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Coating of graphite flakes with MgO/carbon nanocomposite via gas state reaction

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ABSTRACT

Coating of graphite flakes with MgO/carbon nanocomposite was carried out via gaseous state reaction between mixture of Mg metal, CO gas and graphite flakes at 1000 °C. XRD and FE-SEM analysis of coating showed that the coating was comprised of MgO nano particles and amorphous carbon distributed smoothly and covered the graphite surface evenly. Thermodynamic calculations were employed to predict the reaction sequences as well as phase stability. The effect of coating on water wettability and oxidation resistance of graphite was studied using contact angle measurement and TG analysis, respectively. It was demonstrated that the reaction between Mg and CO could result in MgO/C nanocomposite deposition. The coating improved water wettability of graphite and also enhanced the oxidation resistance of graphite flakes significantly. Also the graphite coating showed significant phenolic resin-wettabilty owing to high surface area of such hydrophilic nano composite coating. The importance of graphite coating is explained with emphasis on its potential application in graphite containing refractories.

1. Introduction

Graphite as a source of carbon is widely used in various applications such as refractories and composites due to its low wettability by molten metal/slag and high thermal shock resistance [1–3]. However, poor water wettability as well as low oxidation resistance limits its potentials applications in several fields such as refractory castables [4]. In addition graphite flakes cannot be mixed with organic binders such as phenolic resin properly due to the surface chemistry characteristics. Hence graphite containing bodies in which resin is added essentially as a binder such as MgO/C refractories or graphite anodes suffer from technological problems in terms of production.

Many methods have been applied to improve the oxidation resistance and water wettability of graphite to be dispersed in liquid media [4]. One of the most efficient methods is modifying the surface of graphite with hydrophilic materials like oxides [5]. Zhang and Lee applied pitch on the surface of graphite to overcome these drawbacks [6]. However, the toxic vapors evolved from pitch decomposition create environmental problems. Also regarding the residual semi-crystalline carbon from pitch, a significant improvement in water wettability of pitch coated graphite is not expected. Ono and Ono improved water wettability of graphite by depositing very fine silicon carbide particles on the graphite flakes via a high-speed impact milling [7]. Zhang and Lee studied the effect of Al_2O_3/SiO_2 coating on water wettability of graphite flakes as well [6]. Other researchers employed different coatings such as TiO_2 [8], SiC [2], SiO_2 [9], ZrO_2 [10] and Al_2O_3 [11] to improve surface properties of graphite. In our previous work, $MgAl_2O_4$ spinel coating was prepared via sol–gel citrate process to improve water wettability and oxidation resistance of graphite [12]. These methods, however, suffer from complexity of coating process and high cost of primary materials. Superior properties of nano structure coatings which present higher specific surface in contact with water molecules have attracted considerable attention in promoting nanocoating on the surface of graphite. Therefore controlling the common method is crucial to promote some nano structure coating on the surface of graphite. Meanwhile some methods such as sol–gel are complicated to be controlled in terms of preparing nanocoating because the slightest deviations results in irreversible consequences. In this paper we introduce a novel method by which a nanocomposite of MgO/carbon coating is applied on flaky graphite particles. In this regard Mg powder exposed to CO gas state and precipitates as a nanocomposite of MgO/carbon on the surface of graphite. Simultaneous precipitation of carbon beside MgO in the coating hinders grain growth and agglomeration of MgO particles at 1000 °C presenting a well distributed nanocomposite as a coating on the graphite flakes.

2. Experimental procedure

Chinese natural graphite flakes (particle size: 150–500 μm, purity >97%, SiO_2 content in ash >80%) and Mg metal powder (150–300 μm, purity >98%) were used

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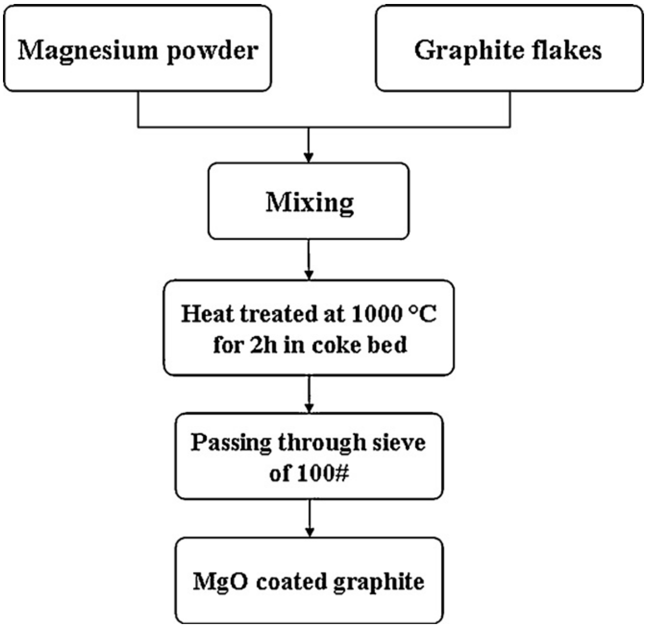

Fig. 1. Flowchart of experimental procedure of MgO/C coating on graphite.

as the starting materials. A homogenous mixture of magnesium powder and graphite flakes by the weight ratio of 1:1 was heat treated in an alumina crucible at 1000 °C for 2 h in a coke bed. The flowchart of procedure is shown in Fig. 1. The phase composition and microstructure of coated graphite was characterized by Philips X-ray diffractometer (with Cu Kα radiation) and FE-SEM model LEO-1530, respectively. Wettability of coated graphite was determined by measuring the contact angle between the graphite pellets (with thickness of 3 mm and diameter of 12 mm) and a drop of water on its surface. Thermogravimetric analysis of natural and coated graphite was also carried out with a Netzsch STA-449C with heating rate of 10 °C/min in static air atmosphere.

3. Results and discussion

XRD pattern of coated graphite is shown in Fig. 2. All peaks in this pattern are attributed to graphite and MgO phases. No residual magnesium metal phase was detected in this pattern. The high intensity of graphite peak in XRD pattern is due to the preferred orientation of (0 0 2) crystallographic planes of graphite flakes which results in high reflection of graphite in this direction. Formation of MgO could be explained by the reaction of magnesium with carbon monoxide (CO originated from the reaction of carbon and oxygen in the coke bed at 1000 °C) at the surface of graphite. In fact because of high partial pressure of $Mg_{(g)}$ over $Mg_{(l)}$ at 1000 °C, $Mg_{(g)}$ could react with CO gas according to reaction (1), resulting in the precipitation of MgO and carbon on the surface of graphite flakes.

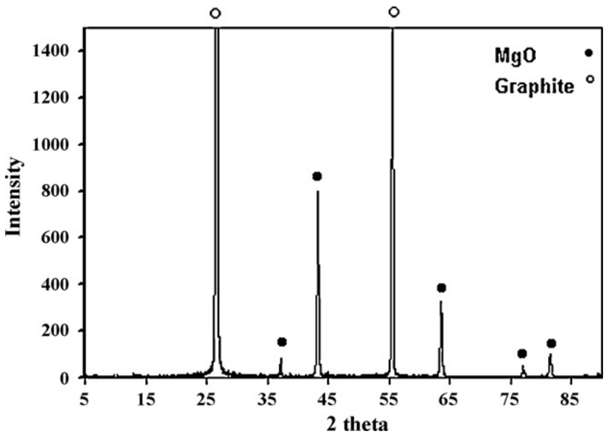

Fig. 2. XRD pattern of the coated graphite surface.

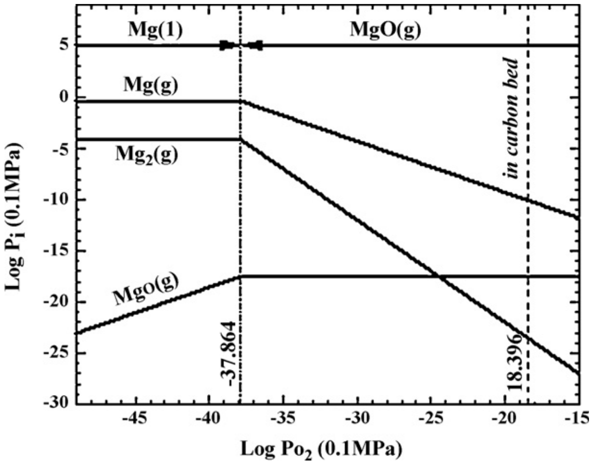

Fig. 3. Equilibrium partial pressure of components in MgO system at 1000 °C.

$$Mg_{(g)} + CO_{(g)} \rightarrow MgO_{(s)}\downarrow + C_{(s)}\downarrow \quad (1)$$

In order to complete above discussion and study the status of Mg and MgO phases under defined conditions, thermodynamic approach was employed.

Fig. 3 illustrates equilibrium partial pressure of gaseous species in MgO system at 1000 °C. High partial pressure of $Mg_{(g)}$ over $Mg_{(l)}$ facilitates easy evaporation of Mg at such elevated temperature. On the other hand the equilibrium partial pressure of oxygen in carbon bed at this temperature (about 10^{-18} bar) is located in MgO stability region. Therefore since partial pressure of $Mg_{(g)}$ over $Mg_{(l)}$ is much more than equilibrium partial pressure of $Mg_{(g)}$ over $MgO_{(s)}$ in carbon bed, consolidation of $Mg_{(g)}$ to $MgO_{(s)}$ is occurred according to reaction (1) leading to the formation of MgO/C composite coating on the surface of graphite flakes. Also at Mg/MgO interface the partial pressure of oxygen is at its minimum value ($PO_2 \approx 10^{-37.864}$ 0.1 MPa) and therefore during consolidation of $Mg_{(g)}$ to $MgO_{(s)}$ the partial pressure of oxygen is too low on the surface of graphite. Accordingly the reaction between Mg and CO is the dominant reaction on the surface of graphite flakes which ends up in the formation of MgO/C nanocomposite coating.

FE-SEM micrographs of as received and coated graphite flakes are presented in Fig. 4. A graphite flake with a smooth surface is indicated in Fig. 4a. In Fig. 4b a typical coated surface is shown illustrating a texture containing MgO particles as nano sized islands on the surface of graphite. Higher magnification images (Fig. 4c) showed that the coating is comprised of MgO cubic particles and amorphous carbon phase which is shown as a dark shadow on MgO particles. Carbon (green arrows in Fig. 4c) and magnesium oxide (yellow arrows in Fig. 4c) in this nano composite coating is formed alongside each other with undistinguishable interface according to Fig. 4c and EDX analysis taken from random points of coated surface. (For interpretation of the references to color in text, the reader is referred to the web version of the article.) Therefore it can be stated that precipitation of carbon between MgO nano particles (according to reaction (1)) has created a composite coating structure. The EDS analysis of coating proved that the coating is contained of Mg, O and carbon constituents.

Considering coating conditions, a proper physical–chemical bonding can be assumed between graphite and the first layer of composite precipitated from vapor phase at 1000 °C. However, we applied an experimental procedure to understand the strength of bonding between coating and graphite using ultrasonication waves. The coated graphite was exposed to ultrasonic waves of

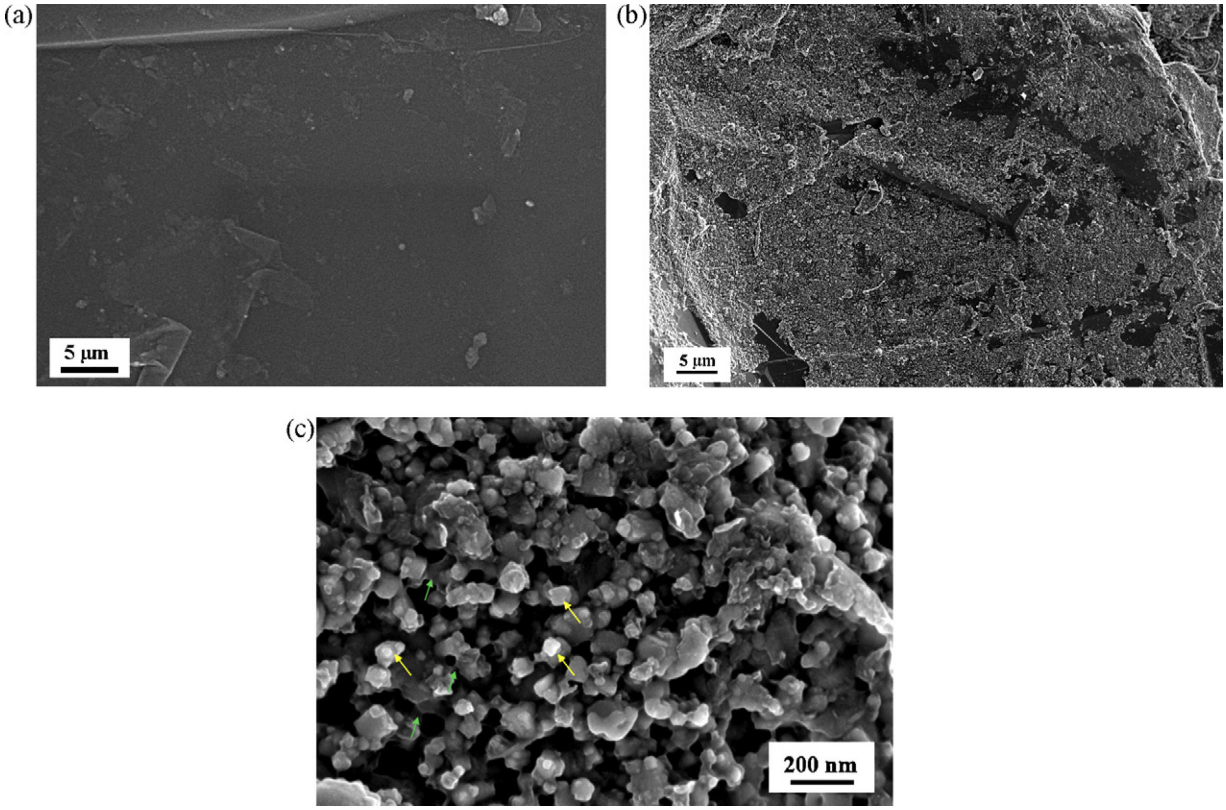

Fig. 4. SEM micrographs of (a) as received and (b and c) coated surface in different magnifications.

400 W power for 10 min and then thermal analysis was carried out for the obtained sample. No significant difference in weight loss before and after exposure to ultrasonic waves proved the proper bonding of the coating and graphite as the substrate. In addition we believed that during the coating process the chemical reaction took place between carbon atoms of the outer surface of graphite and the reactant which may involved with the oxygen atom present at the outer layer of the graphite. Hence the present method of coating has the advantage of better bonding with the substrate in comparison to the other common methods such as sol–gel and precipitation.

In order to evaluate the effect of coating on water wettability of graphite, contact angle between a drop of water and surface of the graphite flakes was measured in 7 min after setting a drop on the surface of samples (Fig. 5). In case of the uncoated graphite the contact angle was measured about 80° and could be assumed to be constant during the test period. However, in case of coated graphite the contact angle decreased to below 40° and reached to almost zero after 6 min. The appreciable decrease of contact angle means the coated surface in converse comparison to primary graphite has a hydrophilic nature and water can wet the surfaces easily. Improvement of water wettability is mainly attributed to the oxide characteristic of the coated graphite surface facilitating its application in castable and concretes refractories [4].

The oxidation behavior of samples was compared by recording the weight losses under flowing air in a TG (thermogravimetery) apparatus (Fig. 6). TG curve of as received graphite shows that the oxidation commences at around 700 °C and the whole sample burns out by 1050 °C while the coated graphite starts to lose the weight at 800 °C with a significantly slower rate. In this case the sample was burned out completely at 1300 °C. This experiment shows that the oxide coating developed on graphite discourages the oxidation. Probably oxidation of graphite and formation of several atomic lay-

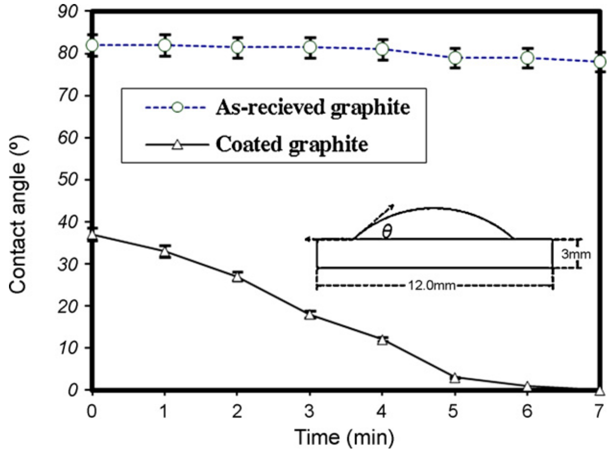

Fig. 5. The contact angle of θ vs. time for as received and coated graphite.

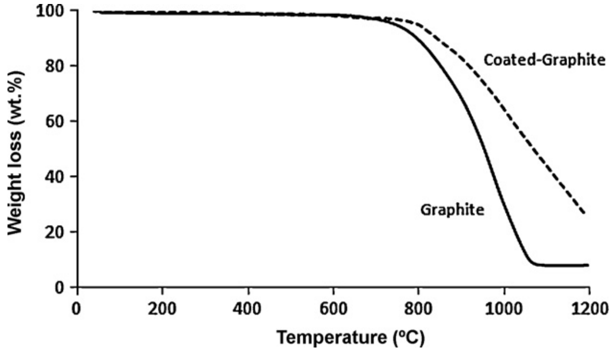

Fig. 6. Weight loss vs. temperature for as received and coated samples.

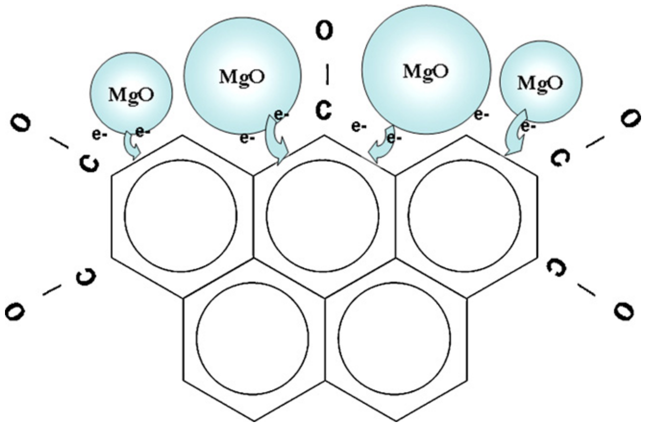

Fig. 7. Schematic image of electron donor effect of MgO on the surface of graphite.

ers of GO in the surface could lead to the formation of appropriate chemical bonding with the first layers of coating. SEM micrographs show that there is a strong bonding between the substrate and coating due to smooth and crack-free coating on graphite.

The improvement of oxidation resistance of graphite coated with MgO seems to have been improved based on two mechanisms realized by two mechanisms. First, the presence of MgO nano particles in coating could protect the graphite surface from oxygen attack as a barrier and thus prevent the surface oxidation. On the other hand MgO could inhibit oxygen and carbon reaction forming C═O bonding). It can also be attributed to the inhibiting effect of MgO on the reaction of oxygen and carbon to form C═O bonding.

As reported by Yamaguchi and Zhang, MgO as an electron donor can stabilize the absorbed oxygen on the surface of graphite resulting in the formation of G–O bonding on the surface of graphite and therefore hindering the formation of CO gas and oxidation of graphite [13]. Fig. 7 illustrates schematically the electron donor effect of MgO and stabilizing oxygen groups on the surface of graphite schematically.

4. Conclusion

The conclusions obtained in this work can be summarized as follow:

1. The flake graphite surface was coated via a simple method using gaseous reaction of Mg and CO at 1000 °C in a coke bed of primary mixture of magnesium powder and graphite flakes.
2. The coating comprised of MgO particles in range of nanometer and traces of amorphous carbon.
3. The coating improved the water wettability and oxidation resistance of graphite significantly. These improvements were granted by establishing an electron donor regions to the surface of graphite.

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