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Effect of additive BaO on corrosion resistance of xCu/(10NiO-$NiFe_2O_4$) cermet inert anodes for aluminum electrolysis

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Abstract: xCu/(10NiO-$NiFe_2O_4$) cermet and 1BaO-xCu/(10NiO-$NiFe_2O_4$) cermet (x=5, 10, 17) inert anodes were prepared as potential inert anodes for aluminum electrolysis and their corrosion resistance to traditional electrolyte was studied with anodic current density of 1.0 A/cm^2 in laboratory electrolysis. The substantial corrosion of metal Cu was observed, many pores appeared on the surface of anode and electrolytes infiltrated inside anodes during the electrolysis. The wear rates of 5Cu/(10NiO-$NiFe_2O_4$), 10Cu/(10NiO-$NiFe_2O_4$), 17Cu/(10NiO-$NiFe_2O_4$), 1BaO-5Cu/(10NiO-$NiFe_2O_4$), 1BaO-10Cu/(10NiO-$NiFe_2O_4$) and 1BaO-17Cu/(10NiO-$NiFe_2O_4$) are 2.15, 6.50, 8.30, 4.88, 4.70 and 4.48 cm/a, respectively. The addition of BaO to 10Cu/(10NiO-$NiFe_2O_4$) cermet and 17Cu/(10NiO-$NiFe_2O_4$) cermet is advantageous because BaO can effectively promote densification and thus improve corrosion resistance. But the addition of BaO to 5Cu/(10NiO-$NiFe_2O_4$) cermet is unfavorable to corrosion resistance because additive BaO at the grain boundary of anode accelerates possibly the corrosion of cermet.
Key words: BaO; inert anode; aluminum electrolysis; cermet; corrosion resistance; wear rate

1 Introduction

The basic requirements for an inert anode include[1]: a low corrosion rate, a good electronic conductor, not contaminating the produced metal to any significant degree, thermal stability at electrolysis temperature as well as exhibiting adequate resistance to thermal shock, and economical feasibility. No material meets all these requirements[2−3] yet. A lot of research work has been carried out to find out a kind of appropriate material as inert anode[4−5]. $NiFe_2O_4$-based cermet, which has the desirable properties of metal and ceramic, and shows a good resistance against corrosion in the molten cryolite and a relatively high electrical conductivity, is one of the most promising materials as inert anode for aluminum electrolysis[6−9].

The corrosion resistance of $NiFe_2O_4$-based cermet as a potential inert anode material for aluminum electrolysis is dependent on its relative density. For conventional sintering, the densification is usually enhanced by increasing the sintering temperature, but the grain coarsening results in low mechanical properties and electric conductivity, especially corrosion resistance[10−11]. Activated sintering is an effective method to gain high relative density for cermets. The impact of lowering the sintering temperature on cermet composition and corrosion resistance was studied. LAI et al[12] observed that for cup-shaped inert anode consisting of cermet 17Ni/83(10NiO-$NiFe_2O_4$) with 100 mm in diameter, the contents of main impurities are Ni 0.1288% and Fe 1.0074%, and the corrosion rate under electrolysis conditions based on the content of impurity Ni in metal aluminum is approximately 8.51 cm/a. TIAN et al[13] revealed that there is preferential corrosion for metal Ni in NiO-$NiFe_2O_4$-based cermet anodes. By considering the corrosion resistance and electrical conductivity, the cermet containing 5%Ni (mass fraction) behaves the best among NiO-$NiFe_2O_4$-based cermet anodes, and should be further studied. XI[14] reported that V_2O_5 can improve the corrosion resistance and Ni_2FeVO_6 distributes along the grain boundary, which

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can control the chemical dissolution of ceramics anode and the reinforced grain boundary can control the grain-boundary corrosion rate. OLSEN and THONSTAD[15] found that the nickel level in the electrolyte did not reach steady state after electrolysis for 4 h and the total contaminant level of anode constituents in the deposited metal was as low as 0.116% (mass fraction). RAY et al[16−17] pointed out that the contaminant level of Cu-NiO-$NiFe_2O_4$ anode in the deposited metal was as low as 0.2 %Fe(mass fraction), 0.1 %Cu (mass fraction) and 0.034 %Ni (mass fraction).

Some metal oxides, such as BaO, may be the selective additives, which do not contaminate the aluminum produced. In order to give some available advices for the choice of anode constituent and good corrosion resistance, *x*Cu/(10NiO-$NiFe_2O_4$) cermet and 1BaO-*x*Cu/(10NiO-$NiFe_2O_4$) cermet (*x*=5, 10, 17) were prepared by cold isostatic pressing followed by pressureless sintering. The effect of additive BaO on the corrosion resistance of *x*Cu/(10NiO-$NiFe_2O_4$) cermets was investigated .

2 Experimental

2.1 Preparation of sample

*x*Cu/(10NiO-$NiFe_2O_4$) cermet and 1BaO-*x*Cu/(10NiO-$NiFe_2O_4$) cermet (*x*=5, 10, 17) were prepared by the conventional ceramic method with reagent grade raw materials of Fe_2O_3, NiO, Cu and BaO. Fe_2O_3 and NiO in the molar ratio of 1.35 were mixed and calcined in a muffle furnace at 1 200 °C for 6 h in a static air atmosphere to form 10NiO-$NiFe_2O_4$ ceramic powder. The synthesized powders, Cu and BaO powder were ground in the medium containing dispersant and adhesive. The mass fraction of BaO was 1%. The dried mixture was compacted at a pressure of 200 MPa to get cylindrical blocks (*d* 20 mm×45 mm) and bars. Then, the cermets were sintered at 1 200 °C for 4 h in nitrogen atmosphere at an efficaciously controlled oxygen partial pressure[18].

2.2 Characterization

Microstructure was analyzed with JSM−6360LV scanning electron microscope and EDX−GENESIS energy dispersive spectrometer. Bulk densities were tested according to the Archimedes' method. Under the operating conditions of laboratory test, the electrolysis cell would not be thermally self-sustaining; it was necessary to provide extra heat by placing the cell in a vertical furnace. The furnace had a minimum cross-sectional diameter of 300 mm. The major components of the cell are shown in Fig.1.

The graphite crucible had an outside diameter of 105 mm and an inner diameter of 65 mm. The alumina

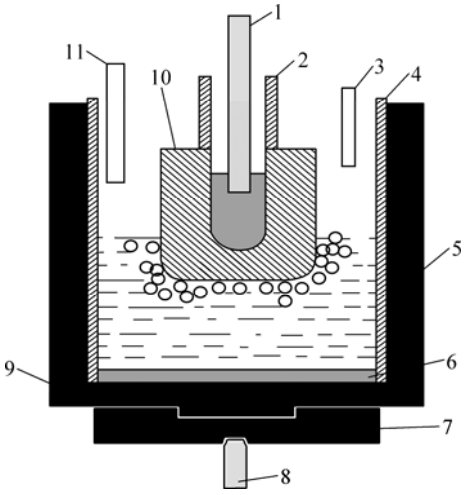

Fig.1 Sketch of electrolysis cell: 1—Anode rod; 2—Alumina sleeve; 3—Bath withdrawing tube; 4—Alumina liner; 5—Electrolyte; 6—Metal aluminum; 7—Graphite mechanical support; 8—Cathode rod; 9—Graphite crucible; 10—Inert anode; 11—Alumina feed tube

liner was 60 mm in inner diameter with a wall thickness of 2.5 mm. This liner extended from the lower crucible edge upward for 160 mm. It contained both the metal cathode pool and the cell electrolyte. The upper liner prevented oxygen generated at the anode from coming into contact with the graphite crucible or the furnace interior. It also defined the current path from the anode to the metal pool and not directly to the sidewall. Two stainless steel rods (diameter 8 mm) were used for electrical connection to the anode and cathode crucible.

The anode rod was insulated from the anode support bar by an insulating ring. In addition to supporting the anode assembly, this bar was used to raise and lower the anode to assure a proper distance between the anode and cathode during the electrolysis. The cathode rod was connected to the bottom of the graphite crucible and insulated from the furnace. The volume above the upper edge of the crucible and extending to the furnace wall was filled with insulating materials such as silica boards and light mass and high insulating fire brick.

2.3 Aluminum electrolysis

The electrolyte was prepared from reagent grade Na_3AlF_6, AlF_3, CaF_2 and $A1_2O_3$. The compositions were 5% CaF_2(mass fraction), 7.43% $A1_2O_3$(mass fraction) and balance cryolite(*n*(NaF)/*n*(AlF_3)=2.30). All compositions were dried at 120 °C for 48 h to remove the water before using. The crucible contained a total of 300 g electrolyte. Metal aluminum (65 g) was added prior to electrolysis. The cell with inert anode was heated to the required temperature of 960 °C and kept for 2 h before immersing the anode and electrifying for 20 min

later. The immersion depth of anode was approximately 20 mm.

During electrolysis, the current was kept at 3 A; the current density of inert anode bottom was 1.0 A/cm^2. The cell voltage and reference voltage between inert anode and aluminum electrode were measured. Bath samples were taken out just before the addition of alumina and further analyzed to determine the level of anode constituents in the melt.

After the test, the anode was raised out of the melt while maintaining polarization so as to prevent reduction of the anode material by dissolved metal. The anode above the electrolyte was cooled with the cell. Some of electrolyte samples taken out during electrolysis were dissolved by $HClO_4$ solution, and analyzed with X-ray fluorescence spectroscope (XRF). The precision of analyses was approximately 10% (mass fraction) for the measured values below 100×10^{-6}, 5% (mass fraction) for values between 100×10^{-6} and $1\ 000\times10^{-6}$, and 3% (mass fraction) above 1×10^{-3}. The anode was sectioned, polished and then analyzed with SEM/EDS.

The equation of corrosion rate of inert anode is

$$W_{\text{loss}} = (m_{\text{b}}w_{\text{b}} + m_{\text{a}}w_{\text{a}})\times10^{-6}\times365\times24/(S_{\text{anode}}\rho_{\text{anode}}t) \quad (1)$$

where W_{loss} is the corrosion rate of inert anode (cm/a); m_{b} is the total mass of electrolyte (g); w_{b} is the mass fraction of impurity of electrolyte (10^{-6}); m_{a} is the total mass of aluminum after electrolysis (g); w_{a} is mass fraction of impurity of aluminum after electrolysis (10^{-6}); S_{anode} is total anode area immersed in electrolyte (cm^2); ρ_{anode} is the relative density of anode (g/cm^3); t is electrolysis time (h).

3 Results and discussion

3.1 Electrolyte test

YOUNG[19] observed that it took approximately 8 h for stoichiometric $NiFe_2O_4$ in cryolite melts to reach steady-state concentration, which is taken to be the solubility. LAI et al[20] showed that such a process would cost 4−6 h. Therefore, in present work all electrolysis experiments lasted for 10 h. As mentioned above, the electrolyte samples were taken out during electrolysis to study the dissolution process of the anode material. The samples were analyzed for the concentration of anode components in electrolyte during electrolysis, and a typical set of results are plotted in Fig.2.

From Fig.2(a), the steady-state of impurity Ba is approximately reached (The precision of analysis is 5%) and the mass fractions are 504×10^{-6}, 592×10^{-6} and 680×10^{-6} for 1BaO-5Cu/(10NiO-$NiFe_2O_4$), 1BaO-10Cu/(10NiO-$NiFe_2O_4$) and 1BeO-17Cu/(10NiO-$NiFe_2O_4$), respectively, when the electrolysis ends, indicating that Ba concentration increases with increasing Cu concentration of inert anode.

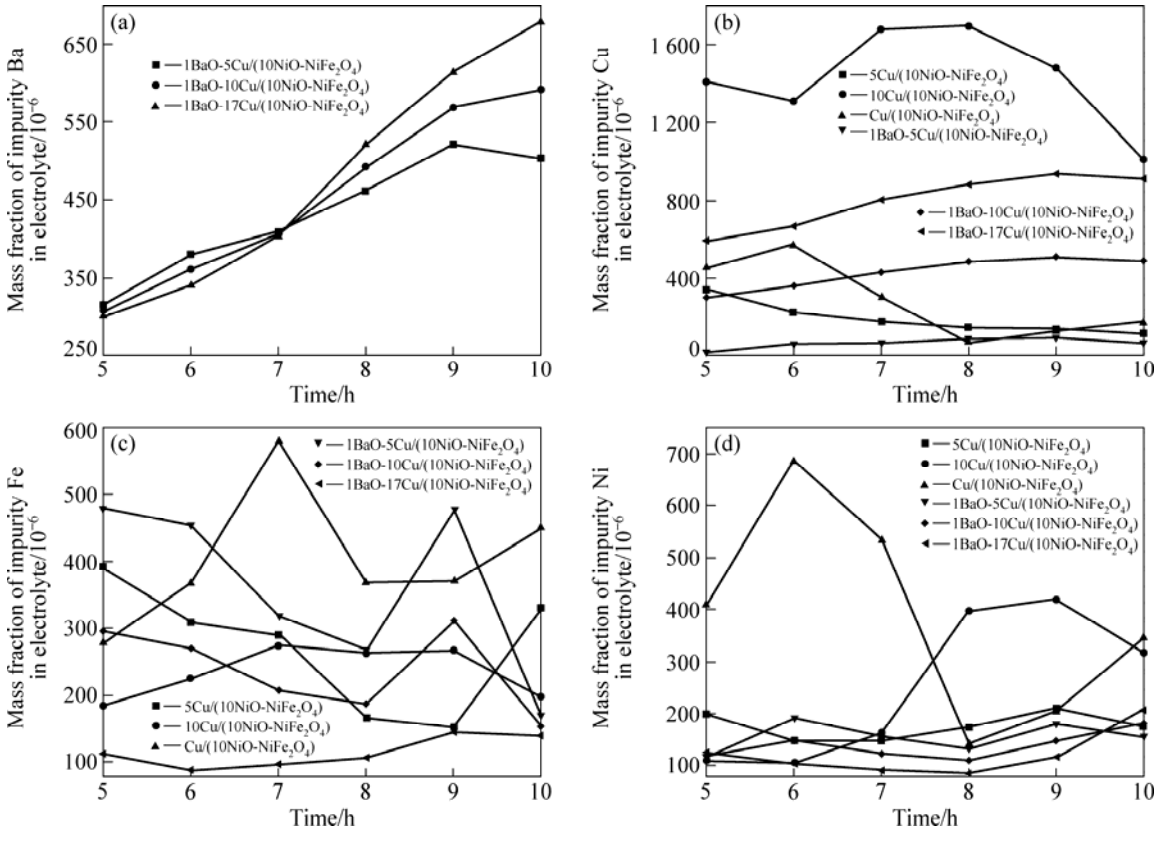

Fig.2