Carbothermic Reduction of Alumina at 1 823 K in the Presence of Molten Steel: a Sessile Drop Investigation

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The carbothermic reduction of alumina was investigated at 1 823 K in the presence of molten steel in argon atmosphere for time periods up to 6 hours. A sessile-drop study was carried out to investigate the influence of operating parameters such as carbon/alumina ratio in the substrate, solute carbon level in the melt and reaction time. With molten steel acting both as a reducing agent and a metallic solvent, we report significant reduction reactions in the Al_2O_3 –22.82 pct C/Fe (0.6 pct C) system, associated generation of CO gas and carbon pick-up by molten steel. The refractory substrate thickness was seen to decrease with time and the metal droplet started to flatten out and spread over the substrate after 5.5 hours. The chemical composition of metal deposited on the substrate was determined to be iron-aluminide; small levels of unreduced alumina and residual carbon were also observed. The carbon level in the metal droplet increased steadily to 1.5 wt pct during initial 3 hours and then decreased to 0.6 wt pct after 6 hours indicating carbon consumption; a small step increase in CO gas generation was also observed after 5.5 hours. While the metal droplet was still predominantly iron after 5 hours, it had completely transformed to iron aluminide after 6 hours of contact. The molten metal was also seen to penetrate deep in the substrate. These experimental results provide unambiguous evidence for a macroscopic carbothermic reduction of alumina occurring at 1 823 K in the presence of molten steel and for the dissolution of product aluminium in molten steel.

KEY WORDS: refractory; degradation; chemical reactions.

1. Introduction

The carbothermic reduction of alumina has been investigated by a number of researchers as an alternative route for aluminium production due to the potential benefits in reduced energy, lower costs and more favourable environmental characteristics than the conventional Hall-Heroult process.^{1–5)} The overall reaction for carbothermic reduction: $\text{Al}_2\text{O}_3 (\text{s}) + 3\text{C} (\text{s}) = 2\text{Al} (\text{l}) + 3\text{CO} (\text{g})$, is known to proceed in the region of 2 473 K for a pressure of one atmosphere.⁶⁾ These high temperatures however promote direct vaporization of aluminium and aluminium bearing compounds. Cox and Pidgeon⁷⁾ investigated Al–O–C system in the temperature range 1 700 K to 2 200 K at reduced pressures and reported on the formation of small quantities of aluminium bearing compounds such as oxi-carbides and carbides ($\text{Al}_4\text{O}_4\text{C}$, Al_2OC , Al_4C_3). A possible occurrence of $\text{Al}_2\text{O}(\text{g})$, $\text{AlO}(\text{g})$ gases has also been discussed in thermodynamical investigations on the system.⁸⁾ Frank *et al.*⁹⁾ investigated the carbothermic reduction of alumina in the temperature range 1 973 K to 2 123 K in the presence of a metallic solvent (Cu and Sn) at pressures between 0.08 to 0.20 atm. The overall driving force for the reduction reaction was determined by the activity of aluminium in the metallic solvent, the temperature and the pressure of CO gas. The reduction was

approximately 80 pct complete in 60 minutes at 2 073 K under a pressure of 0.1 atm.

In a recent study by our group, in-depth investigations were carried out on Al_2O_3 –12.9 pct C refractory in contact with molten steel at 1 823 K in argon atmosphere for periods up to 3 hours (referred to as Paper I hereafter).¹⁰⁾ Using the sessile drop approach, this research was focussed on developing a fundamental understanding of interactions in the Al_2O_3 –C/Fe system at steelmaking temperatures, and to determine their impact on refractory degradation and steel quality. Experimental results showed unambiguous evidence for the occurrence of chemical reactions in the Al_2O_3 –C/Fe ternary system and for the pickup of Al by Fe at 1 823 K. X-ray micro-diffraction studies of the interfacial region provided clear evidence for the formation of small quantities of iron-aluminide after 30 minutes. The formation of these reaction products was explained in terms of the localised carbothermic reduction of alumina in the presence of a metallic solvent Fe, with product aluminium getting removed from the reaction zone through dissolution into molten iron.¹¹⁾ Along with small increases in the rate of CO generation, metal penetration in the refractory substrate and carbon pick-up by molten metal as a function of time, the interfacial region and associated morphology was found to undergo dynamic changes. Video images of the reaction

assembly showed intense activity with increasing time; fine hair-like whiskers were seen deposited all around the metal droplet after 3 hours of contact. SEM/EDS analysis of these whiskers identified them as being oxides of aluminium; the formation of whiskers was explained through reactions of Al_2O gas with CO gas: $\text{Al}_2\text{O} + 2\text{CO} = \text{Al}_2\text{O}_3 + 2\text{C}$.

This study¹⁰⁾ was focussed on the degradation of alumina-carbon refractories, and was significantly different from the conventional approaches used for carbothermic reduction investigations. Most of the studies reported on the carbothermic reduction of alumina have been carried out in the presence of excess carbon with carbon/alumina ratios ranging between 1.5 and 5 at temperatures $> 1973\text{ K}$; a carbon/alumina ratio of 0.15 was used in this investigation at 1823 K . The key issue that needs to be investigated is whether operating parameters such as carbon/alumina ratio in the substrate, solute carbon level in the melt, reaction time can be optimised to significantly increase the yield of aluminium bearing reaction products and their subsequent capture by molten steel. In this article, we report an in-depth investigation on $\text{Al}_2\text{O}_3\text{-C}$ substrates in contact with molten steel at 1823 K for periods up to 6 hours. The aim of this research is to determine optimum conditions for carbothermic reduction reactions in $\text{Al}_2\text{O}_3\text{-C/Fe}$ ternary system at steelmaking temperatures.

2. Experimental

High purity (99.8 pct) fused alumina was mixed thoroughly with synthetic graphite with 5 wt pct phenolic resin as a binder. Refractory substrates were prepared by compacting the mixture in a steel die using a hydraulic press and pressing to a pressure up to 10 MPa. The compacted cylindrical substrates (25 mm diameter, 3–4 mm thick) were baked at 423 K for 48 hours for enhancing their structural integrity. Two carbon concentrations (10, 20 wt pct) were used in the mix, with the total carbon concentration in the substrate determined to be 12.9 and 22.82 wt pct respectively. The increase in the carbon level was attributed to the pyrolysis yield from the binder.¹²⁾ Sessile drop investigations on the $\text{Al}_2\text{O}_3\text{-C/molten steel}$ system were carried out at 1823 K in a laboratory scale, horizontal tube resistance furnace (Fig. 1).¹³⁾ Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone of the furnace with the help of a graphite rod. The weight of the metallic iron Fe (0.6 wt pct C) used was 1.0 gm.; the presence of solute carbon in the iron droplet was to enhance the capture of Al_2O gas within the metal droplet.

The furnace tube was purged with 99.99% pure argon

($\text{O}_2 \sim 3\text{--}5\text{ ppm}$) throughout the duration of the experiment with a flow rate of 1.0 l/min. The furnace was purged with argon for 20 minutes with a slight positive pressure ($\sim 1.3\text{ atm.}$) to ensure no gas could leak into the furnace; oxygen levels in the outgoing gases were measured continuously and were below 2 ppm. The assembly was held in the cold zone of the furnace until the desired temperature was attained and was then inserted into the hot zone. This eliminated any reaction that may occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. The melting of the metal droplet marked the beginning of the reaction time; the $\text{Al}_2\text{O}_3\text{-C/Fe}$ (0.6 pct C) drop assembly was quenched after fixed periods of reaction time (up to 6 hours) by withdrawing the tray into the cold zone of the furnace. Using an IR gas analyser, CO and CO_2 concentrations in the outlet gas mixture were measured continuously. A high resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live phenomena in-situ. The output from the CCD camera was channelled to a digital video recorder (DVD) and a television monitor to record the entire experimental process as a function of time. Experimental results and relevant details of various measurements are presented in section 3.

3. Experimental Results

3.1. Video Images of Reaction Assemblies

A sequence of video images for various reaction assemblies recorded over extended periods at 1823 K is presented in Fig. 2. These include results for three configurations: A: ($\text{Al}_2\text{O}_3 + 12.9\text{ pct C}$) substrates in contact with molten Fe; B: ($\text{Al}_2\text{O}_3 + 12.9\text{ pct C}$) substrates in contact with molten Fe (0.6 pct C), and C: ($\text{Al}_2\text{O}_3 + 22.82\text{ pct C}$) substrates in contact with molten Fe (0.6 pct C) for time periods up to 6 hours. The chemical compositions of various reaction assemblies are summarised in Table 1. Detailed results on configuration A were presented in paper I, and have been included here for comparison. Major differences were observed in three cases. For configuration A, significant activity was observed in the reaction assembly after nearly 75 minutes of contact; a large number of fine alumina whiskers were seen emanating from/around the metal droplet. The formation of these alumina whiskers was attributed to the oxidation of $\text{Al}_2\text{O(g)}$ by CO(g) .¹⁰⁾ There was persistent activity even after three hours of contact. For configuration B, some particulate/gaseous emissions were observed after 1 hour of contact but these tended to decrease with time and no emissions were recorded after 3 hours. This change in visible activity could have been caused by the reduction of $\text{Al}_2\text{O(g)}$ by the solute carbon in the metal droplet and subsequent entrapment of reaction products within the metal droplet.

Fig. 1. A schematic representation of sessile drop experimental arrangement.

Table 1. Chemical compositions of refractory substrates and molten metal.

Configuration	Substrate Composition	Metal composition
A.	$\text{Al}_2\text{O}_3 + 12.9\text{ pct C}$	Fe
B.	$\text{Al}_2\text{O}_3 + 12.9\text{ pct C}$	Fe + 0.6 pct C
C.	$\text{Al}_2\text{O}_3 + 22.82\text{ pct C}$	Fe + 0.6 pct C

Configuration C showed a significantly different behaviour. This assembly had a higher level of C (22.82 pct) in the substrate along with the presence of solute carbon in the metal droplet. No whisker formation was observed in this case. However after 3 hours of contact, the substrate had slightly reduced its thickness (see Fig. 2(C)). The metal droplet started to flatten out and began spreading on the substrate after ~5.5 hours; a large lump of metal was seen

deposited on the substrate and the thickness of the substrate had reduced significantly. As poor wetting between alumina-carbon refractory and molten steel is well known in literature,¹⁴⁾ good wetting observed in this case pointed towards major changes in the composition of either the refractory substrate or the metal droplet. Configuration C was chosen for further investigation and detailed results on this system are reported in the following sub-sections 3.2 to 3.4.

Fig. 2. Video images of molten steel droplets for three configurations: A: ($\text{Al}_2\text{O}_3 + 12.9$ pct C)/Fe; B: ($\text{Al}_2\text{O}_3 + 12.9$ pct C)/Fe (0.6 pct C); and C: ($\text{Al}_2\text{O}_3 + 22.82$ pct C)/Fe (0.6 pct C). Various times indicated in this figure represent reaction times at 1 823 K.

Fig. 3. SEM image and EDS data on the metal deposited on the substrate surface [Al_2O_3 –22.82 pct C/Fe (0.6 pct C)] after 6 hours of reaction at 1 823 K.

3.2. Electron Microscopic and X-ray Diffraction Studies

The metal droplet was detached from the ($\text{Al}_2\text{O}_3 + 22.82$ pct C)/Fe (0.6 pct C) assembly that had been reacted at 1 823 K for 6 hours. The substrate had significantly reduced in thickness (~ 0.5 of initial thickness) and had a thick metallic coating. This substrate was set in epoxy and an SEM investigation was carried out on the top metallic surface without any polishing; corresponding SEM/EDS results are presented in Fig. 3. The EDS analysis identified C, Fe and Al as key constituents of the deposited metal. An x-ray diffraction study was carried out using Philips Diffractometer with Cu $K\alpha$ radiation (50 KV, 40 mA) and results are reported in Fig. 4(B). X-ray diffraction results on configuration A after 30 minutes (see Paper I) have been included as Fig. 4(A) for comparison. There are significant differences in two cases. The x-ray micro-diffraction results in Fig. 4(A) were obtained after identifying local regions of high concentration in the interfacial region using a monocapillary (0.5 mm) attachment; this spectrum contained mostly corundum (alumina) peaks and several low intensity iron aluminide peaks. In Fig. 4(B), the spectrum has changed significantly. Only two low intensity corundum peaks could be seen and the intensity of iron-aluminide peaks had increased significantly. The XRD data reported in Fig. 4(B) was on a large

area without any pre-selection and represents a macroscopic effect. A graphite peak was seen in both cases. Experimental results presented in Figs. 3 and 4 point towards a bulk transformation of Fe (0.6 pct C) melt to iron-aluminide.

3.3. Gas Generation and Carbon Pick-up

The CO gas generated from the reaction assembly was measured continuously with an on-line IR gas analyser. Figure 5(a) shows CO gas data from the ($\text{Al}_2\text{O}_3 + 22.82$ pct C)/Fe (0.6 pct C) assembly at 1 823 K for periods up to six hours. While the overall CO gas generated was generally quite low, increasing in the initial 2.5 hours and stabilising thereafter; a small step increase in gas generation was seen at 5.5 hours. Figure 5(b) shows the carbon pick-up by molten metal measured over extended periods. Reaction assemblies were quenched after fixed periods and the carbon content of quenched metal droplet was determined through LECO* CS-244 C&S analyser (* LECO is a trademark of LECO Corporation, St. Joseph, MI). The carbon pick-up by molten metal increased rapidly with time reaching 1.5 wt pct after 3 hours; however it then started to decrease after 4 hours dropping to 0.6 wt pct after six hours. During the period between 3 to 5 hours, while the solute carbon was being consumed within the metal droplet, the CO gas generation was found to be quite steady. No well-defined correlation could be established between the rate of gas generation and the level of solute carbon in the melt. While both were seen to increase with time in the initial period up to 3 hours, their behaviour was quite different during the period between 3 to 5 hours. A step increase in gas generation at 5.5 hours also did not show a corresponding reflection in carbon solute levels. These results indicate that other factors could be rate controlling in these ternary reactions.

3.4. Interfacial Phenomena

Reaction assemblies were quenched after heat treatment at 1 823 K after time periods of 5 and 6 hours. The entire reaction assembly was set in epoxy for microscopic investigation. The set assembly was then sectioned carefully to

Fig. 4. X-ray diffraction profiles collected from reaction assemblies at 1 823 K: [A] interfacial region of Al_2O_3 -12.9C/Fe after 30 minutes; [B] top surface of ($\text{Al}_2\text{O}_3 + 22.82$ pct C)/Fe (0.6 pct C) after six hours. Various diffraction peaks have been labelled as: C – corundum; G – Graphite; Fe_3Al – iron-aluminium alloy; (hkl) indices have been provided in parenthesis. As most of the peak positions for Fe–Al and Fe_3Al tended to overlap, the stoichiometry of Fe–Al alloy could not be determined from XRD patterns. (hkl) indices for Fe_3Al have been given in this figure.

Fig. 5. CO gas generation and carbon pick-up by the metal droplet during extended contact between Al_2O_3 -22.82 pct C/Fe (0.6 pct C) at 1 823 K.

Fig. 6. SEM image and EDS data on the interfacial region of Al_2O_3 -22.82 pct C/Fe (0.6 pct C) assembly at 1823 K after 6 hours of reaction. Figure 6(a) shows the metal droplet and the region where molten metal was in contact with the substrate. Figure 6(b) shows a higher magnification micrograph of molten metal along with EDS data.

Fig. 7. SEM image and EDS data on the interfacial region of Al_2O_3 -22.82 pct C/Fe (0.6 pct C) assembly at 1823 K after 6 hours of reaction. This micrograph is for the lower part of the metal droplet and the interfacial region deeper in the substrate.

Fig. 8. SEM image and EDS data on the interfacial region of Al_2O_3 -22.82 pct C/Fe (0.6 pct C) reaction assembly at 1823 K after 5 hours of reaction.

expose a cross-sectional view of the Al_2O_3 -C substrate/metal assembly and was again reset in a mould. **Figure 6(a)** shows SEM/EDS images of the upper part of contact region between the ($\text{Al}_2\text{O}_3 + 22.82$ pct C) substrate and Fe (0.6 pct C) droplet after 6 hours of contact. The upper part of this micrograph mainly shows molten metal and the lower part represents the region where molten metal was in contact with the substrate. The metal droplet showed a large number of thin strands embedded in a uniform grey background (see Fig. 6(b) for a magnified image of this region). The EDS analysis on thin strands indicated them to be primarily composed of C; these could probably represent empty spaces that got filled with epoxy during sample preparation. The grey region was identified as iron-aluminide with high aluminium content as estimated from the relative heights of Al and Fe peaks. No oxygen peak was seen in this EDS spectrum. Small quantities of un-reduced alumina were observed in regions close to the substrate surface.

Figure 7 shows SEM/EDS images of the lower part of contact/interfacial region between the ($\text{Al}_2\text{O}_3 + 22.82$ pct C) substrate and Fe (0.6 pct C) after 6 hours of contact. Four distinct regions can be clearly identified in this micrograph. The metal droplet (region A) was quite uniform and predominantly contained Al, Fe, a little C and no oxygen. Region 'B' comprising top layers of the substrate directly in contact with molten metal was composed of alumina, Fe and

a small peak for C. Region 'C' present as small islands in the substrate consisted of un-reduced alumina. Region 'D' which appeared to be in the form of molten puddles, was present in large quantities to depths of ~ 1 mm, and was primarily iron aluminide with a composition very similar to that observed for the region 'A'.

Figure 8 shows SEM/EDS images of the lower part of the contact/interfacial region between the ($\text{Al}_2\text{O}_3 + 22.82$ pct C) substrate and Fe (0.6 pct C) after 5 hours of contact. This micrograph is significantly different from the results reported in Figs. 6 and 7 for a reaction time of 6 hours. Firstly, the metallic region 'A' was predominantly iron with a small C peak. No peak for aluminium could be seen. Secondly, the relative proportions of un-reduced alumina (whitish regions 'B') were much higher after 5 hours as compared to 6 hours. In addition, several dark grey regions containing un-reduced alumina (and carbon) (region 'D') were also seen. A few iron-aluminide puddles (region 'C') that were quite similar to the ones observed after 6 hours were also observed; however the Al peak intensity was quite small and much lower in this case.

4. Discussion

Figure 2(C) clearly shows a reduction in the thickness of the refractory substrate over a period of time, a result indic-

ative of possible chemical reactions and subsequent consumption of its constituents. Detailed experimental results on configuration C: ($\text{Al}_2\text{O}_3 + 22.82 \text{ pct C}$)/Fe (0.6 pct C) system at 1 823 K for periods up to six hours have been presented in Figs. 3 to 8. The spreading of the metal droplet on the refractory substrate after 5.5 hours and associated changes in the wetting behaviour of the metal droplet also point to possible compositional changes either in the metal or in the substrate surface region. Based on SEM/EDS investigations, the metal deposited on the refractory surface after 6 hours was found to predominantly contain Fe, Al and C (Fig. 3). X-ray diffraction (Fig. 4(b)) unambiguously identified this metal as iron-aluminide; a small amount of alumina and graphite were also present.

Detailed results on the interfacial region after 6 hours were presented in Figs. 6 and 7. The metal droplet (Fig. 6(a)) was predominantly composed of iron aluminide; a small C peak was also seen. A large number of thin whiskers that were quite similar to the ones observed for Al_2O_3 –12.9 pct C/Fe after 3 hours (paper I) were also present. These were however mainly composed of carbon, possibly from the epoxy resin during sample preparation. It is quite likely that these whiskers represent blank spaces left behind by the reduction of $\text{Al}_2\text{O}_3(\text{g})$ by the solute carbon in the melt. Some unreduced alumina was also observed on the substrate surface.

Top layers of the substrate surface (Fig. 7, region 'B') were identified as being composed of predominantly alumina and iron. Looking closely at the EDS data in regions 'B' and 'C' in Fig. 7, it can be seen that Al/O ratio (2.24) in region 'B' is slightly higher than the Al/O ratio (1.8) in region 'C'. It is therefore quite possible that the top layer also contains iron aluminide instead of iron; this view is further substantiated by extensive amounts of iron-aluminide observed deeper in the substrate. These experimental observations indicate good wetting between alumina and iron aluminide.

Another point of key interest is the significant differences observed in the micrographs after 5 and 6 hours. The metal droplet was predominantly Fe after 5 hours (Fig. 8, region 'A') and it had completely transformed into iron aluminide after 6 hours (Figs. 6 and 7). In addition, the relative proportions of unreduced alumina in the substrate were much lower during this period. Even though small levels of aluminium were observed deep in the substrate after 5 hours, Al/Fe peak ratio was much smaller (~0.26) compared to that observed after 6 hours (~0.81). The CO gas data (Fig. 5) also showed a sharp increase at 5.5 hours; a flattening of the metal droplet was also observed during this time period (Fig. 2(C)).

No chemical reaction is known to occur between Fe and Al_2O_3 at 1 bar; pressures above 60 GPa and temperatures of 2 200 K were required for iron and alumina to react to form iron oxide and an iron-aluminium alloy.¹⁵⁾ Extreme conditions reversed the direction of this redox reaction through a modification of the chemical nature of iron making it more electropositive than aluminium at high pressures. Previous lowest temperature reported for carbothermic reduction of alumina in the presence of molten Sn was 1 973 K.⁹⁾ Our experimental results provide unambiguous evidence for chemical reactions occurring in the Al_2O_3 –C–Fe ternary system and carbothermic reduction of alumina at 1 823 K.

Experimental observations indicate the time period when key reactions took place in the system to lie between 5 and 6 hours at 1 823 K. A thick layer of unreduced alumina was found in direct contact with metal after 5 hours (Fig. 8). Due to poor wetting between alumina and molten iron, this layer is expected to offer resistance for the penetration of metal in the substrate and inhibit the kinetics of chemical reactions in the system. This alumina layer was seen to be significantly fragmented after 6 hours (Fig. 7). With aluminium bearing gases getting reduced within the metal droplet as indicated by the presence of large number of whiskers (Fig. 6), the composition of metal droplet gets significantly modified with increased levels of aluminium. With good wetting observed between iron-aluminide and refractory substrate (Figs. 2(C) and 7- region 'B'), alumina no longer acts as a barrier to metal penetration in the substrate, leading to further increases in reaction kinetics.

Chemical reactions observed in this study cannot be predicted from the currently available thermodynamic software packages such as FactSage;¹⁶⁾ the in-pur data for the theoretical software needs to be upgraded to take into account these ternary reactions. The formation of various reaction products can be explained in terms of the carbothermic reduction of alumina in the presence of a metallic solvent:¹⁷⁾ $\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO}$. The reaction product aluminium has a very high affinity for liquid iron and will be removed from the reaction zone through dissolution into molten iron.¹¹⁾ With the infinite dilution activity coefficient for aluminium in iron reported as 0.02, the overall reaction rate for the coupled reaction in the Al_2O_3 –C–Fe ternary system would be enhanced significantly.¹⁸⁾ C and Fe are among some of most important elements involved in redox reactions.¹⁹⁾ Both C and Fe were found to operate in tandem, *i.e.*, reduction of Al_2O_3 by C as a first step followed by the continuous removal of reaction products by Fe. Extended contact between alumina, carbon and molten iron has been determined to be an important criterion for the carbothermic reduction of alumina at 1 823 K. Further studies are underway on optimising key operational parameters, reaction configurations and chemical compositions for enhancing the reaction kinetics of chemical reactions in Al_2O_3 –C–Fe ternary system.

5. Conclusion

Carbothermic reduction of alumina has been observed at 1 823 K, in the Al_2O_3 –22.82 pct C/Fe (0.6C) system using a sessile drop approach. Reduction temperature in this study is significantly lower than the previously reported lowest temperature of 1 923 K for the carbothermic reduction of alumina.⁹⁾ Our study shows that chemical interactions taking place in Al_2O_3 –C–Fe system resulted in the transformation of molten iron into iron-aluminide after 5–6 hours of contact. These studies indicate extended contact to be an important requirement for the carbothermic reduction of alumina at 1 823 K in the simultaneous presence of carbon and molten iron. Alumina and carbon are among the key constituents of steelmaking refractories. With reduction of alumina occurring at steelmaking temperatures, these results could play an important role in understanding the degradation of carbon based refractories and contamination of steel with reaction

products.

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