CELL TESTING OF METAL ANODES FOR ALUMINUM ELECTROLYSIS

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Abstract

The technical viability of a nonconsumable anode made of metal is under investigation. Chosen according to selection criteria previously disclosed, the metal anode is designed to form a protective oxide layer that under cell operating conditions is thick enough to prevent chemical attack of the underlying metal yet thin enough to allow electronic current to pass without a substantial increase in cell voltage. Testing involved electrolysis in a 10 A cell fitted with candidate anodes and TiB_2 cathodes. Anode specimens were made of various Cu-Al, Ni-Al, Cr-Al, and Fe-Cr-Al alloys. Test cells operated under the following conditions. Anodic current density was set at a number of values between 0.25 and 2.4 A cm^{-2}. Bath ratio was set at two values, 1.15 and 0.56. When the bath ratio was 1.15 electrolysis was always conducted at a temperature of 970°C, whereas with a bath ratio of 0.56 experiments were performed at 750° and 840°C. Alumina concentration was varied from saturation to exhaustion. Best results were obtained with anodes composed of Cu-Al and Cr-Al alloys, especially when tested at low temperature in melts with a bath ratio of 0.56. Cells generated oxygen and produced aluminum metal containing less than 0.1% copper and chromium, respectively. The longest test lasted 47 hours. Voltages compared favorably with that measured on a cell fitted with a carbon anode.

Introduction

Previous work in this laboratory led to the enunciation of new selection criteria for the identification of materials for use as nonconsumable anodes [1]. These selection criteria were rather different from those employed by others in that not only was the question of anode composition addressed, but a much broader framework for failure analysis was constructed so that important factors such as anode shape and experimental test conditions could be systematically studied. Application of the selection criteria resulted in the choice of a **metal** anode covered by a protective oxide film. More specifically, the anode is designed so that cell operating conditions promote on its 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 article reports the results.

Materials Selection

It is beyond the scope of this article to give a full account of the decision making process that led to the choice of the materials used in this study. Suffice it to state that through application of the selection rules cited above [1] it appeared that it was possible to construct an anode consisting of a metallic body or core covered by a protective oxide layer. In other words, chemistries with the potential to meet all the known requirements were identified. 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). Finally, recognition of the behavior of certain aluminum alloys to form a tenacious oxide film led to the choice of aluminum bronzes (Cu alloys containing between 7 and 15 weight per cent Al) as primary candidates. Pursuant to the choice of Cu-Al alloys, other anode chemistries were investigated: Ni-Al, Cr-Al, and Fe-Cr-Al. The compositions of the various candidates are given in Table I.

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 a particular aluminum alloy can serve as a nonconsumable anode depends upon whether one can 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 anode 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

$$3/2\ O_2\,(g)\ +\ 6\ e^-\ =\ 3\ O^{2-} \qquad (1)$$
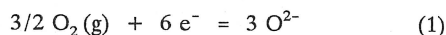
even though the anode is positively charged and is thus electron-deficient. If chemical dissolution of the alumina film is represented by

$$Al_2O_3\ \rightarrow\ 2\ Al^{3+}\ +\ 3\ O^{2-} \qquad (2)$$
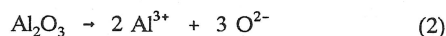
then this reaction may be arrested by maintaining a high chemical potential of **either** O^{2-} or Al^{3+}. Operating at low bath ratio has the effect of increasing the chemical potential of Al^{3+}, $\mu_{Al^{3+}}$, which in turn has the effect of further stabilizing the alumina film. This seems to 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°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°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$_3$Al, 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°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°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

Figure 1 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, Na$_5$Al$_3$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$_3$AlF$_6$	54.6% Na$_3$AlF$_6$
10% AlF$_3$	36.4% AlF$_3$
5% CaF$_2$	0 or 5% CaF$_2$
up to 7% Al$_2$O$_3$	up to 4% Al$_2$O$_3$

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
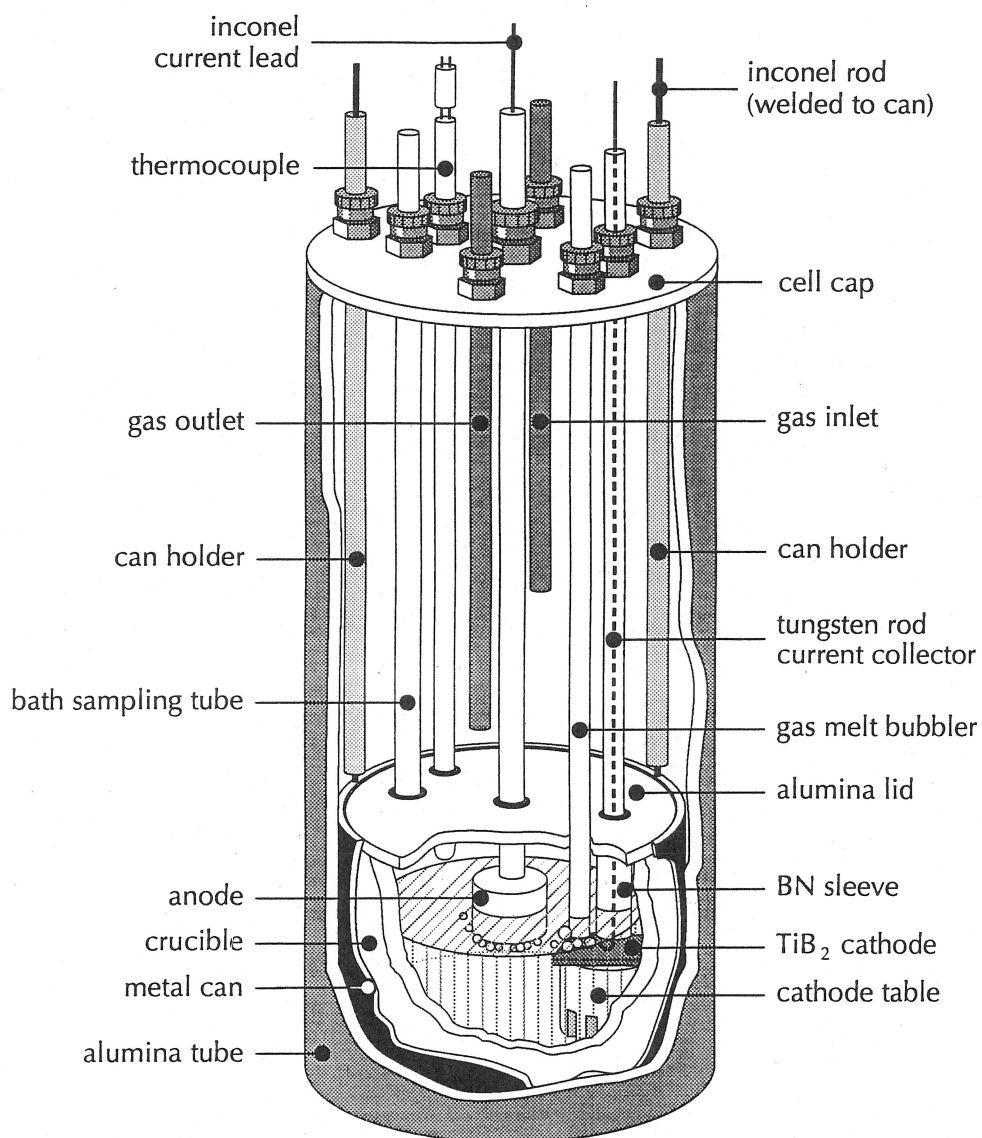
Figure 1. Laboratory-scale aluminum reduction cell for testing anodes.

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. To reduce vaporization losses from the bath and to align the various

cell components the crucible was covered with a lid of pressed alumina fiber or alumina refractory brick. The crucible was then placed in an inconel can which in turn was lowered into a closed-one-end alumina reactor tube inside the furnace. The top of this alumina tube was covered with a 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.

<u>Results and Discussion</u>

To provide baseline data for this investigation the cell was operated with anodes of carbon and platinum. Figure 2 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 3 shows a segment of the voltage trace on platinum. The platinum anode was made of a platinum crucible, 1" in dia. and 2" 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 in Figure 3 the current was set at 7.1 A which represents a current density of 0.7 A cm^{-2}. Cell voltage was measured to be 4.4 V. Evidence of gas bubble evolution is the periodic fluctuation of cell voltage in the amount of approximately 0.015 V, a value smaller than that measured on carbon by a factor of ten. 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]. Also shown in Figure 3 is the trace of the iR drop, i.e., the voltage across the interelectrode gap, which measured approximately 750 mV under the instant conditions.

Figure 4 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}, although most of the time the cell ran at 1 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. On the time interval shown in Figure 4 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 5 shows results obtained later in the same experiment as that cited in Figure 4. On the time interval shown in Figure 5 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 5, 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 6 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. Also given in Figure 6 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.

Figure 7 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 7 the temperature was 840 °C. Even at this temperature it was
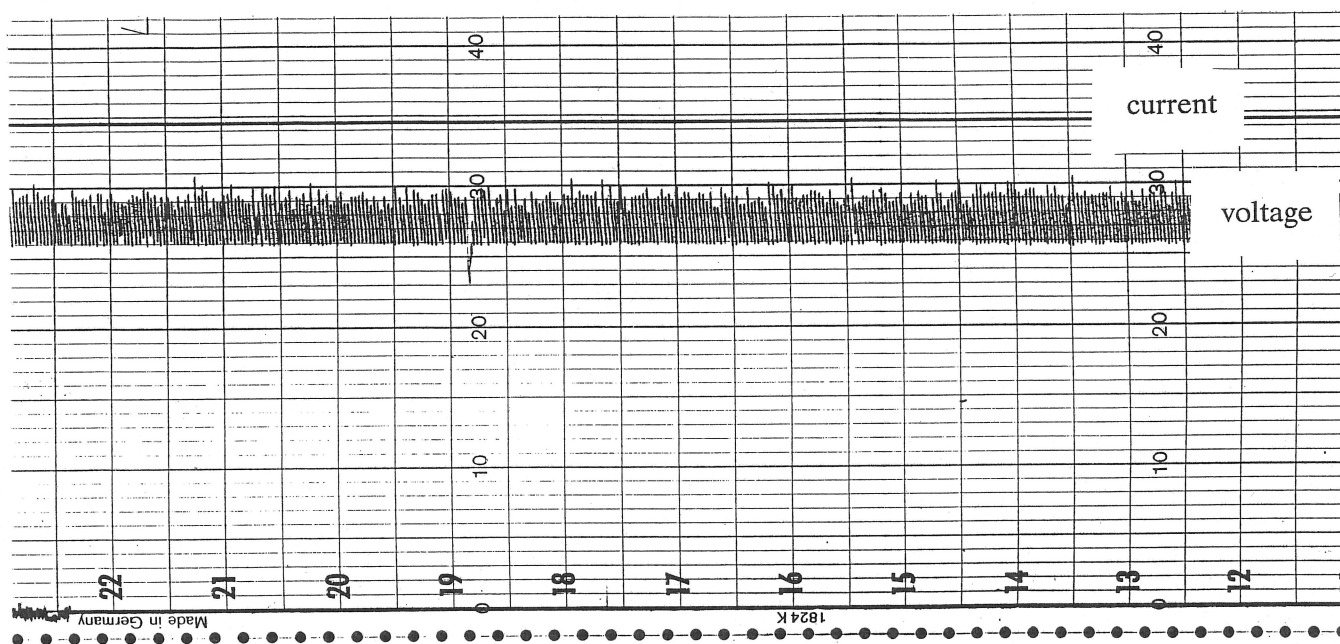
Figure 2. Electrolysis testing of a graphite anode. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Chart speed = 2 cm/min.
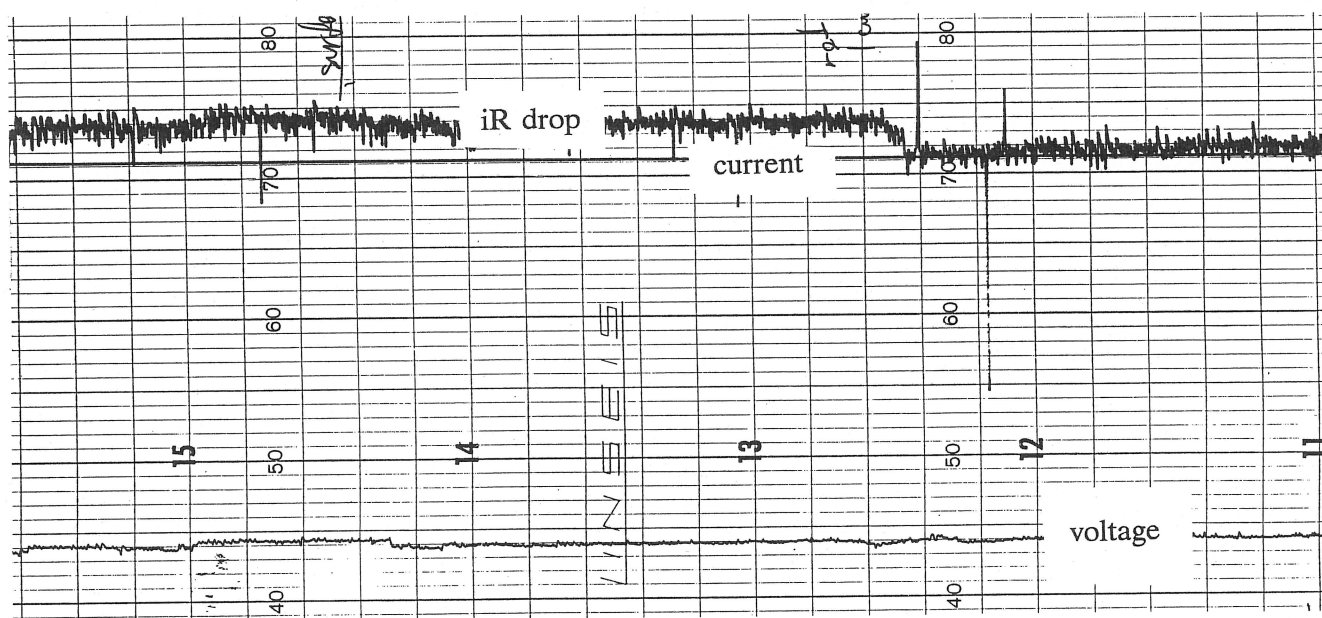

Figure 3. Electrolysis testing of a platinum anode. Current scale: 10 units = 1 A.
Voltage scales: cell voltage, 10 units = 1 V; iR drop, 100 units = 1 V. Chart speed = 5 cm/min.
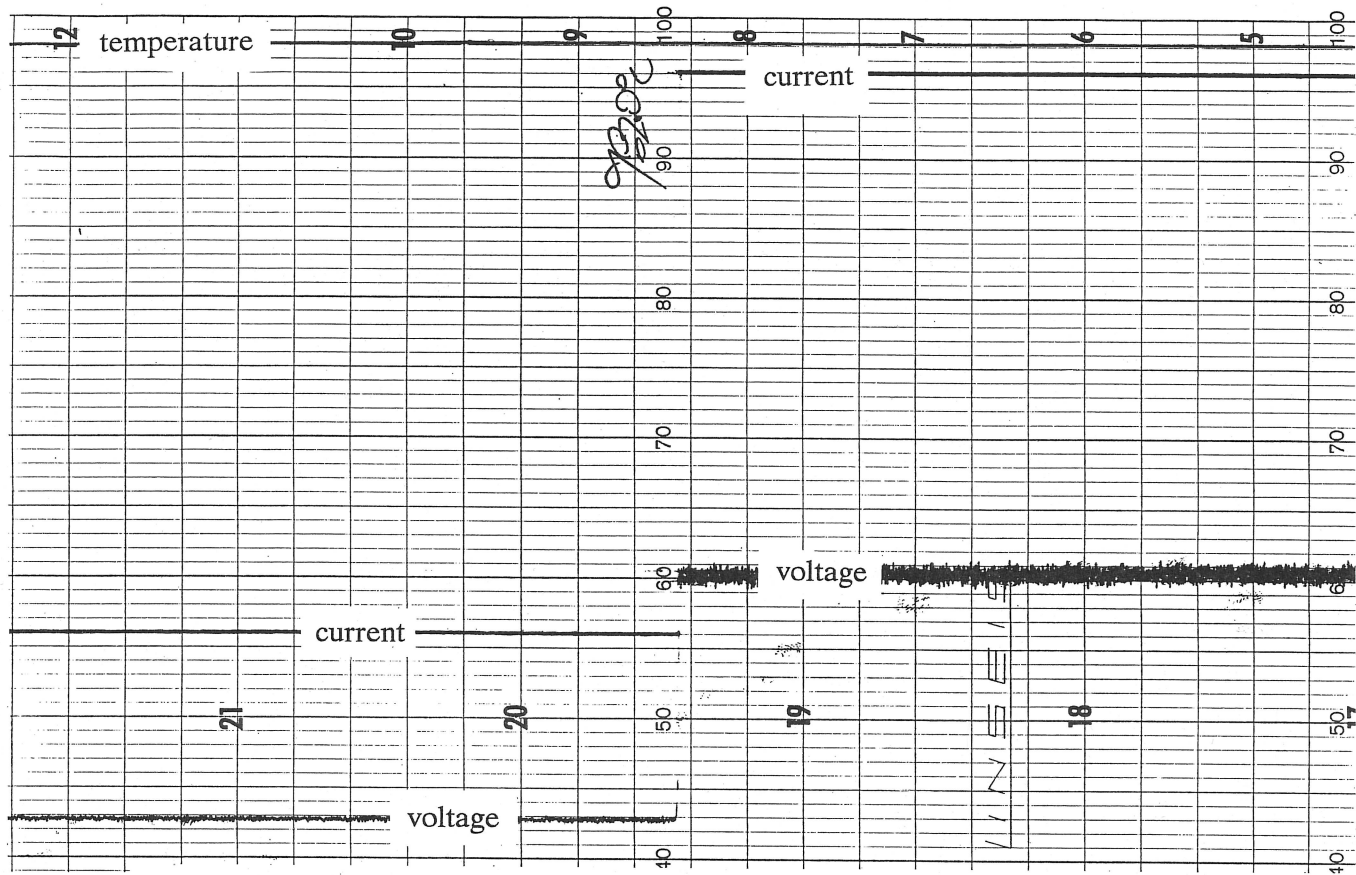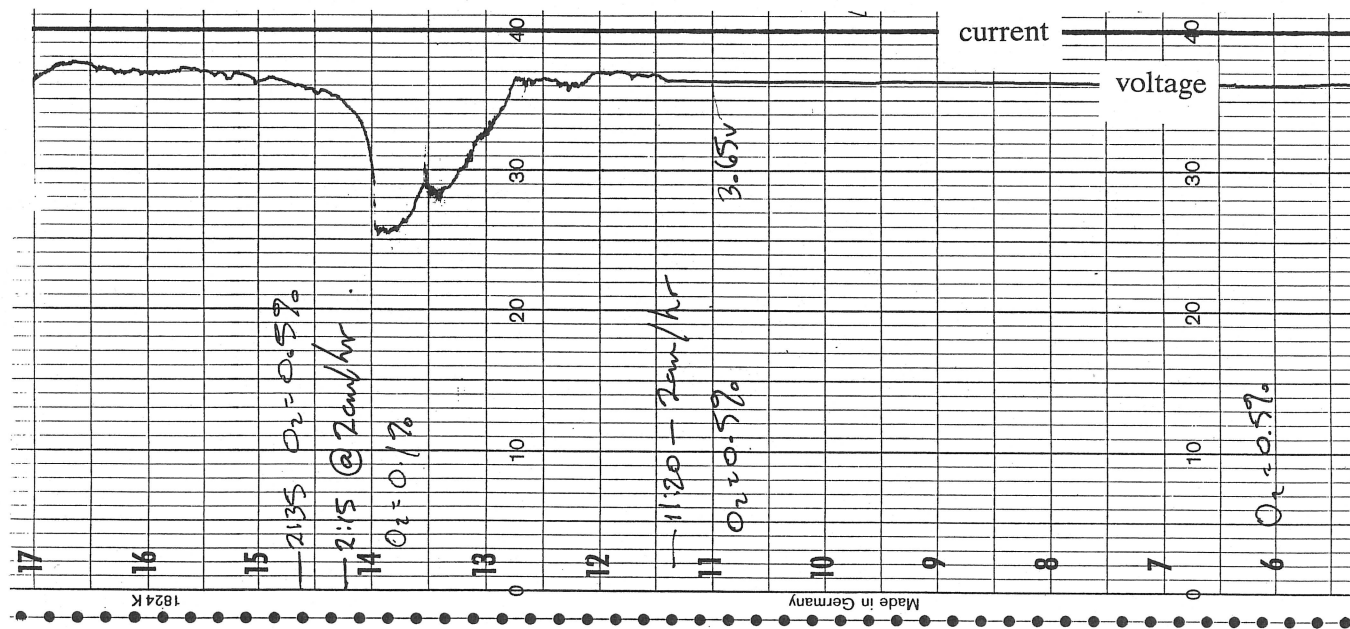
Figure 4. Electrolysis testing of an aluminum bronze anode, copper - 11.8% Al. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Temperature scale: 10 units = 10 K, zero offset at 900°C. Chart speed = 2 cm/min.

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/hr.
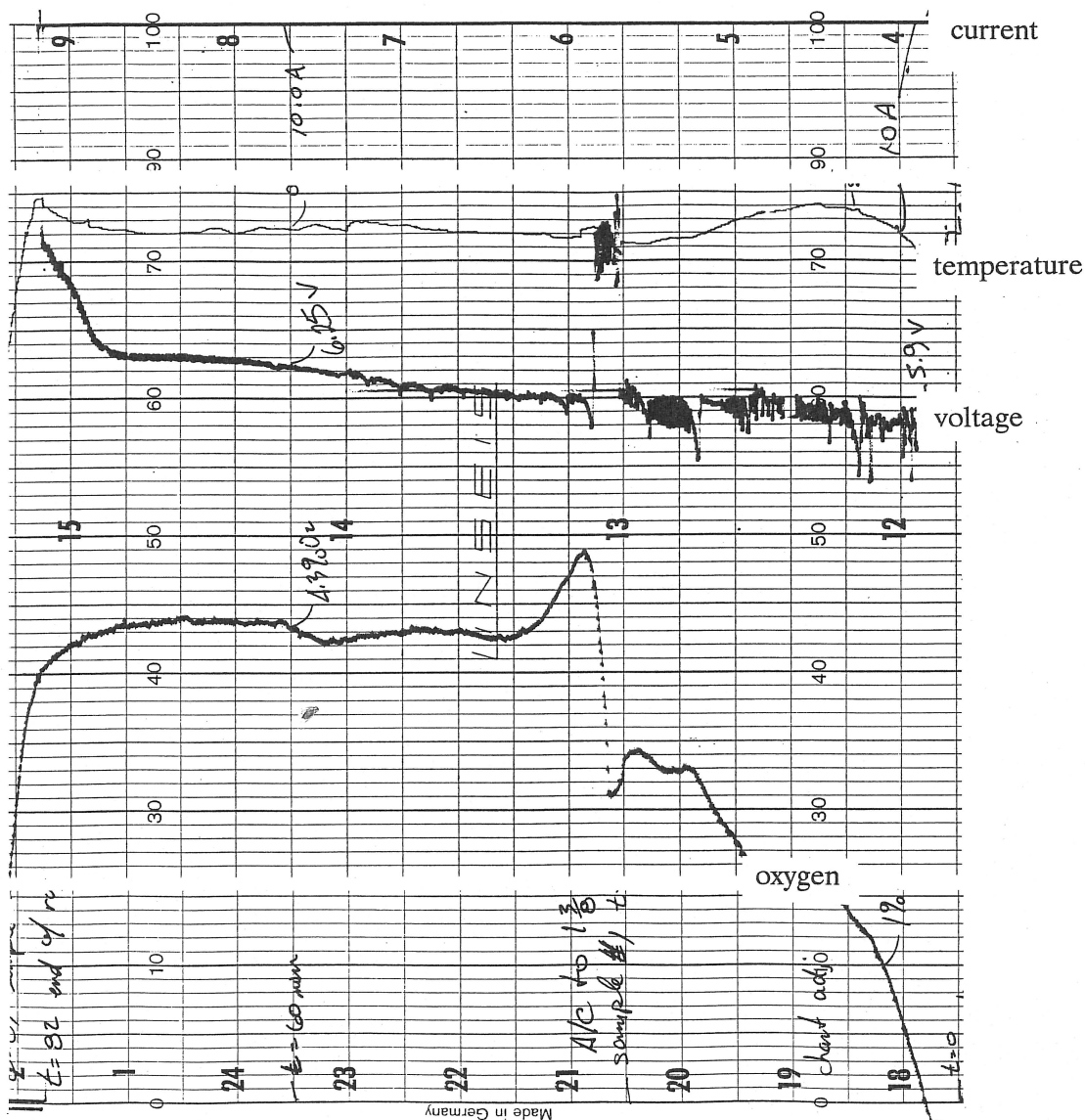
Figure 6. Electrolysis testing of an anode of Hoskins alloy 875, Fe - 22.5% Cr - 5.5% Al - 0.5% Si. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Oxygen scale: 10 units = 1%. Temperature scale: 10 units = 10 K, zero offset at 900°C. Chart speed = 12 cm/hr.

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 8 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 8 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 8 the voltage decreased from 3.3 to 2.7 V. Clearly, this is not the behavior of an anode undergoing catastrophic oxidation.
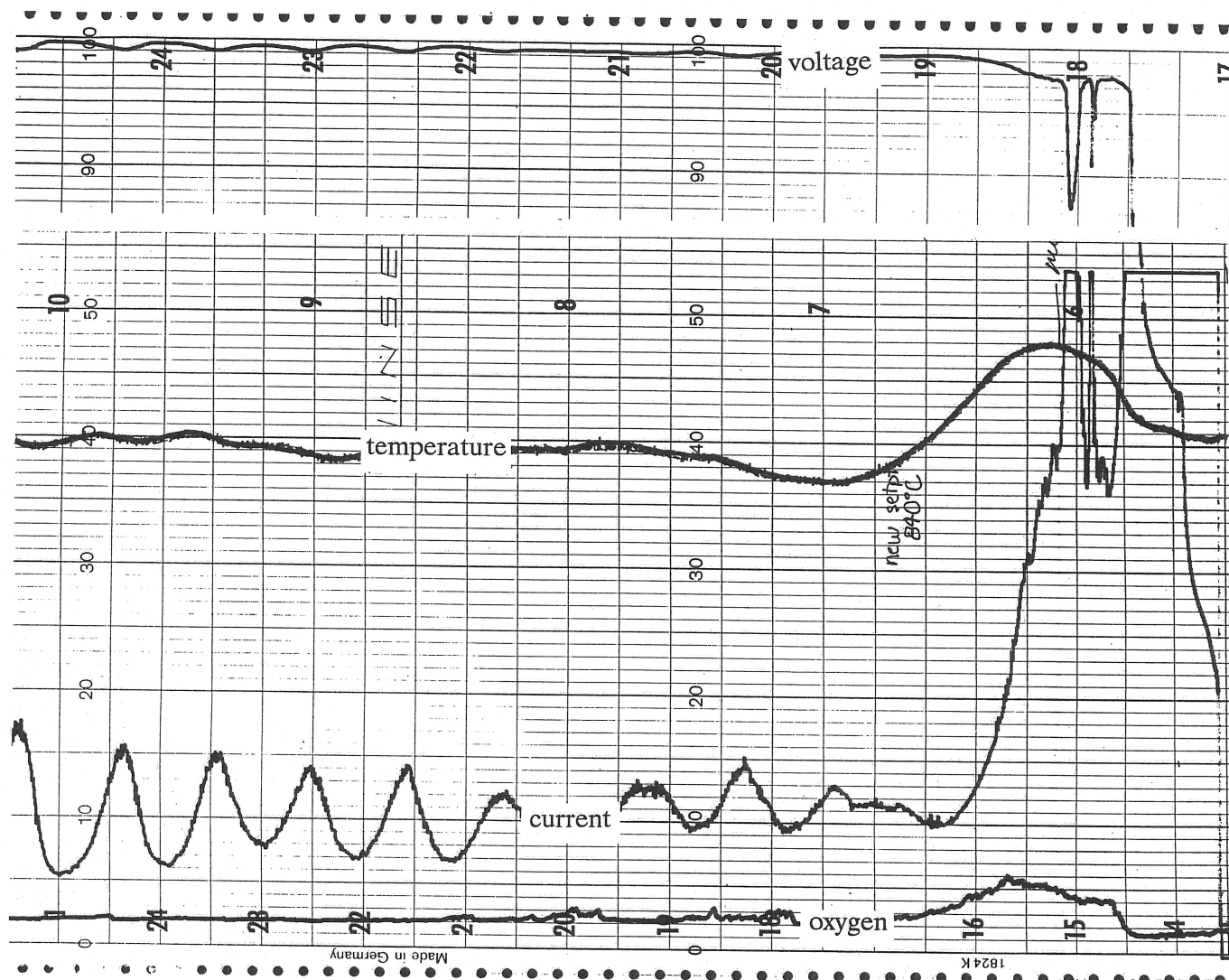
Figure 7. Electrolysis testing of a chromium - aluminum anode, Cr - 50% Al. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Oxygen scale: 10 units = 1%. Temperature scale: 10 units = 10 K, zero offset at 800°C. Chart speed = 12 cm/hr.

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. 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.

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 to be connected with either alumina concentration or current density.

The following are suggested in the way of future research:

1. continued testing at low temperature in low-ratio bath. The anode benefits from the lower temperature which has the
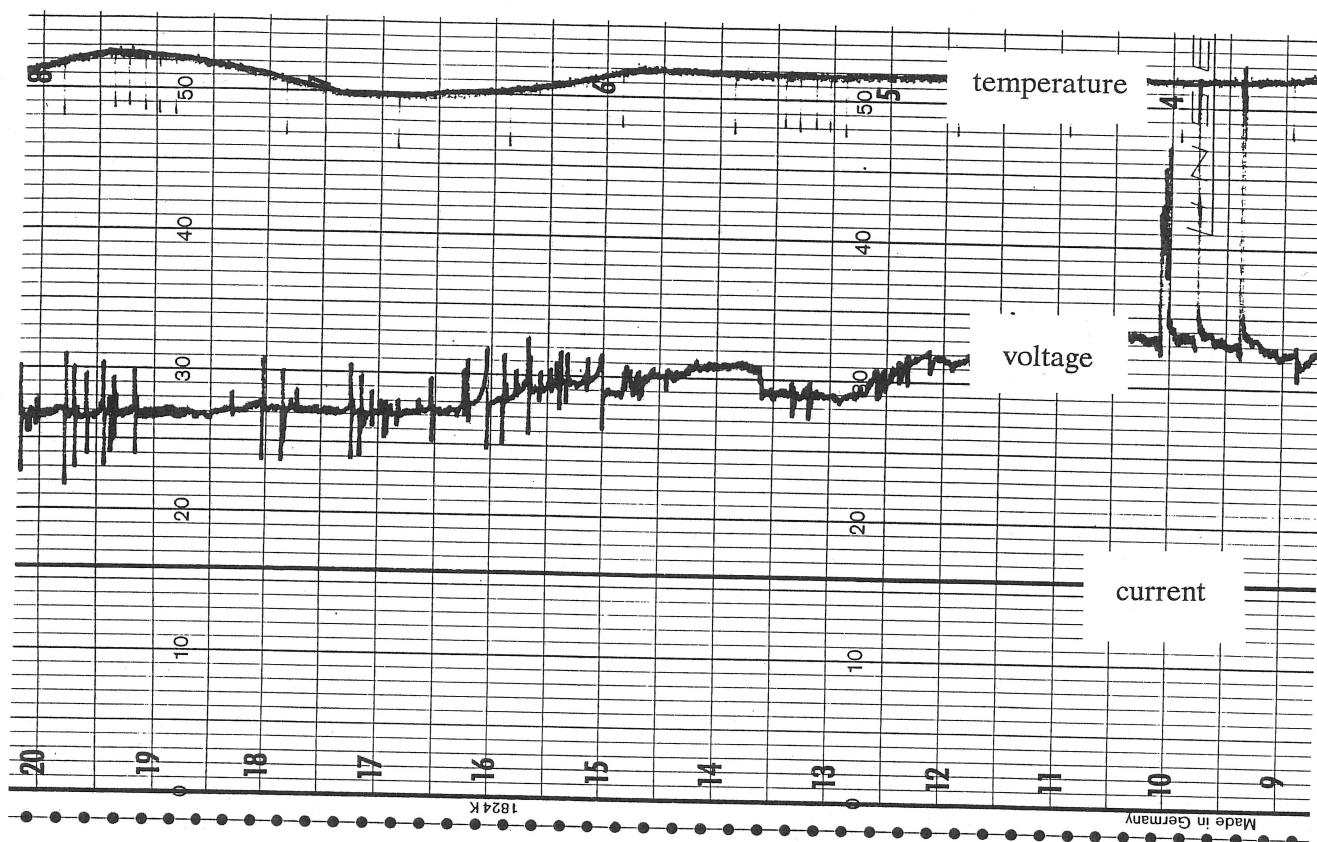
Figure 8. Electrolysis testing of a chromium - aluminum anode, Cr and Al sputtered onto a monolith of Ni - 6% Al. Voltage scale: 10 units = 1 V. Current scale: 10 units = 1 A. Temperature scale: 10 units = 10 K, zero offset at 700°C. Chart speed = 12 cm/hr.

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 anode chemistries, including ternary alloys.

3. longer tests. In order to attain steady state operation and acquire 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 offers by its sheer size more points of access and thus can be more completely instrumented for on-line diagnosis.

Acknowledgements

References

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