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Effect of Ni content on corrosion behavior of Ni/(10NiO-90NiFe₂O₄) cermet inert anode

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Abstract: Ni/(10NiO-90NiFe₂O₄) cermet inert anodes with metal Ni content of 0, 5, 10, 15 and 20 (mass fraction, %) were prepared and their corrosion behavior in Na₃AlF₆-Al₂O₃ melts was investigated in laboratory electrolysis tests. The results indicate that the content of metal Ni in anodes has little effect on the steady-state concentration of impurities Ni and Fe in electrolyte and the values range in $(114-173) \times 10^{-6}$ and $(287-385) \times 10^{-6}$, but the content of impurities in the metal aluminum manifolds. There is preferential corrosion for metal Ni in NiO-NiFe₂O₄ based cermet anodes. Considering the corrosion resistance and electrical conductivity, the cermet containing 5%Ni (mass fraction) behaves best among NiO-NiFe₂O₄ based cermet anodes studied, and should be further studied.

Key words: aluminum electrolysis; inert anode; NiFe2O4 based cermet; corrosion resistance

1 Introduction

It is well known that the Hall-Héroult process, developed in 1886, is the only commercial method for production of aluminum and it has many disadvantages including energy consumption, carbon wasting and environmental pollution. The implementation of new technology based on the inert electrodes could result in significant energy and environmental benefits, and it has become a research focus[1–2]. Despite intensive research efforts, no fully satisfactory inert anode material has been found. Compared with metals and oxides, NiFe₂O₄ based cermet, which seems promising to have the desirable properties of metallic materials as well as those of ceramics, is one of the most promising materials as inert anode for aluminum electrolysis[3–4].

In our previous work, the effect of content of NiO on the corrosion resistance of NiFe₂O₄ based cermet has been studied, and the content of NiO in ceramic phase was determined 10% (mass fraction, the same below)[5]. However, its corrosion resistance to Na₃AlF₆-Al₂O₃ melts is affected not only by the ceramic phase but also

by the metallic phase. Though the results [6-8] showed that Ni was an unacceptable metal phase in cermet inert anode because of its tendency to anodically dissolve, OLSEN and THONSTAD[9] asserted that the mass transfer coefficient of Ni from electrolyte to molten aluminum was 1/2 that of Cu, and the preferential corrosion of metal Ni didn't occur. In addition, according to our previous research [10], the wettability between Cu and NiFe₂O₄ is worse than that between Ni and NiFe₂O₄, which shows better sintering performance. So it is necessary to conduct a systematic study on the effect of Ni content on the corrosion behavior of Ni/(10NiO-90NiFe₂O₄) in aluminum cermets electrolysis.

In this work, 10NiO-NiFe_2O_4 based cermet inert anodes with Ni content of 0, 5, 10, 15 and 20 (mass fraction, %) were prepared by cold pressing-sintering based on our previous works, and their corrosion resistance to cryolite-alumina melts was tested under conventional electrolysis condition. The purpose of this work is to determine which kind of metal content should be selected to improve the corrosion resistance of 10NiO-

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NiFe₂O₄ based cermet inert anodes.

2 Experimental

2.1 Preparation of ceramic and cermets

The raw materials, metal Ni powder, NiO and Fe₂O₃ were all of reagent grade. 10Ni-NiFe₂O₄ based cermet samples were prepared by conventional cold isostatic pressing-sintering process[11]. Proper amounts of NiO and Fe₂O₃ were mixed using a ball mill and then calcined to obtain 10NiO-NiFe2O4 ceramic powder. The calcined ceramic powder was mixed again with different contents (0, 5%, 10%, 15%, 20%) of Ni powder by ball milling in the media containing dispersant and adhesive that were organic to avoid the metal oxidation. Finally, the mixed ceramic-metal powder was dried and isostatic pressed into cylindrical blocks ($d20 \text{ mm} \times 40 \text{ mm}$) at the pressure of 2×10^8 Pa, and sintered at 1 350 °C for 2 h in atmosphere of efficaciously controlled oxygen partial pressure to get the desired cermet samples. The composition and correlative properties of these cermet inert anodes prepared are listed in Table 1.

 Table 1 Composition and correlative properties of inert anode samples

Sample No.	w(Ni)/ %	Diameter/ mm	Relative density/ %	Electrical conductivity $(960 \ ^{\circ}C)/(S \cdot cm^{-1})$
1	0	17.40	92.3	2.88
2	5	17.26	95.4	30.15
3	10	17.28	93.9	35.96
4	15	17.30	92.3	32.02
5	20	17.28	91.8	37.55

2.2 Cell design

A sketch of the experimental cell is presented in Fig.1. A hole was drilled at the bottom of graphite crucible and 90 g metal aluminum was added. Thus, a steady cathode surface could be obtained during electro-



Fig.1 Schematic diagram of experimental cell: 1 Al₂O₃ sleeve; 2 Stainless steel anode rod; 3 Cermet inert anode; 4 Al₂O₃ liner; 5 Graphite crucible; 6 Electrolyte; 7 Metal aluminum; 8 Graphite mechanical support

lysis. Alumina sleeve was set in the graphite crucible and about 800 g electrolyte was contained. Under the operating conditions of the laboratory test, the cell would not be thermally self-sustained. It was necessary to provide extra heat by placing the cell with the anode in a vertical laboratory furnace and the furnace was heated to the desired temperature. The temperature was measured with Pt/Pt-10%Rh thermocouple and controlled to ± 1 °C by TCE-II programmable temperature control unit.

2.3 Electrolysis test

The electrolyte was made up of reagent grade Na₃AlF₆, Al₂O₃ and CaF₂, technical grade AlF₃, with CR (molar ratio of NaF to AlF₃) 2.3, 5.0%CaF₂ and 4% Al_2O_3 . All compositions were dried at 120 °C for 48 h to remove the water before being used. Metal aluminum was added prior to electrolysis. The temperature was monitored at 970 °C, i.e. with superheat of 10 °C. The anode-bath contacting area was controlled by immersing the anode depth, which was 1 cm. The current density of anode bottom was 1 A/cm². The current and the cell voltage were supplied and monitored by a Multi-Purpose Potentiostat/Galvanostat (model 273A/10, Perkin-Elmer Instruments). According to the calculation, the concentration of Al₂O₃ in the bath decreases by 1.5% during lasting 8 h electrolysis if the current efficiency is 85%[12] and Al₂O₃ is not added. Moreover, alumina sleeve also contributes to keep the concentration of Al₂O₃. So, Al₂O₃ was not added during testing.

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 aluminum. The cell was left to cool with the anode resting above the electrolyte. The anodes tested were sectioned, mounted, polished, and analyzed by XRMA (JSM-5600LV). Some samples of bath and the aluminum samples in the bottom hole were analyzed by X-ray fluorescence spectrum (analytic error below 5%) for getting the concentration of Ni and Fe in bath and cathode aluminum.

3 Results and discussion

3.1 Varieties of impurities concentration in bath during electrolysis

DEYOUNG[13] pointed out it took approximately 8 h for stoichiometric NiFe₂O₄ in cryolite melts to reach steady-state concentration, which was taken to be solubility. LAI et al[14] pointed that this process would last 4–6 h. Therefore in present work, all electrolysis experiments lasted 8 h. The varieties of the concentrations of impurities, which were corroded from

 $Ni/(10NiO-90NiFe_2O_4)$ cermet inert anode components into the melts, are listed in Table 2 and Table 3.

Table 2 Concentrations of impurity Fe in bath during electrolysis for different cermet anodes

Sample	w(Ni)/	Concentration/10 ⁻⁶				
No.	%	6.5 h	7 h	7.5 h	8 h	Average
1	0	304	306	306	303	304
2	5	381	397	388	377	385
3	10	316	322	323	315	319
4	15	348	347	328	330	338
5	20	284	286	290	289	287

Table 3 Concentrations of impurity Ni in bath duringelectrolysis for different cermet anodes

Sample	w(Ni)/	Concentration/10 ⁻⁶				
No.	%	6.5 h	7 h	7.5 h	8 h	Average
1	0	116	112	113	115	114
2	5	114	123	135	146	129
3	10	147	153	153	146	149
4	15	176	176	169	171	173
5	20	133	132	135	135	133

From Table 2, for the cermet inert anodes investigated, the contents of metal Ni are 0%, 5%, 10%, 15% and 20%, and the steady-state concentrations of impurity Fe in the bath are about 304×10^{-6} , 385×10^{-6} , 319×10^{-6} , 338×10^{-6} and 287×10^{-6} respectively, which are far below the solubility (580×10^{-6}) mentioned by DEYOUNG (bath ratio 1.1, with 6.5% Al₂O₃, 1 000 °C)[13].

The data listed in Table 3 show that, for the cermet inert anodes investigated, the steady-state concentration of impurity Ni in the bath ranges between 114×10^{-6} and 173×10^{-6} . And the content of metal Ni in cermet makes little effect on the steady-state concentration of impurity Ni in the bath during the electrolysis of 10NiO-NiFe_2O_4 based cermets. That is to say, with the content of metal Ni in 10NiO-NiFe_2O_4 based cermet increasing, there is little effect on the steady-state concentration of impurities Ni and Fe in the bath. It should be noted that the concentrations of impurities Ni and Fe decrease when the content of metal Ni is 20%. The reason may be that the corrosion control process is changed. Of course, the exact reason requires to study further.

3.2 Effect of metal Ni content on content of impurities in metal aluminum

The content of anode constituents Fe and Ni in the metal aluminum recovered at cathode after testing is listed in Table 4. It is very obvious that the content of impurities in metal content aluminum increases when the metal Ni is added. In the content range of 0-20% of

metal Ni, the contents of impurity Fe and Ni vary in $(2\ 300-4\ 088) \times 10^{-6}$, $(198-1\ 519) \times 10^{-6}$, respectively. It should be noted that the content of impurity in metal aluminum is the highest when the content of metal Ni is 15%, and the total content of impurities is $5\ 556 \times 10^{-6}$, which corresponds with the concentration of impurities in the bath. The reason is not clear and should be studied further.

Table 4 Content of impurities in metal aluminum after testingSample No.w(Ni)/%Concentration of impurities/10⁻⁶ENi

	$w(N_1)/\%$ -	<u>.</u>			
Sample No.		Fe	Ni		
1	0	2300	198		
2	5	3561	1298		
3	10	3978	1519		
4	15	4088	1468		
5	20	3958	1312		

Notice: Contents of impurities Ni and Fe in metal aluminum before electrolysis are 34×10^{-6} and 1360×10^{-6} .

In addition, the mass ratio of impurities Fe to Ni in metal aluminum neither ranges from 3 to 8, as DEYOUNG mentioned[13], nor are about 1.4 as that in cermets, but 2.6-11.6. The following reasons may explain the phenomenon. Firstly, the addition of Ni and NiO restrains the dissolution of Fe from anodes, and decreases the mass ratio. Secondly, the polarized corrosion mechanism of ceramic phase in the cermets, affected by chemical dissolution, electrochemical corrosion and so on, is probably different from the static corrosion mechanism (unpolarized corrosion mechanism), which is only controlled by chemical dissolution. Thirdly, the transferring velocity for different impurities from electrolyte to molten aluminum is different, and the velocity of impurity Fe is about twice that of impurity Ni[8].

3.3 Microstructure of cermet inert anodes after electrolysis

To obtain more information about the corrosion process, the cermet inert anodes 1, 2, 3 and 5 are sectioned, mounted and polished after electrolysis experiments. The back-scattered images of the cermet inert anodes are shown in Fig.2.

From Figs.2(a) and (b), the corrosion of inert anodes is not obvious. However, comparing Figs.2(c) and (d) with (b), though the metallic phase Ni and other phases are distributed evenly in the uncorroded area, it can be found obviously that the metal phase Ni is leached preferentially, and there is a lot of holes and pores left. The distribution of metallic phase near the surface is complex and it may be regarded as three layers that are preferential corrosion layer, transition-layer and the body respectively. This may imply that the corrosion



Fig.2 SEM backscattered images of cermet inert anodes at anode bottom after electrolysis: (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 5

resistance will weaken with the content of metal increasing, and the cermet inert anodes containing low content metal should be selected. In addition, there are some metal grains in the sample 1, which were introduced during preparation process.

Generally speaking, the cermet inert anodes investigated may deteriorate in operating Hall cells by a number of possible mechanisms such as chemical dissolution, electrochemical corrosion, reduction by dissolved metal aluminum, electrolyte penetration, and grain boundary attack. Normally, a thin oxide coating would be always present on the anode surface. However, under electrolysis condition, it should be further noted that the Ni metal present in the anode may fluorinate:

$$3Ni(s)+2AlF_3(s)=3NiF_2(s)+2Al(l)$$
(1)

As for influence of alumina concentration and electrolysis temperature, the decomposition voltage of reaction (1) at 965 °C is 1.912 V, which is lower than 2.240 V for oxygen production under same condition. Thus, the metallic phase Ni is corroded preferentially and pores are left.

About the electrolyte penetration, it may result from two reasons. The first one is due to pores left by the electrochemical dissolution of metallic phase when anode is polarized, or the metallic phase oxidation and the following preferential chemical dissolution, and bath penetrates into these pores by capillary effect. The second one is the selective dissolution of Fe, since in the ceramic phase of the NiFe₂O₄-based cermet inert anode, impurity Fe has a fairly high solubility in cryolite molten compared with Ni. To restrain or eliminate effectively the above-mentioned factors, which are adverse to resistance corrosion of inert anode, it is necessary to improve the relative density and decrease the content of metallic phase.

4 Conclusions

1) With the content of metal Ni in cermet inert anodes increasing from 0% to 20%, there is little effect on the steady-state concentration of impurities Ni and Fe in the bath, and the values are $(114-173) \times 10^{-6}$ and $(287-385) \times 10^{-6}$. But the contents of impurities Ni and Fe in the metal aluminum manifold and range in $(198-1519) \times 10^{-6}$ and $(2 300-4 088) \times 10^{-6}$, respectively.

2) The microstructure of inert anodes after electrolysis shows that the metallic phase Ni in cermet inert anodes is found to be corroded preferentially and produces many holes and pores, and the distribution of metallic phase near surface can be regarded as preferential corrosion layer, transition-layer and the body.

3) From the post-examination with SEM study of cermet inert anodes and the content of impurity in metal aluminum recovered at cathode, the low content of metal

Ni cermet inert anode should be selected to improve its corrosion resistance. Considering the corrosion resistance and electrical conductivity, the cermet containing 5% metal Ni behaves best among NiO-NiFe₂O₄ based cermet anodes studied, and should be studied further.

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