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Interfacial Reactions between Alumina and Carbon Refractories and Molten Iron at 1,823 K

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Abstract: High temperature interactions of alumina–carbon refractories with molten iron were investigated at 1,823 K in argon atmosphere. These studies were specifically focussed on the decomposition of alumina in the simultaneous presence of carbon and iron, and associated refractory degradation. Refractory mixtures were prepared by blending 90 wt% alumina with 10 wt% synthetic graphite; 5–15 wt% iron powder was then mixed with the refractory mixture. Using phenol formaldehyde as a binder, pellets were prepared from various blends; these were heat treated at 1,823 K for 30 min in Ar atmosphere. The presence of molten iron significantly enhanced the decomposition of alumina resulting in an enhanced refractory degradation as well as the formation of a new reactant product. This product was identified as a Fe–Al intermetallic phase from SEM/EDS (scanning electron microscopy/energy-dispersive spectroscopy) and x-ray microdiffraction investigations.

Keywords: alumina, molten iron, refractory degradation, interfacial phenomena

Introduction

Carbon-based oxide refractories are used extensively in a range of ironmaking and steelmaking applications due to their thermomechanical properties and excellent resistance to chemical attack by slag or molten steel [1, 2]. Alumina–carbon refractories are among a major class of refractories used for applications such as submerged entry nozzles, ladle shrouds, slide gate plates, etc. [3]. In addition to high temperatures, the effects of mechanical stresses, thermal cycling, erosion and corrosion by hot gases, molten metal and slag can cause the deterioration of refractories during their service life [4]. Refractory

interaction with molten steel/slag involves metal penetration, depletion of carbon from the refractory and subsequent refractory degradation [5]. Factors that influence the penetration of liquid metal into the pores of a refractory are temperature, refractory, slag compositions, porosity and gaseous atmosphere. The depth of penetration of molten metal into the refractory and the strength of bonding of the metal film with the refractory depends significantly on the wetting behavior of the refractory with molten iron [6]. Slags tend to react with the oxides inside the refractory while molten iron preferentially dissolves carbon from the refractory [7]. The depletion of carbon from the contact surface leaves behind a porous region, which can cause aggregate particles to be removed from the hot face into molten metal leading to impurity inclusions. Due to increased porosity as well as metal contamination, these reactions result in a reduced resistance to chemical attack [8].

Another significant factor affecting refractory degradation is the chemical interaction between alumina and carbon. Lefort et al. observed the formation of Al (g) and an associated increase in CO generation during reactions of alumina with graphite between 1,573 and 1,673 K [9]. Heyrman and Chatillon showed that the reaction of Al_2O_3 –C specimens produced CO, Al (g) and Al_2O (g) gases [10]. Halmann et al. have also reported similar findings in the temperature range of 1,700–2,200 K with additional products being AlO and CO_2 gases [11–13]. Ramachandran et al. have used thermodynamic predictions to show that Al vapors formed will be deposited in steel as inclusions during interactions of alumina–carbon system with iron [14]. Klug et al. have reported on the interaction of alumina and graphite during firing at 1,823 K which resulted in bright particles of alumina surrounded by a light gray matrix of $\text{Al}_4\text{O}_4\text{C}$. They have also reported that $\text{Al}_4\text{O}_4\text{C}$ was found to be an intermediate product with final products being AlO/Al₂O and CO/CO₂ gases [15]. Although Cox and Pidgeon proposed that the reactions between alumina and carbon were solid–solid reactions, the observations by Klug et al. indicate that vapor-phase reactions also had a strong influence on reaction kinetics [13].

Sasai and Mizukami have reported that the equilibrium partial pressures of Al_2O , and AlO gases were seen to decrease in the order of $p_{\text{AlO}} < p_{\text{Al}_2\text{O}}$ [16]. They

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expressed the likelihood of reactions occurring as follows: $\text{Al}_2\text{O}_{3(s)} + 2\text{C}_{(s)} = \text{Al}_2\text{O}_{(g)} + 2\text{CO}_{(g)}$, and $\text{Al}_2\text{O}_3(s) + \text{C}(s) = 2\text{AlO}(g) + \text{CO}(g)$. The overall reaction could be described as $\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al}_2\text{O} + \text{CO}_2$ and $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$. Hauck and Potschke proposed that alumina deposits on the surface of refractory submerged-entry nozzles had originated from the Al₂O gas from the reduction of alumina by graphite [17]. Yoshimori et al. reported that suboxide gases generated from the alumina-carbon refractory played an important role as carrier gases for aluminum vapors and oxygen; these suboxide gases are likely to diffuse out of the nozzle [18]. Reactions at the metal-refractory interface are likely to be $\text{Al}_2\text{O}_{(\text{refractory})} = 2\text{Al}_{(\text{Fe})} + \text{O}_{(\text{Fe})}$ and $3\text{Al}_2\text{O}_{(\text{refractory})} = 4\text{Al}_{(\text{Fe})} + \text{Al}_2\text{O}_{3(\text{Fe})}$. This reaction could occur in the early stages of contact, when originally dissolved oxygen in the iron melt is the only source of oxygen. Even though a partial decomposition of alumina has been observed in several studies, the carbothermic reduction of alumina has known to occur only at temperatures >2,273 K or at high pressures [19].

In a previous study from our group, the sessile drop approach was used to investigate the interactions between the alumina-carbon refractory and molten iron at 1,823 K. Experimental results on wettability, carbon depletion and metal penetration provided clear evidence for chemical reactions taking place between alumina, carbon and molten iron at these temperatures [20]. Limited research has been carried out on Al₂O₃-C/Fe system with a specific focus on phase transformations associated with the decomposition of alumina in the simultaneous presence of carbon and iron. During experiments using the sessile drop approach, there was however a limited contact between refractory constituents and molten iron due to poor wettability between alumina-carbon refractory and molten iron.

This paper reports an in-depth investigation on high temperature interactions taking place in Al₂O₃-C, Al₂O₃/Fe and Al₂O₃-C/Fe systems at 1,823 K with focus specifically on the decomposition of alumina and its corresponding influence on interfacial reactions and the nature of products formed. Detailed results are reported on scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) investigations; these experimental findings are supplemented with thermodynamic analysis on these systems. The influence of iron concentration and enhanced contact area between iron and refractory constituents was investigated. Iron powder was mixed in a range of proportions with alumina and carbon mixtures to form pellets. These reactant compositions are somewhat different from those used during standard steelmaking practices. During steelmaking,

iron melt containing dissolved oxygen is in a direct contact with Al₂O₃-C refractory; there was however no free oxygen present in molten iron in this study.

Experiment

About 99.7% pure alumina (CT-3000, supplied by ALCOA, Australia) was used for its high purity, fine particle size (~2 µm) and ease of compaction along with electrolytically pure iron powder. Detailed chemical analysis of the iron powder has been provided in Table 1. A 100 mesh synthetic graphite (99.1% fixed carbon and 0.2% ash) was used as the carbon source to isolate the influence, if any, of ash impurities. Phenolic resin was used as a binder to improve the green strength of the pellet. Experiments were carried out on Al₂O₃-C, Al₂O₃/Fe and Al₂O₃-C/Fe refractory systems. Alumina-carbon refractory mixtures were prepared in 90% Al₂O₃: 10% C proportion (labeled hereafter as AS1) as per the procedure described previously [20]. About 100% Al₂O₃ was used for Al₂O₃/Fe investigations. For investigations on the Al₂O₃-C/Fe system, the iron powder was added in 5, 10 and 15 wt% ratios into AS1 blends to study the influence of enhanced contact with iron; these specimens were labeled as AS1-5Fe, AS1-10Fe and AS1-15Fe. The composition of these pellets has been provided in Table 2. Investigations on the interfacial behavior of all these pellets were carried out in a laboratory scale, horizontal tube resistance furnace at 1,823 K for 30 min under Ar flow (1.0 L/min). A schematic diagram of the experimental setup is shown in Figure 1. Initially, the pellet was held on a specimen holder, which was pushed in the furnace with the help of a stainless steel rod. The assembly was

Table 1: Chemical composition of iron powder.

Element	Mn	Si	Al	Ca	Cr	Cu	Ni	V	Fe
(Wt%)	0.02	0.29	0.07	0.11	0	0	0.2	0.08	Balance

Table 2: Composition of AS1-iron-blended substrates.

Sample label	Al ₂ O ₃ -C ratio (wt%)	Fe (wt%)	Binder (wt%)	Calculated value	
				Wt% Al ₂ O ₃	Wt% C
AS1-5Fe	90:10	5	5	88.3	11.7
AS1-10Fe	90:10	10	5	88.8	11.2
AS1-15Fe	90:10	15	5	89.2	10.8

Figure 1: A schematic representation of the experimental arrangement.

held in the cold zone of the furnace until the desired temperature (1,823 K) 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. After 30 min of exposure in the hot zone at 1,823 K, the tray assembly was pulled back into the cold section of the furnace effectively quenching the sample and halting further reactions.

To examine the chemical transformations within the pellet, the reacted assembly was set in epoxy resin which was then polished to a 1 μm finish. The polished samples were examined by SEM (model S-3400X, Hitachi, Tokyo, Japan). EDS was used to identify the elemental distribution in the selected region. Phase changes were investigated using x-ray microdiffraction (selected area diffraction) based on epitaxial technique. X'pert epitaxy technique can be used for detecting small concentrations of reaction products and texture through diffraction space maps based on area, texture and one or two-axes scans. This software has specific tools that can extract information from the near-surface region, lattice mismatch between layers and substrate, alloy composition of the layer, layer thickness, composition, uniformity and substrate curvature. The epitaxial software uses high-intensity colors to highlight the peak position area. It is also more sensitive to the near-surface region. Detailed procedure of conducting x-ray microdiffraction analysis has been given elsewhere [21].

Results and discussion

Interactions of Al_2O_3 -C system

Figure 2 shows the microscopic examination of 100% alumina and AS1 substrate heat treated at 1,823 K for 30 min. Figure 2(a) represents a well-sintered body of alumina particles. Figure 2(b) represents alumina-carbon interaction where several microcracks/pores could be seen; these have been marked in red. The change in morphology during alumina-carbon interactions can be attributed to high temperature interaction between alumina and carbon in the presence of Argon gas as well as to the curing of phenolic resin into active carbon. SEM image in Figure 2(b) clearly indicates that the alumina matrix was well sintered in the regions where carbon was not in close contact with gray particles of alumina. However, microcracks were observed in regions where carbon was in direct contact with alumina. This change could be attributed to the generation of suboxide gases through the partial decomposition of alumina with carbon and their passage through the refractory matrix [16, 22].

The EDS analysis of the AS1 refractory pellet (Figure 3(a)) shows the interaction between alumina and carbon. Position "A" shows high alumina content with very little carbon representing unreacted alumina. The analysis of position "B" shows the simultaneous presence of aluminum and carbon; a significant reduction in the oxygen peak indicates the disintegration of alumina and the subsequent removal of oxygen through the formation of CO/CO_2 gases [23]. The presence of aluminum and carbon was observed only in those regions, where alumina was in close proximity with significant amounts of carbon. A further confirmation of EDS results was provided by XRD analysis. The XRD pattern of heat-treated AS1 substrate is shown in Figure 3(b). A number of diffraction peaks were observed in addition to the diffraction peaks for synthetic graphite and alumina; the secondary product formed was

Figure 2: (a) Alumina (100%) and (b) alumina-graphite (AS1) pellet after heat treatment at 1,823 K for 30 min indicating microcracks/porous regions (marked as red).

Figure 3: (a) SEM image and EDS analysis of AS1 sample and (b) XRD pattern of AS1 substrate showing various diffraction peaks. These peaks have been labeled as corundum, C; graphite, G; aluminum carbide, Al_4C_3 .

identified as Al_4C_3 . These Al_4C_3 peaks were observed at peak locations of 31.783° and 40.214° as stand-alone peaks, while at 43.483° , 57.444° and 59.712° , Al_4C_3 peaks were also observed in conjunction with alumina peaks. Generally, low intensities for Al_4C_3 peaks indicate that these compounds were formed in very small quantities.

Although the complete carbothermic reduction of alumina is expected to occur at temperatures above 2,073 K; the thermodynamic feasibility of these reactions has been investigated in the temperature range of 1,803–1,923 K. Ramachandran et al. have reported thermodynamic predictions on the addition of 20 wt% of carbon into the (Al, O) system in the presence of 0.1 mol of Ar (g) in the temperature range 1,773–1,923 K. They have reported on the generation of two predominant Al-containing vapor species: Al_2O (g) and Al (g) along with a high concentration of CO (g) [14]. Balmenos et al.

performed thermochemical calculations on alumina–carbon interactions under vacuum to predict that almost all Al_2O_3 was converted into Al (g) and CO (g) around 1,773 K [24]. The dissociation of alumina with carbon has also been reported to occur at 1,803 K with the free energy ΔG° calculated as $\Delta G^\circ = -1,515,000 + 377 T$ (K) [25, 26]. Given the thermodynamic feasibility of these interactions at 1,823 K, pellets under investigation would have experienced a partial decomposition of alumina into Al_2O (g) or Al (g) leading to the formation of small amounts of Al_4C_3 . The presence of phenol binder provided an additional carbon source in the system. Kanno et al. have reported that during the heat treatment in oxide refractory system, the phenol binder devolatilizes to form a reinforcing carbon framework and the active carbon thus formed reacts to form secondary compounds (carbides and/or oxycarbides) in a nonoxidizing medium [27].

$\text{Al}_2\text{O}_3/\text{Fe}$ system

Pure alumina substrate was reacted with iron by using the sessile drop method at 1,823 K for 30 min in the presence of Ar (g). Microscopic and diffraction analysis confirmed that no interaction had occurred between alumina and iron [23]. A detailed study by Kapilashrami had reported that contact angles of Al_2O_3 with molten iron were generally nonwetting and in the range of 100 – 141° at 1,803–1,873 K in inert gas atmospheres of helium, argon, hydrogen gases and under vacuum [28]. Due to the nonwetting behavior of alumina with iron, there will be minimal contact between two species. It is therefore unlikely that any appreciable reaction will occur between alumina and liquid iron at 1,823 K. $\text{Al}_2\text{O}_3/\text{Fe}$ reactions have been reported to occur only at temperatures $>2,273$ K and at high pressures [19]. Figure 4(b) shows the

diffraction pattern of 100% $\text{Al}_2\text{O}_3/\text{Fe}$ system; there was no evidence for the formation of additional reaction products.

Another study was conducted where 5 wt% phenolic resin was added into Al_2O_3 (3 g) substrate. This resin-cured sample was reacted with iron at 1,823 K in a horizontal tube furnace for 30 min. Microscopic investigations showed the penetration of a small amount of iron into the alumina substrate (Figure 4(a)). EDS analysis of the sample in positions “A” and “B” indicated unreacted iron and alumina, whereas the position “C” indicates the alumina–carbon region. Position “D” shows the presence of iron, aluminum and carbon. XRD analysis of the sample as shown in Figure 4(c) revealed the presence of three new diffraction peaks at 41.223° , 47.969° and 70.18° ; these peaks were identified as Fe_3AlC . This result indicates that even a small amount of carbon from phenolic

Figure 4: (a) SEM image and EDS analysis of 100% alumina sample containing 5% phenolic resin and iron at 1,823 K for 30 min, (b) XRD pattern of 100% alumina sample interacted with iron showing only alumina peaks (corundum, C) and (c) XRD pattern of 100% alumina sample interacted with 5% phenolic resin and iron at 1,823 K for 30 min using sessile drop arrangement. This pattern shows a few peaks in addition to alumina peaks.

resin had reacted with alumina and created channels within alumina causing the penetration of iron through pores and the formation of the reaction product Fe_3AlC . Further investigations are underway to understand the role of active carbon from phenolic resin and its impact on the kinetics of alumina–carbon interaction.

Al_2O_3 -C/Fe system

Microscopic investigation and EDS analysis of the refractory pellet AS1-5Fe (Figure 5(a)) showed the combined effect of carbon and iron, which is expected to play a significant role for chemical reactions in the system. Chemical reactions were observed in those regions

where iron had penetrated deep in the alumina–carbon matrix. At position “A” the elemental analysis showed that whenever Fe was in close proximity with regions containing alumina and carbon, there was clear evidence for alumina decomposition. Similar results were observed at several other locations in the matrix as well in regions where molten iron had completely covered the surface of alumina–carbon regions. Figure 5(b) and 5(c) shows the microstructure and EDS analysis of the samples AS1-10Fe and AS1-15Fe. The concentration of iron in these systems was much higher than in AS1-5Fe. While the typical elemental analyses observed were quite similar to those observed for AS1-5Fe, the ratio of Fe/Al peak heights was found to increase with increasing Fe levels in the initial pellet.

Figure 5: Microstructure and EDS analysis of (a) AS1-5Fe, (b) AS1-10Fe and (c) AS1-15 Fe pellets after heat treatment. Alumina (gray region), carbon (dark region) and Fe–Al reaction product (white region) can be seen clearly in these micrographs.

Figure 6: EDS analysis of AS1-5Fe and AS1-10Fe pellets showing the formation of Al_4C_3 in the carbon-rich regions.

Figure 6 shows carbon-rich regions of AS1-5Fe and AS1-10Fe samples in the presence of iron. Microscopic results show that the presence of iron had an impact on morphology and chemical nature of alumina decomposition such that Al and C were observed at position “A” with trace amounts of iron. The combined presence of C and Fe can enhance the kinetics such that Al_2O_3 gets decomposed into Al_2O and AlO gases and its subsequent reduction into Al (g) with iron saturated carbon. Ar (g) can also act as a carrier gas for aluminum vapors [14, 18] to form either a compound with solid carbon or with liquid iron. The formation of Al (g) has previously been reported in other studies in the presence of carbon saturated iron. [29].

To validate results obtained from the EDS analysis of pellets with increasing amount of iron, an epitaxial mapping was drawn for AS1-5Fe, AS1-10Fe and AS1-15Fe systems [21]. The results are shown in Figure 7(a), 7(b) and 7(c); these reveal that with increasing iron levels in the system, the proportion of secondary product containing Fe and Al had also increased. These images also show that the concentrations of products formed were much higher than in that observed in the sessile drop arrangement due to a much enhanced contact between reacting species [23]. Microdiffraction analysis of these samples showed the presence of additional phases in AS1-5Fe, AS1-10Fe and AS1-15Fe samples (Figure 8(a), 8(b) and 8(c)).

This additional phase (identified as cubic aluminum-iron alloys) was present at stand-alone peak positions of 30.840° , 44.187° , 64.258° and 81.289° ; these peaks were in addition to alumina and carbon peaks. Aluminum-iron alloy (Fe_3Al) also shared peaks at 26.628° and 54.851° with key graphite peaks. The presence of Fe_3Al phase has provided unambiguous confirmation for the reduction of alumina at 1,823 K.

The probability of Fe_3Al diffraction peaks belonging to iron peaks was also considered, as the location of some of Fe diffraction peaks was quite close to Fe_3Al peaks in the diffraction pattern. Diffraction peaks of iron (JCPDS No. 085-1410) are observed at peak positions of 44.354° , 64.528° and 81.657° ; and JCPDS No. 006-0696 shows diffraction peaks of iron to be at peak positions 44.674° , 65.023° , 82.335° and 98.949° . These Fe peak positions are, however, slightly different from the peak positions observed in our $\text{Al}_2\text{O}_3\text{-C/Fe}$ system, which were located at 26.628° , 30.840° , 44.187° , 54.851° , 64.258° and 81.289° . All these peaks provide an excellent match to the diffraction pattern of JCPDS No. 45-1203 for Fe_3Al . No pure Al or Al_4C_3 was observed in these samples, thereby indicating that both of these were intermediate phases and had later transformed into a more stable Fe-Al phase. These results clearly show that reduced Al had reacted either with molten iron or with solid carbon to form Al_4C_3 . The Al_4C_3

Figure 7: Epitaxial mapping of reacted pellets at 44.19° for locating the position of Fe_3Al reaction product [(a) AS1-5Fe, (b) AS1-10Fe and (c) AS1-15Fe].

phase, however, was not detected in the diffraction pattern probably due to rather its small concentration.

These results show that molten iron has played an important role in the carbothermic reduction of alumina at

1,823 K. The role of iron was further analyzed through off-gas analysis, where interaction with alumina, carbon and iron generated far more CO/CO_2 gases than those produced during a blank run of AS1 substrate [23]. It was observed from

Figure 8: XRD pattern of refractory pellets [(a) AS1-5Fe, (b) AS1-10Fe and (c) AS1-15 Fe] after heat treatment at 1,823 K for 30 min showing Fe_3Al as reaction product other than corundum (C) and carbon (G).

Al_2O_3 -C interactions that a small part of alumina had changed to aluminum and formed Al_4C_3 . In the presence of molten iron, Al (g) formed during the carbothermic reduction of alumina showed a tendency to be absorbed within the molten iron. These findings indicate that gas-liquid reactions were more likely to occur than gas-solid reaction in this system. Reduction reactions are likely to occur via gas transport mechanism between alumina and carbon source. A similar observation has been reported by Heyrmanz et al. and Frank et al. [10, 30]. If AlO and Al_2O gases are formed due to the carbothermic reaction of alumina, subsequent carbon pickup by iron would lead to a further reduction of these suboxide gases into aluminum gas, which is later absorbed by Fe to form Fe-Al alloys.

Both theoretical and experimental results have shown a partial conversion of alumina into aluminum and its subsequent interaction with iron or carbon to form carbides. These studies also show that Al (g) formed had partially reacted with Fe, and molten iron had picked up both Al and carbon during these interactions. Khanna et al. have reported on another aspect, highlighting that C and Fe are among some of most important elements involved in redox reactions [23]. While it is well known that the presence of even small amounts of carbon can affect the kinetics of chemical reactions, it is difficult to predict how the simultaneous presence of two reducing agents will have a significant effect on reduction reactions under conditions wherein carbon is present along with molten iron. Iron also contributes as a solvent metal to lower the temperature for the carbothermic reduction of alumina. This feature is similar to observations on molten tin and copper by Frank et al. [30], which were used as solvent metals to lower the temperature for the carbothermic reduction of alumina.

Conclusions

The interaction of alumina with carbon in the presence of Ar gas showed the dissociation of alumina to a minor degree and the production of a small quantity of Al_4C_3 during microscopy and diffraction investigations. Al_2O_3 /Fe interaction, however, did not show such dissociation from XRD analysis. The interaction of Al_2O_3 /Fe in the presence of phenolic resin as binder, however, showed a small amount of metal penetration at the metal/refractory interface. Diffraction analysis further confirmed the formation of a secondary product due to the interaction among alumina, carbon from the resin and molten iron. Microscopic analysis of Al_2O_3 -C/Fe system showed that the interaction between alumina and carbon had increased significantly in the presence of iron. A partial decomposition of alumina was observed in the refractory pellets where iron was in close proximity of refractory constituents; elemental analysis showed the presence of Al, C and Fe in the iron penetrated regions of the refractory. Diffraction analysis of reacted refractory pellets confirmed the reaction product to be a cubic aluminum-iron alloy.

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