Effect of Metallic Content on Properties of $NiFe_2O_4$ Matrix Cermet Inert Anodes for Aluminum Electrolysis

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Abstract- $NiFe_2O_4$ matrix cermet inert anodes for aluminum electrolysis were prepared with Cu-Ni mixed powders as toughening metallic phase and 15NiO-85$NiFe_2O_4$ as ceramic matrix via powder metallurgy two-step sintering method. The mixed metallic contents varied from 10 to 18 (mass fraction, %) with 2% intervals. The phase composition, microstructure of composite and the effect of metallic content on the density, porosity, fracture toughness and bending strength were studied in details. The results show the densities of cermets increase with metallic content increase while decrease for porosities. The fracture toughness and bending strength first increase and then decrease with the increase of metallic content. When the metallic content was 16%, the maximum values of fracture toughness and bending strength were 105.19MPa and 2.73MPa•$m^{1/2}$ respectively. The results imply that the cermet containing 16% metals should be further studied to confirm the optimal metallic content for $NiFe_2O_4$ matrix cermet inert anodes used in aluminum electrolysis.

Keywords- $NiFe_2O_4$; inert anode; cermet; metallic content; fracture toughness

I. INTRODUCTION

It is well-known that the Hall-Héroult process, developed in 1886, is the only commercial method for production of aluminum from alumina. Though the techniques and equipments and many other aspects have greatly improved in the process of aluminum electrolysis, the use of carbon anode has not changed till now. The disadvantages caused by using carbon anode for aluminum electrolysis, including energy consumption, carbon wasting and environmental pollution, have come into sufficient notice. Inert anode and its techniques, which could result in significant energy and environmental benefits, have become the research focus of international aluminum and material field [1-4]. Despite intensive research efforts, no fully satisfactory inert anode material has been found. Compared with metals and oxides, $NiFe_2O_4$-based cermet, which possesses their putative ability to combine the features of ceramics and metals, namely, chemical inertness and electronic conductivity, is a promising candidate as an inert anode for aluminum electrolysis [5-7]. Although cermet anodes combine the advantages of metals and ceramics, they also inherit their shortcomings. For high conductivity and mechanical properties, the content of metallic phase should be as high as possible, whereas, the corrosion resistance would decrease. Therefore, the metallic phase content plays a crucial role in properties of inert anode. Recently, an intensive and extensive work was concentrated on the electric conductivity and corrosion behavior of $NiFe_2O_4$ matrix cermet consisting of Cu or Cu-Ni. Previous works showed that the metallic content was mainly 17%Cu. Cu-Ni alloy shows better properties for Ni could improve the wettability between Cu and $NiFe_2O_4$ and promote the sintering process [8].

In this study, 85Cu-15Ni/(15NiO-85$NiFe_2O_4$) cermets were fabricated by powder metallurgy two-step sintering method. The effects of metallic content on the density, porosity, bending strength and fracture toughness of the cermets were investigated in details.

II. EXPERIMENTAL SECTION

A. Preparation of Cermets

x(85Cu-15Ni)/(15NiO-$NiFe_2O_4$) cermet composites were fabricated by conventional cold pressing and sintering process with reagent grade raw materials of Fe_2O_3, NiO, MnO_2, V_2O_5, Cu and Ni. A proper amount of Fe_2O_3 and NiO powders, with 1%MnO_2 and 0.5%V_2O_5, were mixed in planetary muller for twenty-four hours using distilled water as dispersant. The dried mixtures with 4% PVA binder were molded by cold pressing under 60MPa and then calcined in a muffle furnace at 1000℃ for 6h in air to form the 15NiO-85$NiFe_2O_4$ matrix material. Through crushing

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and screening, the matrix materials were separated to different size of particles, namely, 0.50mm~0.35mm, 0.105mm~0.074mm, and <0.074mm. Particle gradation design is showed in Table I, with different contents (10%, 12%, 14%, 16% and 18%) of metal (85Cu-15Ni). The mixtures were put into glass beaker, using anhydrous alcohol as dispersant to avoid the metal oxidation, and mixed thoroughly under vigorous mechanical stirring and ultrasonication at room temperature. Finally, adding with 4% PVA binder, the dried mixtures were made into cuboid compacts (60mm×12mm×10mm) by cold pressing under 200MPa and sintered subsequently at 1200℃ in the air atmosphere for 6h to produce cermets. The flow chart of preparation process is shown in Fig .1.

TABLE I DESIGN OF PARTICLE GRADATION (MASS FRACTION)

Matrix content			Metallic content
500μm~350μm (42%)	105μm~74μm (18%)	<74μm (40%)	
37.80%	16.20%	36.00%	10%
36.96%	15.84%	35.20%	12%
36.12%	15.48%	34.40%	14%
35.28%	15.12%	33.60%	16%
34.44%	14.76%	32.80%	18%

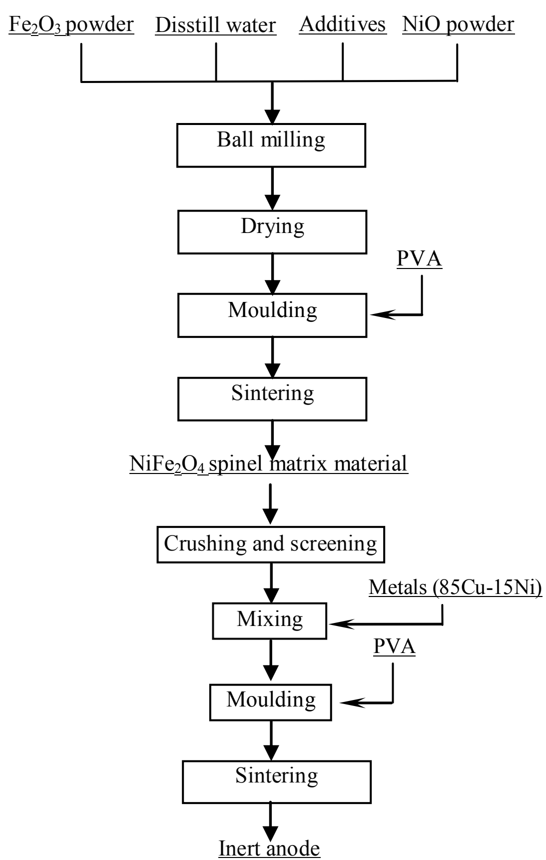

Figure 1 Flow chart of preparing cermet.

B. Characterization

The bulk density and porosity of the obtained cermets were tested using Archimedes' method with deionized water as the immersion medium. Phase composition of the composite was identified by X-ray diffraction analysis using X' Pert Pro X-ray diffractometer. The fracture toughness of the sintered samples was determined by single-edge notched bending (SENB) at ambient conditions [9]. Three-point bending strength was tested by using INSTRON4206−006 electron mechanical experimental machine with span of 30mrn and cross-head speed of 0.5 mm/min. Microstructure of fracture surfaces was analyzed on SSX-550 scanning electron microscopy (SEM).

III. Results and Discussion

A. Phase Analysis

The X-ray diffraction pattern of (85Cu-15Ni)/ (15NiO-85$NiFe_2O_4$) cermet is plotted in Fig .2. From Fig .2, it can be seen that the major detected peaks include those of $NiFe_2O_4$, NiO and (Cu, Ni), which shows that the inert anode material is of the desired phase composition.

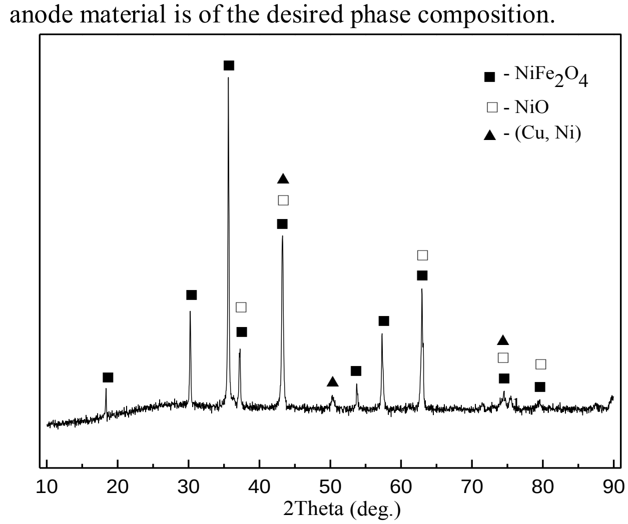

Figure 2 XRD pattern of NiFe2O4 matrix cermet.

B. Effect of metallic content on bulk density and porosity

The changes of density and porosity with metallic content are delineated in Fig .3. From Fig .3, it can be found that in the range of 10-16% metal alloy, the higher the metallic content is, the higher the density and the lower the porosity is. When the metallic content is over 16%, the density decreases and the porosity increases slightly.

The density increases with the increase of metallic content in proper range, due to the density of 85Cu-15Ni alloy is higher than that of 15NiO-85$NiFe_2O_4$ ceramic. On the other hand, in this research, the sintering temperature (1200℃) is somewhat higher than the melt point of 85Cu-15Ni alloy (1175℃), therefore, the cermets are undergone liquid sintering process. The existing metallic phase in the sintering process can be filled in the blanks between the NiO-$NiFe_2O_4$ ceramic grains by capillarity. So the porosity decreases with the increase of metallic content. However, when the metallic content is as much as 18%, it can be found that the metal is overflowed on the surface of sample, which increases the porosity and decreases the density.

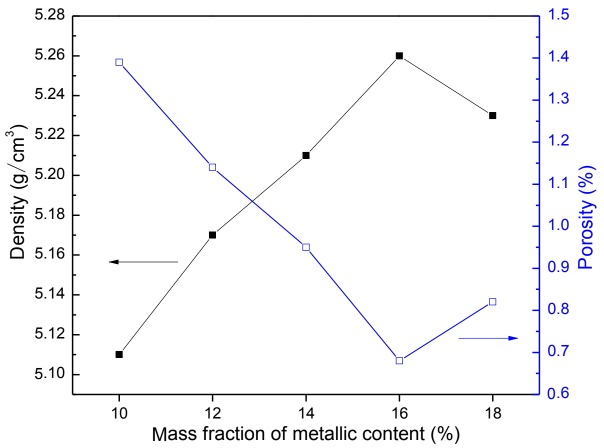

Figure 3 Effect of metallic content on density and porosity.

C. *Effect of metallic content on mechanical properties*

The mechanical property is significant to desirable inert anode material. In general, proper metal will improve the mechanical property on cermet. Given low metallic content, it is hard for cermet to exhibit the advantage of metallic strengthening and conductivity improving. However, the predominance of corrosion resistance of cermet decreases with the increase of metal content because the metal dissolves in cryolite melt prior to the ceramic matrix. In this research, only the mechanical properties of cermet were discussed, and the electrical conductivity and corrosion resistance of cermet will be researched in details later.

Fig .4 illustrates variation of bending strength and fracture toughness versus the metallic content. As the figure depicts, the change trend of bending strength is the same as that of fracture toughness. As the metallic content increases, the bending strength and fracture toughness increase and maximum values of both are obtained when the metallic content is 16%, after which the both values slightly decrease. The maximum values of bending strength and fracture toughness are 105.19MPa and 2.73MPa•m$^{1/2}$, respectively.

Generally speaking, the bending strength of cermets is related to several factors such as ceramic grain size, porosity, metallic phase dispersion, the bond between ceramic phases and metallic phases. Eqns. (l) and (2) illustrate that decreasing grain size and porosity can increase material strength [10, 11]:

$$\sigma = \sigma_0 \exp(-bP) \quad (1)$$

$$\tau = \tau_0 + Kd^{-1/2} \quad (2)$$

where P is porosity, σ is strength for sample with porosity of P, σ_0 is strength for sample without pores, b is a constant, and τ is material strength, τ_0 is yield stress, K is a constant and d is grain size.

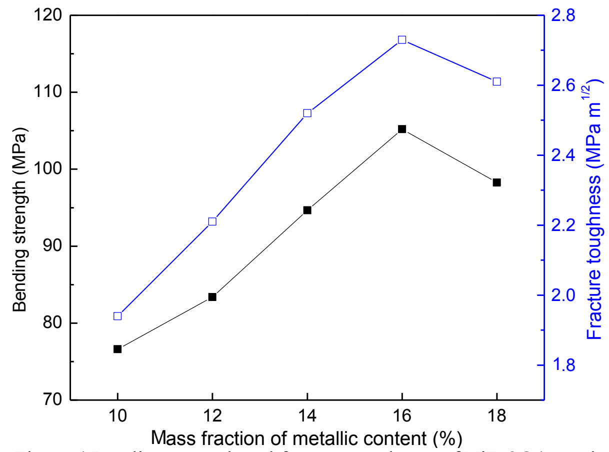

Figure 4 Bending strength and fracture toughness of NiFe2O4 matrix cermet with various metallic contents.

Fig .5 displays the fracture surfaces of (85Cu-15Ni)/(15NiO-$NiFe_2O_4$) cermets with various metallic contents. As shown in Fig .5, there is no obvious change on ceramic grain size (5-20μm) for the composites with various metallic contents. As discussed above, the existing liquid phase is beneficial to the decrease of porosity. From equation (1), the strength is inversely proportional to porosity. The smaller the porosity is, the higher the bending strength is. Additionally, the homogeneous dispersion of metal phase can improve interfacial contact between ceramic and metal and promote function of metallic toughening. From Fig .5, as the metallic content increases, the more metallic phase exists between ceramic grains and disperses evenly. However, the overflowing of metallic phase makes the loss of metallic phase between ceramic grains, leaving large pores, and weakens the strength.

The toughening of cermet mainly depends on metallic particle [12]. The crack always extends through the way with low energy. It is hard for crack to extend through metallic phase but easy to extend across the interface between ceramic and metal due to the relatively low fracture energy. The homogeneous dispersion of metal phase, additionally, increases the interface between ceramic and metal. Consequently, these both increase the extending distance and resistance of fracture growth and strengthen the function of the bridging toughening and crack deflection toughening simultaneously. However, the increased porosity, when the metallic content is over 16%, slightly weakens the fracture toughness of cermets.

IV. CONCLUSION

1) As metallic content increases from 10% to 16%, the higher the metallic content is, the higher the density and the lower the porosity is. When the metallic content is over 16%, the density decreases and the porosity increases slightly, owing to the overflowing of metallic phase in the sintering process.

2) The change trend of bending strength and fracture toughness is consistent with that of density. A maximum bending strength of 105.19MPa and maximum fracture toughness of 2.73MPa•$m^{1/2}$ are presented when the metallic content is 16%.

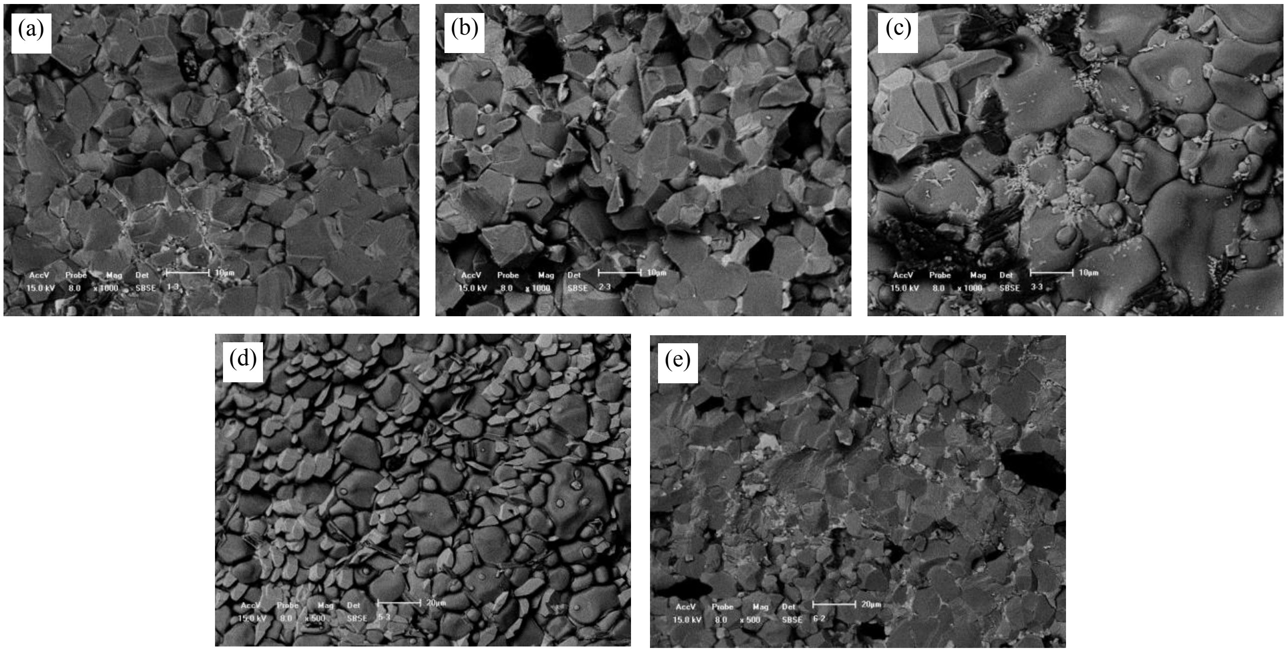

Figure 5 SEM photographs of (85Cu-15Ni)/(15NiO-$NiFe_2O_4$) cermets with various metallic contents: (a)10%, (b)12%, (c) 14%, (d) 16% and (e) 18% (mass fraction).

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