

Introduction

The production of aluminum presently consumes about 15 kW-hr/kg, largely in the form of electrical energy. This can be compared to the 2 kW-hr/kg requirement for blast furnace production of iron. The theoretical requirement, according to the reaction



is 5.6 kW-hr/kg at 977°C, yielding an energy efficiency of 37%. The electrolysis step alone consumes 64% of the total energy used, the Bayer process for the production of alumina consumes 14%, and anode preparation 10%. The cost of aluminum production has risen along with the price of electricity; in order for U.S. producers to stay competitive with other producers who have substantially lower energy costs, the energy efficiency of the process must be increased. Improvements in this regard include increasing the current efficiency and decreasing the cell voltage. The largest contribution to cell voltage is the voltage drop across the electrolyte, about 1.8 V, which is dependent upon electrolyte conductivity and electrode separation. Probably the only way to decrease electrode separation is to replace the carbon electrodes with a wettable cathode and a nonconsumable anode.

An anode material that would maintain its dimensions would be a considerable improvement over carbon because it would not be necessary to allow for uneven wear of the anode by exaggerating the interelectrode spacing through the elimination of prebaking. An inert anode material would have the following properties: high electrical conductivity, resistance to chemical attack by the electrolyte, and stability with respect to O₂ gas at 1 atm pressure. Despite intensive research efforts, no satisfactory inert electrode material has been found. Most candidate materials have been oxide-based, and in particular have been based on oxides that have low solubilities in cryolite. The base oxides of most compositions being investigated are SnO₂ (Swiss Aluminum Ltd., Sumitomo Chemical Co. Ltd., Great Lakes Carbon Corp.), Cr₂O₃ (Sumitomo), Fe₂O₃ (Sumitomo, Swiss Aluminum, Diamond Shamrock, Aluminum Co. of America, Great Lakes Carbon), Y₂O₃ (Diamond Shamrock), and ZrO₂ (Swiss Aluminum). These oxides are usually compounded with others in order to improve their physical and electrical properties.

Candidate anode material formulations are usually based upon electrical conductivity and melt solubility data. Following bench-scale Hall cell tests, changes in composition are made. This method of empirical formulation has not yet been fully successful. Part of the problem lies with the incomplete data base for these materials; as well, test methods have been largely empirical. The present research addresses both issues.

In particular, the concentration dependence of electrical conductivity of candidate anode materials based upon Fe₂O₃ is under investigation. Furthermore, the corrosion of these materials under simulated Hall cell operating conditions is being studied. The aim of the project is to introduce a scientific method of materials selection and formulation. This requires an improved data base for these materials. Two aspects of the project are particularly noteworthy. The first is that single crystal samples will be tested, enabling the measurement of intrinsic properties in experiments not influenced by grain boundaries, porosity, etc. The other aspect is the development of a stable reference electrode for use in cryolite melts.

Experimental

Sample compositions have been taken from the systems NiO-Fe₂O₃ and CoO-Fe₂O₃. The component oxides are mixed, pressed to a cylindrical shape, and then sintered so that they can be used as feed rods to the crystal growing apparatus. This apparatus uses the floating zone melting technique with a 1 kW CO₂ laser as a heat source. The growth chamber is maintained at a pressure of 1 atm O₂ and counter-rotation is usually applied. Typical crystals are about 5 mm in diameter and at least 5 cm in length. Complete characterization consists of metallographic examination of sections parallel and perpendicular to the growth axis, X-ray powder and Laue back-scattering examination, chemical analysis, and SEM examination. Mossbauer spectroscopy will be applied to single phase materials in order to gain some information concerning the cation distribution on the crystal lattice. To date most laser-processed compositions are from the NiO-Fe₂O₃ system. The composition 59.6 mol% Fe₂O₃ has yielded a single-phase material consisting of iron-rich spinel. Other compositions containing as much as 57 mol% NiO have a second NiO-rich wustite phase. This second phase appears to align itself along the growth axis. Formulations containing dopants such as CuO will also be subjected to floating zone melting.

Samples for electrical conductivity measurements will be machined from these crystals. The technique used for measurement will be the four point DC technique applied over a temperature range to 1550°C for a variety of oxygen pressures.

A bench-scale Hall cell has been designed and built to enable the study of the electrochemical corrosion of candidate materials under a simulated industrial environment. The cell has three electrodes: a test anode, a counter-electrode or cathode, and an aluminum reference electrode. The electrolyte is held in a crucible of either alumina or pyrolytic boron nitride, depending upon the degree of melt saturation with respect to Al₂O₃. A grade HBN boron nitride cylinder holds the test specimen and contains the reference electrode and a thermocouple well. A concentric cylinder of Mo foil serves as the cathode. The whole electrode assembly is lowered into the premelted electrolyte. There is an argon atmosphere in the cell. Specimens are tested at a current density of 1 A/cm². An IR current interrupter is used to measure potentials between electrodes. When combined with the stable reference electrode, this apparatus measures overpotentials during electrolysis. The traditional weight loss measurements will also be made, then samples will be subjected to structural analysis. Graphite samples have been studied to date. A comparison of overvoltage measurements with the literature validates the test procedure and demonstrates the stability of the reference electrode.

Discussion

While not discussed above, electrical conductivity measurements as a function of temperature have been made for a candidate cathode material, titanium diboride³. The conductivity measurements of the spinel oxides will be interpreted in terms of the "polaron glass" model, which relates lattice structure to electrical properties. The goal is to develop some predictive capacity in the model, to guide future choices of composition.

In the case of the NiO-Fe₂O₃ system, the maximum conductivity is known to occur at the spinel composition Fe₃O₄. However, this oxide also has a high solubility in cryolite. The spinel NiFe₂O₄ is expected to be less soluble, but its conductivity is also lower than that of Fe₃O₄. In an attempt to find a composition that combines the attributes of each spinel, specimens have been

prepared at various values of x in the system $Ni_xFe_{3-x}O_4$. While these samples are being tested in terms of their conductivity, samples having identical composition and structure will be tested as electrodes in the bench-scale Hall cell. This means that the composition dependence of the physical properties can be directly linked to the behavior of the material in the electrolysis cell.

References

1. K. Billehaug and H. A. Øye, "Inert Anodes for Aluminium Electrolysis in Hall-Heroult Cells," *Aluminium (Düsseldorf)* 57(2), pp.146-150; 57(3), pp. 228-231 (1980).
2. J. S. Haggerty, "Production of Fibers by a Floating Zone Fiber Drawing Technique," NASA Report CR-120948 (1972).
3. A. D. McLeod, J. S. Haggerty, and D. R. Sadoway, "Electrical Resistivities of Monocrystalline and Polycrystalline TiB_2 ," *J. Am. Ceram. Soc.*, 67(11), pp. 705-708 (1984).

Acknowledgement

The authors thank Dr. H. R. Baumgartner of PPG for supplying polycrystalline TiB_2 plate. The technical assistance of Mr. Paul McGrath in growing the TiB_2 single crystals is noted.

This material was prepared with the support of the U. S. Department of Energy (DOE) Grant No. DE-FG07-831D12380. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.