

Corrosion behavior of Cu-Ni-Ag-Al alloy anodes in aluminium electrolysis^①

XU Jun-li(徐君莉), SHI Zhong-ning(石忠宁), QIU Zhu-xian(邱竹贤)
(School of Materials & Metallurgy, Northeastern University, Shenyang 110004, China)

Abstract: The behavior of Cu-Ni-Ag-Al alloy used as anode for aluminum electrolysis was directly visualized in a two-compartment see-through cell during electrolysis, and its performances were tested at 850 °C in acidic electrolyte molten salts consisting of 39.3% NaF-43.7% AlF₃-8% NaCl-5% CaF₂-4% Al₂O₃ for 40 h in a laboratory cell. The results show that nascent oxygen oxidizes the anodic surface to form oxide film at the beginning of electrolysis. X-ray diffraction analysis of alloy surface show that the oxide film on the anodic surface consists of CuO, NiO, Al₂O₃, CuAl₂O₄ and NiAl₂O₄. However, SEM image shows the oxide film is porous, loose and easy to fall into electrolyte and to contaminate aluminum. The corrosion mechanism of metal anodes was analyzed.

Key words: metal anodes; aluminum electrolysis; oxide film; porous; corrosion mechanism

CLC number: TF 821

Document code: A

1 INTRODUCTION

There are large amount of CO₂ and dangerous gas(CF₄) released by using carbon anode in aluminum electrolysis. While the use of inert anode could help to suppress the emission of greenhouse gases, as shown in the following equations:



Replacement of carbon anodes by inert materials has been a subject of research in aluminum electrolysis. And research on inert anode is mostly focused on the choice of anode materials^[1]. Cermets have for a long time been viewed as one of the most promising groups of materials for inert anodes^[2-4], and many of them have been patented for aluminum electrolysis, but none of them is yet in commercial use^[5]. This is mainly because they are weak on their electronic conductivity and resistant thermal shock, and the joint with the power is also difficult^[6]. Compared with cermet anodes, metal anodes take advantage on these aspects. In addition, metal anodes are easy to fabricate and present fewer difficulties in service^[7-10]. However, many metals react with oxygen evolved on anodic surface and show poor resistance in molten electrolyte^[11]. Therefore, the main concern on metal anodes is the stability of the surface film, which should have performance of preventing attack of the underlying metal either by molten electrolyte or oxygen^[1]. The purpose of this paper is to discuss the reason why aluminum is contaminated, and to illustrate the forming process of oxide film on the anodic

surface and their dissolution mechanism in molten electrolyte with Cu-Ni-Ag-Al alloy used as anode in aluminum electrolysis.

2 EXPERIMENTAL

2.1 Fabrication of metal anodes

Cu, Ni, Ag and Al were used for prepare the anode materials, as Cu can enhance electronic conductivity, Ni shows good resistance in molten cryolite, and the addition of aluminum is known to improve the oxidation resistance^[11-13]. Mass ratio among Cu, Ni, Ag and Al is 63: 21: 5: 11. Cu, Ni and Ag were reagent grade, and Al was pure flake. These materials were melted in a furnace under the protection of argon at 1 280 °C, and then forged into a carbon mould. There was a screw on the top of the anode to be connected to the power supply by inconel rod.

2.2 Experiment settings

Two different methods were used to research on alloy anode behavior during aluminum electrolysis. Visualizing electrolysis were carried out in a two-compartment see-through cell. Electrolysis lasted for 40 h was also performed in a laboratory furnace. Both electrolysis tests were conducted in molten electrolyte consisted of 39.3% NaF-43.7% AlF₃-8% NaCl-5% CaF₂-4% Al₂O₃ at 850 °C. Electrolytes were all dried before use. Schematics of the experimental settings are presented in Fig. 1.

3 RESULTS AND DISCUSSION

3.1 Visualizing electrolysis testing

① **Foundation item:** Project(G1999064903) supported by the National Key Fundamental Research and Development Program of China

Received date: 2003 - 06 - 19; **Accepted date:** 2003 - 11 - 24

Correspondence: XU Jun-li, PhD; Tel: + 86-24-83680245; E-mail: jl Xu@163.com

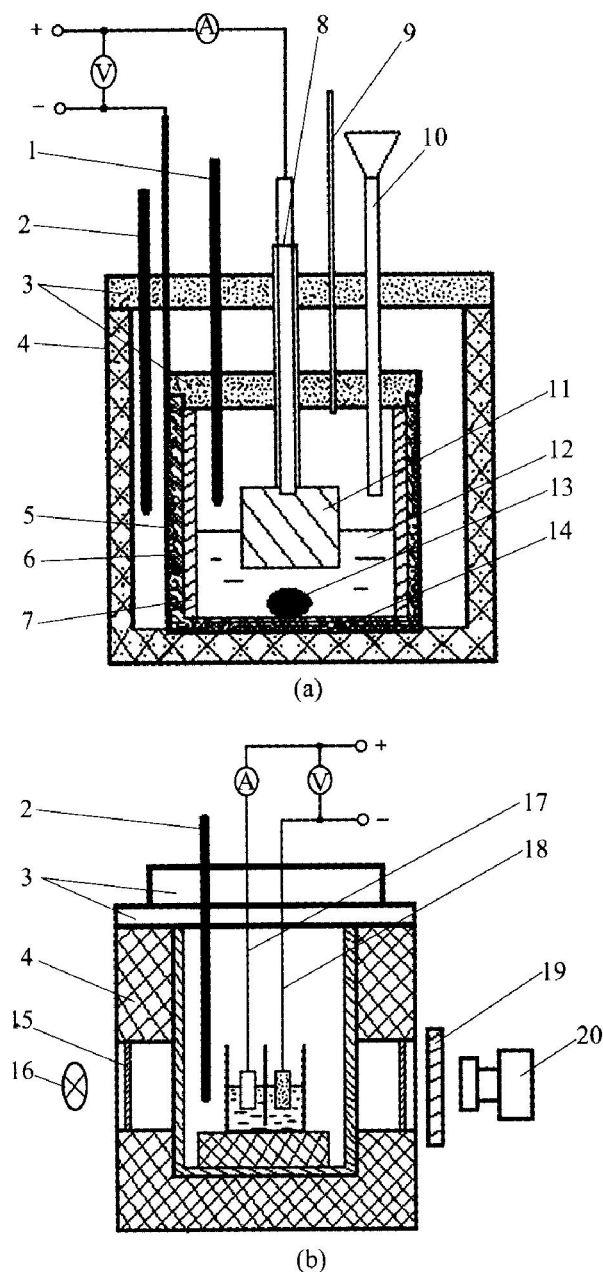


Fig. 1 Schematics of experimental settings

- (a) —Laboratory cell;
 (b) —Two-compartment see through cell
 1—Measuring thermocouple;
 2—Temperature controller thermocouple;
 3—Attemperator; 4—Electric furnace;
 5—Iron crucible; 6—Graphite crucible;
 7—Alumina insulative sleeve liner;
 8—Anode rod & alumina sleeve;
 9—Vent pipe; 10—Alumina feeder tube;
 11—Alloy anode; 12—Electrolyte melt;
 13—Liquid aluminum; 14—Carbon cathode;
 15—Quartz windows; 16—Adjustable lamp;
 17—Anode rod; 18—Cathode rod;
 19—Glass windows; 20—Camera

No gas bubble was found on anodic surface when current density was increased gradually from 0 to 0.36 A/cm^2 during the electrolysis at the velocity of $0.045 \text{ A}/(\text{cm}^2 \cdot \text{min})$; while there were current flowing through electrolyte, and aluminum fog produced in cathodic compartment, as shown in Fig. 2.

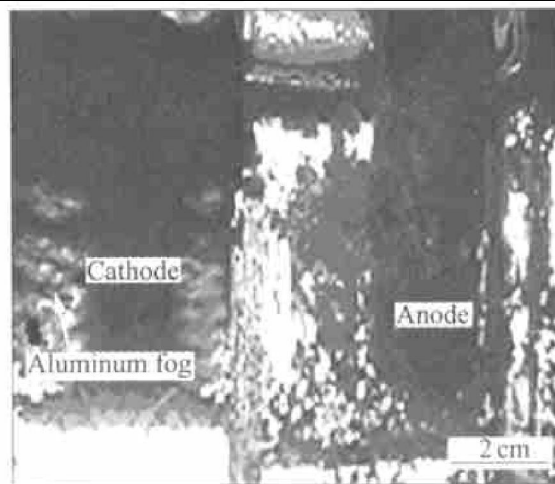


Fig. 2 Phenomena at beginning of aluminum electrolysis

At the beginning of electrolysis, a little oxygen generated at the low current density, and the amount of oxygen was not adequate for nascent oxygen to oxidize the anodic surface to form oxide film. Thus, there was no oxygen bubble evolved on the anodic surface.

After current density was set at 0.36 A/cm^2 , there were thick foam on the molten electrolyte surface and oxygen evolved as gas bubbles. In high current density, oxygen evolving velocity was faster than metal oxidizing velocity, so there were oxygen evolved. When current density decreased to 0.24 A/cm^2 at the velocity of $0.045 \text{ A}/(\text{cm}^2 \cdot \text{min})$, there were still oxygen bubbles evolved. It was shown that the metal was oxidized at very low velocity. This is because when the metal oxide film was thick enough, oxygen atom transporting to underlying metal was restricted, and then the alloy anode was protected by oxide film.

3.2 Laboratory-scale electrolysis testing

The relationship of cell voltage with electrolysis time is plotted in Fig. 3 when the anodic current density was 1 A/cm^2 .

As shown in Fig. 3, cell voltage was stable during the course of electrolysis, while gas bubble evolved drastically around anode. After electrolysis, the product of Al deposited at the bottom of electrolyte, which contained 95.6% Al, 4.0% Cu and 0.4% Ni analyzed by electron probe microanalyzer (810 type). The impurity (Cu) content is high in product of aluminum since copper in alloy anode reacts with oxygen to form Cu_2O and CuO , and the solubility of them are high in molten cryolite. Copper ion is deoxidized at the vicinity of cathode and deposited into aluminum. In addition, Cu may be displaced by Al.

3.3 Composition and structure of oxide film

After electrolysis, oxide film on anodic surface is

analyzed by X-ray diffractometry, and the result is shown in Fig. 4.

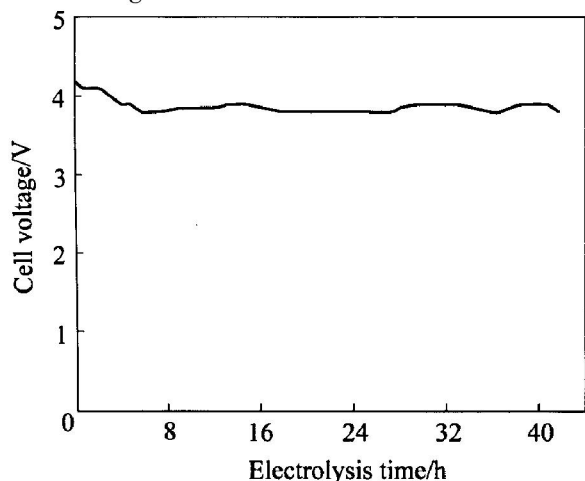


Fig. 3 Fluctuation of cell voltage with electrolysis time

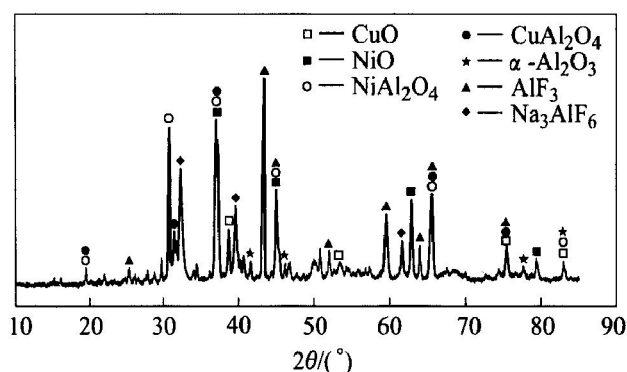


Fig. 4 XRD pattern of oxide film

From Fig. 4, it can be seen that the composition of oxide film is complicated. There exists mixed metal oxides (CuO, Al₂O₃, NiO) and their compound oxide spinels (CuAl₂O₄, NiAl₂O₄). Besides, there are AlF₃ and Na₃AlF₆, which come from electrolyte.

SEM image of the anodic surface is shown in Fig. 5. The oxide film is porous material and it is

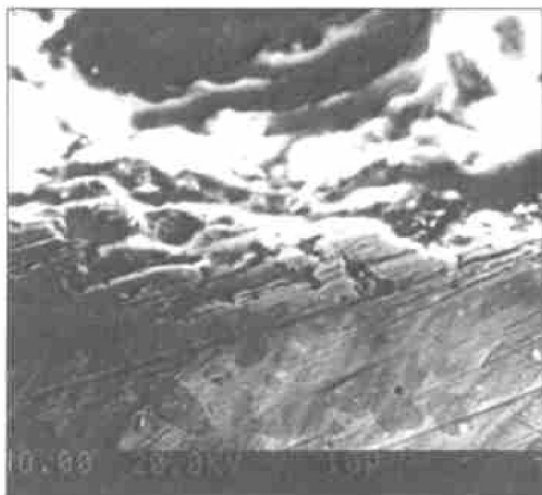


Fig. 5 SEM image of Cu-Ni-Ag-Al anode surface

not compact enough. So it may be fall into electrolyte since it is pushed by the flow of the electrolyte and the anodic bubbles. The electrolyte may also attack the underlying metal of the anode by penetrating through the porous oxide film. This is one of the reasons why aluminum is contaminated. How to form a compact oxide film is the most challenge of metal anode.

3.4 Corrosion mechanism

The schematic of the corrosion mechanism of metal anode is shown in Fig. 6. During the course of electrolysis, AlO₂⁻F⁻ complex anions and F⁻ anions were transported to anode under the electromagnetic action, and oxygen atom discharged on the surface of metal anode^[14]. Then oxygen reacted with anode to form metal oxides on anodic surface. Anodic reaction was different with change of the concentration of alumina. At high alumina concentration, anode reaction may be the following equation:

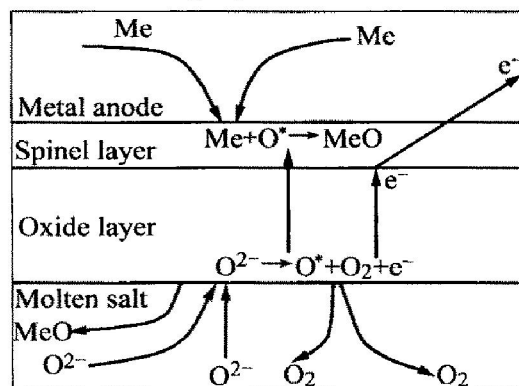
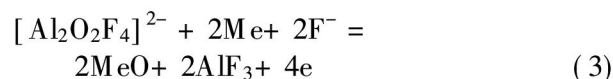


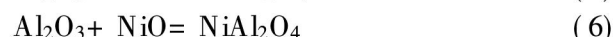
Fig. 6 Illustration of course of erosion of anode surface



At low alumina concentration, the anode reaction may be written as:

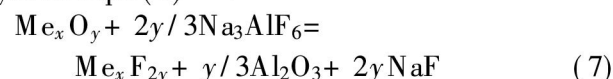


At high temperature, Al₂O₃, CuO may react with NiO further, forming spinels as the following equations:



Spinel is an ionic compound, which has high melting point and chemical stability. It can prevent from the attack of molten electrolyte at high temperature.

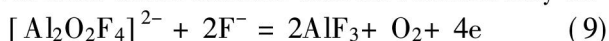
Some oxide films fall into electrolyte because the loose layer is pushed by the flow of electrolyte and anodic bubbles, and some of metal oxide films dissolve in the molten electrolyte since they react with electrolyte as Eqn. (7)^[15]:



Metal oxide may also react with aluminum dissolved in electrolyte by following displacement equation:



When the metal oxide is thick enough, oxygen evolves from anode surface. Anodic reaction may be



4 CONCLUSIONS

1) At the beginning of electrolysis, oxygen oxidizes metal surface firstly to form oxide film, and it helps to prevent the alloy anode to be oxidized further.

2) Oxide film consists of metal oxides and spinels. The forming of spinels is beneficial to resistant molten electrolyte.

3) Oxide film is porous, loose and easy to fall into electrolyte and to dissolve, which makes aluminum be contaminated.

REFERENCES

- [1] Sadoway D R. Inert anodes for the Hall-Héroult cell: the ultimate materials challenge[J]. JOM, 2001, 53(5): 34 - 35.
- [2] Sadoway D R. Materials systems approach to selection and testing of nonconsumable anode for the Hall cell [A]. Boxall L G. Light Metals [C]. Warrendale: TMS, 1990. 403 - 407.
- [3] Kvand H. Inert electrodes in aluminum electrolysis cells [A]. Eckert C E. Light Metals [C]. Warrendale: TMS, 1999. 369 - 376.
- [4] Hryn J N, Pellin M J. A dynamic inert metals anode [A]. Eckert C E. Light Metals [C]. Warrendale: TMS, 1999. 377 - 381.
- [5] Laurent C, Torstein A U, Bouvet S. Visualizing gas evolution on graphite and oxygen evolving anodes[J]. JOM, 2002, 54(5): 41 - 45.
- [6] Hryn J N, Sadoway D R. Cell testing of alloy anode for aluminum electrolysis [A]. Das S K. Light Metals [C]. Warrendale: TMS, 1993. 475 - 483.
- [7] Duruz J J, Nora V, Crotta O. Cells for the Electrowinning of Aluminium Having Dimensionally Stable Metal Based Anodes [P]. WO 0006802, 1999 - 01 - 08.
- [8] Duruz J J, Nora V, Crottaz O. Nickel-iron Alloy Based Anodes for Aluminium Electrowinning Cell [P]. WO 0006803, 1999 - 01 - 08.
- [9] Nora V, Duruz J J. Slow Consumable Non-Carbon Metal-Based Anodes for Aluminium Production Cells [P]. WO 0006805, 1999 - 01 - 08.
- [10] Duruz J J, Nora V. Metal-Based Anodes for Aluminium Electrowinning Cells [P]. WO 0142534, 1999 - 01 - 09.
- [11] Sekhar J A, Deng H, Liu J, et al. Micropyrethically synthesized porous non-consumable anodes in the Ni-Al-Cu-Fe-X system [A]. Huglen R. Light Metals [C]. Warrendale: TMS, 1997. 347 - 354.
- [12] HUANG Naibao, LIANG Chenghao, TONG Dawei. Effect of inhibitors on corrosion behavior of copper-nickel in concentrated lithium bromide solution at high temperature [J]. Trans Nonferrous Met Soc China, 2002, 12(3): 424 - 428.
- [13] Lakshmikantha M G, Sekhar J A. An investigation of the effect of porosity and diluents on micropyrethic synthesis [J]. Metall Mater Trans A, 1993, 24A: 617 - 627.
- [14] Grjotheim K, Kvande H, LI Qingfeng, et al. Metal Production by Molten Salt Electrolysis [M]. Xuzhou: China University of Mining and Technology Press, 1998. 79 - 81.
- [15] QIU Zhuxian. Theory and Application of Aluminium Electrolysis [M]. Xuzhou: China University of Mining and Technology Press, 1998. 428 - 431.

(Edited by YANG Bing)