

## ELECTROCHEMICAL BEHAVIOR OF CERMET ANODES IN Na<sub>3</sub>AlF<sub>6</sub>-K<sub>3</sub>AlF<sub>6</sub>-BASED LOW-MELTING ELECTROLYTES FOR ALUMINIUM ELECTROLYSIS

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### Abstract

The anodic behavior of 5Cu/10NiO-90NiFe<sub>2</sub>O<sub>4</sub> cermet in Na<sub>3</sub>AlF<sub>6</sub>-K<sub>3</sub>AlF<sub>6</sub>-based low-melting electrolytes was investigated for use as inert anodes for aluminium electrolysis. The electrochemical techniques, cyclic voltammetry and Tafel anodic polarization analysis, were performed to determine the reactions. Two anodic processes were observed at the cermet anodes: dissolution of Cu and oxygen evolution. The activity of anodic oxide films (CuO) on cermet anodes was calculated as 0.15 using values of the reversible potential obtained from the Tafel analysis, which suggested a lack of surface oxide stabilization. The exchange current density obtained for cermet anodes was 0.19 A cm<sup>-2</sup>. The porous surface caused by the depletion of Cu during anodic polarization could be the reason for blocking the oxygen evolution on cermet anodes.

### Introduction

Over the years, many types of inert anodes have been tested for aluminium smelting. However, development of a 'non-consumable' anode for the aluminium industry with an acceptable corrosion rate is made difficult by the aggressive nature of the cryolite electrolyte towards most metals, refractory hard metals and ceramic oxide composition [1]. The Cu-containing cermets (NiFe<sub>2</sub>O<sub>4</sub> spinel, NiO and a metallic phase which was mostly Cu) have been investigated as one of the most promising materials for inert anodes due to their combination of the properties of ceramics and metals, and their low solubility in cryolite [2-5].

Since low temperature electrolysis could offer a more favorable operating environment for inert anodes, by decreasing the dissolution rate, a large amount of research has been carried out [6-13]. Through electrolytic tests, we have found 5Cu/10NiO-90NiFe<sub>2</sub>O<sub>4</sub> cermet anodes show good anti-corrosion properties in 22wt%K<sub>3</sub>AlF<sub>6</sub>-50wt%Na<sub>3</sub>AlF<sub>6</sub>-28wt%AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>(saturated) mixed cryolite systems at 820-840°C [14]. For further clarification of the corrosion mechanism, it is necessary to study the electrochemical behavior of these cermet anodes in cryolite-alumina melts or even in melts without oxide added, which still have low and reproducible residual oxide content [15]. In the present work, 5Cu/10NiO-90NiFe<sub>2</sub>O<sub>4</sub> cermet anodes were polarized in an oxide-saturated or melt without oxide added. The aim of the experiments was to characterize the oxidation reactions occurring on the anodes.

### Experimental

All experiments were carried out in an alumina tube reactor, which was filled with high purity argon atmosphere. Spectrographic graphite crucibles (78 mm in inner diameter, 144 mm in height) were used as the container and counter electrode. Na<sub>3</sub>AlF<sub>6</sub>, K<sub>3</sub>AlF<sub>6</sub>, AlF<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were all analytical

grade chemicals. The fluorides (400 g) were mixed according to the demands, and placed in a graphite crucible, heated to 110°C and dried under vacuum for 24 h. Then the temperature was increased slowly to the melting point 818°C [16] under argon, kept for two hours, then increased to 830°C. This temperature was maintained for electrochemical measurements.

A three-electrode system was used for the electrochemical measurements. A cermet anode rod (17.0 mm diameter) was used as the working electrode. The cermet anodes were prepared by School of Metallurgical Science and Engineering, Central South University, China. The working electrode was dipped about 5 mm into the molten salt. The actual immersed height was determined at the end of the run. The graphite crucible was used as the counter electrode, and an aluminum electrode was used as the reference electrode [17]. All potentials in this paper are given with reference to this Al<sup>3+</sup>/Al electrode. The electrochemical measurements were performed using a universal potentiostat/galvanostat, Model 273, controlled via a personal computer executing the electrochemical software Echem M270.

### Results and Discussion

At first, in order to assign reactions to the oxidation processes, the reversible potentials of some reactions related to the present study were calculated according to equation (1) and tabulated in Table I.

$$\Delta_r G_m^0 = -nFE^0 \quad (1)$$

Where  $\Delta_r G_m^0$  is the standard molar Gibbs free energy of the reaction,  $n$  is the electron transfer number,  $F$  is the Faraday's constant,  $E^0$  is the standard potential of the reaction and all the activities were assumed to equal unity. Since the measured potentials are expressed vs the Al<sup>3+</sup>/Al reference, the corresponding cell reactions lead to the formation of the anodic products and aluminium as cathodic product. These calculations were then compared to electrochemical measurements.

Table I. Calculated reversible potentials for reactions at 830°C

| Possible reactions  | $\Delta_r G_m^0$<br>/kJ mol <sup>-1</sup> | $E$ (vs Al <sup>3+</sup><br>/Al) / V |
|---|---|--------------------------------------|
| 2Al <sub>2</sub> O <sub>3(diss)</sub> = 4Al <sub>(l)</sub> + 3O <sub>2(g)</sub>                                     | 2535                                      | 2.19                                 |
| 2AlF <sub>3(diss)</sub> = 2Al <sub>(l)</sub> + 3F <sub>2(g)</sub>   | 1228                                      | 4.24                                 |
| 3Cu <sub>(s)</sub> + Al <sub>2</sub> O <sub>3(diss)</sub> = 2Al <sub>(l)</sub> + 3CuO <sub>(s)</sub>                | 1095                                      | 1.89                                 |
| 6Cu <sub>(s)</sub> + Al <sub>2</sub> O <sub>3(diss)</sub> = 2Al <sub>(l)</sub> + 3Cu <sub>2</sub> O <sub>(s)</sub>  | 1004                                      | 1.73                                 |
| 3Cu <sub>2</sub> O <sub>(s)</sub> + Al <sub>2</sub> O <sub>3(diss)</sub> = 2Al <sub>(l)</sub> + 6CuO <sub>(s)</sub> | 1186                                      | 2.05                                 |
| 3Cu <sub>(s)</sub> + 2AlF <sub>3(diss)</sub> = 2Al <sub>(l)</sub> + 3CuF <sub>2(s)</sub>                            | 1217                                      | 2.10                                 |

Figure 1 shows a cyclic voltammogram obtained at the cermet anode over the potential range 1.5 to 3.6 V vs  $\text{Al}^{3+}/\text{Al}$ . Under the investigated conditions, it seems that only two anodic processes should be possible: (i) discharge of  $\text{O}^{2-}$  or other oxygen-containing species; (ii) dissolution of Cu or oxide film formation at the cermet surface. Taking into consideration that the experiments were restricted to a maximum potential of 3.6 V, it can be concluded that the discharge of  $\text{F}^-$  (or corresponding complex-ion species) takes place only at more positive potentials [18]. In the region of increasing current (Figure 1), two anodic processes were observed. The first, from 1.7 to 2.2 V, corresponded to a Cu related reaction, where the current density was lower than  $0.04 \text{ A cm}^{-2}$ . The second, from 2.2 to 3.6 V, should correspond to the evolution of oxygen [19, 20], which can be further demonstrated by the shape of the voltammogram in the negative-going sweep direction from 3.6 to 2.2 V, where the voltammogram of the reverse scan is rather similar to that of forward scan. It shows a high degree of irreversibility. Then the current was almost zero until the cathodic current appeared, which was attributed to reduction of surface oxide and/or dissolved copper near the anode surface.

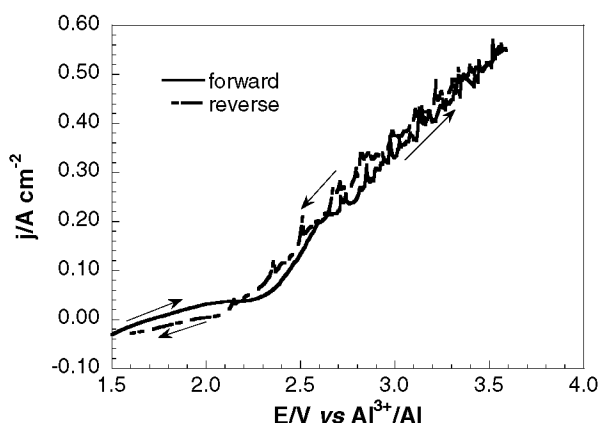
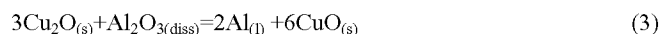
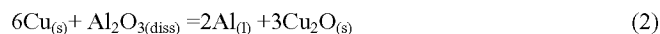


Figure 1. Cyclic voltammograms on cermet anode in 22wt% $\text{K}_3\text{AlF}_6$ -50wt% $\text{Na}_3\text{AlF}_6$ -28wt% $\text{AlF}_3$ - $\text{Al}_2\text{O}_3$  (sat) melt. Temperature:  $830^\circ\text{C}$ ; sweep rate:  $0.05 \text{ V s}^{-1}$ .

In order to obtain more information on the anodic reactions, Tafel plots were drawn using the data from both the forward and reverse sweep of the current-voltage curve (see Figure 2). The observed reversible potentials ( $RP$ s) for copper anodic reactions are easy to obtain since the anodic and cathodic branches meet at a given value of potential [1]. Reversible values are 1.68 and 1.92 V respectively from the forward and reverse sweep, which can be attributed to the two steps of anodic oxidation of copper in the surface layer of the cermet anode:



The anodic dissolution of Cu as  $\text{CuF}_2$  could happen since the calculated reversible potentials in Table I are very close. However in the present systems we studied, copper oxides were preferred, especially in the oxide saturated melts [21, 22].

These observed  $RP$  values are different from the calculated ones, 1.73 and 2.05 V (Table I). One possible reason is that different melts could have different IR drop, which would cause a shift in

potential. To avoid this, we used the automatic IR compensation function of the electrochemical system when we performed the measurements. Another reason is that for the calculated (theoretical) values, the activities of dissolved oxides are supposed to be 1. According to reactions (2) and (3), the observed metal oxide activities ( $a_{\text{oxide}}$ ) can be estimated by the following Nernst equations [1]:

$$RP(\text{observed}) = RP(\text{calculated}) + \frac{RT}{2F} \ln a_{\text{Cu}_2\text{O}} \quad (4)$$

$$RP(\text{observed}) = RP(\text{calculated}) + \frac{RT}{2F} \ln \frac{a_{\text{CuO}}}{a_{\text{Cu}_2\text{O}}^2} \quad (5)$$

The oxide activities calculated as  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are 0.35 and 0.15 respectively. These low values suggest a lack of surface oxide stabilization, that is, the discharge of copper led to the formation of various oxides, as films, which dissolved in the cryolite under our experimental conditions. Our previous corrosion test results showed no copper or its compound found in the corrosion layer, which meant the metallic Cu in the original surface of the anode was totally depleted during electrolysis. This result is identical to the analysis in the present work. See reference [14] for a detailed description of the electrolysis test.

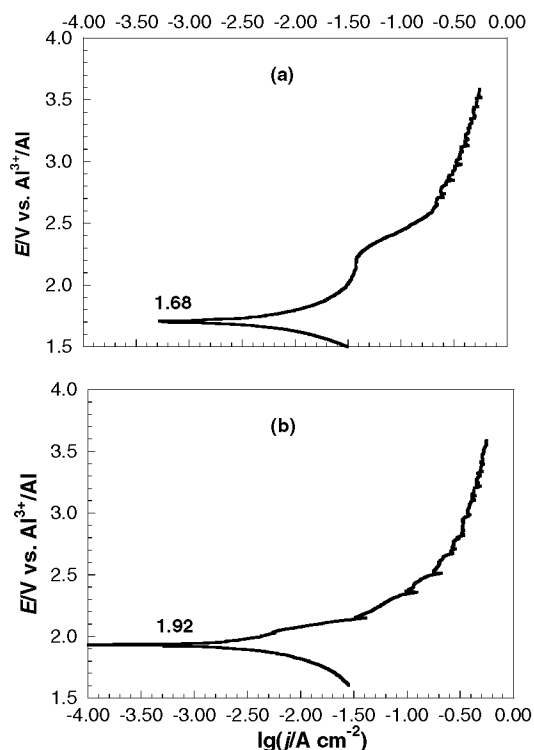


Figure 2. Polarization curves for cermet anode in 22wt% $\text{K}_3\text{AlF}_6$ -50wt% $\text{Na}_3\text{AlF}_6$ -28 wt% $\text{AlF}_3$ - $\text{Al}_2\text{O}_3$  (saturated) melt. Temperature:  $830^\circ\text{C}$ ; sweep rate:  $0.05 \text{ V s}^{-1}$ . (a) forward sweep (b) reverse sweep.

Similar results were obtained by Russell [1] and Lorentse et al. [21], whereas Windisch et al. [22] found that upon oxidation of a  $\text{NiFe}_2\text{O}_4$ +17wt%Cu cermet anode, a layer of  $\text{Cu}_2\text{O}$  was formed on

the copper surface, and subsequently this layer reacted with alumina in the electrolyte, forming  $\text{CuAlO}_2$  on the outer part of the  $\text{Cu}_2\text{O}$  layer, but not on the metal surface. They also found that at low concentrations of alumina, the metal surface was not completely covered by  $\text{Cu}_2\text{O}$ , or the  $\text{Cu}_2\text{O}$  layer was unstable. In the present work, the amount of Cu was much lower, and even in the alumina saturated melt, the metal oxide was still unstable. When the anode was polarized, the exposed metal grains dissolved anodically with the formation of copper cations, which subsequently transferred to the cathode, followed by reduction and dissolution into aluminum. Since the metallic phase did not form a continuous network in the anode, the electrochemical process should slow down rapidly when the exposed Cu in the outer region of the anode had dissolved. The ceramic matrix of the cermet anodes, being in an electrochemically stable state, underwent only chemical dissolution. After the metallic phase in the surface layer was depleted, the anode corrosion process should be controlled by chemical dissolution of the oxide phase. Chemical and electrochemical attack at the cermet/melt interface cause cermet anodes to corrode in cryolite-alumina melts.

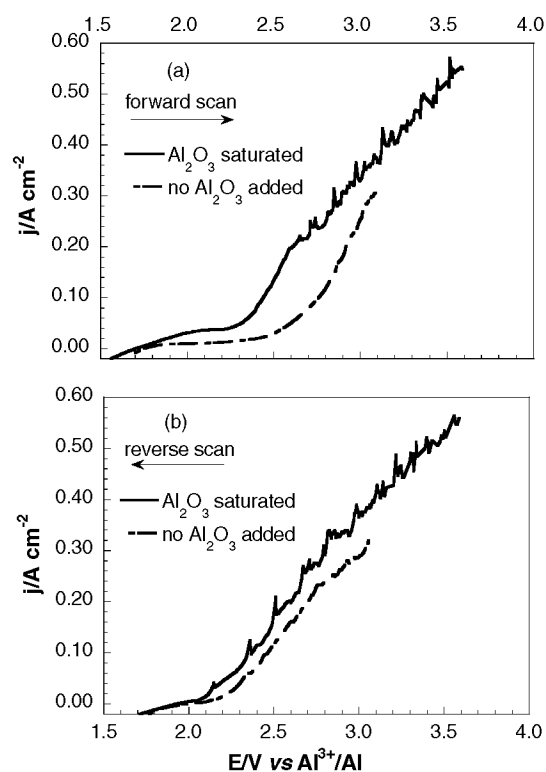


Figure 3. Comparison of cyclic voltammograms on cermet anodes in 22wt%  $\text{K}_3\text{AlF}_6$ -50wt% $\text{Na}_3\text{AlF}_6$ -28wt% $\text{AlF}_3$ - $\text{Al}_2\text{O}_3$  (saturated/without) melts. Temperature: 830°C; sweep rate: 0.05  $\text{V s}^{-1}$ .

Voltammograms of cermet anodes in alumina saturated melts and melts without oxide added are compared and shown in Figure 3. In order to show the voltammograms clearly, the forward sweep and the reverse sweep were drawn separately. For the forward sweep, as the amount of alumina decreased, the current density of copper dissolution reaction decreased, and the potential of oxygen generation was delayed. For the reverse sweep, as the metallic phase Cu in the surface layer of the cermet anodes was corroded preferentially during the anodic sweep, the current density of the

copper dissolution reaction both decreased almost to zero. This further supported our suggestion on the corrosion mechanism of cermet anodes.

The Butler-Volmer equation is usually used to describe the relationship between electron transfer rate and potential. When there is no mass transfer effect, at sufficiently large overpotential, e.g. at the potential range of oxygen evolution in the present study, the Butler-Volmer equation takes the following form [23]:

$$j = j_0 e^{\alpha n f \eta} \quad (6)$$

where  $j$  is the redox current density,  $j_0$  is the exchange current density at formal potential,  $n$  is the electron transfer number,  $\eta$  is the overpotential, which is defined as  $E-E^0$ ,  $f$  is  $F/RT$  and  $\alpha$  is the electron transfer coefficient. Equation (6) is usually presented as a Tafel plot. From the Tafel plot, the exchange current density can be extracted from the intercept  $\lg j_0$ .

For the oxygen evolution reactions on cermet anodes in alumina saturated melts, the cyclic voltammograms indicated high irreversibility, i.e. the reactions were slow and mass transfer effects were probably small. We could therefore estimate the apparent exchange current densities  $j_0$  by a simple Tafel plot analysis on the rising portion of the CVs (Figure 4). From extrapolation of the Tafel linear variation of  $\lg j$  with the electrode potential,  $E$ , to the standard oxidation potential ( $E=E^0$ ), we obtained the apparent exchange current density  $j_0 = 0.19 \text{ A cm}^{-2}$ , which indicates the electron transfer rate on cermet was slow. This could be attributed to the porous cermet surface [24] caused by the depletion of copper when anodically polarized, which blocked the oxygen evolution.

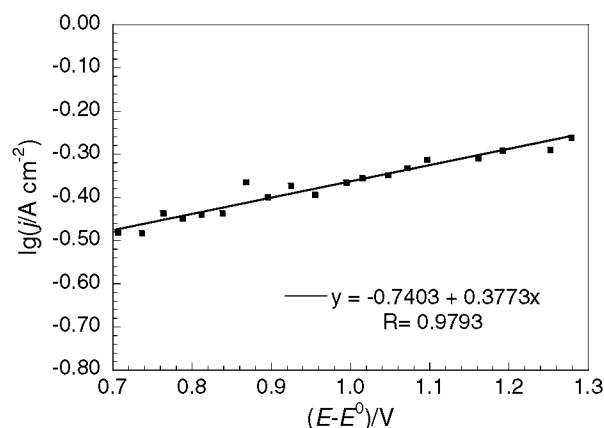


Figure 4. Tafel plot of cermet anode in 22wt% $\text{K}_3\text{AlF}_6$ -50wt% $\text{Na}_3\text{AlF}_6$ -28wt% $\text{AlF}_3$ - $\text{Al}_2\text{O}_3$  (saturated) melts. Temperature: 830°C; sweep rate: 0.05  $\text{V s}^{-1}$ .

## Conclusions

Comparative experiments were carried out on 5Cu/10NiO-90NiFe<sub>2</sub>O<sub>4</sub> cermet anodes in 22wt% $\text{K}_3\text{AlF}_6$ -50wt% $\text{Na}_3\text{AlF}_6$ -28wt% $\text{AlF}_3$ - $\text{Al}_2\text{O}_3$  (saturated/without added oxide) melts at 830°C. The results showed two anodic processes occurred on cermet anodes, which were the dissolution of Cu and the oxygen evolution. The activity of anodic oxide films ( $\text{CuO}$ ) on cermet anodes was calculated as 0.15, which suggested a lack of surface

oxide stabilization. A very low exchange current density ( $0.19 \text{ A cm}^{-2}$ ) obtained for cermet anode could be probably attributed to the porous surface caused by the depletion of copper when anodically polarized.

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