Metal-Solvated Carbothermal Production of Aluminium

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Abstract

Commercial aluminium production by electrolysis of alumina dissolved in cryolite is carried out in Hall-Héroult cells. Several attempts have been made by other investigators to develop alternate routes that are more intense and reduce pollutants \cite{1-4}. At CSIRO Process Science and Engineering, a program investigated the carbothermal reduction of alumina. An experimental study was conducted at the kilogram-scale in a reactor designed to operate up to 2000°C and down to about 10 kPa. Experiments employed a bed of C-Al\textsubscript{2}O\textsubscript{3} pellets contacting a bath containing tin or copper as a solvent metal. The experiments confirmed the feasibility of smelting alumina with high recoveries of aluminium metal to an alloy at temperatures as low as 1750°C and furnace pressures up to about 45 kPa. A key finding was that the method of contacting the charge with the solvent had a significant influence on the extent of undesirable side reactions and loss of aluminium to the gas. The reaction rate was increased with higher temperature, lower reactor pressure and lower concentration of aluminium in the alloy. The amount of aluminium lost to the fume decreased at lower temperatures and higher pressures. Losses were lower with copper than with tin as the solvent.

1. INTRODUCTION

The overall reaction for carbothermal reduction is:

\[
\text{Al}_2\text{O}_3 (s) + 3 \text{ C (s)} \rightarrow 2 \text{ Al (l)} + 3 \text{ CO (g)}
\]  

For which:

\[
\Delta G = 1342.91 - 0.5822 T = -RT \ln \left( \gamma_{\text{Al}} x_{\text{Al}} \right) \frac{p_{\text{CO}}}{a_{\text{Al}_2\text{O}_3} \gamma_{\text{C}} x_{\text{C}}} 
\]

where \( \gamma \) is the activity coefficient, \( x \) is the concentration, \( a \) is the activity and \( p \) is the partial pressure.

The values for Gibbs free energy given in equation 2 were calculated using HSC Chemistry for Windows Ver. 5.1 \cite{5}. This reaction only proceeds above about 2030°C when both \( a_{\text{Al}} \) and \( p_{\text{CO}} \) are at unity. However, the reaction can proceed at lower temperatures if any of \( \gamma_{\text{Al}}, x_{\text{Al}} \) or \( p_{\text{CO}} \) is lowered. In practice, this can be achieved by reducing the pressure in the reaction system, dissolving the aluminium in another metal, and selecting the solvent metal such that there is a substantial reduction in the activity coefficient of aluminium. Additional reduction in \( p_{\text{CO}} \) can also achieved by diluting it with a purge gas. Dissolving the aluminium into a suitable alloy is termed metal solvation. A thermodynamic study of a number of potential
solvent metals was undertaken. Tin, copper and nickel were selected as potential candidates, although only tin and copper were used in the experimental study.

However, there are a number of side reactions that can compete with the production of aluminium and which must be reduced or eliminated in a potential process. The chief of these side products are the carbide (Al$_4$C$_3$) and oxycarbide (Al$_4$O$_4$C) and the gaseous compounds (Al$_{(g)}$ and Al$_2$O$_{(g)}$).

2. METHODOLOGY

An experimental apparatus was designed that could achieve temperatures up to 2000°C and operating at pressures down to 15 kPa in a leak-tight system. The apparatus is shown in Figure 1. The reactor comprised of a silica tube that contained machined graphite parts for holding the reactants which were insulated by graphite and zirconia felts. The reactor top was sealed by a water-cooled brass flange. The reactor was heated by an induction heater and temperature was controlled using either a type-R thermocouple or a two-colour pyrometer. The reactor was pumped down using an oil-sealed rotary vacuum pump and the pressure was measured by a pressure transducer and controlled by manually operating the control valve.

The starting alloys were pre-melted and generally weighed about 500 g. Alumina and carbon black powder were well mixed in the stoichiometric ratio according to equation 1, and the pellets were extruded after mixing with a binder. The pellets were thoroughly dried before use and were about 3-4 mm in diameter. The pelletised charge ranged from 10-60 g.

After weighing all the graphite parts, metal and reactants, the reactor was loaded, sealed and leak tested. The reactor was purged with argon for the duration of the experiment and then heated at 10-15°C/min to the set temperature. After the meal was melted, the pellets were contacted with the metals by three methods. These were as a floating raft on the surface, by mixing using argon injection through a lance or by being submerged with perforated graphite disc. Reactor pressure was reduced between 1500°C and the set temperature. Progress of the reaction was measured by analysing the product gas stream for CO$_2$ and CO. The experiment proceeded for various periods or until the reaction was completed, and then the reactor was cooled while purging. After cooling, the reactor was disassembled and all

![Figure 1: Schematic diagram of the experimental apparatus](image-url)
The alloy, pellet residue and fumes were sampled and analysed for aluminium and solvent metal as well as unreacted alumina. Pellet residues were also qualitatively analysed by XRD to determine the extent of side reactions. The extent and rate of reaction (expressed as the percentage of charge reacted and the percentage of charged reacted per minute respectively) were calculated by integrating the amounts of CO2 and CO generated over time. Examples of temperature, pressure and CO generation over time are shown in Figures 2 and 3.

### 3. RESULTS AND DISCUSSION

Experiments were performed to examine the types of reactions that occur in the absence of a solvent metal at 15 and 30 kPa reactor pressures at 1800°C. Figure 4 shows $p_{CO}$ against time while superimposed over the thermodynamically expected phase regions. The experiment at 15 kPa is well into the region where Al$_4$C$_3$ should predominate and this is confirmed in Table 1. At 30 kPa the material is in the region where Al$_4$C$_3$ and Al$_4$O$_4$C can coexist and again the XRD results show this to be the case. Fume losses were also as expected, with 56% of aluminium lost from the charge at 15 kPa and 21% at 30 kPa. These losses to the vapour phase are in broad agreement with thermodynamic calculations.

These experiments were repeated with the pellets in the presence of a solvent metal over a wide range of temperatures and pressures. Two types of experiments were conducted: some with pellets floating on the surface and others in which the pellets were stirred into the molten metal by argon injection. Experiments with a floating pellet raft showed evidence of side reactions occurring in the pellets while in those with stirring the residue essentially remained as Al$_2$O$_3$ and C. Stirring also significantly suppressed fuming, as did higher reactor pressure as seen in Figure 5.

<table>
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<tr>
<th>Sample</th>
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<th>Some</th>
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<tbody>
<tr>
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<td>Fume Al$_4$O$_4$C</td>
<td>Al$_4$C$_3$</td>
<td>C</td>
<td></td>
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<td></td>
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<td>Al$_2$O$_3$, C</td>
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<tr>
<td></td>
<td>Pellet Residue Al$_4$O$_4$C</td>
<td>Al$_4$C$_3$, Al$_2$O$_3$, C</td>
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Figure 2: Typical temperature and pressure trace
Figure 3: Example of CO trace and cumulative CO generation
Subsequent experiments used a perforated graphite disc to physically submerge the charge while allowing the CO gas to escape the bath. These experiments explored a wide range of conditions and the variables investigated included temperature, pressure, alloy composition, solvent metal and alumina type.

Figure 5 compares methods of contacting the solvent metal and the charge over a range of reactor pressures and shows that submerging the charge further suppresses fume rate as compared to stirring the melt and charge, and a floating charge. Figure 6 shows the effect of time on recovery to pellets, metal and fume based on analytical results rather than using the rate of CO generation to track reaction rate.

The experimental results largely agree with what would be expected from thermodynamic modelling. As expected the variable with the greatest effect is temperature. While the carbothermal reaction can occur at lower temperatures, the rate rapidly increases at about 1700-1750°C as seen in Figure 7. The reaction at 1750°C is slow and becomes about five times faster at 1800°C, while there is a 70% improvement when further increased to 1850°C.

Figure 8 shows the effect of pressure. The reaction rate is approximately doubled when the pressure was reduced from 30 kPa to 15 kPa. However, operating at 15 kPa increased the amount of fume about four times and pellet loss of 24% due to dust generation was observed.

Figures 9 and 10 show examples of the effects of alloy starting composition on reaction rate for both tin and copper alloys. Increasing the amount of aluminium in the alloy increases both $\gamma_{\text{Al}}$ and $x_{\text{Al}}$, thereby reducing the driving force of the reaction. Reduction with tin in particular was adversely affected, as the degree of solvation provided by $\gamma_{\text{Al}}$ was not high. For Al-Sn alloys, $\gamma_{\text{Al}}$ is slightly above unity at 2000 K [6]. In Al-Cu alloys, $\gamma_{\text{Al}}$ is well below unity [7]. For example it is about 0.2 at 30 mol% Al at 2000 K. Therefore, while reaction rate decreases in both systems when there is more aluminium in the alloy, the tin alloys are affected to a greater degree.
Figure 5: Comparison of contact method on the rate of aluminium fuming

Figure 6: Effect of run time on the recovery of aluminium to metal and fume at 1800°C and 30 kPa

Figure 7: Effect of temperature on the reduction rate at 45 kPa

Figure 8: Effect of pressure on the reduction rate at 1800°C

Figure 9: Effect of starting alloy composition on the reduction rate at 1800°C with tin
Another consequence of the high activity of aluminium in the tin alloys is the formation of Al₄C₃ in these alloys between 5 and 10 wt% Al. This is evidenced by loss of aluminium from the starting alloy (reduced to 8 wt% from an initial 10 wt% Al for example). Carbide formation also causes the solidified alloy to stick to the graphite crucible and to be brittle. High aluminium activity also increases fuming of aluminium at higher aluminium levels. In Al-Cu alloys, fume losses were nearly 10% at 35 wt% Cu with some losses beginning to be observed at 20 wt% Cu. Some carbide formation was suspected at 20 and 35% Cu.

Figure 11 contrasts tin and copper alloys with no aluminium in the starting alloy. As mentioned previously, the activity of aluminium in an Al-Cu alloy [7] is much lower than in an Al-Sn alloy [6] of similar aluminium concentration, and consequently the driving force for the reaction in the copper system should be significantly greater. Therefore, the observation that the reduction rate is slower with copper as the solvent contradicts the expected behaviour. A mechanism by which the solvent metal could affect the reaction rate remains unknown.

Most experiments used analytical-grade alumina in the pellets. Towards the end of the experimental work, a sample of Bayer alumina was obtained and used in a number of experiments. Figure 12 shows the reduction rate reduced significantly when Bayer alumina was used as the alumina source. Examination of the two types of alumina showed some morphological differences. Particle sizing showed the d₅₀ of the AR-grade alumina was 75 μm while for the Bayer alumina it was 101 μm. Although the Bayer alumina particles were coarser, this is unlikely to have been the sole cause of the reduction in reaction rate.
Microscopy revealed that the Bayer alumina consisted of blocky particles with few internal voids. In contrast, the AR-grade material had particles with a very open structure. It is unclear whether the AR-grade particles are agglomerates or a spongy single particle with large well-connected channels. The dimensions of the sub-grains in the AR-grade alumina were in the order of 3-6 µm and the voids of a similar size or larger, which greatly increased the surface area in this material.

4. SUMMARY

An experimental study of metal-solvated carbothermal production of aluminium showed that aluminium metal can be produced by capturing it in a solvent metal. The experiments showed the importance of the reacting charge contacting the solvent metal efficiently so that side reactions are avoided and fume losses reduced.

The effects of process variables on the reaction rate are largely in line with what is expected thermodynamically. The process requires temperatures above 1750°C and ideally above 1800°C to proceed. Reducing the reactor pressure increases the reaction rate but it should be noted that pressures below about 30 kPa are impractical due to significant losses of aluminium to the gas phase.

Increasing the amount of aluminium in the alloy reduces the reaction rate, particularly in the case of tin as the solvent. There are limitations to the concentration of aluminium that can be captured without carbide formation in carbon saturated system or unacceptable losses to the gas phase. With tin, this upper limit may be less than 5 wt% Al while with a copper solvent it could be above 20 wt% as long as carbide formation can be avoided.

The reduction rate was significantly decreased when Bayer alumina was used instead of analytical-grade alumina. This would have significant practical implications for an industrial process. Lastly, practical solutions for recovering aluminium from alloys at an industrial scale will need to be addressed.

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References