Role of Ash Impurities in the Depletion of Carbon from Alumina–Graphite Mixtures in to Liquid Iron

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Due to their excellent thermal shock and slag resistance at high temperatures, alumina–graphite refractories are used extensively in the steel industry. The degradation of carbon based refractories through carbon depletion is an important issue and a fundamental understanding of refractory behaviour at high temperatures is crucially important. Natural flake graphite, with ash impurity levels ranging from 1 to 10%, is used extensively in the commercial preparation of alumina–carbon refractories. This study investigates the role played by ash impurities in the depletion of carbon from the refractory composite. Two natural graphites, respectively containing 2.1% and 5.26% ash, were used in this study. Substrates were prepared from mixtures of alumina and carbon over a wide concentration-range. Using a sessile drop arrangement, carbon pick-up by liquid iron from alumina–natural graphite mixtures was measured at 1550°C and was compared with the carbon pick-up from alumina–synthetic graphite mixtures. These studies were supplemented with microscopic investigations on the interfacial region. Very high and similar levels of carbon dissolution were however observed from both alumina–natural graphite mixtures, with carbon pickup by liquid iron from mixtures with up to 30 wt% alumina reaching saturation. A sharp reduction to near zero levels was observed in the 30 to 40 wt% alumina range. Along with implications for commercial refractory applications, these results are discussed in terms of poor wettability between alumina and liquid iron, interactions between ash impurities and alumina, and formation of complexes in the interfacial region.

KEY WORDS: alumina–carbon refractories; natural graphite; carbon dissolution; steelmaking.

1. Introduction

High temperature metallurgical processes are among the major consumers of refractories, with the iron and steel industry utilizing >60% of all refractories used.1) Among these, carbon-bonding oxide refractories, e.g., magnesia–carbon, alumina–carbon, zirconia–carbon etc, are an important component due to their special properties such as excellent slag resistance because of the nonwetting carbon/graphite and improved thermal shock resistance because of high thermal conductivity and crack propagation resistant microstructure.2–5) In oxide–carbon refractories, the carbon content may range anywhere from as low as 4–5 wt% to as high as 30–35 wt%4). When hot metal comes in contact with a refractory, it can dissolve carbon from the contact surface leaving behind a porous region. The degradation of carbon based refractories through carbon depletion is an important issue as it can result in a decreased refractory resistance to chemical attack, carbon pick-up by steel, and inclusions in molten metal. Significant costs are associated with refractory consumption and degradation. A fundamental understanding of refractory behaviour at high temperatures and research into the service life of carbon-bearing refractories is of crucial importance to the steelmaking industry.

A wide variety of carbonaceous materials including coal-tars, coal-tar pitches, phenolic resins, coke, natural and synthetic graphite are used as a source of carbon/binders in the manufacture of commercial refractories.5) Natural flake graphite is used extensively in the commercial preparation of alumina–carbon refractories because of its pressing characteristics—it presses much easier than synthetic graphite or coke. In addition to the high carbon content, carbon based materials for refractory applications should have ash content as low as possible. Currently there is no general consensus on the optimum level of ash impurities in carbons for refractory applications. It is reported that in Europe, refractory producers use natural graphite that has carbon content under 90%. In the United States, most producers use graphite that contains a minimum of 94% carbon.6) Using two natural graphites with significantly different ash composition and concentrations, the focus of this article is on clearly identifying the role played by ash impurities in carbon depletion and refractory degradation. An in-depth investigation is reported on the depletion of carbon from alumina–graphite mixtures into liquid iron at 1550°C.

The dissolution of carbon into liquid iron generally involves two stages: phase boundary reactions at the carbon/melt interface leading to the dissociation of carbon atoms, followed by mass transfer through the adjacent boundary layer into the bulk liquid.7) Investigations on pure
graphite, both experimental and theoretical, have provided a great deal of information about carbon dissolution and various factors affecting dissolution rate, and have generally identified mass transfer in the melt as the rate controlling mechanism. In the case of natural graphite, the dissolution of carbon atoms leaves behind an ash-enriched region, which can cause interface blockage and a reduction in the effective contact area for carbon dissolution. Wu et al. have reported an in-depth FESEM and EDS investigation of the natural graphite/molten iron interfacial region. Interfacial deposits after contact for 3 and 7 min were identified as alumina and calcium oxide indicating the deposition of ash components in the interfacial region. For contact times in excess of 10 min, EDS results indicated the presence of some complex phases containing Fe, Ca and S. FESEM images showed there were two main phases present at the reaction interface: a predominantly iron rich oxide phase and another that was depleted of iron. With increasing reaction time, the surface was increasingly covered with iron depleted phases, indicating a slow deposition of ash components and/or other reaction products on the reaction interface. After 30 and 60 min of contact, these deposits were found to cover approximately 50% of the surface.

Orsten and Oeters have shown that the role played by the ash composition is quite important and can significantly influence the rate of carbon dissolution. Addition of specific materials such as CaO or CaF₂ to lower the melting temperature of ash below the bath temperature was found to significantly enhance the overall dissolution rate as liquid ash gets flushed away by the melt. Stationary rod studies of carbon dissolution from coke into liquid iron by Mourao et al. detected a viscous slag-like layer at the interface. This layer was composed of Al, Ca, Si, K, Na, Ti and P, and these elements were assumed to be in the form of oxides. These authors however did not provide the ash composition for the coke, therefore the changes in the ash layer during carbon dissolution could not be determined. It was suggested that a slag-like layer on the surface of the coke cylinders reduced the interfacial area available for carbon dissolution, and therefore reduced the dissolution rate of carbon. In a recent study, Cham et al. have carried out an in-depth investigation on the influence of mineral matter on the dissolved carbon from a large number of metallurgical coke specimens and have reported wide variation in carbon dissolution kinetics. The chemical composition/concentration of ash were found to have a significant influence on dissolution rate constants. It is generally agreed that ash can form an interfacial layer between molten iron and carbonaceous materials during carbon dissolution if its liquidus temperature is higher than the bath temperature, thereby limiting the area of contact between carbon and liquid iron resulting in a slower rate of carbon dissolution. The additional presence of large amounts of alumina in an alumina–graphite refractory substrate could significantly influence the composition of ash deposits in the interfacial region and affect the dissolution of carbon from the substrate.

In this article, we report a systematic study on mixtures of alumina with two natural graphites containing different ash contents/composition. Using the sessile-drop method, experimental results are reported on carbon transfer from alumina–graphite mixtures into liquid iron at 1550°C, along with detailed microscopic investigations on interfacial deposits. Experimental results from both natural graphites are compared with the corresponding results from synthetic graphite-alumina/liquid iron system, and are discussed in terms of alumina concentrations, poor wettability between alumina and liquid iron, ash content/composition and the deposition of complexes in the interfacial region.

2. Experimental

2.1. Material Characteristics

Alumina–graphite composites used in the experimental work were prepared in the laboratory from commercially available natural graphites and alumina. Particle sizes for both natural graphites (labelled as NG1 and NG2) and alumina were less than 50 μm. Proximate and ash analysis for carbonaceous materials are given in Tables 1 and 2 respectively. Fused bead X-ray fluorescence method, with a relative accuracy of ±1%, was used for ash analysis. Electrolytically pure iron and 99.8% pure alumina were used in these investigations. Carbon concentration in the composite pieces ranged from 60 wt% to 100 wt%, balance being alumina. While typical maximum concentrations of carbon in alumina–graphite composites are generally <35 wt%, much higher local concentrations of carbon could be present in the natural graphite/molten iron interfacial region.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Natural Graphite NG1</th>
<th>Natural Graphite NG2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>97.6</td>
<td>93.42</td>
</tr>
<tr>
<td>Volatiles</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Ash</td>
<td>2.1</td>
<td>5.26</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.05</td>
<td>0.02</td>
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Both natural graphites were supplied by Asbury Graphite Mills, N.J., U.S.A

<table>
<thead>
<tr>
<th>Ash Component</th>
<th>Natural Graphite NG1</th>
<th>Natural Graphite NG2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>16.4</td>
<td>7.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.6</td>
<td>37.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>17.6</td>
<td>13.1</td>
</tr>
<tr>
<td>CaO</td>
<td>8.9</td>
<td>24.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.63</td>
<td>0.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.8</td>
<td>0.79</td>
</tr>
<tr>
<td>MgO</td>
<td>10.5</td>
<td>14.9</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.40</td>
<td>0.58</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.07</td>
<td>0.34</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>0.21</td>
<td>0.15</td>
</tr>
</tbody>
</table>
ent in the some surface regions of the refractory due to corrosion at the slag–gas or slag–metal interfaces during steelmaking. Following the experimental procedure used previously for alumina–synthetic graphite/liquid iron system, the composite refractory test pieces were produced by thoroughly mixing powders of desired compositions and then compressing them with a load of about 9 tonnes to produce squares with sides 23 mm and a height of 3–5 mm.

2.2. Carbon Dissolution and Microscopic Investigations

Carbon dissolution investigations on the alumina–graphite/liquid iron system were carried out in a laboratory scale, horizontal tube resistance furnace using the sessile drop approach. A schematic diagram of the experimental set up is shown in Fig. 1. Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone in the furnace with the help of a stainless steel rod. The assembly was held in the cold zone of the furnace until the desired temperature (1550°C) was attained and was then inserted into the hot zone. This eliminated any reaction that could occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. Melting of iron marked the beginning of the contact time. Once the liquid metal droplet had been exposed to the refractory substrate for the desired time (40 min), the tray assembly was pulled back into the colder section of the furnace effectively quenching the iron droplet and halting further reactions. The furnace tube was purged with argon throughout the duration of the experiment with a flow rate of 0.5 L/min. The wetting image of the liquid melt on the solid substrate was monitored and recorded in-situ by a CCD camera, which was connected to a date/time generator, a digital video recorder, and a colour TV. The image from the CCD camera was recorded on a DVD for subsequent analysis. To examine the new phases formed at the interface, the underside of the droplet (which effectively represents the interface) was inspected using a Scanning Electron Microscope (SEM), and analysed with Energy Dispersive Spectroscopy (EDS). After examining the droplets by EDS, the carbon and sulphur contents in various quenched iron specimens were determined using a LECO CS444* carbon sulphur analyser.

3. Experimental Results

3.1. Microscopic Investigations on Alumina–Graphite/Liquid Iron System

Detailed SEM/EDS investigations were carried out on the interfacial region between liquid iron droplet and alumina–graphite substrates after 40 min of contact. Results for substrates containing two natural graphites NG1 and NG2 and a wide range of alumina concentrations are shown in Fig. 2 and Fig. 3 respectively. For 100% natural graphite (NG1) there was a sporadic coverage in form of small number of particulates generally containing Ca. Ca and Fe were the only two elements identified in the interfacial region (Fig. 2(a)). For alumina–graphite system containing 10% alumina in the substrate, we have shown SEM/EDS images from two different regions. While one region shows significant peaks corresponding to Ca, S, Fe along with a small Al peak (Fig. 2(b)), another region shows a strong aluminium peak along with significant peaks of Fe, Ca, S and Mg indicating the simultaneous presence of these components in a small region of space. With 20% alumina, while the surface coverage was still sporadic, small regions containing high concentrations of Al, Mg, Ca, S, Fe could be clearly identified (Fig. 2(c)). Similar results were observed for 70% alumina substrates (Fig. 2(d)) with a relatively stronger Al peak. An interesting feature regarding the interfacial region was the absence of silica, considering that silica was a principal component of ash in the materials investigated. Silica is known to undergo reduction either in-situ by the solid carbon in the substrate or with solute carbon in liquid iron.

There were significant differences in the interfacial products in case of natural graphite NG2. For 100% natural graphite (NG2) (Fig. 3(a)), the interfacial region was covered extensively with deposits which predominantly contained Ca and S. Small peaks corresponding to O, Mg and Fe could also be seen. With the presence of 10% alumina in the substrate (Fig. 3(b)), surface coverage reduced by a significant extent with concentrations of Ca and S reducing to half the levels observed for 100% NG2; a peak corresponding to Al was detected indicating the presence of alumina in the interfacial region. With 25% alumina present in the substrate (Fig. 3(c)), there was a significant coverage of interfacial region predominantly by alumina; other peaks (Ca, S, Fe) had reduced significantly. With 40% alumina,
Fig. 2. SEM and EDS images for alumina–natural graphite (NG1) mixtures/liquid iron system after 40 min of contact. Figures 2(a) to 2(d) clearly show the deposition of reaction products in the interfacial region for a range of alumina concentrations in the substrate.
regions containing little alumina, or predominantly alumina could be clearly identified (Fig. 3(d)).

3.2. Carbon Dissolution Studies on Alumina–Graphite/Liquid Iron System

Experimental results on carbon dissolution from alumina–graphite mixtures into liquid iron at 1550°C are shown in Fig. 4, with the corresponding results for synthetic graphite–alumina mixtures included for comparison. These results indicate the amount of carbon depleted into liquid iron after 40 min of contact. A very high level of carbon dissolution was observed with carbon pick-up by liquid iron nearly reaching saturation values. For up to 30 wt% alumina, the carbon dissolution from alumina–natural graphite mixtures was quite high with carbon values in the melt in excess of 5 wt%. However a sharp fall to near zero
was observed for higher alumina concentrations. Two significant observations can be made about these results. Firstly, carbon dissolution from system containing natural graphite was much higher than the corresponding dissolution from the system containing synthetic graphite. Secondly, there was hardly any difference in the carbon dissolution behaviour for two natural graphites, despite significant differences observed in the corresponding interfacial products. These findings are discussed further in greater detail in the next section.

4. Discussion

The presence of alumina was expected to strongly retard the dissolution of carbon from alumina–graphite refractory mixtures. In the presence of alumina, poor wetting between alumina and liquid iron has a strong influence on carbon dissolution. According to the atomistic model of alumina–graphite/liquid iron system, alumina and liquid iron are strongly repulsive with a tendency towards being mutually exclusive. With alumina strongly inhibiting the penetration of liquid iron in the refractory matrix, the contact between carbon and iron gets strongly reduced leading to low rates of carbon dissolution.

However in the case of alumina–natural graphite mixtures, there was almost no influence of alumina on carbon dissolution for alumina concentrations up to 30 wt%. Natural graphites used in this study were highly crystalline with generally high rates of carbon dissolution in to liquid iron. Even though the presence of ash deposits in the interfacial region can slow down the kinetics of carbon dissolution to a certain extent, the carbon pickup by liquid iron for 100% NG1 and NG2 had reached the saturation value of 5.6 wt% after 40 min of contact (Fig. 4). Both natural graphites contained a wide range of ash impurities. Lee et al. have reported on in-situ refractory interactions between ash impurities and alumina. Of the two natural graphites under investigation, NG2 had a high concentration of basic fluxes such as CaO and MgO. As high concentrations of CaO and MgO will tend to reduce the fusion point of ash and increase its fluidity, there is strong likelihood of formation of a liquid slag like layer as a complex combination of various oxides that solidifies upon cooling. In a low magnification SEM image of the interfacial region for 100% NG2 (Fig. 3(a)), a layer of fused ash appears to cover the interfacial region between the refractory substrate and liquid iron. NG1, on the other hand, contained much lower levels of CaO, 8.9% as against 24.9% in NG2, and contained lower levels of MgO as well. Low concentrations of basic fluxes are likely to result in much higher fusion temperatures thereby reducing the likelihood of a liquid slag like layer in the interfacial region. Only a sporadic distribution of reaction products could be observed in the interfacial region for 100% NG1 (Fig. 2(a)), which was significantly different from the interfacial region for NG2.

With the addition of alumina in varying concentrations to both NG1 and NG2, interfacial regions remained significantly different thereby indicating the important role played by ash impurities. In the presence of alumina, complexes of alumina with ash oxides were observed in the interfacial region (Figs. 2(b)–2(d) and Figs. 3(b)–3(d)). EDS analysis of these complexes indicated the presence of Ca, Mg, Al, Fe, O and S in close vicinity. It is therefore quite likely that alumina in the refractory mixture interacts with various oxides present as ash impurities and forms complexes/slag. Based on the compositions of both natural graphites, the phase equilibrium was computed at 1 550°C using FactSage package. The results of these computations indicate the likely presence of following alumina based products: MgAl2O4, Al2Fe2O6, CaAl12O19, CaAl2Si2O4. Although the relative proportions of various reaction complexes may change with ash composition, these calculations show that alumina can chemically bind with a range of ash impurities at these high temperatures. One of the basic assumptions used in developing the atomistic model for alumina–synthetic graphite/liquid iron system, which treated alumina as being chemically inert, will no longer hold in the presence of ash impurities.

As alumina is chemically bound in various complexes, it looses its individual capacity to stop the penetration of liquid iron in the refractory matrix. As liquid iron can easily come in contact with carbon present in the alumina–natural graphite refractory mixture, there is no specific hindrance from alumina to carbon dissolution apart from ash deposits/complexes in the interfacial region. The depletion of carbon from alumina–natural graphite mixtures into liquid iron was completely unaffected by the nature/concentration of ash impurities present in two natural graphites, with both NG1 and NG2 giving rise to very similar levels of carbon depletion. High levels of carbon dissolution were therefore observed from natural graphite–alumina mixtures until much higher concentrations of alumina in the refractory mixture became effective in reducing the penetration of liquid iron in the refractory matrix. Similar carbon dissolution behaviour observed from two natural graphites with distinct concentrations/compositions and significantly different deposits in the interfacial region highlight the importance of alumina–impurity interactions. If the impurities present in the carbonaceous material can chemically bind with alumina to form reaction complexes, these are likely to be

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**Fig. 4.** Carbon dissolution from mixtures of alumina with two natural graphites, NG1 and NG2, into liquid iron at 1 550°C. The results from synthetic graphite have also been included for comparison.
highly detrimental for the alumina–carbon product with high levels of carbon depletion from the refractory matrix.

5. Conclusions

A detailed investigation has been carried out on the role of ash impurities in the dissolution of carbon from alumina–natural graphite mixtures into liquid iron. Carbon dissolution from mixtures of alumina with two natural graphites into liquid metal was measured at 1550°C, and was compared with carbon dissolution from alumina–synthetic graphite mixtures. Carbon dissolution studies were supplemented with microscopic investigations on the interfacial region. Main findings of this investigation are:

1) Both natural graphites under investigation, NG1 and NG2, showed high levels of carbon dissolution into liquid iron. The presence of up to 30% alumina had negligible effect on carbon dissolution from alumina–natural graphite mixtures with carbon concentration in the melt reaching >5 wt%. However a significant reduction in carbon dissolution was observed for alumina in the concentration range 30 to 40 wt%. The overall carbon dissolution behaviour of two graphites was found to be quite similar.

2) Natural graphites under investigation had significant differences in their ash composition, which was reflected in the nature of deposits observed in the interfacial region. While a small number of sporadic deposits were observed in the case of alumina–NG1 mixtures, a layer of fused ash appeared to cover the interfacial region in case of NG2. However in both cases, EDS analysis of the interfacial region indicated the presence of Ca, Mg, Al, Fe, O and S in close vicinity. It is therefore quite likely that alumina in the refractory mixture interacts with various oxides present in ash impurities and forms complexes/slag deposits in the interfacial region.

3) The evidence suggests that the modification of the interfacial region through formation of slag phase/complexes between ash oxides and alumina was an important driver for carbon dissolution from alumina–natural graphite composites. The formation of complexes between ash oxides and alumina significantly affected the interaction between alumina and liquid iron. Bound in complexes at the interface, alumina could no longer prevent the penetration of liquid iron in the refractory matrix, thereby resulting in high rates of carbon dissolution.

4) As natural graphite is used extensively in commercial steelmaking refractories, these results point towards the inherent difficulties associated with the usage of natural graphite due to chemical interaction between ash impurities and alumina and interfacial phenomena. The presence of ash impurities, even in small concentrations, can significantly degrade alumina–natural graphite refractories through rapid depletion of carbon into liquid iron.

Acknowledgements

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