atmosphere. The phase compositions of samples were studied using a PW-3040 Philips X-ray diffractometer with Cu Kα radiation. The JCPDS cards 08-0415, 21-1152, and 47-0867 were used to identify graphite, $MgAl_2O_4$ spinel, and ammonium nitrate, respectively.

Further, a field emission scanning electron microscope (FE-SEM, LEO®-1530) equipped with energy dispersive spectroscopy (EDS) analyzer and transmission electron microscope (TEM, LIBRA®-200) were used for microstructural observation.

Electrokinetic behavior (zeta-potential) of dispersed powder in water was investigated by an acoustic spectrometer (DT-1200, Dispersion Technology Co., USA).

The quantity measurement of the water-wettability of samples was studied by two different techniques. According to the first technique after Yu et al. [8], 5 g of uncoated and coated samples were put into a graduated cylinder containing 100 ml distilled water. After 30 min the volume of sediment (SV) and the floating ratio (FR) were calculated by Eqs. (1) and (2):

$$\mathrm{SV}\,(\mathrm{cm}^3/\mathrm{g}) = \frac{\text{volume of sediment layer}}{\text{weight of sediment layer}} \tag{1}$$

$$\mathrm{FR}\,(\%) = \frac{\text{weight of floating graphite}}{\text{total weight of graphite}} \times 100 \tag{2}$$

Both SV and FR values depend on water-wettability of graphite powders behavior, so that by improving the water-wettability either of SV and FR show a decline in values [8]. In the second method, the water-wettability of samples was directly estimated by observation of the contact angle of a deionized 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). Before measuring of contact angles, graphite powders were pressed using unidirectional hydraulic press into a cylindrical mould (pressure = 450 MPa).

3. Results and discussion

In order to elucidate the nature of the compound formed on graphite surface, the synthesis of $MgAl_2O_4$ spinel via citrate–nitrate route was carried out without introducing the graphite and keeping all parameters as before. Fig. 2 shows the XRD patterns of synthesized material in different heat treatment conditions along with the precursor. When the material dried up at 180 °C (precursor), it virtually contained ammonium nitrate as crystalline phase while the other phases were amorphous and not detectable by XRD. Decomposition at 450 °C leaves an amorphous product with just a little sign of crystalline $MgAl_2O_4$ spinel (Fig. 2b). Firing at 900 °C, however, promotes the formation of $MgAl_2O_4$ spinel as shown in Fig. 2c.

The surface of coated graphite flakes with 2 wt.% $MgAl_2O_4$ spinel were then observed by FE-SEM as shown in Fig. 3. The graphite body as demonstrated in Fig. 3a is almost completely covered with $MgAl_2O_4$ spinel. At higher magnification (Fig. 3b), it is quite clear that the coating is even but rather

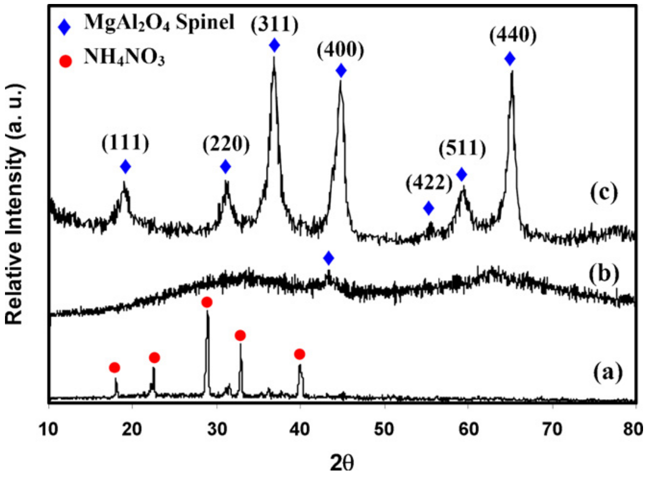

Fig. 2. XRD patterns of precursor (a), and calcined powder at 450 °C in air atmosphere (b), and 900 °C in argon atmosphere (c).

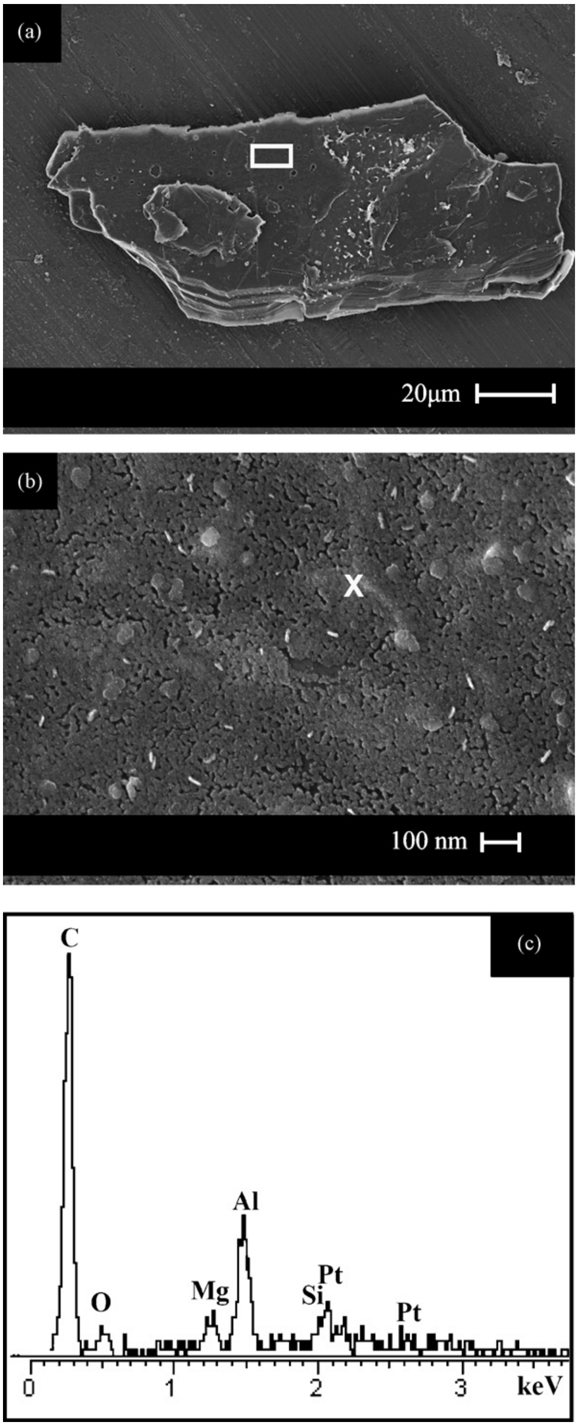

Fig. 3. FE-SEM micrograph of surface of graphite coated with 2 wt.% of spinel (a), microstructure of the coating (b), and EDS analysis of point "×" (c).

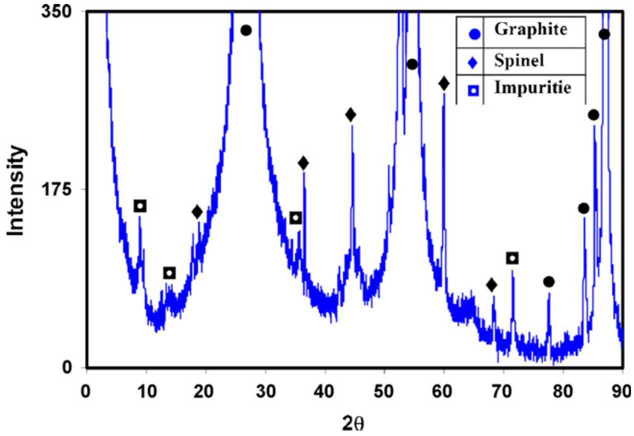

Fig. 4. XRD pattern of the graphite coated with 2 wt.% $MgAl_2O_4$ spinel.

porous. The EDS analysis shown in Fig. 3c clarified that the coating composition consists of Al, Mg, and oxygen. The intensive carbon peak is an indication that the coating is either porous or thin so that the underneath carbon is seen by bombarding electron beam.

A typical XRD pattern of coated graphite with 2 wt.% spinel is shown in Fig. 4. This pattern was prepared by high resolution XRD method where a very slow scanning rate enables the trace structures be detected. This sample as mentioned before was prepared by heat treatment at 900 °C in argon atmosphere. At least three peaks of XRD pattern of $MgAl_2O_4$ spinel, namely (3 1 1), (4 0 0), and (4 4 0) planes can be clarified. Those peaks are well compared to $MgAl_2O_4$ spinel JCPDS card no. 21-1152 as well as the pattern shown in Fig. 2c. There are some unknown peaks which may belong to the impurities of natural graphite and we will refer to them later. The XRD pattern indicated that the coating is not thick enough to weaken the diffracted beam coming out of sample surface.

In order to characterize the coating structure TEM was employed. Fig. 5 illustrates the TEM micrographs of as-received and coated graphite with 2 wt.% $MgAl_2O_4$ spinel. The TEM images also demonstrate that a thin layer of nanocrystalline $MgAl_2O_4$ spinel could cover the surface of graphite flakes (Fig. 5b). The inserted selected area electron diffraction (SAED) patterns in Fig. 5 also prove magnesium aluminate spinel formation on the surface of graphite particle.

Fig. 6 depicts the thermogravimetric curves for coated and uncoated samples. The as-received graphite starts to oxidize below 700 °C with an oxidation rate of 0.066 g/°C. The oxidation of coated graphite samples with 1 and 2 wt.% of spinel begins respectively at about 790 and 850 °C and continuous with a much lower oxidation rate of 0.057 and 0.048 g/°C. The coating postpones and reduces the oxidation of graphite. The oxidation of graphite shows that the coating has not a monolithic and dense structure to stop the oxidation perfectly.

The XRD pattern of remaining part after oxidizing the coated sample at 900 °C for 6 h is demonstrated in Fig. 7. It shows that the main phase in the coating is $MgAl_2O_4$ spinel. Also the impurities left in the formed ash are mainly silica, potassium aluminum silicate, sodium silicate, and potassium silicate. It is interesting to notice that the significant amount of graphite, despite of such a long time oxidation in air atmosphere, has remained in the sample. This is also a good indication that the coating despite of its porous structure has created a anti-oxidation barrier.

The FR as well as SV of coated samples with different amount of $MgAl_2O_4$ spinel as coating in comparison with as-received graphite were also measured (Fig. 8). The coating has

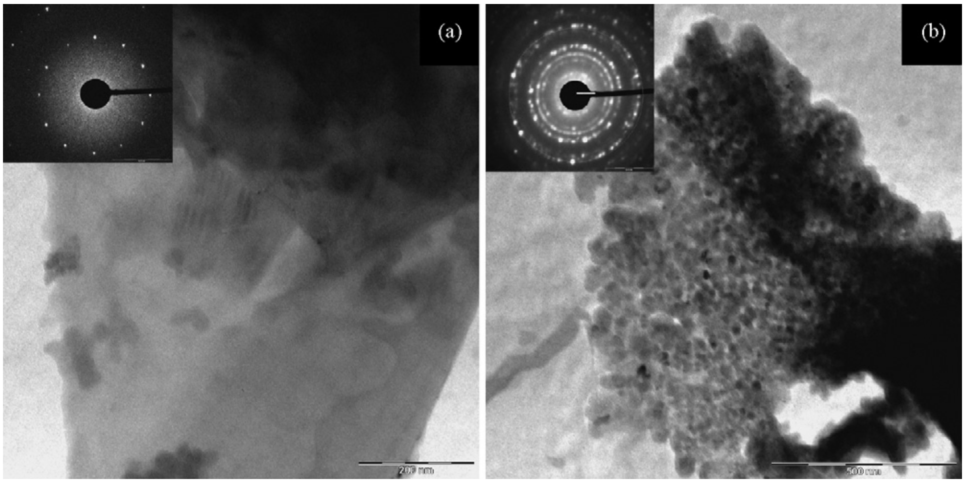

Fig. 5. TEM micrographs and inserted selected area electron diffraction (SAED) patterns of as-received graphite (a), and coated graphite with 2 wt.% $MgAl_2O_4$ spinel (b).

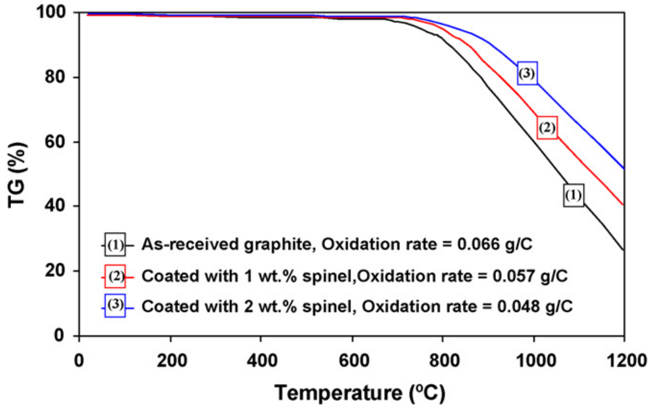

Fig. 6. Oxidation behavior of as-received and coated graphite samples with different amounts of $MgAl_2O_4$ spinel in static air atmosphere.

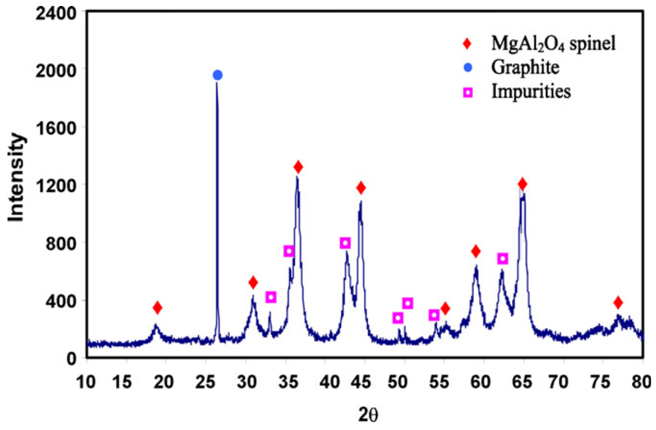

Fig. 7. XRD pattern of the relict part of coated graphite with 2 wt.% spinel after oxidation at 900 °C in air atmosphere.

changed the graphite surface characteristics and created a water-wettable system. The SV is slight decreasing which indicate a better packing of sediment part and less coagulation. This is notable that when coating amount is over 1.5 wt.%, the FR and SV are both without variation.

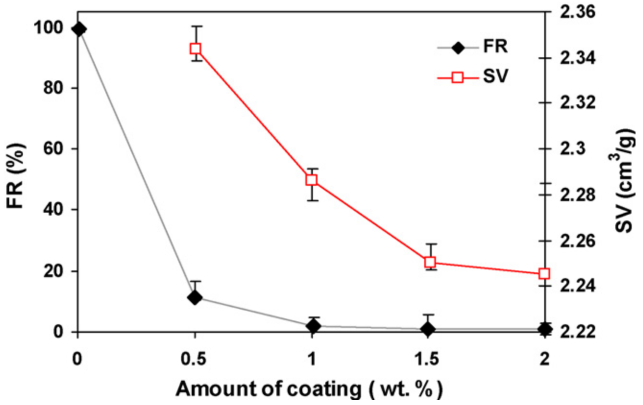

Fig. 8. Variations of FR and SV of graphite with the amount of coating.

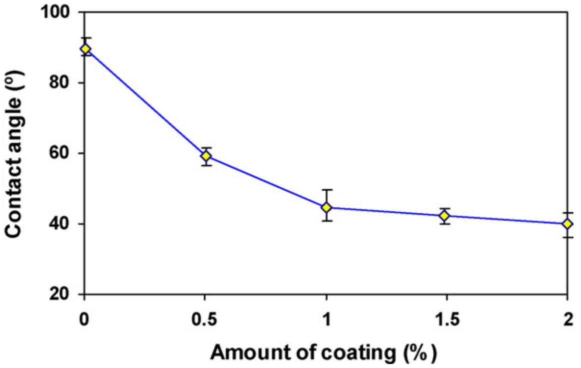

Fig. 9. Variation of contact angles vs. amount of the coating.

Fig. 9 demonstrates the variation of contact angle of water drop on the surface of graphite samples. While the angle for uncoated sample is over 88° for the sample with only 1 wt.% coating declines to about 40°. This measurement is also in accordance with FR measurements.

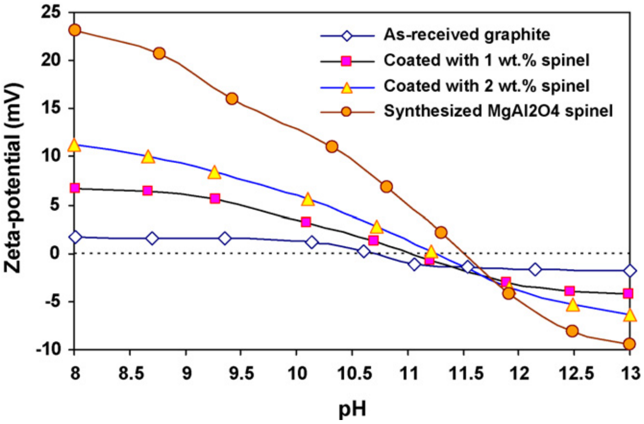

Fig. 10. Zeta-potential of synthesized $MgAl_2O_4$ spinel at 900 °C, as-received, and coated graphite with different amount of $MgAl_2O_4$ spinel in 0.01 M KCl solution (solid portion of suspension = 6 wt.%, particle size < 80 μm).

Electrokinetic behavior of coated and uncoated graphite particles is demonstrated in Fig. 10. The coating changes the graphite electrokinetic properties significantly. By increasing the amount of coating, the isoelectric points (IEPs) of coated samples are shifting towards the synthesized $MgAl_2O_4$ spinel powder.

4. Conclusions

1. An oxide coating was applied on graphite surface through nitrate–citrate route and subsequent heat treatment.
2. The coating structure was characterized by XRD, SEM, and TEM as a porous and nanocrystalline magnesium aluminate ($MgAl_2O_4$) spinel oxide.
3. The surface characteristics of graphite, namely water-wettability and oxidation resistance were altered to an oxide type by coating nature.
4. The water-wettability characteristic and the oxidation behavior of coated graphite particles showed their potential for application in carbon containing refractory castables.

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