PRODUCTION OF ALUMINIUM, MAGNESIUM AND ALUMINIUM-MAGNESIUM ALLOYS BY DIRECT ELECTROCHEMICAL REDUCTION OF THEIR SOLID OXIDES

Antony Cox and Derek J. Fray

Department of Materials Science and Metallurgy
University of Cambridge
England CB2 3QZ

ABSTRACT

A variable composition Al:Mg alloy was made by reducing magnesium oxide tablets that were floating on a liquid aluminium cathode. Forced convection would be required to form a uniform alloy in pools deeper than 10mm due to diffusion limitations. Calcium was also deposited into the alloy by cathodic reduction of calcium ions from the salt. Reducing the calcium activity by introducing a second salt or even replacing calcium chloride completely may alleviate this parasitic reaction. In cells without the liquid cathode, increasing the calcium oxide activity in the salt encouraged calcium deposition reducing the current efficiency of the electrochemical reduction process. The subsequently formed free calcium metal did not reduce alumina or magnesia very easily with barely any penetration into the oxide tablet. An ~ 30wt% reduction of alumina was achieved by using highly porous alumina tablets. Producing magnesia tablets of comparable porosity and strength was not possible resulting in virtually no reduction.

INTRODUCTION

The extraction of metals from raw materials is often a costly and labour intensive process. The main methods used are electrowinning and thermal reduction. However, the raw material as mined usually requires intensive pre-processing consisting of a myriad of stages. For example, many electrowinning processes require a metal halide where the raw mineral needs to go through many treatment stages: roasting, acidification, holding, precipitation, chlorination, filtration and drying to name but some. In the case of titanium, the oxide needs to be chlorinated and then reduced with liquid magnesium in a steel reactor. This method: The Kroll Process, is a hazardous and very costly method and may only produce titanium batch-wise which is why titanium, a metal very abundant in the earth's crust, is so expensive. Thermal reduction methods such as this one are also very expensive, labour intensive and require various purification and subsequent distillation.

A novel process to produce metals and metal alloys by direct electrochemical reduction of their solid oxides has been invented at the University of Cambridge. The metal oxide is made the cathode of a cell and placed in a molten salt electrolyte. A voltage is applied that is below the decomposition of the salt but sufficient to ionise the oxygen and mobilise the oxide ions from the metal oxide lattice into the salt with
subsequent discharge on the anode. A salt is required whose oxide has solubility to allow sufficient oxyanion transport commensurate with the rate of reduction. The operating temperature of the cell can be varied by mixing calcium chloride: an electrolyte known for its oxygen solubility, with sodium chloride that lowers the melting point of the salt. The process can thus be performed between 500 and 1000°C, the choice depending on kinetic and practical factors and whether, as in some cases; there is a desire to produce the metal in solid or liquid form.

A very useful feature of this technique is that the oxide can be pressed or cast into a template so that a metal or metal alloy of a particular shape can be formed in-situ. Furthermore, by controlling sintering temperatures, particle sizes and other experimental parameters, a metal may be produced in a certain form: e.g. a dense or porous structure, a sponge etc.

The process eliminates intense mineral processing, reduces energy consumption, produces oxygen or carbon dioxide on the anode as opposed to chlorine in many electrowinning processes, and allows for in-situ formation of alloys. The latter step alone is quite an achievement.

Metals that have already been successfully produced by the process include titanium [1], niobium [2], chromium, nickel, zirconium, silicon and uranium. The process has been successfully extended to a whole repertoire of other metal oxides and mixed oxides to form alloys including niobium-tin, titanium-aluminium, manganese-nickel-gallium (Ni2MnGa) and intermetallic compounds such as Ni2Al and Nb3Sn. Many other metals, alloys and compounds show promise to be produced by this novel route. Other research groups around the globe have also investigated this field. Okabe and co-workers [3] electrochemically de-oxidised titanium metal and Sadoway and co-workers [4] are investigating the electrowinning of refractory metals from molten oxide mixtures.

The prospect of reducing alumina and magnesia is a challenging one compared to transition metal oxides, which reduce very easily [1,2]. These two oxides are very poor electronic conductors, which will restrict the reduction of the oxide to an essentially 2-dimensional process. This puts a greater requirement on metal-oxide contact, which will at the very least be tentative when these metals are formed in the liquid phase due to poor wetting. Furthermore, magnesia, in particular, shows a thermodynamic stability approaching that of calcium oxide, which could further hinder reduction.

Pertinent thermodynamic data [5,6,7] for the electrolytic reductions at 900°C are as follows:

\[
\begin{align*}
\text{Al}_2\text{O}_3 & = 2\text{Al}(l) + 1.5\text{O}_2(g) & \Delta G_{\text{dec}} & = +1303 \text{ kJmol}^{-1} \\
& & V_{\text{dec}} & = -2.25 \text{V} \\
\text{Al}_2\text{O}_3 + 6e^- & = 2\text{Al}(l) + 3\text{O}^{2-} & \Delta G_{\text{cathode}} & = +4617 \text{ kJmol}^{-1} \\
& & E^{\theta}_{\text{cathode}} & = -7.98 \text{V (vs SHE)} \\
1.5\text{O}_2(g) + 6e^- & = 3\text{O}^{2-} & \Delta G_{\text{anode}} & = +3314 \text{ kJmol}^{-1} \\
& & E^{\theta}_{\text{anode}} & = -5.73 \text{V (vs SHE)}
\end{align*}
\]
\[
\begin{align*}
\text{MgO} &= \text{Mg}(l) + 0.502 \text{O}_2(g) \\
\Delta G_{\text{dec}} &= +473 \text{ kJmol}^{-1} \\
V_{\text{dec}} &= -2.45 \text{V}
\end{align*}
\]

\[
\begin{align*}
\text{MgO} + 2e^- &= \text{Mg}(l) + \text{O}_2^2^- \\
\Delta G_{\text{dec}} &= +1578 \text{ kJmol}^{-1} \\
E^0_{\text{cathode}} &= -8.18 \text{V (vs SHE)}
\end{align*}
\]

\[
\begin{align*}
0.5\text{O}_2(g) + 2e^- &= \text{O}_2^2^- \\
\Delta G_{\text{dec}} &= +1105 \text{ kJmol}^{-1} \\
E^0_{\text{anode}} &= -5.73 \text{V (vs SHE)}
\end{align*}
\]

Pertinent thermodynamic data [5,6,7] for the chemical reductions at 900°C are as follows:

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3\text{Ca}(l) &= 2\text{Al} + 3\text{CaO} \Delta G = -235\text{kJmol}^{-1} \\
\text{MgO} + \text{Ca}(l) &= \text{Mg}(l) + \text{CaO} \Delta G = -40\text{kJmol}^{-1}
\end{align*}
\]

where \(\Delta G_{\text{dec}}\) is the free energy of decomposition, \(V_{\text{dec}}\) is the decomposition potential, \(\Delta G_{\text{cathode}}\) is the free energy of the cathodic reaction, \(E^0_{\text{cathode}}\) is the corresponding standard electrode potential, \((\text{SHE})\) standard hydrogen electrode, \(\Delta G_{\text{anode}}\) is the free energy of the anodic reaction and \(E^0_{\text{anode}}\) the corresponding standard electrode potential.

**EXPERIMENTAL**

**Tablet Preparation**

Alumina tablets were prepared from powders of particle sizes ranging from 0.2μm to 40 μm and pressed into tablets with dies of diameter 9 and 20mm using a linear press. They were sintered at various temperatures and times to produce a range of tablets that varied in porosity from 0% to 45%. Magnesia tablets were also prepared in a similar manner from a powder of particle size 20μm (0 to 20%).

Sample tablets from each of the pure oxides were pre-weighed, immersed in water for 2 hours, shaken to remove excess water and weighed again. This would indicate whether it was possible for the salt to penetrate into the bulk of the oxide. Figure 1 shows some of the alumina tablets after sintering:

![Image of Alumina Tablet](image)

**Figure 1.** Alumina tablet prior to reduction

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Liquid Cathode Cell

Aluminium pellets were placed in the bottom of a tall graphite crucible. A Kanthal wire current collector was attached to the crucible by drilling and tapping into the crucible rim. This avoided obtrusive cathode connector wires to the tablets and pellets. Porous magnesia tablets and pellets (20%) were laid across the metal pellets and pre-dried calcium chloride was powder added to the brim of the crucible. The latter was lowered into an Inconel reactor cylinder (pre heated to 250°C) that in turn was located in a kiln. The reactor and lid were cooled by attachment of aluminium fins to the neck of the vessel. Figure 2 shows the cell:

![Figure 2. Simple schematic of cell](image)

The lid of the reactor was bolted into place, a seal being established using a rubber "O" ring. The connector and gas leads were threaded through silicone rubber bungs, as was an alumina-sheathed thermocouple. The salt and apparatus were further dried overnight and the temperature then gently ramped to 900°C to melt the aluminium and salt. The aluminium formed a pool at the bottom of the crucible 30mm in height, 40mm in diameter. Pre-dried argon was also fed (0.15 lmin⁻¹) into the reactor to prevent oxidation of the aluminium phase, any subsequently formed magnesium and the graphite crucible. Once the salt was molten (this could be observed from glass windows fabricated into the lid), the graphite anode was carefully lowered so that the end of the alumina-sheathed rod was submerged half way into the salt phase. A pre-electrolysis was immediately performed at 2V until the current decayed to less than 50mA. During this time the temperature of the salt was allowed to stabilise. After ~1 hour, the cell voltage was increased to 3.2V and a reduction was performed for 24 hours. The above procedure was repeated with porous alumina tablets and pellets.
Alumina Tube Cell

A Kanthal™ wire loop was tightly inserted into a 5mm diameter alumina tube (99% alumina, 0% porosity) ensuring good physical contact between the wire and the walls of the tube. The reactor was sealed and the assembly, crucible and calcium chloride dried for 12 hours at 250°C. The temperature was increased to 900°C and the graphite anode and alumina tube lowered into the melt. A voltage of 3.2V was applied across the top of the electrodes for 24 hours. The most resistive element of the circuit was the Kanthal wire, which at 1 Amp produced a voltage drop of 500mV, so the true voltage at the electrodes was probably of the order of 2.7V.

In an effort to improve the electrical contact area between the oxide and the current collector, Kanthal wire was tightly wrapped around another alumina tube and a 5mm strip of Ti90Al6V4 wedged through the alumina tube. Kanthal wire was also wrapped tightly around this strip, which was continuous with the wire wrapped around the tube. Figure 3a shows a photo of the cathode and Figure 3b the cell assembly. Since TiAlV was used as a cathode current collector, corrosion should be alleviated. Two graphite anodes were used in order to improve the current density. Again, pure calcium chloride was used at 900°C.

The graphite crucible was replaced with a steel one in order to reduce the carbon particulate content of the salt and eliminate silicon and phosphorus contamination produced from the binder in the graphite.

Steel Cup Cell

The practical difficulties of making an electrical contact to the oxide was addressed by using a small stainless steel crucible into which the oxide tablet was placed. The working temperature was also lowered to 600°C by modifying the salt composition to 65wt% calcium chloride and 35wt% sodium chloride forming a low melting point eutectic. Reductions were performed on ~10mm cubes of the ceramic oxide. Alumina sponge (which is a macro-porous material) and micro-porous magnesia were used. Figure 4 shows the two materials and the steel cup container:

Figure 3a. Ti:Al:V and Kanthal wire current collector making a tight contact with alumina tube
Figure 3b. Simple schematic of cell

Figure 4. Stainless steel cup containing macro-porous alumina sponge and micro-porous magnesia
In an attempt to investigate possible oxyanion mass transport restrictions to the anode, additions of 1 wt% and 5 wt% calcium oxide to the salt were investigated. Nickel oxide was also mixed with alumina and calcium oxide to try to facilitate the reduction process. The following pellets were prepared for use in the following salts:

1) NiO(40wt%):CaO(20wt%):Al₂O₃(40wt%) in CaCl₂(62wt%):NaCl(33wt%):CaO(5wt%)
2) CaO(20wt%):Al₂O₃(80wt%) in CaCl₂(62wt%):NaCl(33wt%):CaO(5wt%)
3) MgO in CaCl₂(64wt%):NaCl(35wt%):CaO(1wt%)
4) Al₂O₃ in CaCl₂(64wt%):NaCl(35wt%):CaO(1wt%)

Mixtures 1) and 3) were sintered for 12 hours at 1200°C and mixtures 2) and 4), 12 hours at 1400°C. The pellets were stored in an oven at 250°C.

The oxide tablet was placed in a steel crucible as in the last set of experiments but this time the crucible was peppered with 1mm holes to assist salt drainage after the experiment. Nickel wire was also attached to the crucible for mixtures 2) to 4), but Kanthal wire was still used for mixture 1) to prevent confusion over differentiating between nickel from reduced nickel oxide and that from corrosion of the wire.

The total resistance in the circuit was estimated by measuring the resistance of the cathode busbar from top (the metal wire) to bottom (the steel crucible). The resistance of the anode was estimated by measuring the resistance lengthwise through the nickel wire and graphite. The procedure from hereon was basically the same as that described in the previous set of experiments. However, for the pure oxides, the pre-electrolysis and reduction voltages were achieved by gradually scanning from 0V to 3.5V at 0.05mVs⁻¹ to investigate the effect of reaction equilibrium times.

RESULTS AND DISCUSSION

Tablet Preparation

When the oxide tablets were immersed in water, the increases in weight ranged from 15wt% to 28wt%. All the alumina tablets showed weight gains in the range 22 to 28wt% indicating substantial porosities. The magnesia tablets were slightly less porous, showing weight gains in the range 15 to 20wt%. These results inferred that the tablets ought to imbibe salt adequately, particularly given the high charge density of the salt making it more able to absorb into materials than water.

Liquid Cathode Cell - Magnesia

From an initial mass of 2.53g of magnesia, only 0.1g of pellet fragments could be recovered, indicating virtually complete reduction. The theoretical yield is 1.6g of magnesium metal. SEM and EDX analysis of the aluminium block revealed the following data:
Table I. Top of alloy (in contact with salt and magnesia tablets)

|       | Sample 1 / wt% | Sample 2 / wt% | Sample 3 / wt% | Sample 4 / wt% |
|-------|----------------|----------------|----------------|----------------|
| Mg    | 2.65           | 2.35           | 1.15           | 0.95           |
| Ca    | 7.15           | 7.30           | 7.43           | 6.93           |

Table II. Middle of alloy block

|       | Sample 1 / wt% | Sample 2 / wt% | Sample 3 / wt% | Sample 4 / wt% |
|-------|----------------|----------------|----------------|----------------|
| Mg    | 0.00           | 0.01           | 0.31           | 0.23           |
| Ca    | 7.01           | 7.11           | 7.20           | 11.59          |

Table III. Bottom of alloy block

|       | Sample 1 / wt% | Sample 2 / wt% | Sample 3 / wt% | Sample 4 / wt% |
|-------|----------------|----------------|----------------|----------------|
| Mg    | 0.00           | 0.06           | 0.00           | 0.00           |
| Ca    | 1.48           | 3.98           | 1.59           | 0.65           |

The theoretical homogeneous magnesium content of the alloy is 2.5wt% for 100% current efficiency. The data indicates that magnesia was reduced and alloyed with the aluminium. The composition is non-uniform so diffusion alone is not enough to form a uniform alloy necessitating the need for forced convection in the alloy pool. An unfortunate result is the calcium presence in the alloy. Aluminium has a strong affinity for calcium and the decomposition voltage for magnesium oxide is closer to calcium oxide by some 200mV compared to alumina. A possible solution to this problem is to reduce the calcium activity in the salt, or better still, find an alternative salt to calcium chloride.

**Liquid Cathode Cell - Alumina**

In the alumina reduction experiment, 0.55g from an initial 1.885g of oxide was reduced. The theoretical yield of aluminium after 4 hours of reduction for a mean current of 0.5A is 0.336g based on 100% current efficiency. Also, based on the stoichiometry of the overall reduction reaction:

\[
\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 1.5\text{O}_2
\]

0.55g of alumina would produce 0.291g of aluminium, indicating that the current efficiency is less than 100% that is commensurate with calcium deposition. However, the experiment demonstrates that using a liquid aluminium cathode pool, it is possible to reduce porous alumina tablets using this cell arrangement as well as magnesia.
Non-porous Alumina Tube Cell

The weight loss from the alumina tube was insignificant indicating little or no reduction had taken place. The tube had taken on a slightly dark exterior appearance, but subsequent EDAX analysis showed this to be only carbon, probably from erosion of the graphite anode.

This experiment suggests that porosity is important in the reduction process. In a porous oxide, the salt will permeate so presenting a vast surface area to the progressing head of metal. In a non-porous oxide, the reduction can only occur at the surface so a much smaller surface area of salt and metal is presented to the oxide. This vastly increases the chances of losing the three-phase contact after which the reduction will terminate. The poor electronic conductivity of alumina serves to compound the problem.

Non-porous Alumina Tube Cell - Wire Wrapping

There was evidence of some reduction on the surface of the tube in immediate contact with the wire. This thinning of the tube is illustrated in Figure 5:

Figure 5. Non-porous alumina tube after reduction

However the reduction did not penetrate very far into the bulk of the material.

Another contributory factor to the poor reduction is that liquid aluminium probably does not easily wet the oxide and salt surfaces, which would also present phase contact problems. For this reason, it was decided to use a low melting point salt and form solid aluminium particles.

Steel Cup Cell - Low Melting Point Salt - Micro-porous Magnesia and Macro-porous Alumina Cubes

The use of nickel wire reduced the iR drop across the cell from 1.75Ω to 0.5Ω. There was very little reduction in the porous magnesia cube, although EDAX analysis did detect some surface magnesium. The alumina sponge was not reduced at all. The lack of reduction on the alumina sponge is not surprising since there was no micro-porosity in the material. The poor reduction on the magnesia is unusual and with solid metal particles
being formed rather than liquid, phase contact should have been improved. The following points should be considered:

There may be a mass transport limitation on the oxyanions from the oxide lattice. The effect of increasing the calcium oxide activity is addressed in the next section.

In order to work below the melting point of the metals, the operating temperature used was 600°C. It may be that the kinetics of the reduction process are too sluggish to work at this temperature: in particular the transport of the oxyanion out of the oxide lattice into the bulk salt.

**Steel Cup Cell - Low Melting Point Salt - Alumina Tablet - 1wt% Calcium Oxide Addition**

The tablets used were highly porous (~50%) and large (20mm x 3mm) and because of this were beginning to form a slurry when recovered from the steel cup. The tablet was recovered as a slurry and was washed with water to reveal grey particles suspended in a white solid matrix as shown in Figure 6:

![Figure 6. Alumina and aluminium powder mixture](image)

When added to warm concentrated hydrochloric acid (70°C), hydrogen gas was produced - as would be expected from aluminium metal. When a sample of the material was placed in warm concentrated sulphuric acid and also in dilute nitric acid, no gas was produced. Aluminium is one of only a few metals that display this pattern of behaviour with these acids. Subsequent EDAX analysis showed aluminium metal to be present.

However, this result was not consistent. Some tablets were virtually unreduced. One possible explanation is that the elevated oxide levels are causing the electrolytic decomposition of calcium oxide forming a parasitic cathodic reaction. Indeed, calcium metal was sometimes detected by EDAX, but more often than not, the calcium probably reacted with the water during the recovery stage. The effervescence observed during recovery would support this.

Copious quantity of calcium carbonate detected in the salt as a white solid. It probably forms by one or a combination of the following mechanisms:
ANODE
\[ C + O_2(g) \rightarrow CO_2(g) \]  \hspace{1cm} (1)

SALT
\[ CO_2(g) + CaO(i) \rightarrow CaCO_3(i) \] \hspace{1cm} (2)

SALT (Cooling)
\[ CaCO_3(i) \rightarrow CaCO_3(s) \] \hspace{1cm} (3)

OR

ANODE
\[ C + 3O^{2-} \rightarrow CO_3^{2-} + 4e^{-} \] \hspace{1cm} (4)

SALT (Cooling)
\[ Ca^{2+} + CO_3^{2-} = CaCO_3(s) \] \hspace{1cm} (5)

When the salt is cooled, calcium carbonate will precipitate out of the salt coating the oxide pellet and any metal formed. This hampered the analysis, but should not have impeded the reduction since calcium carbonate is soluble in the melt at working temperature and shows little cathodic behaviour at the working temperature.

So the most likely explanations for the non-reproducible reduction are that the temperature was often too low for solid-state electrochemical reduction. Calcium metal formed from dissociation of calcium oxide was probably in this case, responsible for the observed reduction.

Steel Cup Cell - Low Melting Point Salt - Magnesia Tablet (1wt% Calcium Oxide Addition) and NiO40:CaO20:Al2O3 Tablet (5wt% Calcium Oxide Addition)

None of these tablets reduced very well. The best result was obtained for NiO40:CaO20:Al2O3. The nickel oxide probably assisted the reduction since it is much easier to reduce than alumina. Free aluminium and nickel were detected ~500um into the surface. The SEM micrographs in Figure 7a and 7b show the oxide before and after reduction:

![Figure 7a. SEM micrograph of NiO40:CaO20:Al2O3 prior to reduction](image)
Again, the calcium oxide, being present at such high activity, probably parasitically decomposed reducing the current efficiency. Higher temperatures are also probably needed: i.e. 900°C as opposed to 600°C. The current trace shown in Figure 8 is typical of an oxide reduction. The oscillations at towards the latter part of the reduction are probably a mixture of oxygen and carbon dioxide gases that have accumulated on the anode. Tapping the anode restored the current plateau.

As discussed in the introduction, in the case of magnesia, even if calcium metal is deposited, reduction via this route is only a borderline case with the free energy of reduction being a tentative −40 kJ mol⁻¹.

Figure 7b. SEM micrograph of NiO₄₀:CaO₂₀:Al₂O₃ after to reduction

Figure 8. Current trace for reduction of NiO₄₀:CaO₂₀:Al₂O₃
CONCLUSIONS

Magnesium oxide was reduced in the liquid cathode cell producing an Al:Mg alloy. The composition could be varied from 0.3 to 2.5wt% since the metal phase was not mixed. Calcium contamination was evident but this may be overcome by lowering the calcium activity in the salt by adding another salt such as sodium chloride. Magnesium was not detected in the salt.

Porosity seems to be important in the direct electrochemical reduction of alumina and magnesia. If liquid aluminium forms on non-porous oxides of these metals, its progress into the bulk of the oxide becomes impeded and is restricted to just the surface at the interface between the oxide and metal contact wire. This may be due to non-wetting between the oxide and the metal. At temperatures at or below 600°C when solid metal forms, the kinetics of the reaction are probably too sluggish for any significant reduction to occur. There was significant reduction in the highly porous, friable alumina as evidenced in the oxide/metal slurry recovered after the experiment. Reduction of pure magnesia was only achieved using the liquid aluminium cathode that would favourably modify the equilibrium of the reduction due to dissolution of the magnesium product by the aluminium.

As well as increasing the porosity, there was some improvement in alumina reduction when calcium oxide (1wt%) was added to the salt due to chemical reduction of alumina by calcium that was in turn formed due to electrolytic dissociation of calcium oxide. The low porosity coupled with the fact that calcium does not reduce magnesia very easily probably explains the virtual absence of reduction in this oxide. This means that reduction of magnesia may only be achieved via the solid-state electrochemical mechanism, whereas alumina, under the right conditions, may be reduced electrochemically and chemically. Future work will focus on high temperature experiments (>900°C) using highly porous oxides in low calcium activity salts where electrochemical reduction should predominate, 3-phase contact maximised and solid state diffusion rates increased.

ACKNOWLEDGEMENTS

The authors are grateful to Corus for their generous financial contribution to this project.

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