

AN INERT METAL ANODE FOR MAGNESIUM ELECTROWINNING

J.F. Moore⁺, J.N. Hryn⁺, M.J. Pellin⁺, W.F. Calaway⁺, and K. Watson⁺⁺⁺Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439⁺⁺Noranda Technology Centre, 240 Hymus Boulevard, Pointe-Claire, Quebec, Canada H9R 1G5RECEIVED
JAN 18 2000
OSTIAbstract

Results from the development of a novel type of anode for electrowinning Mg are reported. A tailored alloy system based on the binary Cu-Al can be made to form a thin alumina layer on its surface that is relatively impervious to attack by the molten chloride melt at high temperature. This barrier is thin enough (5-50nm) to conduct electrical current without significant IR loss. As the layer slowly dissolves, the chemical potential developed at the surface drives the diffusion of aluminum from the bulk alloy to reform (heal) the protective alumina layer. In this way, an anode that generates Cl₂ (melt electrolysis) and O₂ (wet feed hydrolysis) and no chlorocarbons can be realized. Further, we expect the rate of loss of the anode to be dramatically less than the coke-derived carbon anodes typically in use for this technology, leading to substantial cost savings and ancillary pollution control by eliminating coke plant emissions, as well as eliminating chlorinated hydrocarbon emissions from Mg electrowinning cells.

Introduction

The development of inert (non-carbon) anodes for the electrolytic production of magnesium is recognized to be of importance in the metals industry. First, the cost and pollution associated with coke plant carbon electrode production can be eliminated. Second, since an inert anode would be dimensionally stable, cells could be redesigned to reduce the anode-cathode distance and therefore IR loss. Finally, unwanted CO₂ and chlorinated hydrocarbon (CHC) emissions from the cell can be eliminated if there is no carbon source. Due to the adverse environmental significance of CHCs, they are discussed in a separate section below, followed by a section describing our approach to developing an inert anode.

CHCs

Chlorinated hydrocarbons (CHCs) are a broad group of organic compounds that contain at least one chlorine atom. There are a number of subgroups of CHCs that are classified according to their general molecular arrangement. The most important CHC subgroups with regard to magnesium production are[1]:

- Chlorophenols, containing one benzene ring, at least one hydroxyl (OH) group and at least one substituted chlorine atom.
- Chlorobenzenes, containing one benzene ring and at least one substituted chlorine atom. The most important compound with regard to magnesium production is hexachlorobenzene (HCB). Another important chlorobenzene is pentachlorobenzene (5CB).
- Polychlorobiphenyls (PCBs), containing 2 benzene rings and at least one substituted chlorine atom.
- Polychlorinated dibenzofurans (PCDFs), containing 2 benzene rings linked by an oxygen atom in a furan arrangement and at least one substituted chlorine atom.
- Polychlorinated dibenzo-p-dioxins (PCDDs), containing 2 benzene rings linked by 2 oxygen atoms in a dioxin arrangement and at least one substituted chlorine atom.
- Octochlorostyrene (OCS).

In general, CHCs are considered to be toxic. The compounds are highly lipophilic (soluble in fat), tend to bioaccumulate in the food

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

chain and have been shown to cause a variety of biological and toxic responses including immunological and hepatic toxicity, carcinogenic and teratogenic effects.[2] Despite this potential, there is currently no clear indication of increased disease in the general population attributable to CHCs.[3]

The PCDFs and PCDDs are considered to be harmful to human health at very low concentrations. The other CHCs are less toxic but are a cause for concern due to bioaccumulation through the food chain. A system of Toxicity Equivalent Factors (TEQs) is used to rank the relative toxicities of the PCDFs and PCDDs, and to determine the overall toxicity of a complex mixture. The most toxic of the dioxins and furans are those isomers with chlorine atoms at the 2, 3, 7 and 8 positions (e.g. 2,3,7,8-tetrachlorodibenzodioxin [furan]).[1]

There is an ever-increasing global awareness with regard to persistent organic pollutants (POPs) of which the CHCs are a subgroup. Members of the United Nations Economic Commission for Europe (UN-ECE) completed negotiations in February 1998 on a legally binding protocol on POPs under the Convention on Long-Range Transboundary Air Pollution (LRTAP).[4] The UN-ECE region covers the Russian Federation, the Newly Independent States, Central and Eastern Europe, Western Europe, Canada, and the United States. The objective of the LRTAP protocol is to control, reduce, or eliminate discharges, emissions, and losses of POPs. Specific protocol obligations include the application of best available technology to limit air emissions from major stationary sources of dioxins (including PCDDs), furans (including PCDFs), hexachlorobenzene, and polycyclic aromatic hydrocarbons.

The formation of CHCs in magnesium plants using the electrolytic process has been recognized as an environmental issue since the 1970s. Norsk Hydro's Porsgrunn plant in Norway decreased emission of HCB + 5CB + OCS in water effluent from 150 kg/week in 1970 to 0.1 kg/week in 1991.

There appears to be a general lack of understanding of the mechanisms of formation of CHCs in industrial processes. This is especially the case for the magnesium industry. The focus on dealing with CHCs therefore appears to be concentrated on destruction of the CHCs that form, rather than on controlling and minimizing their formation.

Dellinger[5] prepared a report that discusses the possible sources of CHCs in the electrolytic production of magnesium. In summary, he concluded that the most probable mechanism for CHC formation is reaction between chlorine from the electrolysis cell and the carbon anodes to form CCl_4 , followed by gas phase reactions with hydrogen and oxygen containing species to form a range of CHCs. Reactions with free carbon were not ruled out, but were determined to be of minor importance.

Inert Anode Concept

Previous approaches to inert anodes for aluminum production have not been adopted. Clearly, there are noble metals which could be used but are prohibitively expensive. Ceramic metal composite electrodes have been shown to work, but have poor conductivity and can crack due to the stress of thermal cycling. Coatings are inherently susceptible to damage and undercutting.

In previous studies on aluminum electrowinning, copper and its alloys have outperformed other metal-based anodes. [6,7] In the research performed by Hryn and Sadoway, CuAl binary alloys were found to operate as anodes for extended periods of time without significant dissolution.

Recent surface and thin film studies provide insight into the mechanism that could allow the binary CuAl to function as an inert anode material. Copper alloys such as the aluminum bronzes have been known for some time to 'self-heal'. These materials form a surface of dramatically different composition than the bulk material, due to the difference in surface free energy of the various components and their oxides [8]. In this case, the more volatile and reactive component, Al, will surface segregate and oxidize to preferentially form a thin Al_2O_3 surface oxide. A unique feature of this protective layer is that it is self-limited in thickness. Depletion of aluminum from the near-surface region reduces the supply to the surface until a copper-rich sublayer is formed, effectively stopping further oxidation. (See Figure 1).

Briefly, our approach to an inert anode for electrowinning Mg is to use a copper-aluminum-based alloy of optimized composition that has undergone an initial hot oxidation treatment. We believe that our approach provides a novel, workable scheme for forming a protective layer on an inexpensive, easily produced metal alloy. This layer, consisting largely of Al_2O_3 , is resistant to chemical attack by the molten chloride salt under an applied potential, but is thin enough to allow for substantial conduction of current from the oxidized surface species.

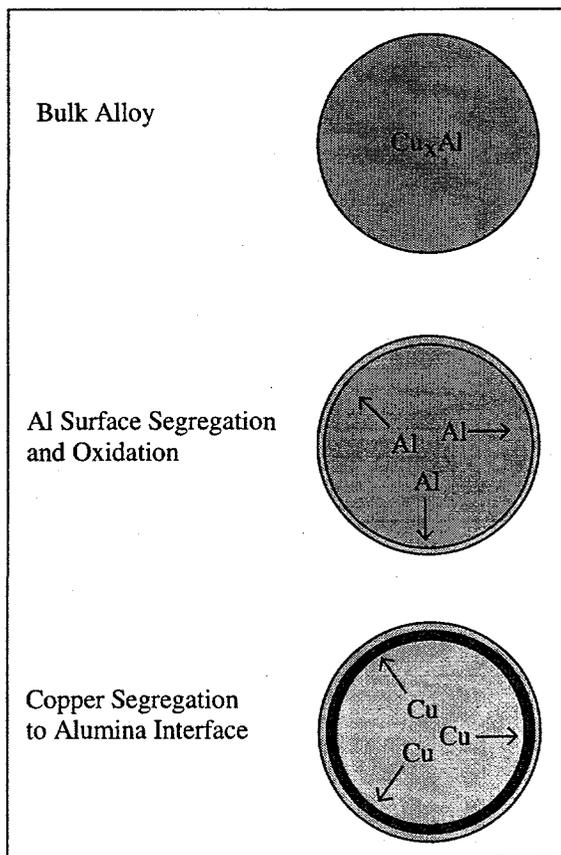


Figure 1: Formation of a Protective Alumina Film by Heat Treatment.

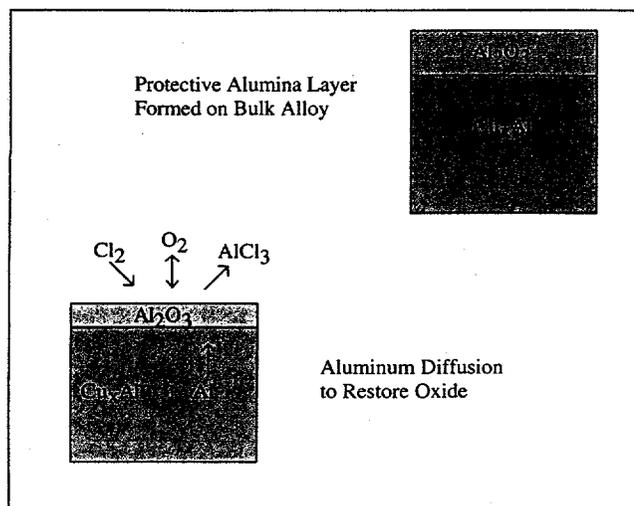


Figure 2 Dynamic Healing of the Protective Alumina Layer

Depending on the water content of the MgCl₂ feed, this protected anode can be expected to operate in two regimes. In a perfectly dry feed, the Al₂O₃ film is thermodynamically stable and therefore does not dissolve. In a wet feed, there is the possibility of Al₂O₃ dissolution at a low rate, but the induced chemical potential and source of oxidation provided by water (or its hydrolyzed components), enhances diffusion of aluminum from the bulk material. (See Figure 2).

The aluminum bronzes selected for initial study comprise two binary compositions. These alloys share a number of desirable characteristics for this application, including:

- Low cost
- Simple preparation
- Sufficiently high melting point
- High bulk electrical conductivity
- Thermal shock resistance
- High fracture toughness
- Inability to produce CHCs

The compositions selected are Cu with 17 at.% and 23 at.% Al, which at the cell operating temperature (720°C) represent the α (fcc) and β (bcc) solid solution phases, respectively.[9] Although the α phase alloy is stable to room temperature, the β phase is known to separate below 567°C into a mixed α and γ phase. The addition of certain ternary components at concentrations as low as 0.5 at.% is sufficient to stabilize the β phase to room temperature, which has important implications for anodes that are heat treated prior to use.

Experimental Approach

Alloys are formed by repeated melting and mixing in a furnace. We have built a furnace with a purgable atmosphere that can be agitated during heating to facilitate mixing. Alloy blocks of the CuAl(23 at.%) binary were purchased for initial melt tests.

We are currently testing the Cu - 23 at.% Al with anodes of 100g scale in 1kg melts against plain carbon steel cathodes. The

experiment consists of a melt furnace (see Figure 3) with steel containment, an inner quartz containment sheath, a quartz beaker for the melt, an o-ring sealed aluminum cap with feedthroughs for thermometry, electrodes (anode, cathode, reference), gas in/out, and illumination. An important feature of our cell is the ability into the cell. With the water-cooled cap and hollow stainless steel leads used for the electrodes, less than 30°C operation can be maintained at the top of the cell with the melt at 720°C. Computer control of the current source allows I-V measurements to be made.

Melt compositions were typically NaCl (50 wt.%), MgCl₂ (30 wt.%), CaCl₂ (19 wt.%), and CaF₂ (1 wt.%). High purity anhydrous salts were obtained from Alfa Chemical. Melting and subsequent anode tests were always performed under dry nitrogen or argon purge.

Another important feature of our experiment is the spectroscopic analysis of the off-gas. An argon purge is maintained throughout cell operation. The off-gas flows through two 10cm spectrometer cells, coupled to IR and UV-vis spectrometers. The IR spectrometer is a Mattson Galaxy FTIR that scans over the 4500-400cm⁻¹ range, providing sensitive detection of HCl, CO₂, H₂O, and numerous CHCs. An Ocean Optics SD-2000 UV-vis spectrometer is fiber-optically coupled to the second absorption cell that is physically located inside the FTIR frame. The UV-vis spectrometer is sensitive to electronic absorption for species such as Cl₂ that do not have a dipole moment, and therefore are not measurable in the IR.

A unique facility for studying the formation of thin oxide layers on these alloys and for depth profiling of the residual anode after melt testing is available. Coupled with an X-ray Photoelectron/Auger Spectrometer (XPS/AES) with angle-resolved and sputter depth profiling is an instrument known as SARISA (surface analysis by resonant ionization of sputtered atoms). This instrument can accurately measure atomic concentrations while depth-profiling a material, unlike SIMS, which suffers from a substantial matrix effect reducing its ability to quantify insulating layers such as the oxides of interest here. SARISA has recently achieved near part per trillion detection limits, yet can also measure near unity sample concentrations with

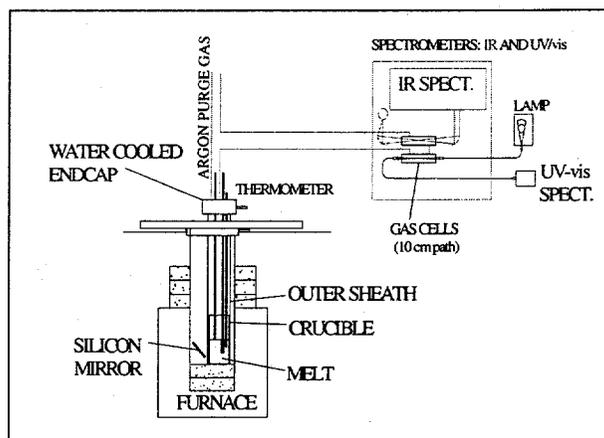


Figure 3: Schematic of Bench Scale Cell with Off Gas Analysis.

the same experimental conditions, yielding close to 9 orders of magnitude dynamic range. SARISA simultaneously measures SIMS along with the neutral yield for comparison.

While accurate depth profiles for short length scales (1-1000nm) can be measured by XPS or SARISA, long-range depth profiles are measured on cross cut samples by energy dispersive x-ray (EDX) spectroscopy. Surface microstructure has been determined for selected samples by scanning electron microscopy. The SEM/EDX instrument is capable of 100nm structure resolution and has 1% detection limit for most elements.

The salts in use in the experiments were also analyzed by inductively coupled plasma atomic emission for metal content.

Results

Results for the heat treatment of a set of alloys and melt testing under potential are described. Table 1 shows the surface EDX measurements for three alloys before and after heat treatment at 900°C in air. The EDX is sensitive to the top 0.5µm of material, but not to low z elements such as O. Both the α-phase and β-phase alloys were seen to double their Al content in the near-surface region upon heat treatment, probably due to the growth of an alumina layer. The addition of 0.5% atomic of a ternary component to the β-phase alloy enhanced this effect, yielding nearly 80% Al in the near surface. This ternary component furthermore was apparently partitioned in the oxide film, since its signal did not change upon heat treatment.

Table 1: Near-surface compositions for polished and heat-treated alloys. Al diffusion to the surface can be enhanced by stabilizing the α-CuAl phase to lower temperatures.

Nominal composition	%Cu	%Al	%Ternary
α-Cu _{0.83} Al _{0.17}	79.7	20.3	--
α-Cu _{0.83} Al _{0.17} heat treated	59.5	40.4	--
β-Cu _{0.77} Al _{0.23}	71.4	28.6	--
β-Cu _{0.77} Al _{0.23} heat treated	48.8	50.4	--
Cu _{0.77} Al _{0.23} Ternary _{0.005} (β-stabilized to 25°C)	69.5	30	0.4
Cu _{0.77} Al _{0.23} Ternary _{0.005} heat treated	19.6	79.3	0.4

An example of the off-gas analysis is indicated in Figure 4. The electronic absorption of Cl₂ is clearly measured near 330nm. This peak grew in over a 30-second period after starting a 5A current flow through a test cell with graphite electrodes. Given the flow rate of the purge gas, this peak represents a concentration in the effluent of about 3%. The expected production rate of Cl₂ at this current is about 4L/hr, and we could realistically measure levels about 40 times lower than that shown, giving us a detection limit of 0.1L/hr for Cl₂.

Angle-resolved XPS of the α-phase CuAl is shown in Figure 5. The data are integrated XPS intensities for the Al (1s) and Cu (2p_{3/2}) peaks measured at various angles from normal incidence

(longer mean sampling depth) to 60 degrees from normal (shorter mean sampling depth, hence greater surface sensitivity). The data demonstrates clearly that the surface has segregated aluminum. This effect can be understood as an expression of minimal surface free energy, and has been previously observed using other techniques on single crystal alloys [10].

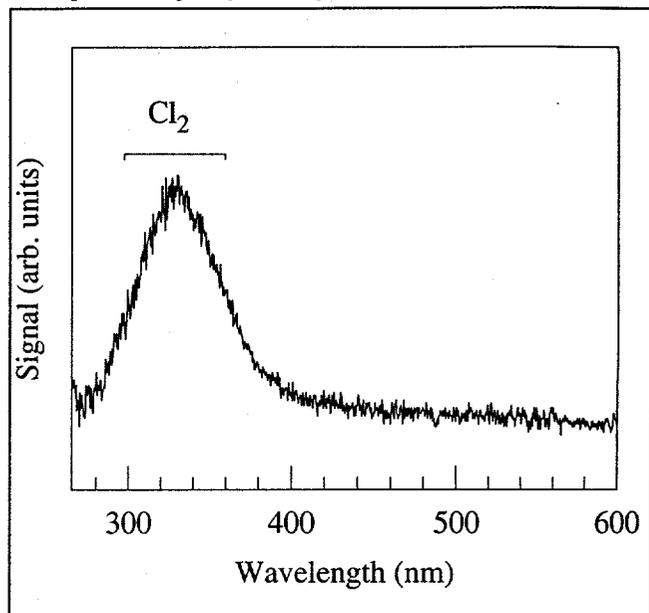


Figure 4: Chlorine production apparent in uv-vis spectrum of off gas with carbon anode.

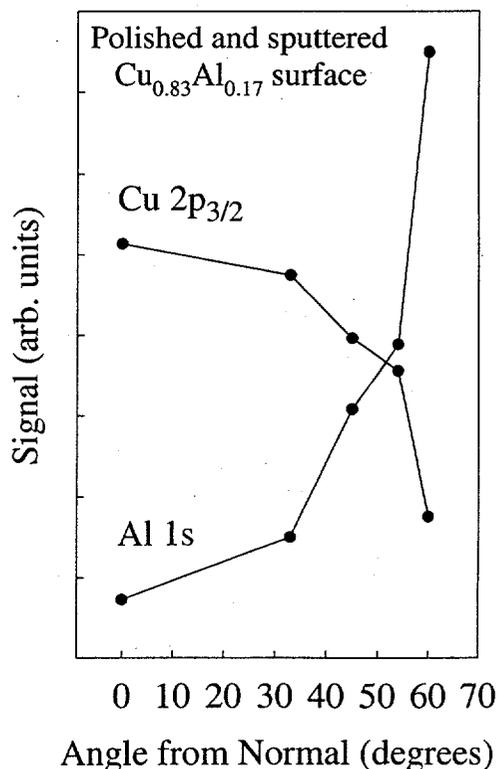


Figure 5. XPS Shows Al Surface Segregated in Clean Alloy.

Although the surface layer may be aluminum rich, the top 3nm of material is initially copper dominated, presumably representative of the bulk composition, as shown in Figure 6 (grey curves). Upon successive exposures to oxygen, the aluminum and oxygen were seen to increase and the copper is diminished (not shown). Finally, the same sample was heat treated in air at 900°C for 4 hours. The curves in black show the final composition of the near surface region, which is at least 99% Al₂O₃. Results for the other alloys studied were similar, with Al₂O₃ being the primary but not always the exclusive constituent of the surface.

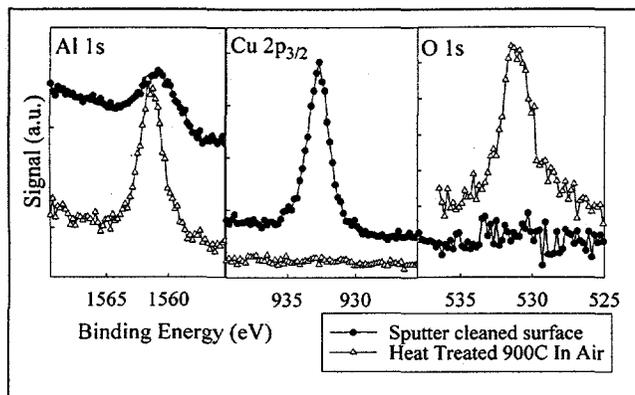


Figure 6. CuAl surface before and after heat treating. The Al diffuses to the surface to oxidize, excluding the Cu.

Initial depth-profile studies using SARISA and the XPS instruments yielded complimentary information about the composition and depth of the oxide films. The depths were typically 4-5nm regardless of heat treatment conditions, although there was considerable variability in Al/Cu content of the oxide. The XPS data consistently showed that the copper oxide in the film was Cu₂O when present. SARISA was able to measure quantitatively the Cu content in the alumina film, which was generally reduced but often as much as 50% of the bulk concentration. The ideal conditions for generating a relatively pure alumina layer were rapid heating and cooling to the 900°C treatment temperature in air.

We have also measured the diffusion rate of Al in the α -phase alloy under unpolarized, wet melt (worst case) conditions. In this case, the protective layer was rapidly lost and the surface became copper rich. A cross section measured by EDX shows a diffusion profile several microns deep into the alloy after only 30 seconds (see Figure 7). An exponential fit to this profile gives a diffusion constant of 10^{-10} cm²/sec. This implies that for a heat treated CuAl alloy used as an anode, the surface can dissolve at up to 1 μ m/sec (initially) before the dynamic reformation of the Al₂O₃ is compromised. In practice the dissolution rate should be much lower than this. Furthermore, for longer times, the implication is that significant quantities of aluminum can diffuse through long distances (mm) of the bulk alloy, driven by the aluminum depletion near the surface.

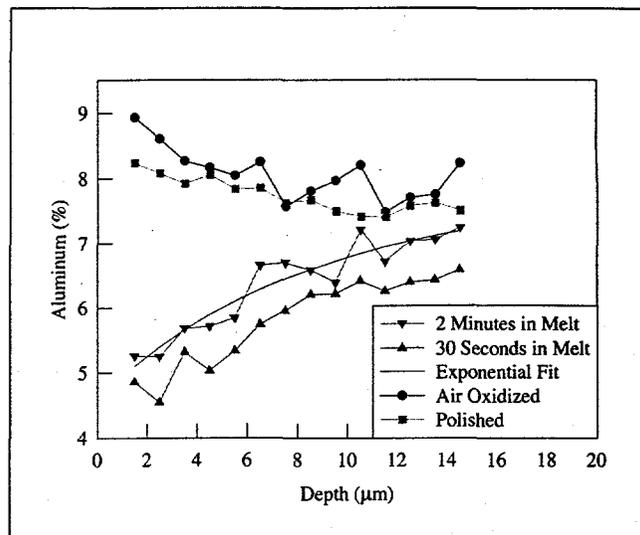


Figure 7. Depth profile of Cu-Al showing rapid Al diffusion in a wet melt, unpolarized. The rapid diffusion of Al allows the oxide layer, under anodic conditions, to reform.

Discussion

The results above show that while it is possible to grow a predominantly Al₂O₃ layer on the surface of the dilute CuAl alloys, there is often some fraction of Cu₂O present. It was observed in preliminary work that the nature of the alloy surface depends on the heat treatment conditions (temperature, oxygen level, and cooling rate). Previous studies showed that for the thermodynamically stable phase to form (Al₂O₃, in this case), the temperature and oxygen level must be in a regime where the diffusion of aluminum to the surface is greater than or equal to the arrival rate of oxygen molecules.[11,12] If the temperature is too low for a given oxygen environment (e.g. air), the rate of oxidation exceeds the aluminum diffusion flux, and the primary component (copper) will oxidize.

Future work

Preliminary cell tests have shown that we can electrowin Mg using a CuAl alloy anode. Stability and reproducibility remain concerns, since in some cases dissolution of copper was observed. We believe that the surface oxide in our initial tests is strained relative to the bulk metal, inducing cracks that lead to film breakdown. We plan to investigate the addition of ternary components to control the composition, thickness, and thermal expansion properties of the oxide so that it can be more adherent and will not suffer breakdown.

Conclusion

We introduce the concept of an inert metal anode for Mg electrowinning in molten chloride baths. By controlling oxidation conditions during anode preparation, for example heating to a sufficiently high temperature, we were able to form pure Al₂O₃ passivating films on a β -CuAl alloy. We expect that under certain cell conditions these films will protect the anode from dissolution,

and slow etching of this layer should be followed by growth of new oxide by transport of Al from the bulk alloy.

[12] Wei Wang, W.A. Lanford, and S.P. Murarka, "Completely passivated high conductivity copper films made by annealing Cu/Al bilayers" *Applied Physics Letters* 68, 1622 (1996).

Acknowledgements

This work was supported by the U.S. Department of Energy, Argonne National Laboratory Directed Research and Development (LDRD) Program under Contract W-31-109-ENG-38.

References

- [1] L. Ongstad, et. al., "Environmental Aspects of Magnesium Production by Electrolysis", *Advances in the Production and Fabrication of Light Metals and Metal Matrix Composites, International Symposium Proceedings, CIM Conference, 1992*, pp. 231-244.
- [2] M. Hansson, et. al., "Occupational Exposure to Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in a Magnesium Production Plant", *Occupational and Environmental Medicine*, 1995; 52, pp. 823-826.
- [3] J. Johnson "EPA's Dioxin Reassessment", *Environmental Science and Technology*, Vol. 29, No. 1, 1995, pp. 26A-31A.
- [4] "New Protocol on Persistent Organic Pollutants Negotiated under the UN Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution", U.S.EPA, April 1998.
- [5] B. Dellinger, "Formation and Destruction of Chlorinated Hydrocarbons Within the Magnolia Magnesium Refining Process", Report prepared for MMI, September, 1997.
- [6] C.F. Windisch, Jr. and S.C. Marschman, "Electrochemical Polarization Studies on Copper and Copper-containing Cermet Anodes for the Aluminum Industry" *Light Metals (Warrendale, PA)*, 1987, 351-5.
- [7] J.N. Hryn and D.R. Sadoway, "Cell Testing of Metal Anodes for Aluminum Electrolysis", *Light Metals (Warrendale, PA)*, 1993, 475-83.
- [8] J. Ferrante "An Auger Electron Spectroscopy and LEED Study of Equilibrium Surface Segregation in Copper-Aluminum Alloys", *Acta Metallurgica*, 19 (1971) 743-748.
- [9] J.L. Murray "The Aluminum-copper System", *International Metals Reviews*, 30 (1985) 211-233.
- [10] A. Laudet, M. Jardinier-Offergeld and F. Bouillon, "Use of Oxygen Auger Line Relative Intensities for Characterization of Surface Oxides on Oxidized Metals and Alloys" *Surface and Interface Analysis* 8, 83 (1986).
- [11] L. Zhu, E. Zur Muhlen, D.J. O'Connor, and B.V. King, "An investigation of oxygen adsorption on α -Cu_{0.82}Al_{0.18}(100) using low energy ion scattering" *Surface Review and Letters* 3, 1241 (1996).