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A DYNAMIC INERT METAL ANODE*

J.N. Hryn and M.J. Pellin

Argonne National Laboratory
Energy Systems Division
9700 South Cass Avenue, Bldg. 362
Argonne, IL 60439-4815

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Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois, USA 60439

Abstract

A new concept for a stable anode for aluminum electrowinning is described. The anode consists of a cup-shaped metal alloy container filled with a molten salt that contains dissolved aluminum. The metal alloy can be any of a number of alloys, but it must contain aluminum as a secondary alloying metal. A possible alloy composition is copper with 5 to 15 weight percent aluminum. In the presence of oxygen, aluminum on the metal anode's exterior surface forms a continuous alumina film that is thick enough to protect the anode from chemical attack by cryolite during electrolysis and thin enough to maintain electrical conductivity. However, the alumina film is soluble in cryolite, so it must be regenerated in situ. Film regeneration is achieved by the transport of aluminum metal from the anode's molten salt interior through the metal wall to the anode's exterior surface, where the transported aluminum oxidizes to alumina in the presence of evolving oxygen to maintain the protective alumina film. Periodic addition of aluminum metal to the anode's interior keeps the aluminum activity in the molten salt at the desired level. This concept for an inert anode is viable as long as the amount of aluminum produced at the cathode greatly exceeds the amount of aluminum required to maintain the anode's protective film.

Introduction

Aluminum is produced by an electrolytic reduction process that was invented 100 years ago by Hall and Héroult. In the Hall-Héroult process, electric current is passed through a 960°C bath of molten sodium aluminum fluoride (cryolite) containing dissolved aluminum oxide (alumina). Molten aluminum metal is produced at the cathode, and carbon dioxide and other gases are evolved at the anode, consuming that anode. Consumable carbon anodes are a source of significant air pollution and energy inefficiency in aluminum production. Substantial research has been conducted to find an alternative for the carbon anode, specifically to find what has been referred to as a nonconsumable or inert anode (i.e., one that supports an electron transfer reaction without being consumed by any type of chemical reaction). To date, despite major research efforts both within and outside the aluminum industry, no satisfactory anode material has been found.

Using nonconsumable anodes in the Hall-Héroult cell for aluminum production would offer environmental, energy, and economic benefits. Carbon anodes used in aluminum production are consumed, evolving CO_2 and CO, as well as unwanted emissions of perfluorocarbons (CF_4 and C_2F_6). The manufacture of carbon anodes also occasions unwanted emissions of polynuclear aromatic hydrocarbons (PNAH), volatile organic compounds (VOC), HF, SO_x, COS, NO_x, CO, and CO_2.[1] All these emissions could be avoided if a suitable nonconsumable alternative to the carbon anode were found, because, during electrolysis, nonconsumable anodes would evolve only oxygen gas. Further benefits of replacing carbon anodes with nonconsumable alternatives include improved energy efficiency because of a lowering of cell voltage. Recognizing that oxygen-evolving nonconsumable anodes would mean a one-volt increase in the theoretical cell voltage required to produce aluminum, the net operating cell voltage will still be lower with nonconsumable anodes because of a lower anode overpotential, a moderate decrease in the anode-to-cathode distance, and improved conductivity within nonconsumable metal anodes. Although measurable energy savings can be realized when retrofitting existing cells with nonconsumable metal anodes, greater energy savings are possible when such anodes are utilized in advanced cell designs, with so-called wettable cathodes. The decrease in emissions and the elimination of the costs associated with environmental compliance, as well as the improved energy efficiency, of cells fitted with nonconsumable anodes will result in improved economics for aluminum production.

For the most part, previous investigations on nonconsumable anodes have focused on oxide-based ceramic anodes and cermet anodes (nickel-ferrite and copper metal dispersions).[2-15] However, using metals, rather than ceramics or cermets, as the nonconsumable anode material offers several advantages. These include (a) improved electrical conductivity (yielding an energy savings of 5% because of decreased anode resistance), (b) improved fracture toughness, (c) improved thermal shock resistance, (d) elimination of nonuniform current distribution or interconnected porosity problems, and (e) ease of fabrication into complex shapes for use in efficient cell designs (allowing for future energy and cost savings as new cell designs are created). Over the years, many metals were considered as candidates for nonconsumable anodes, but apart from a few expensive noble metals (e.g., gold, platinum, iridium), metals were found to corrode in operating Hall-Héroult cells.

Metal Alloys as Inert Anodes

Although pure metals had been tested in the past, it was Sadoway who first suggested alloys that form protective reaction layers could be used as inert anodes in aluminum production.[16] Selection criteria were developed for materials to be used as inert anodes, and these criteria led to the selection of Cu-Al and related alloys for electrolysis testing. It was thought that a stable oxide layer on the anode surface would protect the underlying alloy from corrosion during electrolysis.

Experimental work conducted at MIT by Hryn and Sadoway [17] has shown that copper-aluminum (Cu-Al) and related alloys are promising nonconsumable alternatives to carbon anodes. When acting as anodes in operating Hall-Héroult cells, these alloys generated oxygen on their surfaces and operated at a constant voltage for several hours. Copper levels in the aluminum product varied, but at times they were below detection limits (<0.1%). Further, it has been observed that (a) Cu-Al alloy anodes operate for extended periods without corroding; (b) occasional spontaneous cell upsets occur, as evidenced by a decrease in the cell voltage; and (c) normal cell operation is restored without intervention. These observations were made on anodes during electrolysis testing in near-alumina-saturated conditions (tests in alumina crucibles) and, perhaps more importantly, in alumina-unsaturated conditions (tests in pyrolytic boron nitride [PBN] crucibles). For tests conducted in PBN crucibles, the alumina concentration varied from near-alumina-saturation conditions at the beginning of the tests to near-alumina-starvation conditions at the end of the tests since, during electrolysis testing, alumina was not fed to the cells. It was assumed that a protective film had formed on the surface of these anodes, and that this film would occasionally breakdown and reform (self-heal) spontaneously. However, the mechanisms of protective film formation and self-healing in operating Hall-Héroult cells were not uncovered. Nevertheless, the tests demonstrated that certain Cu-Al alloys could function as anodes in operating electrolysis cells without degrading, even when the alumina concentration in the electrolyte was far below saturation.

Interest in the use of metal anodes as nonconsumable alternatives to carbon anodes has grown since the MIT work was presented in 1992. The key technical impediment to the future development of metal alloy anodes as replacements for carbon anodes is the present lack of understanding of the stability of the alloy surface at the cryolite-metal anode interface.

Corrosion Resistance in Metal Alloy Anodes

Self-Limiting Barrier Film

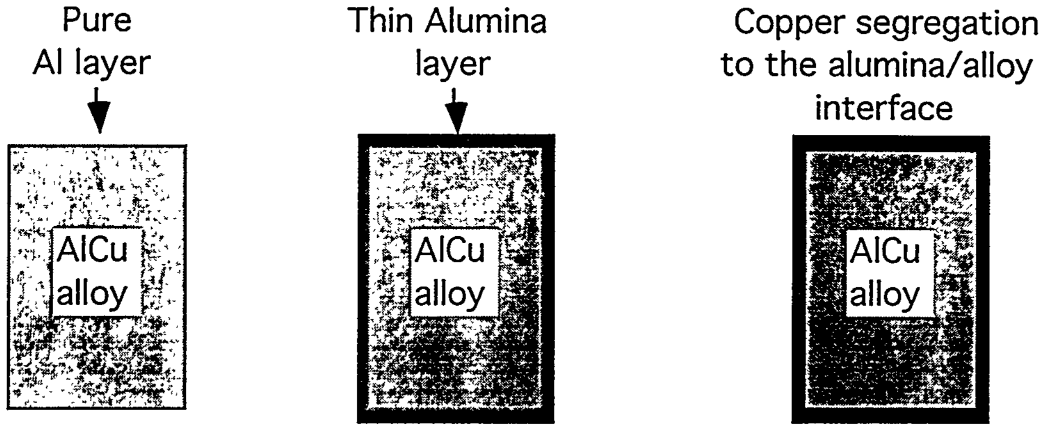
Certain metal alloys, when acting as anodes in operating Hall-Héroult cells, can have dramatically reduced oxidation rates when compared with the bulk metal and yet maintain a coherent oxide film that cannot reach thicknesses that are resistive. Such alloys utilize the varying surface free energies of their constituents to form surface layers that are significantly different in composition than the bulk alloy. The surfaces of such alloys, when scratched, damaged, or accidentally dissolved, will reform (self-heal) during cell operation. Aluminum is the anode constituent of choice for the protective film, because its eventual dissolution will not contaminate the aluminum metal product. Since aluminum is molten at the cell operating temperature, only aluminum-containing alloys with melting points above the operating temperature of Al electrolysis cells are candidate materials. In such alloys, Al segregates to the anode surface to participate in the formation of a passive layer.

Although thermodynamic considerations suggest that any base metal could be used as long as Al is present in the alloy, other considerations lead us to the specific choice of copper. Copper-based alloys are favored for two reasons: (a) their advantageous bulk properties, which include conductivity, fracture toughness, malleability, etc., and (b) their lattice spacing, which is such that alumina on properly prepared alloys has been found to grow in a self limiting manner. When using Cu alone, or some other base metal alloys with Al, as an anode in an electrolysis cell, the resistive oxide layer can grow thick and insulating with time, as evidenced by an increasing cell voltage (at constant current) until the anode is no longer conductive.

As depicted in Figure 1a, an appropriately annealed Cu-Al alloy has initially a surface layer of pure aluminum (measured in ref. [18] and calculated by using known surface energies by the formalism in ref. [19]). Air oxidation of the alloy at temperatures of up to 700°C [18] rapidly produces a 5-10-nm-thick surface film of Al_2O_3 that remained stable for extended periods. While Cu films annealed at 400°C become very rough in 30 minutes, alloys containing as little as 1% Al remain smooth. Air oxidation experiments at MIT produced similar results. One proposed mechanism that may be responsible for this stability and self-limiting film growth is copper segregation into the alumina/alloy grain boundary. This segregation seems to stabilize the growth of grains in polycrystalline material.

Oxidation Rate Reduction

While the formation of a barrier oxide that remains adherent over a wide temperature is an important property of these remarkable alloys, it is not the only property responsible for corrosion resistance. Recent surface corrosion studies of dilute Al in Cu alloys provides insight into the reason this particular alloy is useful in an extremely corrosive environment.[20-26] While these surface oxidation studies (up to 700°C) were performed only on dilute alloys of interest to the microelectronics industry, they demonstrate that small amounts of alloying metals (such as Al) can dramatically increase the corrosion resistance of Cu metal. In the environment of an operating Hall-Héroult cell, this corrosion resistance may be extremely useful in making the anode inert. The suggested mechanism for high-temperature air-oxidation resistance of the alloy can be understood by considering first the oxidation of pure Cu metal.



(a) Annealled in Ar (b) Oxidized (c) Cu segregation

Figure 1. Oxidation sequence of AlCu alloys. (a) In a vacuum, AlCu alloys containing greater than 1 ppm Al will have a surface concentration of Al that exceeds 99.9 atomic % (black line in figure). This surface segregation is a result of the relative volatility of Al and the broken symmetry at the surface. (b) Following high-temperature exposure to oxygen, the alloy will produce a thin (~6 nm) film of Al_2O_3 that resists further oxidation (gray layer in figure). (c) Production of the oxide will be accompanied by a buried layer precipitation of a monolayer or two of pure copper (red layer in figure).

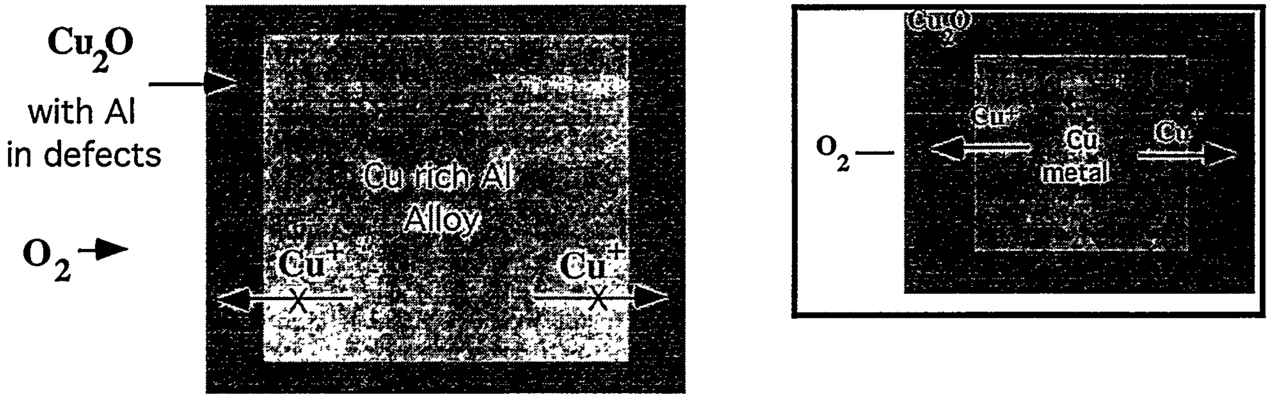


Figure 2. Addition of small amounts of Al and certain other metals to Cu metal reduces the corrosion rate by several orders of magnitude. One mechanism responsible for this reduction results from the incorporation of Al atoms at defect sites in the growing Cu oxide. Cu oxide films grow by defect-mediated transport of Cu^+ through the oxide film to the surface where it can be oxidized (see inset). Since Cu oxide grows with few defect sites, small concentrations of additives are effective in surface passivation.

It has been known for half a century that copper oxide grows primarily by transport of Cu^+ through the growing oxide layer to the surface where it can react with oxygen.[27] This growth mechanism is illustrated in Figure 2. The transport of Cu^+ through the film is believed to occur via ions hopping between defects in the Cu_2O.[27] One successful method of reducing the oxidation rate of copper has been to control the concentration of the vacancies available for migration. Since the concentration of these vacancies is small, this can be accomplished with a very low concentration of dopant.[20-26] Among the dopants tested, Al, Mg, and B reduced the corrosion rate of Cu by factors exceeding 250, even for dopant concentrations equivalent to one part per thousand.

Means of Metal Anode Protection

The formation of a protective surface on the Cu-Al alloys that were tested as inert anodes by Hryn and Sadoway is best thought of as a dynamic process. Over the range of operating conditions that were investigated (from alumina starvation to alumina saturation), both of the corrosion-resistance mechanisms of Al in Cu alloys likely came into play. It is important not to forget that the corrosion resistance arises not just from barrier layer formation, but also from the blocking of Cu ion transport. This combination of properties makes the Cu-Al alloy system quite flexible. However, because of the wide range of cell conditions during aluminum electrowinning, the appropriate alloy concentrations must be optimized carefully. One implication is that previous experiments may have used alloy concentrations that were far from optimized. The two key parameters in the evolution of the surface of the anode are the oxide dissolution rate and the Al diffusion and segregation rate.

Consider conditions in which the dissolution rate of alumina >> diffusion rate of aluminum. In such a situation, the alumina surface of the anode would quickly dissolve, exposing a Cu surface. The corrosion rate of this copper surface would be reduced from that of pure Cu by more than two orders of magnitude by the presence of even a small amount (<0.1%) of Al in the near-surface region. Moreover, it is not necessarily true that copper dissolution into the melt will occur in this case. Even if copper is exposed to the cryolite, its oxidation will be gettered by any nearby Al, since the free energy of formation of Al_2O_3 is so much larger than that of Cu_2O. In this case, copper is oxidized, the oxygen is gettered by aluminum, and then the alumina dissolves. Thus, one gains a dissolution rate for aluminum which is limited by the oxidation rate of copper.

The other limiting case (diffusion rate >> dissolution rate) is more consistent with the observations of Hryn and Sadoway. As noted above, air oxidation of Cu-Al alloys produces an Al_2O_3 layer that is self-limiting at 5-10 nm. If this is also true during Al electrolysis, then the film thickness would stop before its resistance became unacceptably large, as is the case with other metal anodes. Unfortunately, the segregation of Al is not constant in this case; Al is drawn from deeper and deeper within the alloy and eventually this film will dissolve. This phenomenon might explain the disruption observed during the past study.

Concept for a Dynamic Inert Metal Anode

Our understanding of the oxidation of Cu and its dilute Al alloys is significantly better than it was 5 years ago.[18, 20-24, 28-36] The fact that a Cu-Al alloy can function as an inert anode in alumina-unsaturated baths is no longer surprising. Although we know that alumina dissolves in the molten cryolite salt bath, we do not believe that the film is highly soluble in the bath. Anode protection could be due to the nature of the anode's film's microstructure, which may result in a slow dissolution rate, combined with the diffusion and segregation of aluminum from the interior of the metal anode to the anode surface at a rate equal or greater than the alumina dissolution rate, thereby providing enough aluminum to the anode/bath interface to maintain the protective film.

If the rate of alumina dissolution is high, the amount of material dissolving into the bath becomes substantial and cannot be adequately replenished from the bulk alloy. To maintain the film, the segregating metal (Al) must be added to the anode during electrolysis. This can be achieved by adding aluminum (molten at operating temperatures) to the interior of a cup-shaped anode. The added aluminum will then diffuse through the solid copper-aluminum alloy wall of the anode to the bath/film interface, where it is oxidized the form the protective film. This aluminum will end up in the electrolyte as film dissolution occurs. Therefore, what is envisioned is that aluminum metal added to the interior of a cup-shaped anode moves through the anode wall, then through the oxide film, and eventually ends up in the electrolyte. It is this diffusion of aluminum that maintains a protective film on the anode in aluminum electrolysis.

Pure aluminum metal added to the interior of a cup-shaped anode will have a chemical activity that is close to unity (Raoultian scale). At the molten aluminum/anode interface in the interior of the anode, the copper alloy anode material will begin to dissolve into the molten aluminum. At some point, aluminum will begin to diffuse into the anode, causing phase changes in the anode and the formation of intermetallic compounds. This process will destabilize the physical integrity of the anode. Therefore, the aluminum added to the interior of the anode should have a low enough chemical activity to prevent phase changes from occurring in the anode alloy. Dissolving the aluminum in a molten salt before adding it to the anode interior should reduce the chemical activity sufficiently. The aluminum activity in the molten salt can be set by controlling the salt composition and the amount of aluminum dissolved in the salt. For example, the activity can be set to the value of the aluminum-rich boundary of the alpha copper phase. In that case, the aluminum will diffuse through the anode without causing destabilizing phase changes within the alloy anode.

Also, segregation is not limited to Al. Minor impurities or additives may also segregate and be incorporated into the anode's protective film. Appropriate selection of additives can even improve the conductivity of the film, should the self-limiting film be too resistive.

Research at Argonne National Laboratory

We believe that understanding metal alloys and their oxide films will lay the basis for using nonconsumable metal alloys to replace the consumable carbon anodes presently used in aluminum production. Surface characterization is key to understanding the complex nature of how metal alloy anodes remain inert in Hall-Héroult cells. There is no experimental evidence supporting the hypothesis that an oxide layer is present during cell operation; in-situ analysis of operating anodes may be the only way to confirm this possibility. Is dissolution occurring at a rate that is slower than diffusion and oxidation of the aluminum? This is a complex question, the answer to which depends not only the dissolution rate of alumina into the cryolite melt, but also upon the rate of oxidation of aluminum. The liberation of oxygen at the anode requires an understanding of alloy oxidation via both gas-solid and liquid-solid reactions. During cell operation, oxygen bubbles adhering to the anode may be controlling oxidation of the segregating aluminum. Thus, studies of alloy oxidation in controlled oxygen environments may be necessary to sort out what is occurring at the anode surface. We believe that the complex question of the structure and composition of the anode surface in contact with the melt can only be answered by direct experimental measurements in combination with measurements on anodes in more controlled environments. We are conducting such experiments to study these questions.

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