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Improvement of oxidation resistance in graphite for MgO-C refractory through surface modification

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Abstract: Graphite, used as a carbon source in a conventional magnesia–carbon (MgO–C) refractory, was modified with an acid reagent, resulting in a negative charge on the surface of graphite, to enhance the coating efficiency of aluminum (Al) phase, which was compared to the pristine graphite through its dispersibity and oxidation behavior. The graphite particles with and without surface modification were added, respecticely, in an Al(NO₃)₃ suspension used as a coating reagent, and then filtered at room temperature. The modified graphite shows better disperbility than the pristine graphite, indicating that the coating efficiency of Al precursor is enhanced in the modified graphite. With respect to oxidation behavior, the modified graphite without the coating layer is totally reacted with oxygen at heat treatment of 900 °C in air. However, the Al-coated graphite starts to react with oxygen at heat treatment of 900 °C and fully reacted with oxygen at heat treatment of 1000 °C, showing the gray and white colors, respectively. It is verified that the Al layer is individually and uniformly formed on the surface of graphite and the oxidation resistance of graphite is enhanced owing to the increased coating efficiency of Al precursor.

Key words: refractory; graphite; surface modification; aluminum; coating

1 Introduction

Magnesia-carbon (MgO-C)refractory is extensively used in basic furnance, electric arc furnance, and steel ladles for its many desirable properties, such as the corrosion resistance by less wettability with a molten metal and the excellent thermal shock resistance by its low thermal expansion, high thermal conductivity, and low elasticity, due to the presence of graphite used as a carbon source [1, 2]. However, the mechanical and thermal properties of the MgO-C are continuously deteriorated owing to the spalling phenomena and pore generation by the oxidiation of graphite. Therefore, antioxidants having a notably reactivity with oxygen are requisitely added into the MgO-C batches during fabrication to impede the oxidation of graphite [3, 4]. Academically, almost graphite must not react with oxygen until the oxidation of antioxidant is considerably progressed. However, pore generation at inner site of MgO–C refractory is unavoidable phenomenon because antioxidant can't effectively obstruct the oxidation of graphite in real environments and has disadvantages, such as volume expansion, limited content, and high cost.

Therefore, in previous work, graphite was coated with the coating reagent of metal precursor, especially aluminum (Al) precursor, to adequately obstruct the approach of oxygen to graphite [5]. In the MgO–C refractory prepared with the Al-coated graphite, the reaction between graphite and oxygen was interrupted by the barrier effect of Al layer formed on the surface of graphite. In the coating process, the coating reagent

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should be homogeneously coated on the surface of graphite to get the sufficient coating effect [6]. Four key points should be considered for the preparation of graphite with a high coating efficiency: 1) the coating process of a metal precursor onto graphite is performed in an aqueous solution to increase the dispersibility of metal precursor on the surface of graphite [7,8]; 2) the surface of graphite is purified and modified with an acid to give the hydrophilic group to the surface of graphite; 3) the metal precursor having a high solubility with water is used to improve the coating efficiency; and 4) metal with a high reactivity with oxygen is selected.

In this work, to enhance the coating efficiency of Al precursor onto graphite, the surface of graphite was modified with an acid reagent [9]. The coating efficiency of Al precursor on the surface of graphites with and without modification was investigated through its dispersibility, and the oxidation behaivor of the Al-coated graphite with modification was discussed based on its microstructure and phase analysis after combustion tests.

2 Experimental

The aluminum nitrate (Al(NO₃)₃) (3 mol/L, Sigma-Aldrich Korea, Yongin, Korea) was used as a metal precursor [10]. Platy graphite, usually used in the commercial MgO-C refractory, was suspended into the mixture of the sulfuric and nitric acids (3:1, volume ratio) used as a modification reagent for the surface of graphite. The mixture was sonicated for 3 h and stirred for 24 h. After stirring, the acid-treated graphite was filtered and washed with a distilled water until pH=7, and then graphite was dried at 80 °C for 48 h. The process for preparing the Al-coated graphite is shown in Fig. 1. Firstly, Al(NO₃)₃ was dissolved in an aqueous solution. The graphite particles modified by the acid were mixed with the Al(NO₃)₃ solution, and then stirred at room temperature for 1 h. The graphite coated with Al precursor was filtered, and then dried at 80 °C for 1 h. The prepared powder was pre-heat treated at 300 °C for 1 h under H₂ atmosphere to increase the adhesion of Al precursor onto the surface of graphite.

The combustion tests for the modified graphite particles before and after coating with Al precursor were conducted in a range of 500–1000 °C for 1 h. The microstructure observation and elemental analysis for the particles were performed using a scanning electron microscope (SEM; Model JSM-5610; JEOL, Tokyo, Japan) and an energy dispersive X-ray spectrometer (EDS; energy resolution 133 eV; Oxford Inst., Oxford, UK), respectively. The phase analysis after combustion tests was performed using an X-ray diffractometer (Model PW 3040, Philips X-pert MPD, Eindhoven, Netherlands).



Fig. 1 Schematic diagram for fabricating Al-coated graphite through acid treatment

3 Results and discussion

3.1 Dispersion of graphite and coating of Al phase

To obstruct effectively the oxidation of graphite in the MgO-C refractory, the Al precursor should be uniformly and homogeneously coated on the surface of graphite and the coating efficiency of Al precursor should be enhanced [11,12]. Therefore, the surface of graphite was modified by the acid to provide the hydroxyl group of anion on the surface of graphite. To confirm the effect of surface modification, the graphite particles without and with modification were dispersed in an aqueous solution, including the Al-coated graphite particles [13]. The stability of the graphite without and with surface modification is shown in Fig. 2. After acid treatment, the surface modified graphite is well dispersed in the water without any aggregation after 3 d (Fig. $2(b_1)$), probably meaning that the hydroxyl group with a negative charge is generated on the surface of graphite by the acid [14]. However, the pristine graphite is precipitated within a few minutes (Fig. $2(a_1)$). The pristine graphite coated with Al precursor is more quickly precipitated than the modified graphite coated with Al precursor in a short period (Figs. $2(a_2)$ and (b_2)), and then the modified graphite particles coated with Al precursor is again precipitated as time passes (Fig. $2(b_3)$) owing to the disappearance of charge by the reaction between the graphite with anion and the Al precursor with cation. It indicates that Al precursor is well coated on the surface of graphite. Namely, the adhesion of Al precursor onto graphite is driven by the attractive force



Fig. 2 Photographs showing dispersibility of graphite particles (Numbers 1, 2 and 3 indicate the graphite particles without coating layer, with coating layer after 3 min and 3 d, respectively): (a_1-a_3) Pristine graphite; (b_1-b_3) Modified graphite.

between counter ions, which affects the dispersion of hetero-phase [15]. The mass gain for the surface modified graphite is larger than that for the pristine graphite in the coating of Al precursor, showing 1.5% and 1.9% (mass fraction) based on Al element, respectively. It is confirmed that the surface modification for graphite increases the coating efficiency of Al precursor. Therefore, it is desirable for following experimental to work with the surface modified graphite.

The results of microstructure and element analysis for the surface modified graphite particles without and with the coating layer are shown in Fig. 3, as a function of heat treatment. In the graphite without the coating layer, only O and C elements are detected (Fig. $3(a_1)$). In Fig. $3(b_1)$, Al element is evenly detected on the surface of graphite. However, the Al layer can't be distinctly distinguished, because the coated Al layer is an amorphous phase after pre-heat treatment at 300 °C. After heat treatment at 1000 °C, the polygonal Al₂O₃ particles converted from the amorphous Al layer are completely covered on the surface of graphite, as shown in Fig. $3(b_2)$, assuming that the Al precursor is uniformly coated on the surface of graphite. After heat treatment at 1000 °C, the graphite particles without and with the coating layer show the different aspects. Various impurities are detected for the graphite without the coating layer (Fig. $3(a_2)$), indicating that the graphite without the coating layer is easily decomposed. However, in the graphite with the coating layer, only Al, O and C elements are detected with increasing Al and O elements and decreasing C element after heat treatment. Therefore, it can be inferred that the oxidation of graphite will be suppressed by the Al layer formed on the surface, making the oxygen barrier layer.

3.2 Oxidation behavior

Photographs after combustion tests for the modified

graphite particles without and with the coating layer are shown in Fig. 4. In the case of the graphite coated with Al precursor, firstly the pre-heat treatment is progressed at 300 °C. As the temperature increases in combustion test, the graphite without the coating layer is decomposed and oxidized as shown in Fig. 4(a), showing the gray and brown colors at 700 and 900 °C, respectively. Actually, the graphite without the coating layer starts to react with oxygen at 700 °C, and fully reacts at 900 °C. However, when the graphite was coated with Al precursor as shown in Fig. 4(b), the graphite shows a sound condition in combustion test at 700 °C, and starts to react with oxygen at 900 °C. Finally, the Al-coated graphite, actually the coating layer, fully reacts with oxygen at 1000 °C, showing a white color. It means that the coating layer (Al precursor layer) has a valuable effect as antioxidant owing to the continuous and homogeneous coating onto the surface of graphite, delaying the oxidation of graphite. The mass loss of the Al-coated graphite is below 10% (mass fraction) after combustion test at 1000 °C. Therefore, it can be said that the coating process can enhance the oxidation resistance of graphite even though the mass gain by the oxidation of coating layer is considered.

3.3 Phase analysis

XRD results for the modified graphites without and with the coating layer are shown in Fig. 5, as a function of heat temperature. The graphite peaks are detected in the graphite without the coating layer before heat treatment, which nearly disappears after heat treatment at 1000 °C. However, the graphite peaks are clearly detected till heat treatment at 900 °C for the graphite with the coating layer. The alumina (Al₂O₃) and graphite peaks coexist after heat treatment at 1000 °C, with some amorphous peaks, indicating that the graphite is decomposed and the coating layer is not fully crystallized.

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Fig. 3 SEM morphologies and results of EDS analysis for modified graphite particles (Numbers 1 and 2 indicate before and after heat treatments at 1000 °C for 1 h): (a_1, a_2) Without coating layer; (b_1, b_2) With coating layer



Fig. 4 Photographs of modified graphite particles (Numbers 1 to 4 indicate the modified graphite particles after combustion test at 500, 700, 900, and 1000 °C, respectively): (a_1-a_4) Without coating layer; (b_1-b_4) With coating layer



Fig. 5 XRD results of modified graphite particles without and with coating layer: (a) Modified graphite without coating layer before heat treatment; (b) Modified graphite without coating layer after heat treatment at 1000 °C for 1 h; (c) Modified graphite with coating layer after heat treatment at 500, 700 and 900 °C, respectively; (d) Modified graphite with coating layer after heat treatment at 1000 and 1200 °C, respectively

Finally, the Al-coated graphite is fully transformed to Al_2O_3 at 1200 °C. The results are well consistent with the results of combustion tests. As results of phase analysis, it is verified that the oxidation resistance of graphite can be enhanced by the coating of Al precursor. In this work, the methodology for increasing the coating efficiency of Al precursor onto the surface of graphite has been proposed. However, lots of works, such as effects of metal precursor species and pre-heat treatment temperature on the thermomechanical properties of the MgO–C refractory, are still remained to optimize the coating process of metal precursor for applying the graphite to the MgO–C refractory, including coating morphology on the surface of graphite with an acid treatment.

4 Conclusions

Graphite was modified with acid treatment to enhance the coating efficiency of Al precursor. The surface modified graphite shows better dispersibility than the pristine graphite. The modified graphite particles coated with Al precursor are precipitated as time passes, owing to the disappearance of charge by the reaction between the graphite with anion and the Al precursor with cation. It is verified that Al precursor is well coated on the surface of graphite. The evidence for coating of Al precursor can be observed in the results of microstructure and element analysis. The surface modification for graphite increases the coating efficiency of Al precursor onto the surface of graphite, showing mass gains of 1.5% and 1.9% (mass fraction) in the graphite without and with surface modification, respectively. The pristine graphite starts to reacts with oxygen in combustion test at 700 °C, and then fully reacts at 900 °C. However, the Al-coated graphite shows a sound condition in combustion test at 700 °C, and starts to react with oxygen at 900 °C. The Al-coated graphite is retained in combustion test of 1000 °C, even though the color is changed to white. These results mean that the coating layer is homogeneously and continuously coats on the surface of graphite, delaying the oxidation of graphite. In addition, the graphite phase in the Al-coated graphite is detected till 900 °C, and the Al₂O₃ and graphite peaks

coexist at 1000 °C. Finally, the Al-coated graphite is fully transformed to Al_2O_3 at 1200 °C. Consequently, the Al-coated graphite with a high oxidation resistance is successfully prepared with the surface modification of graphite, and the Al-coated graphite developed in this work will enhance the oxidation resistance of MgO–C refractory.

References

- ZHANG S, LEE W E. Influence of additives on corrosion resistance and corroded microstructures of MgO–C refractories [J]. Journal of the European Ceramic Society, 2001, 21: 2393–2405.
- [2] HASHEMI B, NEMATI Z A, FAGHIHI-SANI M A. Effects of resin and graphite content on density and oxidation behavior of MgO-C refractory bricks [J]. Ceramics International, 2006, 32(3): 313–319.
- [3] ZHANG S, MARRIOTT N J, LEE W E. Thermochemistry and microstructures of MgO-C refractories containing various antioxidants [J]. Journal of the European Ceramic Society, 2001, 21: 1037–1047.
- [4] SADRNEZHAAD S K, MAHSHID S, ASHEMI B H, NEMATI Z A. Oxidation mechanism of C in MgO–C refractory bricks [J]. Journal of the American Ceramic Society, 2006, 89: 1308–1316.
- [5] KIM E H, JO G H, LIM H T, BYEUN Y K, JUNG Y G. Development of MgO–C refractory having high oxidation resistance by metal coating process [J]. Journal of Nanoscience and Nanotechnology (In-press).
- [6] BUTTRY D A, ANSON F C. New strategies for electrocatalysis at polymer-coated electrodes reducton of dioxygen by cobalt porphyrins iImmobilized in nafion coatings on graphite electrodes [J]. Journal of the American Society, 1984, 106(1): 59–64.
- [7] KIM E H, LEE D, PAIK U G, JUNG Y G. Size effect in Ni-coated

TiC particles for metal matrix composites [J]. Journal of Nanoscience and Nanotechnology, 2011, 11: 1746–1749

- [8] KIM E H, LEE J H, JUNG Y G, LEE C G, LEE M K, PARK J J. Preparation of Ni-coated TiC particles using potential hydrogen (pH) for dispersion into a molten metal [J]. Progress in Organic Coatings, 2011, 70: 310–317.
- [9] PANDEY P C, UPADHYAY S U, SHUKLA N K, SHARMA S. Studies on the electrochemical performance of glucose biosensor based on ferrocene encapsulated ORMOSIL and glucose oxidase modified graphite paste electrode [J]. Biosensors and Bioelectronics, 2003, 18: 1257–1268.
- [10] HOU C H, LIANG C, YIACOUMI S, DAI S, TSOURIS C. Electrosorption capacitance of nanostructured carbon-based materials [J]. Journal of Colloid and Interface Science, 2006, 302: 54–61.
- [11] LIU X G, QU Z Q, GENG D Y, HAN Z, JIANG J J, LIU W, ZHANG Z D. Influence of a graphite shell on the thermal and electromagnetic characteristics of FeNi nanoparticles [J]. Carbon, 2010, 48: 891–897.
- [12] WANG Z, LIU J, LIANQ Q, WANG Y, LUO G. Carbon nanotubemodified electrodes for the simultaneous determination of doamine and ascorbic acid [J]. Analyst, 2002, 127: 653–658.
- [13] KNOX J H, WAN Q H. Chiral chromatography of amino- and hydroxy-acids on surface modified porous graphite [J]. Chromatographia, 1995, 40: 9–14.
- [14] ABIMAN P, CROSSLEY A, WILDGOOSE G G, JONES J H, COMPTON R G. Investigating the thermodynamic causes behind the anomalously large shifts in pKa values of benzoic acid-modified graphite and glassy carbon surfaces [J]. Langmuir, 2007, 23: 7847–7852.
- [15] KIM E H, JUNG Y G, PAIK U G. Microstructure and mechanical properties of Al₂O₃ composites with surface-treated carbon nanotubes (CNTs): Dispersibility of modified carbon nanotubes (CNTs) on Al₂O₃ matrix [J]. Journal of Nanoscience and Nanotechnology, 2012, 12: 1332–1336.

石墨表面改性对 MgO-C 耐火材料抗氧化性能的改善

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摘 要: 石墨常作为传统 MgO-C 耐火材料的碳源。石墨在经酸化剂改性后,可在表面产生负电荷,从而增强铝相的涂覆率。从弥散度和氧化性能方面对改性后的石墨与天然石墨进行了比较。首先,将经过和未经过表面改性的石墨颗粒分别添加至酸化剂 Al(NO₃)₃ 悬浮液中,并在室温下过滤,得到改性后的石墨。试验表明:改性后的石墨较天然石墨具有更好的弥散性,其 Al 相涂覆率得到了增强。在氧化性能方面,优化后的石墨没有 Al 涂层时, 霍 900 ℃ 热处理时与空气充分氧化;而有 Al 涂层时,则在 900 ℃ 时开始氧化,在 1000 ℃ 时充分氧化,并分别变为灰色和白色。可见,由于 Al 涂层在石墨表面均匀覆盖,Al 相涂覆率的提高增强了石墨的抗氧化性能。 关键词:耐火材料;石墨;表面改性;铝;涂层