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ADVANCED MATERIALS FOR THE ENERGY EFFICIENT PRODUCTION OF ALUMINUM

Final Report

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Introduction

Aluminum metal is not found in nature in its elemental state. Instead, it is tightly bound with other elements and must be extracted from them. Commercially, aluminum is produced from naturally occurring aluminum compounds by the electrolytic reduction of aluminum oxide, which is obtained from bauxite ore by the Bayer process through digesting crushed bauxite ore in strong caustic soda solution at high temperatures. In 1886 Charles Martin Hall in the United States, and Paul Héroult in France, independently developed the currently employed electrolytic process for extracting aluminum from aluminum oxide. This process, known today as the Hall-Héroult process, transformed aluminum from a precious metal into a common structural material. The process is still the only process used commercially for primary extraction of aluminum metal and is fundamentally the same as it was originally disclosed by Hall and Héroult in 1886.

In this process electric current is passed through a bath of molten electrolyte containing aluminum oxide. An important feature of the Hall-Héroult discovery was that cryolite, a double salt of aluminum and sodium, would dissolve aluminum oxide at temperatures of around 1000°C, and that the dissolved aluminum oxide could be electrolytically reduced to form molten aluminum metal.

The electrolytic reduction is performed in heavy metal cells or pots known as Hall-Héroult cells. These cells have massive carbon anodes normally formed in the shape of large blocks suspended above the cell and capable of being lowered into the electrolyte. The floor of the cell is lined with carbon and functions as the cathode. Direct current is passed from the carbon anodes through the electrolyte to the cathode. The carbon anodes are systematically consumed by a chemical reaction occurring in the cell. This reaction can be represented as

Aluminum produced by the Hall process is very pure, in the vicinity of 99.8%. The main impurities are traces of iron and silicon.

Despite its capability to produce high purity aluminum, the Hall process has always suffered from a number of important problems. One set of problems arises from the use of consumable carbon anodes. These anodes are expensive to produce, and the cost of producing them adds significantly to the overall cost of the aluminum produced by the Hall process. In addition, in the so-called pre-bake furnaces where the raw materials are treated to form the large anode blocks vast quantities of energy are consumed and a substantial amount of pollution is generated. In the Hall cell the anodes are consumed, approximately 0.45 pounds of carbon per pound of aluminum product, with attendant continuous change in shape. This makes it difficult to maintain uniform anode current loading. Furthermore, anode consumption also makes it difficult to maintain proper anode-cathode spacing during operation of the Hall cell. Additionally, the anode-cathode spacing is typically greater than required because of the uncertainty of the consumable anode's shape and the need to maintain a deep molten aluminum pool. Such spacing results in an inordinate consumption of electrical energy, owing to the voltage drop across the molten salt electrolyte. Finally, accompanying the consumption of the anode there is the production of the gaseous oxides of carbon, carbon monoxide and carbon dioxide, which are vented to the earth's atmosphere.

To address the problems caused by carbon anodes, substantial research has been conducted in an effort to find an alternative, particularly to find what has been referred to as an inert anode, i.e., one that supports an electron transfer reaction without being consumed by any type of chemical reaction. In spite of enormous effort by people both within the aluminum industry and outside it, at the time the present study began no fully satisfactory anode material had been found [1].

In a pair of articles by Billehaug and Øye the attempts to discover a nonconsumable anode prior to 1980 have been reviewed [2,3]. Since then, the major efforts have been the following. Alcoa, under sponsorship from the U.S. Department of Energy, Office of Sponsored Programs, examined a variety of mixed oxides and cermet materials. The ceramic phase was nickel ferrite, while the metal phase was ferronickel or copper. A prime example was the cermet consisting of 17 weight per cent copper and 83 weight per cent mixed oxide composed of 51.7 weight per cent NiO and 48.3 weight per cent Fe_2O_3 [4]. This work was terminated by Alcoa in 1985 at which time the Battelle Pacific Northwest Laboratory began to study these materials [5]. Great Lakes Carbon tested cermets in which the ceramic phase was composed of hexagonal ferrite such as $\text{BaNi}_2\text{Fe}_{15.84}\text{Sb}_{0.16}\text{O}_2$ and the metal phase was composed of, for example, $\text{Ni}_{0.7}\text{Cu}_{0.3}$ [6]. Moltech, formerly ELTECH Electrosearch, has been investigating the behavior of a coating composed of cerium oxyfluoride [7]. Lastly, in 1983 with support from the U.S. Department of Energy, Office of Sponsored Programs, research began at MIT. The initial approach was to investigate mixed oxide materials such as nickel, cobalt and manganese ferrites under carefully controlled synthesis and service conditions [8]. Over time these original ferrite chemistries were rejected for reasons given below. Following the DOE sponsored study and just prior to the start of the present investigation, the work at MIT was sponsored by a venture capital firm in Boston and concentrated on anode embodiments of the form of an oxidized reaction layer on a metal monolith.

In an article published in Light Metals 1987, the principal investigator claimed that "the search for inert anode materials has proved to be one of the most difficult challenges for modern materials science" and therefore that a totally different approach had to be adopted [9]. Specifically, it was felt that the problem had to be posed in a way that considered the conditions in an industrial cell during all phases of operation. The term, "dynamic materials system," was coined to describe this image of the Hall-Héroult cell. The consequent analysis was based upon an assessment of the thermodynamics and kinetics of the process viewed from a global perspective. On the basis of this approach a new set of criteria was enunciated for the selection of anode materials. The result was the discovery not only of chemistries previously ignored for this application but also of new anode designs for Hall cells. In an effort to validate these materials selection criteria and to demonstrate the viability of these design concepts tests were conducted at MIT in cells at the 1-ampere scale and in the research and pilot facilities of an American aluminum producer at the scales of a 10-ampere cell and a 100-ampere cell. In the light of the results from these tests and in response to further theoretical analysis at MIT the criteria for materials selection were revised. As well, a much broader framework for success/failure analysis was constructed. The revised the set of materials selection criteria and how they fit into this broader framework were reported in Light Metals 1990 [10].

An application of these new selection criteria resulted in the choice of a metal anode covered by a protective oxide film. More specifically, the anode is designed so that the operating conditions of the cell promote on the anode's surface the formation of an oxide layer that is both thick enough to prevent chemical attack of the underlying metal and yet thin enough to allow electronic current to pass without a substantial increase in cell voltage. To assess the viability of this concept, specimens of various candidate alloy compositions were subjected to electrolysis testing. This document describes the experiments and report the results.

Materials Selection

At the outset of this work the plan was to design a composite material consisting of a metallic core covered by an oxidized surface reaction layer. The reaction layer must satisfy the chemical and electrochemical requirements specified in the selection criteria and simultaneously provide an adequate level of electronic conductivity. The initial choices of candidate anode materials systems were

- * perovskite structure oxides on metal alloy: LaCrO_3 on LaCr
- * spinel structure oxides on metal alloy: MgCo_2O_4 on MgCo

Both LaCrO_3 and MgCo_2O_4 are known to exhibit a high degree of electronic conductivity at elevated temperatures. The oxides of lanthanum and magnesium fully satisfy the selection criteria.

It became apparent in the early stages of the investigation that to prepare anode test specimens of composite materials according to the above formulations would be extremely difficult. Rather than risk paralyzing the electrolysis testing for lack of proper specimens it was decided to search for analogous chemistries that conformed to the same selection criteria as LaCrO_3 and MgCo_2O_4 . Accordingly, CaTiO_3 and CaFe_2O_4 were chosen; the other contenders at this point were the analogous compounds in which Ca is replaced by Mg or Al. The Ca-containing variants were selected owing to the availability of fundamental property data and ease of procuring material from domestic suppliers. The goal was to choose compounds known to be chemically and electrochemically stable at Hall-cell operating temperatures and known to possess the requisite electronic properties. To narrow the field of candidate materials even more, preference was shown towards alloys containing elements that are already present in Hall bath, i.e., Na, Ca, and Al (along with Mg and Li in some instances). Both the spinel, CaFe_2O_4 , and the perovskite, CaTiO_3 , exhibit n-type semiconductivity, and the latter can be made much more conductive (and p-type) by doping with Nb^{5+} introduced as Nb_2O_5 .

The initial plan was to prepare anode test specimens from the oxide powder by hot isostatic pressing (HIP) onto a stainless steel core. Stainless steel was chosen because it does not undergo phase transformation over the temperature and pressure cycles of HIP-ping. However, the steel tubes used as the container in standard HIP-ping practice were unacceptable in this work owing to the fact that they would allow the stainless steel core would move out of position during

vacuum sealing. It was decided to use instead of steel tubes, evacuated Vycor™ capsules lined with platinum foil. Vycor™ was selected because its softening point falls in the right part of the temperature range employed for consolidation of the powders. By using this HIP-ping procedure it would be possible to guarantee composition of the anode surface layer. The plan was to prepare at a later date test anodes by growing oxide surface layers onto metal monoliths of Ca-Fe or Ca-Ti alloys.

In the midst of preparing these specimens came the recognition that the Al-bearing variants of these compounds might be much easier to prepare owing to the peculiar nature of Al_2O_3 films when they form on metals. In his treatment of the kinetics of oxidation of metals Wagner cited as one example the copper-aluminum system [11]. He made the point that alloys containing less than 4 weight per cent aluminum would be subject to so-called "internal oxidation," where islands of aluminum oxide form inside the copper matrix. For alloys containing more than 4 weight per cent aluminum one could expect the formation of a surface layer of aluminum oxide. Copper oxide does not form owing to the fact that alumina is so much stabler; put another way, in the presence of aluminum, under certain conditions copper can be made immune to oxidation. The standard free energies of formation of copper oxide and aluminum oxide at 970°C are -94 kJ/mol of O_2 and -853 kJ/mol of O_2 , respectively. The 970°C isotherm of the copper-aluminum-oxygen phase diagram is plotted in Figure 1 (b). This shows that in the presence of pure oxygen at a pressure of 1 atmosphere the oxide in equilibrium with copper-aluminum alloys containing even up to 60 mole per cent aluminum is the two-phase mixture of CuO and CuAl_2O_4 (see top of the diagram starting from extreme left). However, when such an alloy is first exposed to molten cryolite the oxide is expected to dissolve. When the new oxide forms it will consist of only pure alumina for all but the most dilute solutions, i.e., copper containing less than several parts per million aluminum. The question for the present investigation was this: if the newly exposed metal is covered with a film of pure alumina, will this film remain in place to protect the underlying metal from further oxidation and at the same time allow electronic current to pass without a substantial increase in electrical resistance? Alternatively, will the initially formed alumina film, which at 970°C and 1 atmosphere oxygen pressure is metastable, resist conversion to the mixed copper-aluminum oxide? If so, then this alloy system would satisfy all the requirements of an inert anode. On this basis, then, aluminum bronzes (Cu alloys containing between 7 and 15 weight per cent Al) were chosen as primary candidates for nonconsumable anodes. Pursuant to the choice of Cu-Al alloys, other anode chemistries were investigated: Ni-Al, Cr-Al, and Fe-Cr-Al. Table I gives the exact compositions. These alloys were chosen because they follow the formula of M-Al, where M is a solvent metal in which aluminum dissolves to form preferably a single-phase solid solution; additionally, M is more noble than aluminum so that the surface oxide is alumina, and not the mixed oxide containing both M and aluminum. In many respects this is the principle behind the design of alloys for use as components in jet engines, e.g., CoCrAlY and FeCrAlY. These are essentially Co-Cr and Fe-Cr alloys doped with Al and Y, which have a much greater affinity for oxygen than do Co, Fe, and Cr. Exposure to oxygen results in the formation of an oxide comprised mainly of alumina and yttria. The use of the combination of Al and Y is dictated by the need to match the lattice parameters of the metal and the oxide film. The figure of merit in this instance is the Pilling-Bedworth ratio which is the ratio of the volume of the oxide divided by the volume of the metal components

contained therein. Perfect lattice matching is achieved with a PB ratio of 1. If PB is less than 1 as is the case with the oxides of the alkali metals, the oxide film forming on the metal's surface does not provide complete coverage and the metal is not protected against total consumption by oxidation. If PB is greater than 1, the oxide film provides complete coverage for the metal; however, if PB is too high, e.g., in excess of 2, tensile stresses develop between the metal and the surface film and in the extreme cracking and delamination can occur. Hence, good engineering practice suggests that the lattice constants be tailored for the highest degree of similarity.

Table I Anode Compositions

Cu-Al	Ni-Al	Cr-Al	Fe-Cr-Al
*Cu-15% Al	*Ni-31.4% Al	*Cr-50% Al	*Fe-22.5% Cr
*Cu-11.8% Al			-5.5% Al
*Cu-7.5% Al			-0.6% Si

*weight per cent

Whether aluminum bronze can serve as a nonconsumable anode depends upon whether it is possible to maintain a protective film on the material. In other words, can Hall cell operation establish conditions that not only allow film formation but also prevent its destruction? Observations in the present investigation suggest that the answer to this question is affirmative. Film formation on a working anode occurs because evolving oxygen reacts with the aluminum in the alloy. This selective oxidation of aluminum can be attributed to the pronounced difference in the free energies of formation of alumina and the oxides of the other constituents of the alloy. For example, in the case of aluminum bronze which consists of aluminum and copper, if the current is interrupted for an extended period of time and the alumina film dissolves owing to the fact that the bath is not saturated with alumina, the copper in the anode should not then be chemically attacked by the bath. It remains to be seen whether in order to prevent dissolution of the alumina film it is necessary to operate at alumina saturation of the bath. In support of the opinion that alumina saturation may not be necessary there is speculation that on the electrode surface the oxygen gas fixes the chemical potential of the oxide ion, $\mu_{O^{2-}}$, at a value much higher than that of the bulk electrolyte through the equilibrium

even though the anode is positively charged and is thus electron-deficient. If chemical dissolution of the alumina film is represented by

then this reaction may be arrested by maintaining a high chemical potential of either O^{2-} or Al^{3+} . Operating at low bath ratio has the effect of increasing the chemical potential of Al^{3+} , $\mu_{Al^{3+}}$, which in turn has the effect of further stabilizing the alumina film. This seems to be in conformity with the observation in the present investigation (by no means definitive) that electrolysis in low-ratio bath gave the best results in terms of aluminum purity, i.e., lowest levels of contamination by anode constituents.

Description of the Experiments

Specimen Preparation

Anodes were prepared in the following manner. Copper - aluminum alloys were made by melting reagent grade copper and aluminum in graphite crucibles at a temperature of $1300^{\circ}C$ under an argon atmosphere. The melt was stirred with a graphite rod to ensure mixing of the constituents. To minimize segregation as the melt solidified, the specimen was subjected to air and water quenching. The metal was removed from the crucible, machined into the shape of a cylinder measuring about $3/4$ " in dia. and 1" high, and ground smooth with 600 grit silicon carbide. The specimen was then heat treated at $1000^{\circ}C$ in air for 24 hours to form a protective film. Finally, the specimen was welded to an inconel rod, $1/8$ " in dia.

Nickel - aluminum specimens, $NiAl$ and Ni_3Al , were prepared commercially (Xform Inc., Cohoes, NY). Powder was hot pressed and sintered into cylinders, $3/4$ " in dia. and 1" high, of closed porosity. Before electrolysis testing, the specimen was ground smooth on an alumina grinding wheel and welded to an inconel rod, $1/8$ " in dia.

Chromium - aluminum alloy specimens were made in two ways: casting and sputtering. Castings were prepared by dropping several chromium pellets (chromium powder wrapped in aluminum foil) into aluminum metal held in a graphite crucible at a temperature of 1600 to $1650^{\circ}C$ under a shroud of flowing argon. To ensure mixing of the constituents and dissolution of the chromium the melt was stirred with a graphite rod. To minimize segregation as the melt solidified, the specimen was subjected to air and water quenching. On an alumina grinding wheel the solidified metal was ground into the shape of a cylinder measuring about $3/4$ " in dia. and 1" high. To form a protective oxide film on the surface of the specimen it was annealed at $1000^{\circ}C$ for 24 hours in air. This heat treatment also served to relieve the high level of internal stress in the specimen which was prone to shatter and pulverize if left untreated for several days after casting. Sputtered specimens were prepared by coating an alloy monolith of copper - aluminum or nickel aluminum with alternating layers of chromium and aluminum and annealing to form both the surface alloy and the protective oxide.

The Fe - Cr - Al anodes were fabricated from an ingot of commercially available material (alloy 875, Hoskins Manufacturing Co., Hamburg, MI). Unlike most of the cast alloys mentioned above, Hoskins 875 is machinable; thus, it was possible to make electrical contact by screwing a threaded inconel rod, $1/8$ " in dia., into a hole tapped into the top of the anode. Before electrolysis the

surface of the specimen was ground down to bare metal. To form a protective film the specimen was heat treated in dry oxygen at 1300°C for 24 hours.

Electrolysis Testing and Analysis

Figure 2 shows the apparatus for testing anode specimens. Electrolysis was conducted in a 10 A cell located within an electrical resistance furnace with a nominal 4" bore. A typical experiment began with weighing out the reagent grade (99.9+%) salts comprising the bath (about 300 g total). Table II gives the two bath compositions adopted in this study. Chiolite, $\text{Na}_3\text{Al}_3\text{F}_{14}$, was used where possible. Some experiments were conducted at 970°C in a melt representative of industrial Hall bath, i.e., bath ratio of 1.15 and 5% CaF_2 , while others were conducted at 750° and 840°C in so-called "low-ratio" bath, i.e., bath ratio of 0.56, with or without CaF_2 . The concentration of alumina was varied: in some experiments the bath was at alumina saturation while in others the concentration of alumina was less than half of this value. Tests conducted at alumina saturation could be performed in an alumina crucible. Otherwise, a crucible of pyrolytic boron nitride was used.

Table II Electrolyte Compositions

representative Hall bath (bath ratio = 1.15)	"low-ratio" bath (bath ratio = 0.56)
78% Na_3AlF_6	54.6% Na_3AlF_6
10% AlF_3	36.4% AlF_3
5% CaF_2	0 or 5% CaF_2
up to 7% Al_2O_3	up to 4% Al_2O_3

Throughout most of this study there was no starter cathode consisting of an aluminum puddle or heel. Instead, a shard of TiB_2 measuring approximately 1" square and 1/4" thick served as the cathode. Liquid aluminum wets this material. In a typical experiment it took only about 20 minutes of electrolysis to coat the shard of TiB_2 with metal. In the early experiments the TiB_2 sat on the bottom of the crucible. Later, in an attempt to guarantee that the impurity levels found in the aluminum produced during the test were representative and not experimental artifacts, the TiB_2 shard was placed on a table made out of an inverted alumina crucible, 1" in dia. and about 1" tall. Insulated from the bath with pyrolytic boron nitride tubing, a tungsten rod acting as current collector completed the circuit between the cathode and the power supply. The electrical connection was simply a pressure contact.

Once the crucible had been charged with the electrolyte and the cathode shard placed on the table, the thermocouple, anode and insulated tungsten current collector were positioned above the salts. The crucible was covered with a lid of pressed alumina fiber or alumina refractory brick which helped to minimize vaporization losses from the bath and to align the various cell components. The crucible was then placed in an inconel can which in turn was lowered into a clos-

ed-one-end alumina reactor tube inside the furnace. The top of this alumina tube was covered with cap made of 1/4" thick aluminum plate. Ports in the cap provided gas-tight access for the electrodes, the thermocouple, gas inlet and outlet, and bath sampling tube.

Under a flowing argon atmosphere the cell was heated at a rate not exceeding 100 K per hour to approximately 50 K above the electrolysis temperature and held at this temperature for about 3 hours to ensure melting of all the salts. The cathode current collector and the anode were energized prior to immersion into the melt. Then the current collector was connected to the TiB_2 plate, and the anode was lowered into the melt to a depth of 2 to 5 mm. In experiments with low ratio bath it was impossible to conduct electrolysis at current densities greater than about 0.1 A cm^{-2} without experiencing loss of current caused by what is thought to be freezing of electrolyte on the cathode due to shift in bath composition. This was remedied by fitting the cell with an alumina tube, 1/8" in dia., positioned several millimeters above the top surface of the cathode and by bubbling helium through the electrolyte. At the end of the test, the anode was raised out of the bath to break the electrolysis circuit. The temperature was decreased at 80 K per hour to room temperature.

Electrolysis was conducted at constant current (galvanostatically) such that the current density on the anode was typically on the order of 1 A cm^{-2} , although during the course of this investigation anodes were tested at current densities as high as 2.4 A cm^{-2} and as low as 0.25 A cm^{-2} . The active surface area of the cathode varied with the size of the TiB_2 shard but typically exceeded that of the anode by a factor of 1.5 to 2.

A four-channel strip chart recorder logged current, voltage, temperature, and oxygen concentration in the gas stream leaving the cell.

Results and Discussion

To provide baseline data for this investigation the cell was operated with anodes of carbon and platinum. Figure 3 shows a segment of the voltage trace on carbon. The carbon anode was a cylinder of high-purity graphite, just under 1" in dia., fitted with a sleeve of alumina so that only the bottom face was electrochemically active. On the time interval shown, the current was set at 3.45 A which represents a current density of 0.7 A cm^{-2} . Cell voltage was measured to be 2.75 V. Evidence of gas bubble evolution is the periodic fluctuation of cell voltage in the amount of approximately 0.15 V. Figure 4 shows a segment of the voltage trace on platinum. The platinum anode was made of a platinum crucible, 1" in dia. and 4" high. Provided the platinum crucible was only partly immersed, it functioned as a hollow anode of substantial size given the comparatively small amount of platinum metal present in total. There was no insulating sleeve, and so the active area of the anode varied with depth of immersion. On the time interval shown current was set at 7.1 A which represents a current density of 0.7 A cm^{-2} . Cell voltage was measured to be 7.1 V. Evidence of gas bubble evolution is the periodic fluctuation of cell voltage in the amount of approximately 0.05 V. Also given in Figure 4 is the trace of the output of the oxygen sensor measuring the oxygen concentration in the gas leaving the cell which operated under a constant through flow of argon. These experi-

ments show that the magnitude of the voltage fluctuation on carbon is about three times that on platinum. This is in conformity with previous studies in which it has been asserted that carbon dioxide evolution on carbon is a much more highly activated process than oxygen evolution on platinum or even on some of the monolithic ceramic anodes such as tin oxide and nickel ferrite [2].

Figure 5 shows results obtained with an anode of copper containing 11.8 weight per cent aluminum. The electrolyte in this test was the so-called representative Hall bath saturated with alumina, and the temperature was nominally 970°C. The cathode was a plate of TiB_2 sitting on the floor of the crucible. During the course of this experiment the current was set at a number of values so as to vary the anodic current density from as low as 0.25 A cm^{-2} to as high as 2.4 A cm^{-2} . Anode performance as measured by external electrical parameters was excellent, i.e., undistinguishable from that of platinum, and appeared to be insensitive to current density. For most of the test, however, the anodic current density was set at 1 A cm^{-2} . On the time interval shown in Figure 5 the current was set at 9.6 A and 5.6 A which represent current densities of 2.4 and 1.4 A cm^{-2} on the anode. The interelectrode gap at this time was 1". The voltages recorded were 6.0 V at 9.6 A and 4.28 V at 5.6 A. The shape of the voltage trace is very similar to that of the platinum anode tested in the same cell. The main features of note are the absence of drift to higher values and the presence of fluctuations comparable in size to those seen on platinum.

Figure 6 shows results obtained later in the same experiment as that cited in Figure 5. On the time interval shown in Figure 6 the current was set at 4.0 A which corresponds to an anodic current density of 1.0 A cm^{-2} . The steady state voltage at this current was 3.6 to 3.7 V. Figure 6, however, shows a certain curious form of behavior. Approximately 2 hours into the segment shown in Figure 5 the voltage drops to 2.55 V, a value too low to sustain electrolysis of alumina. This is supported by the drop in the oxygen concentration in the exit gas. Then after a period of about 75 minutes the voltage rises back to 3.7 V with the attendant increase in oxygen level in the exit gas, as seen before the voltage drop. What happens when the voltage drops to 2.55 V? If oxygen evolution is not the anodic reaction, what is it? How is it that the anode can recover from this condition? On the basis of the work done during the course of this investigation the answers to these questions remain unknown. However, it is important to recognize that the anode of aluminum bronze has the capacity to recover from failure. This experiment lasted 47 hours before the cell was shut down. Oxygen was produced during some 31 hours. The aluminum metal product was found by EDAX to contain copper in the amount of 1.4% by weight. While this is unacceptably high from a commercial perspective, one must keep in mind the very small scale of these experiments. In subsequent tests with low-ratio bath the copper level was decreased to below 0.1% in the aluminum metal product.

Figure 7 shows results obtained with an anode of iron containing 22.5 weight per cent chromium, 5.5 weight per cent aluminum, and 0.6 weight per cent silicon (Hoskins alloy 875). At a constant current of 10 A the cell voltage rises over 1.25 hours to 6.3 V. Then, the voltage ramps up a full volt to 7.3 V in 5 minutes. This behavior is what one expects when the anode is being covered by a resistive film of increasing thickness. Subsequent examination of the anode confirmed this to be the case. The aluminum metal product contained 0.45 weight per cent iron and 0.1 weight per cent chromium.

Figure 8 shows results obtained with an anode of chromium containing 50 weight per cent aluminum. The electrolyte in this test was the low-ratio bath containing 5% CaF_2 and saturated with alumina. At the time of this test the cell did not have the helium bubbler. Attempts to conduct electrolysis at a temperature of 750°C had failed and thus during the time of the segment shown in Figure 8 the temperature was 840°C . Even at this temperature it was difficult to sustain current at any reasonable value. In spite of a set point current of 5.4 A, the capacity of the power supply has been exceeded and the cell is operating under voltage control at a value of nominally 10 V. Under these conditions, a periodic variation in current is observed. This has been explained in terms of freezing out of bath on the cathode due to the concentration gradients established during electrolysis. Without raising the temperature, the way to avoid this problem is to improve bath circulation. The aluminum metal produced in this test contained chromium in an amount below the limit of detection as analyzed by EDAX, i.e., less than 0.1% by weight.

Figure 9 shows results obtained with an anode of chromium and aluminum sputtered onto the surface of a casting of nickel - 6% aluminum. The electrolyte in this test was the low-ratio bath containing 5% CaF_2 and saturated with alumina, and the electrolysis temperature was 750°C . The bath was stirred by means of helium bubbling through an alumina tube, 1/8" in dia., positioned in the interelectrode gap and with the gas flow directed at the surface of the TiB_2 cathode substrate. Figure 9 shows the current set at 1.6 A which corresponds to a current density of 0.25 A cm^{-2} on the anode and 0.12 A cm^{-2} on the cathode. Over the 1.75-hour period depicted in Figure 9 the voltage decreased from 3.3 to 2.7 V. Clearly, this is not the behavior of an anode undergoing catastrophic oxidation.

Conclusions and Recommendations for Future Work

While the technical viability of metal anodes has not been proven, the experiments conducted during the course of the present investigation look promising. There is no doubt that an anode comprising a metal core and an oxide surface film can function as an anode. The longest test lasted almost 50 hours. On several occasions in low-ratio bath, electrolysis produced aluminum containing immeasurable amounts, i.e., less than 0.1%, of the anode base metal. It is not known whether the key factor in this high level of performance is the low temperature or the high aluminum fluoride level in the bath. While the choice of alloys containing aluminum is justifiable in the light of the relevant thermodynamics, the long-term sustainability of the anode rests on what is clearly metastable at Hall-cell operating conditions.

The nature and mechanisms of failure of the protective film that forms on the anode must be investigated more intensively in order to determine how to adjust anode composition, bath composition and operating parameters so as to extend service lifetime and improve the purity of metal produced in the cell.

Two distinct and distinguishable failure modes have been identified. Mode 1 failure: no current, the onset of which is the unchecked rise in cell voltage. Ex situ inspection reveals pronounced oxidation of the anode metal. Mode 2 failure: no oxygen, the onset of which is the substantial drop in voltage below

what is necessary to electrolyze alumina. There is evidence that even without intervention the anode can recover from this second mode of failure.

The performance of the anodes seemed not be connected with either alumina concentration or current density.

Through the conduct of this investigation it has become evident that the methodology for anode selection can be extended to other materials selection problems. For example, in the production of magnesium by fused salt electrolysis of magnesium chloride, as practiced by the Dow Chemical Co., substantial quantities of carbon are consumed as anodes, approximately 0.1 lb carbon per pound of magnesium product. In trying to find an alternative material in this application, one would have to face the same set of issues described above. Fused salt electrolysis is important in the production of the alkali metals, alkaline earth metals, and the rare earth metals. This latter group is very important from the standpoint of advanced magnetic materials such as iron-neodymium-boron $\text{Nd}_2\text{Fe}_{14}\text{B}$, and as precursors to the so-called high T_c superconducting ceramic materials, e.g., $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$.

In the area of fused salt batteries, the identification of advanced materials for electrodes, separators, diaphragms, and containers would pave the way for the commercialization of this technology. Again, the selection criteria and testing methodology used in the present investigation could play a major role in solving these problems. In this sense, the search for advanced materials for Hall cells can be considered a test vehicle and forms the basis for future studies directed at the problems named in this section.

In connection with the problem at hand, the nonconsumable anode for the Hall cell, the following are suggested for future research:

1. Continued testing at low temperature in low-ratio bath. The anode benefits from the lower temperature which has the potential to modify the nature of the protective film on the exterior of the anode. In addition, the high aluminum fluoride levels in low-ratio bath may help stabilize the protective film.
2. Test other chemistries for the anode, including multicomponent alloys. Prime candidates are the ternary system copper-nickel-aluminum and the superalloys used in jet engine turbines, namely, CoCrAlY and FeCrAlY.
3. Longer tests. In order to attain steady state operation and results unbiased by the initial conditions, testing for extended periods of time is advised.
4. Larger cells. As a corollary to recommendation 3, a larger test cell has a surface/volume ratio more representative of an industrial cell. In addition, a larger test cell has the room for more points of access and thus can be more completely instrumented for on-line diagnosis.

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Publications from this Research

Articles:

1. J.N. Hryn and D.R. Sadoway, "Cell Testing of Metal Anodes for Aluminum Electrolysis," Light Metals 1993, S.K. Das, editor, TMS, Warrendale PA, 1993, pp. 475-483.

Patents:

1. D.R. Sadoway, inventor, Massachusetts Institute of Technology, assignee, "Apparatus for the Electrolytic Production of Metals," U.S. patent no. 5,254,232, October 19, 1993.

Figure 2. Laboratory-scale aluminum reduction cell for testing anodes.

Figure 3. Electrolysis testing of a graphite anode. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed = 2 cm/min.

Figure 4. Electrolysis testing of a platinum anode. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Oxygen scale: 10 units = 1%. Chart speed = 5 cm/min.

Figure 5. Electrolysis testing of an aluminum bronze anode, copper - 11.8% Al.
 Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed
 = 2 cm/min.

Figure 6. Electrolysis testing of an aluminum bronze anode, copper - 11.8% Al.
Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed
= 2 cm/hr.

Figure 8. Electrolysis testing of a chromium - aluminum anode, Cr - 50% Al. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed = 12 cm/hr.

Figure 9. Electrolysis testing of a chromium - aluminum anode, Cr and Al sputtered onto a monolith of Ni - 6% Al. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed = 12 cm/hr.

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