

## Preliminary testing of $\text{NiFe}_2\text{O}_4$ - $\text{NiO}$ - $\text{Ni}$ cermet as inert anode in $\text{Na}_3\text{AlF}_6$ - $\text{AlF}_3$ melts

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**Abstract:** The electrical conductivity of cermet 83(90 $\text{NiFe}_2\text{O}_4$ -10 $\text{NiO}$ )-17 $\text{Ni}$  at different temperatures was measured in air, the operating performance of inert anode was evaluated in a laboratory electrolysis cell with various electrolyte compositions. The results indicate that the electrical resistivity of cermet studied has negative temperature coefficient, which is the characteristic of semi-conducting material. The proper addition of  $\text{AlF}_3$  in the bath can improve the corrosion resistance of cermet inert anode, but excess adding amount will cause the catastrophic corrosion. Post-examination of anodes shows that metal  $\text{Ni}$  leaches preferentially on the anode surface. Chemical dissolution, electrolyte penetration as well as electrochemical dissolution serve as major corrosion mechanisms.

**Key words:** aluminium electrolysis; inert anode;  $\text{NiFe}_2\text{O}_4$  based cermet; electrical conductivity; corrosion resistance

### 1 Introduction

It is well known that the current aluminum reduction cell with carbon consumable anode has many disadvantages. So the concept of inert anode was introduced, with which the disadvantages can be avoided completely.

A lot of research work has been carried out to find out a kind of appropriate material as inert anode[1–3].  $\text{NiFe}_2\text{O}_4$  based cermets, which have the desirable properties of metals as well as those of ceramic and show a good resistivity against corrosion in the molten cryolite and relatively high electrical conductivity, are one kind of the most promising materials as inert anode for aluminum electrolysis[4–6]. Aluminum Company of America, with the support from US Department of Energy, conducted a considerable work about the ferrites and developed the cermets with the composition of  $\text{NiFe}_2\text{O}_4$ -18 $\text{NiO}$ -17 $\text{Cu}$ - (Cu-Ni)[7].

Most industrial electrolytes operate with cryolite-ratios in the range of 2.2–2.7 and cell temperature of 950–970  $^{\circ}\text{C}$ . The lower temperature would be beneficial for reducing the corrosion rate of candidate inert anodes

based on metal or ceramic materials[8, 9]. Many authors have studied the impact of lowering the operating temperature through modifying electrolyte composition. Aluminum fluoride is the most commonly used additive to lower melting point, with up to 30%  $\text{AlF}_3$  in excess of the cryolite composition allowing operation between 800 and 900  $^{\circ}\text{C}$  [10].

In our previous works,  $\text{NiFe}_2\text{O}_4$  based cermets with different contents of  $\text{NiO}$  were tested and the optimized composition was determined. In this work, the cermets 83(90 $\text{NiFe}_2\text{O}_4$ -10 $\text{NiO}$ )-17 $\text{Ni}$  were prepared and their performance was evaluated at different electrolysis temperatures based on the content of  $\text{AlF}_3$ . The purpose was to provide feasible conditions of using and reduce the corrosion rate of  $\text{NiFe}_2\text{O}_4$  based cermet.

### 2 Experimental

#### 2.1 Material fabrication

The raw materials, nickel powder,  $\text{NiO}$  and  $\text{Fe}_2\text{O}_3$  were all reagent grade.  $\text{NiFe}_2\text{O}_4$  based cermet samples were prepared by a cold pressing-sintering process[11]. A proper amount of  $\text{Fe}_2\text{O}_3$  and 10% excess  $\text{NiO}$ , compared with that of the stoichiometric  $\text{NiFe}_2\text{O}_4$ , were mixed and

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then calcined. Metal powder nickel 17% was added to the calcined powder. Finally, the mixture was cold pressed into cylindrical blocks and sintered at 1 300 for 4 h in an atmosphere of efficaciously controlled oxygen partial pressure to get the desired cermet samples. The dimensions of the anodes were about  $d$  42 mm  $\times$  40 mm with relative density above 95%.

## 2.2 Electrical conductivity measurement

Electrical conductivity of  $\text{NiFe}_2\text{O}_4$  based cermet inert anode was determined with a direct current quadripole electrodes measuring apparatus[12]. In this study, test was carried out in an atmosphere of efficiently controlled oxygen partial pressure to avoid the oxidization of metal. The electrical conductivity  $\sigma$  is determined by the following equation[13]:

$$\sigma = \frac{l}{\pi \cdot r^2} \times \frac{I}{U} \quad (1)$$

where  $r$  is the radius of cylinder sample;  $l$  and  $U$  are the interval and voltage drop between two electrodes, respectively;  $I$  is the current intensity through the sample examined.

## 2.3 Electrolysis test

The electrolyte was prepared from reagent grade  $\text{Na}_3\text{AlF}_6$ ,  $\text{CaF}_2$ ,  $\text{Al}_2\text{O}_3$  and technical grade  $\text{AlF}_3$ , the compositions and temperature used in the electrolysis experiments are given in Table 1.

**Table 1** Bath composition and temperature

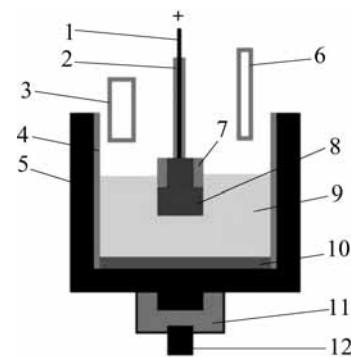
No.	Mass fraction/%				Temperature/
	$\text{Na}_3\text{AlF}_6$	$\text{AlF}_3$	$\text{Al}_2\text{O}_3$	$\text{CaF}_2$	
B1	80.9	9.6	7.5	4.0	960
B2	70.7	18.8	6.5	4.0	900
B3	64.0	30.0	2.0	4.0	800

The electrochemical cell shown in Fig.1 consisted of a graphite crucible lined with a cylindrical alumina sleeve.

The counter electrode consisted of the bottom of graphite and the area was about 60  $\text{mm}^2$ . The temperature was monitored during the experiment using a Pt/Pt+10%Rh thermocouple in a sintered alumina sleeve adjacent graphite crucible sidepiece. To control the immersion surface of anode, a sintered alumina sheath was used.

The current intensity was 30 A, giving an overall current density was 0.75  $\text{A}/\text{cm}^2$ .  $\text{Al}_2\text{O}_3$  was added every 15 min in amounts based on the electrolytic consumption rate at 85% cathodic current efficiency[14]. After electrolysis the anode was raised out of the melt while maintaining polarization so as to prevent reduction of the

anode material by dissolved metal. The cell was left to cool with the anode resting above the electrolyte.



**Fig.1** Electrochemical cell used in test: 1 Anode rod; 2 and 7 Sintered alumina sheaths; 3 Alumina feed tube; 4 Sintered alumina sleeve; 5 Graphite crucible; 6 Bath withdrawing tube; 8 Inert anode; 9 Electrolyte; 10 Melt aluminium; 11 Graphite mechanical support; 12 Cathode rod

Some of the electrolyte samples taken during electrolysis were analyzed with X-ray fluorescence. Anodes used were sectioned, mounted, polished, and analyzed by SEM/EDS.

## 3 Results and discussion

### 3.1 Effect of temperature on electrical conductivity of $\text{NiFe}_2\text{O}_4$ - $\text{NiO}$ -Ni cermet

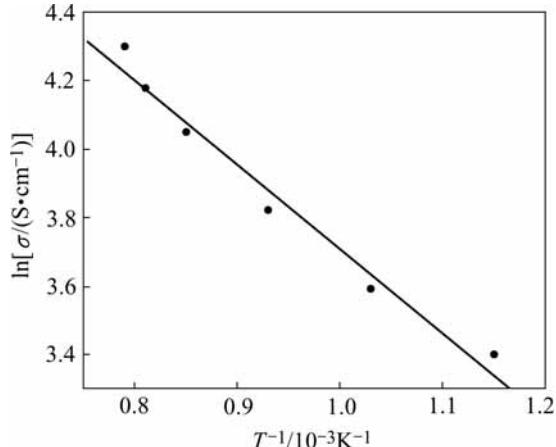
It is necessary for inert anode materials that have good electrical conductivity to realize the purpose for decreasing cell voltage and saving energy. The results show that the electrical conductivity of cermet 83(90 $\text{NiFe}_2\text{O}_4$ -10 $\text{NiO}$ )-17Ni increases with the increasing temperature. For example, the electrical conductivity increases from 29.84  $\text{S}/\text{cm}$  to 68.45  $\text{S}/\text{cm}$  with increasing temperature from 873 K to 1 273 K. The electrical conductivity of material is acceptable as inert anode for aluminum electrolysis.

From Fig.2, the material exhibits the characteristic of semiconductor, and its connection with temperature meets the equation  $\ln \sigma \propto 1/T$ .

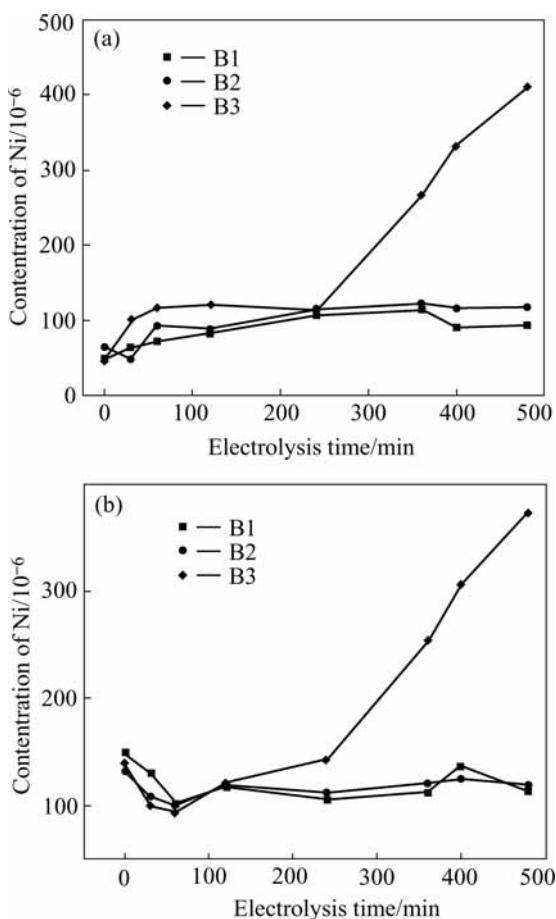
### 3.2 Varieties of Ni and Fe concentration in bath during electrolysis

Fig.3 shows the varieties of concentrations of anode constituents Ni and Fe in the electrolyte during electrolysis lasting 8 h.

As shown in Fig.3, it is clear that cermet 83(90 $\text{NiFe}_2\text{O}_4$ -10 $\text{NiO}$ )-17Ni exhibits a varying degree of dissolution of the anode components in the different bath compositions. When the electrolyte B1 and B2 are used, the steady-state values of Ni are  $101.88 \times 10^{-6}$  and  $117.09 \times 10^{-6}$ , respectively, which are fairly close to the



**Fig.2** Electrical conductivity vs temperature for cermet 83(90NiFe<sub>2</sub>O<sub>4</sub>-10NiO)-17Ni



**Fig.3** Elemental analyses of electrolyte contamination of anode constituents versus time for cermet electrodes

solubility ( $90 \times 10^{-6}$ ) measured by DEYOUNG[15] (bath ratio 1.1, melt with 6.5% Al<sub>2</sub>O<sub>3</sub>, 1 000 °C). While at the current work, the steady-state concentrations for Fe are  $117.70 \times 10^{-6}$  and  $119.0 \times 10^{-6}$ , far below the solubility ( $580 \times 10^{-6}$ ) mentioned by DEYOUNG. For the bath B3, the concentrations of Ni and Fe don't reach steady-state and increase during electrolysis despite of the decreasing temperature from 960 °C to 800 °C. When the testing is

terminated, the values of Ni and Fe concentration in the bath are  $411.45 \times 10^{-6}$  and  $373.24 \times 10^{-6}$ , respectively. The cause may be attributed to the corrosion mechanism of NiFe<sub>2</sub>O<sub>4</sub> based cermet when the electrolyte compositions are changed.

### 3.3 Effect of bath compositions on corrosion resistance

The content of anode constituents Ni and Fe in the metal aluminum recovered at cathode after the tests is listed in Table 2. The values are close in the electrolyte B1 and B2, and differ rather strongly from the electrolyte B3. And the metal obtained in the bath B2 has lower total contamination than that of others, which means that NiFe<sub>2</sub>O<sub>4</sub> based cermet tested has relatively lower corrosion rate. Though it is difficult to give actual corrosion rates based on these results, a conclusion can be drawn that the cermet 83(90NiFe<sub>2</sub>O<sub>4</sub>-10NiO)-17Ni exhibits better corrosion resistance in the bath B2 than that of others.

**Table 2** Metal contamination of anode constituents

No.	Temperature/°C	w(Ni)/%	w(Fe)/%
B1	960	0.0403	0.2224
B2	900	0.0409	0.2017
B3	800	0.0668	0.2584

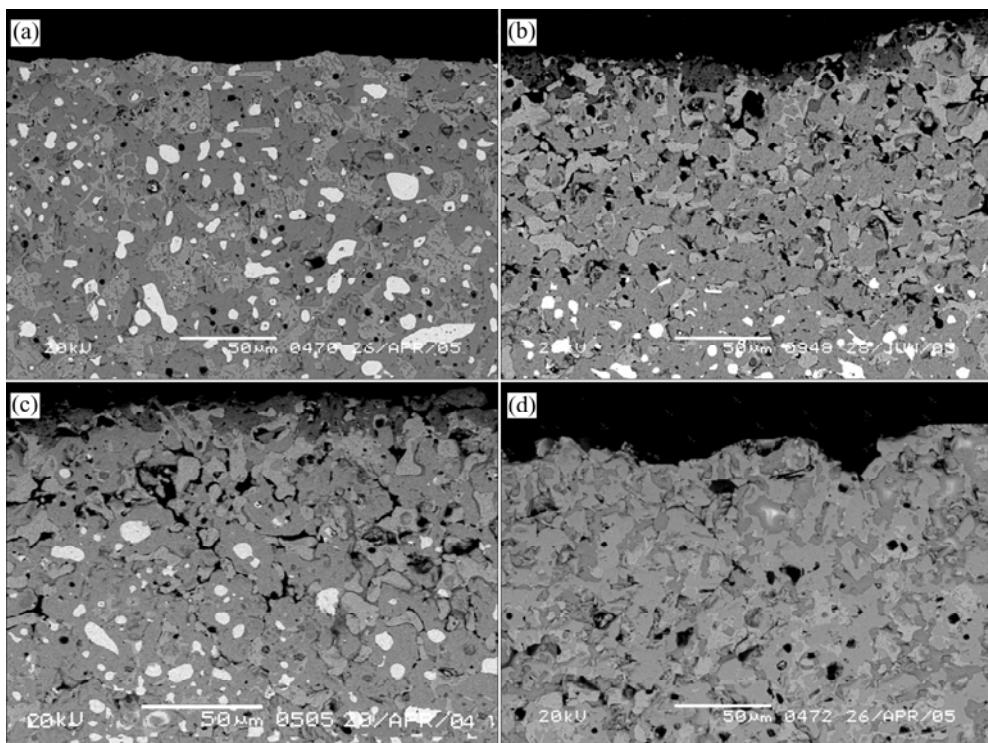
### 3.4 Preliminary study on corrosion mechanism of NiFe<sub>2</sub>O<sub>4</sub> based cermet

To obtain more information about the corrosion mechanism of the cermets, the bottom of anodes B1, B2 and B3, after electrolysis experiment, were sectioned, mounted and polished. The backscattered electron images are shown in Fig.4.

From Fig.4(a), the metal and other phases are distributed evenly and the porosity of anode is low. By comparing Fig.4(a) with Figs.4(b), (c) and (d), it is obvious that the metal phase Ni leaches preferentially, there are a number of holes and pores left and the density of anode surface decreases, especially the anode B3. The analysis of EDS shows that lots of electrolyte has penetrated into the anode and filled in the pores.

Generally speaking, NiFe<sub>2</sub>O<sub>4</sub> based cermet anodes may deteriorate in operating Hall cells by a number of possible mechanisms such as chemical dissolution, electrochemical dissolution, reduction by dissolved metal Al, electrolyte penetration, and grain boundary attack. Under the present electrolysis conditions, chemical dissolution, electrochemical dissolution and electrolyte penetration serve as three major corrosion mechanisms.

The oxide components of the anode NiFe<sub>2</sub>O<sub>4</sub> and NiO are soluble in the electrolyte. The solubility of such oxides are low; but their dissolution and rates of dissolution may determine the corrosion of the anodes.



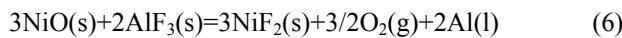
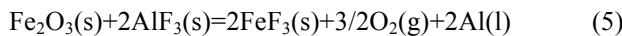
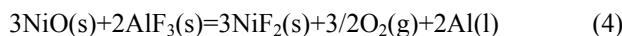
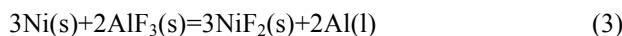
**Fig.4** SEM backscattered images of anode from bottom surface: (a) Anode before electrolysis; (b) Anode B1 after electrolysis; (c) Anode B2 after electrolysis; (d) Anode B3 after electrolysis

The rates of all thermally activated processes decrease with the decrease of temperature. Also, solubility of Fe and Ni oxides in the cryolite melt decreases, as expected, with the decreasing temperature. DEYOUNG's studies [15] also showed that the solubility of Fe and Ni oxides decreases somewhat with decreasing bath ratio. So the corrosion resistance performance of this anode composition could be improved when the bath ratio is decreased properly. But the solubility increases with the decreasing  $\text{Al}_2\text{O}_3$  concentration. If the dissolved oxide is reduced immediately and effectively, the dissolution will continue even though the solubility may be low. Thus, the corrosion of anode will quicken.

The reaction leading to the formation of oxygen at the inert anode and aluminum at the cathode is represented by the following reaction:



However, there are several possible reactions competing with reaction (2) during electrolysis:



With influence of alumina solubility and concentration, the decomposition voltages of reaction (2) at 800 and 965 are about 2.418 V and 2.240

V respectively. From Table 3, the decomposition voltage of reaction (2) is higher than that of reaction (3) and close to those of reactions (4)–(6). Therefore, the metal Ni in the anode will leach preferentially and the cell reactions (3)–(6) will compete with reaction (2) during electrolysis, and will be favored at high aluminum fluoride activity, at lower temperature, and with low alumina level. Thus, the use of low temperature-low ratio electrolyte with this anode composition leads to poorer anode performance.

**Table 3** Decomposition voltages of reactions (3)–(6) at different temperatures

Reaction	Decomposition voltage/V	
	800	965
(3)	1.845	1.912
(4)	2.591	2.586
(5)	2.750	2.745
(6)	2.550	2.552

Activity of aluminum fluoride is  $1.0 \times 10^{-2}$ ,  $1.5 \times 10^{-3}$  at 800 and 965, respectively [16].

About the electrolyte penetration, it may result from two reasons. The first one is that the bath penetrates into the pores due to capillary effects, which is left by the electrochemical dissolution of metal phase, or the preferential dissolution of the oxidation product of the metal phase in the polarized anode. The second one is the selective dissolution of Fe, since in the ceramic phase of

the  $\text{NiFe}_2\text{O}_4$  based anode, Fe has a higher solubility in cryolite, compared with Ni. In the present study, though the anode bulk density is high and electrolysis period is short, the content of metal Ni is high and its leaching leaves lots of pores, so the bath penetration is severe.

## 4 Conclusions

1) Cermet 83( $90\text{NiFe}_2\text{O}_4$ - $10\text{NiO}$ )- $17\text{Ni}$  exhibits characteristic of semiconductor, its electrical resistivity has a negative temperature coefficient. Its electrical conductivity is 68.45 S/cm at 1 273 K, which is acceptable as inert anode for aluminum electrolysis.

2) The proper addition of  $\text{AlF}_3$  in the bath can improve the corrosion resistance of cermet inert anode, but excess adding amount will cause the catastrophic corrosion. Considering the metal aluminium contamination of anode constituents, the anode behaves better in bath B2 than in the others.

3) From the post-examination with SEM/EDS of the anodes, the metal Ni is found to be corroded preferentially and produce many pores. Under present electrolysis conditions, chemical dissolution, electrolyte penetration as well as electrochemical dissolution plays major corrosion mechanisms.

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