

Light Metals Research at the University of Auckland

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Introduction

The Light Metals Research Centre (LMRC) at the University of Auckland was founded in 2002 and followed some twelve years of research in aluminium, titanium and magnesium largely in Engineering led by Profs. Barry Welch and John Chen. Their activity expanded significantly through the 1990s with the involvement of Margaret Hyland and Jim Metson. Following Welch's retirement, a cross-faculty research centre was formed under the interim directorship of Jim Metson and taken over by Mark Taylor when he joined the University in 2003. The Centre was established with the objective of providing world-leading expertise with a full suite of research and development capabilities, and training and education for the global light metals sector. The Centre is located largely within Chemistry, but the emphasis on external (and particularly international) contract research means activities are managed through Auckland Uniservices Ltd., wholly owned by the University of Auckland.

Although both the Bayer process for alumina refining and the Hall-Heroult process for electrolytic reduction are more than a century old, both face major challenges in an increasingly energy- and carbon-constrained world. There are ongoing issues in materials science, process control, energy recovery and reduced environmental impacts that are increasingly part of the industry's viability and licence to operate. Herein, the contributions of the Centre in addressing two particular chemistry-themed challenges encountered in the aluminium production chain are presented. The first case study describes how advanced characterization techniques give insights on how calcination technology affects the phase transformation reactions and phase distribution in smelter-grade aluminas; the second addresses the understanding of the corrosion mechanisms of silicon carbide sidewall refractories, critical to the life of the reduction cell.

Light Metals Research Centre

The LMRC currently employs around 30 research professionals, mostly engineers with some chemists and physicists, and hosts 12 postgraduate students. Some 20 academics from fields that include chemistry, mathematics, industrial psychology, and multiple engineering fields also contribute to the research programmes operating within the Centre. The LMRC is currently engaged in over 40 such projects with 20 industrial, 13 University and 7 Governmental agency partners spanning 15 countries. These projects range from fundamental research to commercialization of industrial technologies, and cover the major industrial growth areas such as in China and the Middle East. Additionally, smelter innovations in older plants are driven by the need to accommodate a changing energy market. Aluminium smelting technology, including alumina production and the environmental impacts

of the industry, is by far the largest part of the research undertaken, with projects also in areas such as titanium processing, magnesium alloy development and surface treatment.

Technical consultancy and research contract services provided through the Centre are supported by research in process fundamentals, aligned with experience in materials science, process control, operations management and scientific method-based process improvement. The Centre also offers tailored industrial training courses and postgraduate qualifications from the University. Long-term research in material science and engineering has made the LMRC into a world leader in Al industry, industrial materials, and process development. For example, it has developed standard quality tests for electrode and refractory materials where chemical and electrochemical corrosion can be tested. Coupled with advanced material characterization methods, they give insights into complex corrosion mechanisms and help in the design of materials with properties better suited to their operating environment.

The LMRC has also been developing and commercializing its own technologies. An example is the Sidewall Heat Exchanger (SHE), a compact and efficient air-driven heat exchanger capable of providing controlled cooling of smelter cell sidewalls. The SHEs enable increased amperage to the reduction cell and the ability to accommodate power modulation, while retaining other operational benefits, including a cooler operating cell and ultimately allowing waste heat recovery of 100-200 kW per cell.

The Microstructure of Metallurgical Grade Aluminas

The Hall-Heroult process produces aluminium metal by electrolysis of alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). For every tonne of primary metal, 1.92 tonnes of alumina are required. Thus, the tonnage of alumina produced rises at approximately twice the rate of growth in metal production. Primary metal production sits at about 40 M tons annually and typically shows *ca.* 3-4% year on year growth.¹ It is worth noting that secondary (recycled) production has grown considerably faster than primary and, since around 2004, has exceeded the production of primary metal.

Around 90 M tonnes of alumina are produced annually, 95% of which is destined for aluminium smelting.^{2,3} The balance is produced primarily for catalysis, refractories and abrasives markets. The largest refineries now produce between 4 and 7 M tonnes of alumina annually. The distribution of the scientific literature on alumina is almost the inverse of this and is dominated by applications in catalysis, and (increasingly) the synthesis alumina in a range of exotic morphologies extending to the nanoscale.

However, the microstructure and properties of metallurgical or smelter grade aluminas (MGAs) are of considerable interest, primarily because of the relationship to alumina refinery operation and in their impacts on the smelting process.

Alumina is produced in the Bayer process by the digestion of bauxite, the precipitation of Gibbsite [$\text{Al}(\text{OH})_3$] from a clarified sodium aluminate solution, and calcination to produce the alumina.⁴ An electron micrograph of a typical Bayer process alumina particle resulting from this process is shown in Fig. 1. The aggregated particle morphology and texture reflect the seeding strategy and precipitation conditions, typical for a Bayer plant, where agglomeration is a faster mechanism of particle growth than the growth of individual crystals.

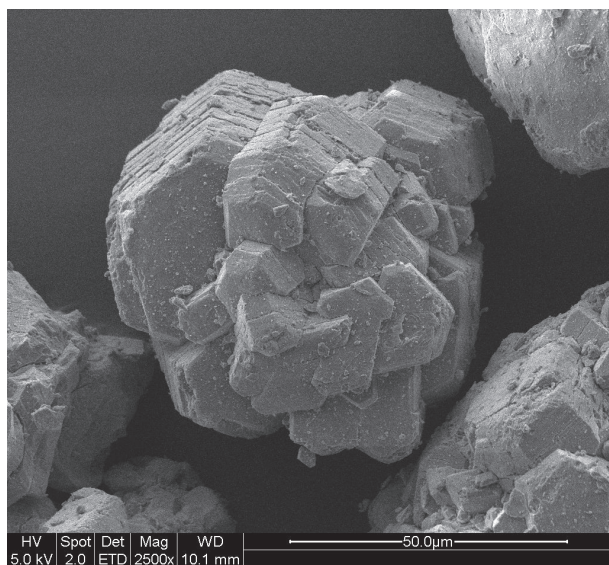


Fig. 1. SEM image of a typical Smelter Grade Alumina grain.

Charge contrast in the Environmental Scanning Electron Microscope (ESEM), or variable pressure SEM, has been shown to be a useful tool in studying gibbsite and alumina microstructure.^{5,6} Previously, the technique has been used to study Gibbsite growth characteristics as slight variations in structure owing to defects and impurities; these result in a contrast difference observable in particle cross sections.⁶ More recent approaches have revealed further internal and structural features that can be related to crystal growth mechanisms. Compositional variations arise from the cycling of growing crystals through precipitation tanks that have a varying Al:Na ratio as the Al is depleted by gibbsite precipitation. Fig. 2 shows a gibbsite cross section where these growth rings are visible through such charge contrast techniques.

Calcination transforms Gibbsite into a range of predominantly transition aluminas (Fig. 3) with the pathway across this phase roadmap and makeup of the final product, dependent on calciner technology.^{7,8} This technology has progressively moved from rotary kilns to more energy efficient gas suspension or circulating fluidized bed processes, in some cases with capacity in excess of 4,000 tonnes per day. Energy consumption is now typically below 3 MJ/kg in such stationary calciners, within about 20% of the theoretical minimum for the calcination of a

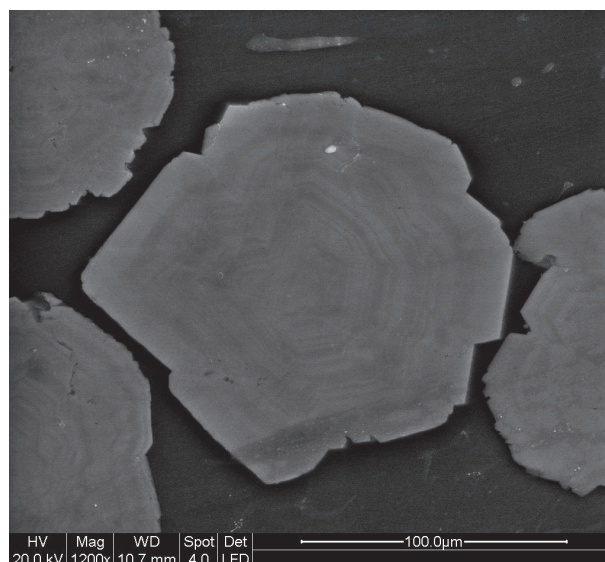


Fig. 2. Charge contrast differences in gibbsite.

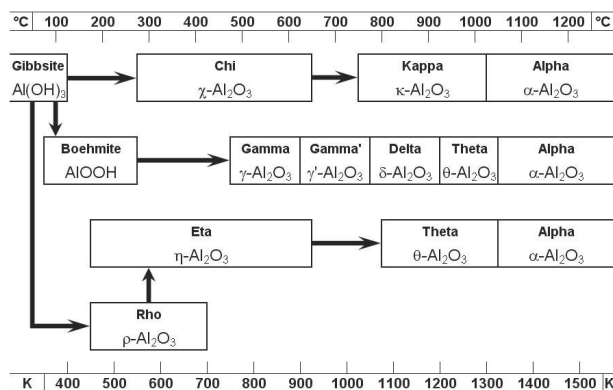


Fig. 3. Gibbsite calcination pathways (adapted from Wefers, *et al.* – see ref.9).

moist Gibbsite. However, contact times between particles and gases at temperatures of up to 1000 °C in the hot zone may be as short as a few seconds; thus, rapid heat transfer into the particle is critical in achieving conversion to alumina. Transformation of gibbsite to the transition aluminas is pseudomorphic, with the original crystal habits, the external dimensions and the morphology largely retained, even though a series of crystallographic phase changes occur. As a consequence, significant porosity develops during the initial heating stages.⁹

The presence of this porosity and the dominance of transition aluminas is key both to the use of the alumina as a medium for dry-scrubbing of cell gases,¹⁰ and in effective dissolution of the alumina in the electrolyte. Before feeding to the reduction cell, alumina is used as the primary medium for cell gas scrubbing. Specific surface areas between 70 and 80 m²/g typically are specified to accommodate scrubber needs.

X-ray diffraction-based structural phase analysis of the MGAs is especially challenging owing to the presence of these metastable, sub-crystalline, transition alumina phases. The gibbsite transformation pathways are often (mis)represented by diagrams such as Fig. 3. The distinction between the transition alumina phases, or forms,

is not as well defined as the diagram might imply. It is generally agreed that θ -alumina is more ordered than δ -alumina, which again is more ordered than the γ -alumina phase.¹¹⁻¹³ However, exactly how the transformation into the more ordered forms proceed is still the subject of debate.^{9,14,15} The formation of γ -, γ' -, and θ -alumina can be seen as waypoints on the gradual transformation into the fully ordered state represented by α -alumina.

A typical X-ray diffraction pattern collected at the Australian Synchrotron for an alumina from fluid bed (CFB) calcination is shown in Fig. 4. For several reasons in wavelength selection and intensity, the synchrotron provides a substantial advantage in data quality for these difficult samples. At the LMRC, the Rietveld refinement approach has been developed to build an SGA model based on the γ -, γ' -, θ -, and α -phases, to allow a quantitative phase analysis.¹⁶ The transition aluminas are modelled based upon literature data for these defect cubic spinel structures, with varying occupancies of the octahedral and tetrahedral aluminium sites. This approach still recognizes that although such a quantitative phase analysis can never be absolutely correct because of the arbitrary boundaries between phases, it can be self-consistent. This has provided a valuable tool in the comparison of aluminas and, in particular, the impacts of calciner technologies and in understanding their behaviour in the smelter.

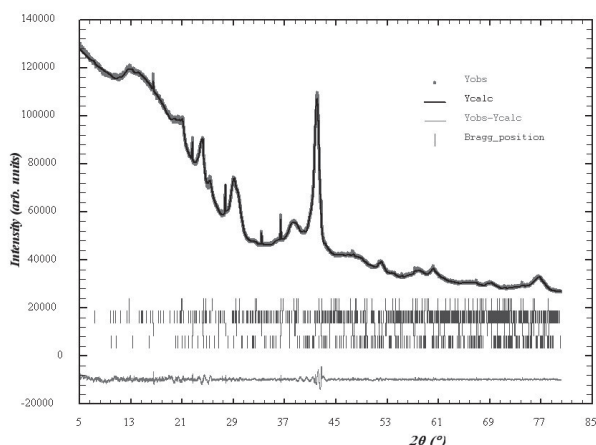


Fig. 4. Synchrotron X-ray powder diffraction pattern of a CFB calcined MGA sample and resulting Rietveld refinement results; the sloping background is a result of the amorphous nature of the quartz capillary used for sample mounting.

The central problem in the short length scale of ordering in these materials has prompted several more novel approaches to address this structural analysis question. We have made considerable use of high field ²⁷Al MAS SS NMR, X-ray Absorption Spectroscopy (XAS) and Atomic Pair Distribution Functions (PDF) derived from neutron diffraction data, in examining the structural relationships within these materials.¹⁷⁻¹⁹ These methods allow an examination of the local chemical environment without the need for crystallographic long-range order. Access to high field SS NMR facilities in the UK, and Synchrotron and Neutron Facilities in Australia and the USA has been central to these studies.

Fig. 5 illustrates data from the soft x-ray line at the Australian Synchrotron, where the near edge X-ray absorption

(XANES) spectrum has been used to probe site occupancy in these materials. It can be seen that resonances characteristic of alpha alumina are present in the industrially calcined samples. Similarly, features related to aluminium in tetrahedral oxygen coordination are also visible in the SGAs. Although useful as a fingerprinting tool for SGA, quantitative analysis of this data is challenging due to the complex multiple scattering interactions in the sample.

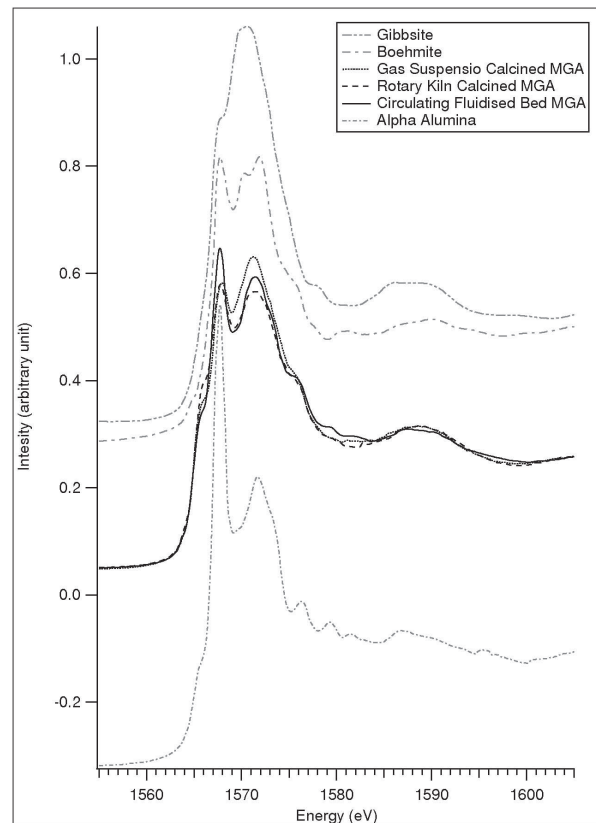


Fig. 5. Al K-edge XANES spectra from a selection of aluminas typical of several calcination technologies, the gibbsite starting material, the oxyhydroxide boehmite, and fully calcined α -alumina (bottom).

An interesting consequence of the rapid heat transfer into particles is the phase differences observed within grains in addition to that between grains. This is beautifully illustrated in the charge contrast ESEM images in Fig. 6, where the lighter coloured surface layer shows evidence of almost complete conversion into α -alumina, while the interior retains the transition alumina structures. The phase assignments associated with the contrast in the images have been confirmed with TEM electron diffraction studies on sectioned samples.⁷ The structure seen in Fig. 6 is expected to have significant impacts on the dissolution behaviour of the alumina when fed to the reduction cell. α -Alumina is known to have poor dissolution characteristics and often sinks to the bottom of the reduction cell, forming a persistent sludge layer. For this reason, modern MGAs typically are specified to have the α content below *ca.* 3%.

These results demonstrate that the speed of modern calciners, and the variation of particle size and morphology, yields a non-equilibrium phase distribution, with clear structural differences both between and within individual alumina grains. This complex mixture of phases presents

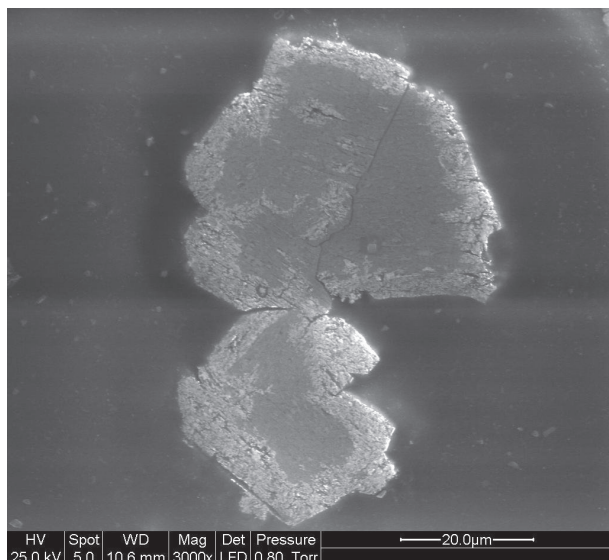


Fig. 6. Environmental SEM image of the cross-section of a relatively small industrial alumina grain showing significant phase differentiation across the section; phase distribution is influenced by the calcination conditions and calciner technology.

significant challenges in understanding their structure, particularly in relation to the performance as a raw material for the smelting process. A holistic approach, where order on different length scales is probed, is necessary for a more complete understanding of these materials.

Sidewall Refractories

Aluminium smelters drive production increases through increasing the amperage of individual reduction cells as well as increasing the number of reduction cells. The largest cells now operate at 500 kA while the largest smelters operate a 1000 or more reduction cells. The life of a cell, typically 5-7 years, is a critical parameter in economic viability, with costs approaching \$0.3 M to rebuild the largest of the cells. Failure occurs usually through erosion of the graphitized or semi-graphitic carbon cathode, or through breaching of the sidewall refractory.

The sidewall in a high amperage cell is typically constructed from cemented blocks of silicon nitride-bonded silicon carbide (SNBSC). This material shows the optimal combination of resistance to molten cryolite, mechanical strength at operating temperature (*ca.* 1000 °C), and sufficient thermal conductivity to shed the required heat load through the sidewall. The latter point is critical as the refractory is protected, not by its corrosion resistance, but by maintaining a frozen layer of electrolyte at the hot face of the refractory. Corrosion resistance of this material, thus, is of considerable interest, as would be the development of a material inert to molten cryolite. The development of such a material would aid in the move towards an insulated cell, and, thus, the ability to reduce the current energy loss through the sidewall as waste heat. To put this in context, current energy consumption across the industry is stalled at a best practice of *ca.* 13 kWh/kg Al, almost exactly twice the theoretical requirement. Given the estimate that between 1 and 2% of the world's electrical power is being used to make aluminium, the potential energy savings are enormous.

SNBSC materials are formed by the high temperature nitridation of a green form containing SiC grains and a Si powder binder (Eq. 1).



This leads to a composite material in which the SiC grains are supported in a Si_3N_4 binder phase. However, not all SNBSC materials are created equal and this leads to unpredictable, and occasionally short, lifetimes in the cell.²⁰ Microstructural analysis of SNBSC materials, before and after use, has been undertaken by X-ray diffraction, solid state Si MAS NMR,²¹ and SEM, to examine the degradation of these materials in a variety of cell environments. These studies identify, for example, significant variations in the α/β Si_3N_4 ratio and porosity in the binder phase, both between manufacturers and as a function of location within an individual refractory brick.²² Typically, higher porosity levels and β Si_3N_4 content are found in the interior part of the brick where during manufacture, the nitridation reaction occurs both later and at higher temperatures.²³

SNBSC samples were tested in a laboratory-scale aluminium reduction cell. A testing rig with some novel features, such as a rotating anode (Fig. 7), was developed to examine corrosion resistance of samples under electrolysis conditions in molten cryolite at up to 1000 °C. Corrosion test results, supported by thermodynamic calculations, identify the Si_3N_4 binder as the reactive phase in these materials, especially in the gas phase above the bath level.

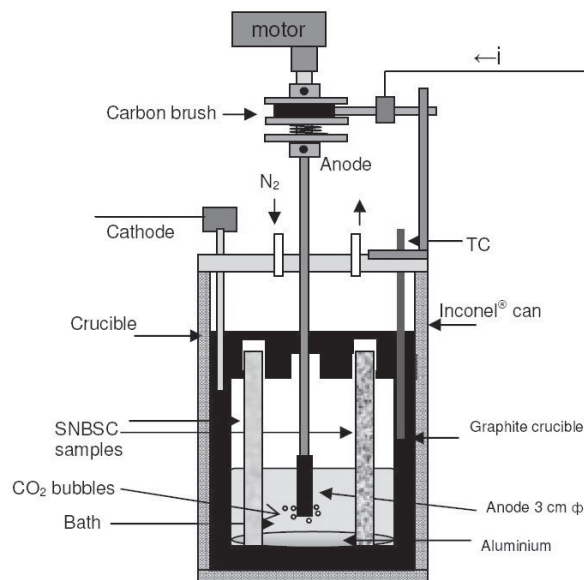


Fig. 7. Laboratory-scale corrosion testing rig.

The phase distribution within the binder is also relevant, with high β Si_3N_4 content showing a statistically significant contribution to the corrosion rate in lab-scale corrosion trials (Fig. 8). The crystal morphology of β Si_3N_4 is suggested as the reason for the high reactivity of these materials. This morphology, characterised by elongated rod-like crystals with hexagonal cross section, presents a higher surface area compared to α Si_3N_4 crystals containing mainly flat matte crystals.

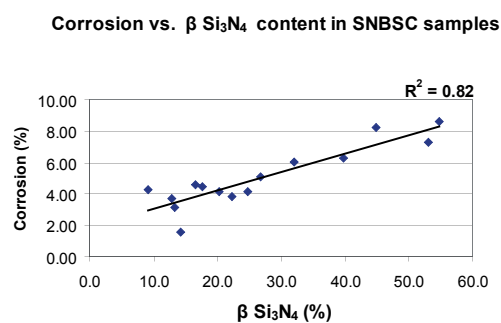


Fig. 8. Corrosion rate (% weight gain owing to the corrosion products) as a function of β Si₃N₄ content of SNBSC samples shows a high correlation.

The proposed corrosion mechanism for SNBSC materials in the aluminium reduction cell atmosphere is based, therefore, on a combination of oxidation of the binder followed by attack of corrosive gases, particularly HF, to produce volatile SiF₄. Thus, the binder phase is initially passivated below the electrolyte level on the sidewall, where exposure to corrosive gases is limited, but occurs more rapidly in the area of the sidewall above the electrolyte/air interface. The intrusion of electrolyte into the refractory and capillary and vapour transport up the sidewall is a key factor in accelerating this reaction.

Although these studies point to improved performance through better temperature control during nitridation, the major gains in sidewall technology will arise from the development of entirely new cryolite resistant materials which do not require a frozen ledge. We are currently looking into such materials in a joint project with several Australian Universities and the Light Metals Flagship programme of CSIRO.

Conclusions

Despite the maturity of the technologies used in alumina refining and aluminium smelting, a range of materials science, process control and performance constraints still limit improvements in energy consumption and the environmental footprint of this industry. The Auckland Light Metals Research Centre has been prominent in both the underpinning research and technical support of the industry to address these challenges.

Metallurgical aluminas, as opposed to those produced for the chemical industry, are poorly understood materials, particularly in the light of very rapid calcination process typically used to produce modern MGAs. The structural analysis of these materials and understanding their performance in the smelter continues to be a challenge, although significant advances have been made over the past decade. Sidewall refractories are another area where reduction cell design and the energy efficiency of the smelting process is constrained by materials science limitations. Although the corrosion of SNBSC refractories is now better understood, we are no closer to a viable sidewall inert to molten cryolite.

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