

Increased surface area of flake graphite by chemical and mechanical treatments

Young-Hwan Kim^a and Sung-Churl Choi^{a,*}

Division of Materials Science & Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Recently, carbon-containing refractories have demonstrated good properties of corrosion and thermal shock resistance, and have become major resources in the steel industry. On the other hand, carbon-containing refractories had some problems in terms of high temperature oxidation and high heat conductivity. To maintain these advantages and solve the problems, it is necessary to increase the carbon surface area. In this paper, flake graphite was laminated in order to increase specific surface area. Flake graphite was evaluated as a raw material. The flake graphite was immersed in diluted acidic solution to form GICs (graphite intercalated compounds), which are inserted into the gap of the graphite layer. After acid treatment, for lamination of the graphite layer, dried GICs were ball-milled. Rod-shaped media could help to reduce the crushing effect and increase the lamination effect during the milling process.

Key words: Refractories, Flake Graphite, Acidic treatment, Graphite Refractories.

Introduction

Flake graphite has some advantages, such as poor wettability with slags, low thermal expansion coefficient and low elastic modulus. [1] In particular, flake graphite can increase heat transfer on the inside of refractories due to its high thermal conductivity. Consequently, graphite-containing refractories have excellent thermal shock resistance. [2, 3] Because of these good thermal and mechanical properties, flake graphite has been used as an additive in oxide refractories. [4-6] Recently, many researchers have studied methods for improving thermal and mechanical properties of graphite-containing refractories. [7-9]

In spite of these advantages, increasing flake graphite content in refractories has some disadvantages. For example, flake graphite is considerably oxidized at 600-700°C and causes porous structure within refractories, leading to erosion. Furthermore, the high thermal conductivity of flake graphite, which provides beneficial thermal shock resistance to refractories, [10] can also lead to heat loss. Eventually, high energy loss by flake graphite increases electricity consumption and refining time in steel-making industries. [11, 12]

Accordingly, it is necessary to reduce flake graphite content in refractories while maintaining their excellent corrosion and thermal shock resistance. For this reason, facile methods for increasing flake graphite surface area are required, as higher surface can improve the thermal shock resistance of refractories. [9, 13-15] Consequently, increasing the surface area of flake graphite can maintain its good

properties and provide similar performance in refractories despite an overall reduction in graphite content.

Thus, in order to increase graphite surface area, we studied mechanical and chemical treatments for flake graphite. To reduce the interlayer bonding strength of flake graphite, GICs (graphite intercalated compounds), which have been used in the manufacture of expanded graphite, were produced by a chemical treatment process, and a mechanical milling process was used to thin the flake graphite.

Experimental Procedure

The starting material was flake graphite (Quingdao Eternal, China, 99% pure), which is typically used in Al₂O₃-C and MgO-C refractories. In this experiment, we applied a solution-based process which has been used to produce expanded graphite. In order to form GICs, a mixture of diluted nitric acid (Junsei Chemical, Mw : 63.02) and sulfuric acid (Junsei Chemical, Mw : 98.08) was prepared (HNO₃ : H₂SO₄ = 4 : 1, volume ratio) and mixed with the flake graphite for 24 hours. The acid-treated flake graphite was rinsed with DI water to remove the residual acid and dried at a room temperature for 24 hours. The GICs, which were produced via chemical treatment, were ball-milled in water for 9 hours. During wet ball-milling, rod-shaped alumina media was used because it is able to shear the layers of the flake graphite.

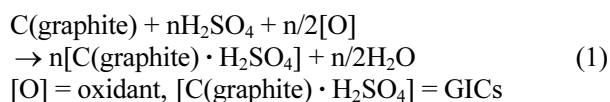
Microstructure images of graphite were acquired using scanning electron microscopy (SEM, JEOL, JSM-6490, Japan). Each sample was mounted using epoxy resin in order to observe cross-sectional images. Likewise, X-ray diffraction (XRD, Ultima IV, Rigaku, Japan, $\lambda_{\text{CuK}\alpha} = 1.54178 \text{ \AA}$) was used to determine the structural properties of graphite. The interlayer distances

*Corresponding author:
Tel : +82-2-2220-0505
Fax : +82-2-2291-6767
E-mail: choi0505@hanyang.ac.kr

(c-axis distance) of flake graphite, GICs and milled GICs were calculated using Bragg's law.

Results and Discussion

Flake graphite can be used to form GICs, which have been used to manufacture expanded graphite, by inserting appropriate intercalants (atoms or molecules) between carbon layers. The chemical reaction of flake graphite with intercalants is shown below.



The GICs, which were formed through reaction (1), consist of carbon layers and intercalant layers overlapped in a periodic structure, such as -C-C-I-C-C-I-C-C- (C : carbon layer, I : intercalant layer). [16] Thus, it was assumed that carbon layers including an intercalant layer have longer interlayer distance compared with other carbon layers. The existence of intercalants in GICs is difficult to determine by SEM. Therefore, to confirm the existence of intercalants in layers, structural properties of GICs were measured by XRD (Fig. 1). If interlayer distance of GICs was greater than that of commercial flake graphite, the existence of intercalants was assumed.

As shown XRD patterns, the (002) peak (c-axis peak, $2\theta = 26.45^\circ$) of GICs was broadened and shifted left compared to the flake graphite peak (Fig. 1(b), Fig. 1(d)). These phenomena indicate that the crystallizability of carbon layers was decreased by insertion of intercalants. In other words, intercalants existed between carbon layers. Moreover, the XRD pattern of the milled GICs was similar to that of the unmilled GICs (Fig. 1(c)). Using XRD pattern data and Bragg's law, calculated interlayer distances of flake graphite, GICs and milled GICs were obtained as 3.367, 3.373 and 3.372 Å, respectively.

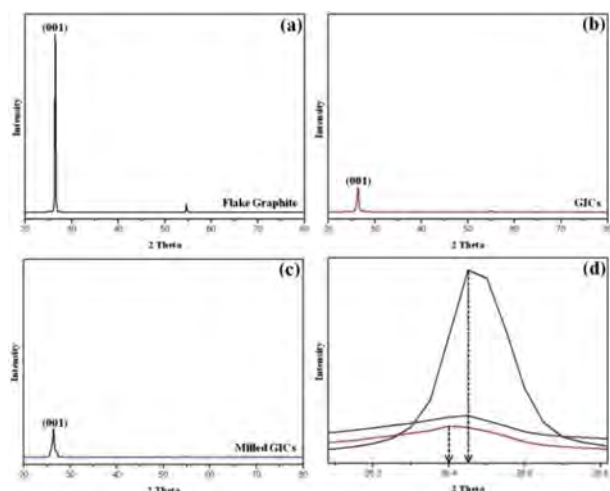


Fig. 1. XRD patterns of flake graphite, GICs and milled GICs.

Flake graphite has a plate-like structure which is composed of stacked carbon layers, as shown in Fig. 2(a). The small picture of Fig. 2(a) shows the cross-sectional SEM image of flake graphite, with an average length of 277 μm and an average thickness of 30 μm. Likewise, the average length and thickness of GICs and milled GICs were measured by cross-sectional SEM images. GICs, which were treated by nitric acid and sulfuric acid, have similar average length as that of flake graphite but were slightly thicker (30.142 μm). It is assumed that increasing the interlayer distance lead to an increase in GICs thickness. In other words, the interlayer bonding strength (c-axis bonding strength) of the GICs was weakened by increasing the interlayer distance between carbon layers.

The GICs, which have weakened interlayer bonding strength, were wet ball milling with DI water to increasing its specific surface area. In this research, instead of spherical-shaped media, rod-shaped media was used in the milling process in order to prevent crushing of the plate-like structure of the carbon layers by increasing the contact area between the GICs and the media. As shown Fig. 2(c), carbon layers of GICs

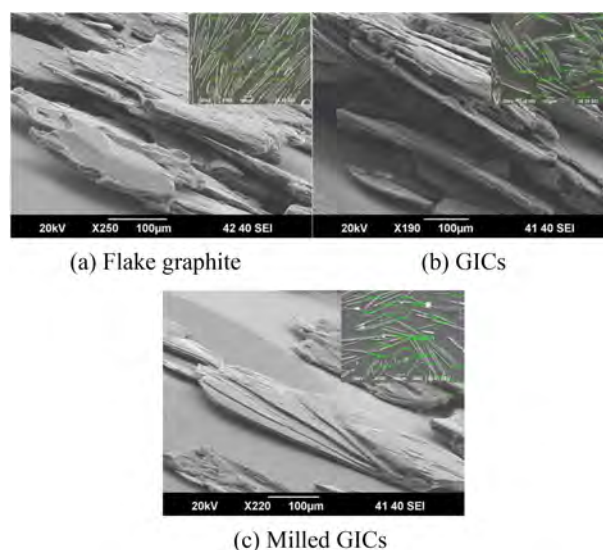


Fig. 2. SEM images; (a) Flake Graphite, (b) GICs, (c) milled GICs.

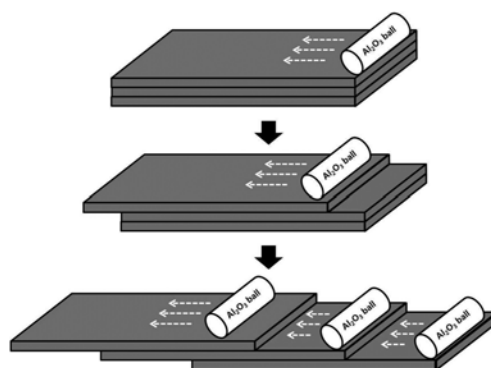


Fig. 3. Schematic diagrams of layer shear effect for GICs.

Table 1. Interlayer distances, length and thickness of each samples.

	Flake Graphite	GICs	Milled GICs
Interlayer Distance (Å)	3.367	3.373	3.372
Length (μm)	277.00	276.87	298.15
Thickness (μm)	30.000	30.142	11.393

were sheared due to a decrease in the crushing effect by the rod-shaped media. Fig. 3 demonstrates the shearing effect of the carbon layers. Rod-shaped media sheared the graphite layers which weakened by acidic treatments. Therefore, the length of milled GICs was increased and the thickness of GICs was decreased. Based on the cross-sectional SEM image of Fig. 2(c), the average length and thickness of milled GICs were 298.15 and 11.393 μm, respectively. We confirmed that milled GICs were longer and thinner than flake graphite.

Table 1 demonstrates the interlayer distance, average length and average thickness of each sample. The interlayer distance of GICs was increased in comparison with that of commercial flake graphite due to insertion of intercalants, as shown in the table. This result shows that GICs have weakened bonding strength between layers. In the case of milled GICs, average length was increased and average thickness was decreased by the shearing effect of weakened carbon layers. As a result, milled GICs have a large specific surface area compared with commercial flake graphite due to chemical and mechanical treatments.

Conclusions

In this research, it was shown that the interlayer bonding strength of flake graphite was decreased using

acidic treatment. In order to weaken the interlayer bonding strength of the flake graphite, GICs were formed. The GICs were ball-milled using rod-shaped alumina media to slide layers of the flake graphite. As milling time increased, the length was increased and the thickness was decreased, due to the slide effect of flake graphite layers by ball-milling process using rod-shaped alumina media. The length and the thickness of milled GICs for 9 hours were 298.15 μm and 11.393 μm, respectively.

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