

Effect of metallic phase content on mechanical properties of (85Cu-15Ni)/(10NiO-NiFe₂O₄) cermet inert anode for aluminum electrolysis

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Abstract: (85Cu-15Ni)/(10NiO-NiFe₂O₄) cermets were prepared with Cu-Ni mixed powders as toughening metallic phase and 10NiO-NiFe₂O₄ as ceramic matrix. The phase composition, microstructure of composite and the effect of metallic phase content on bending strength, hardness, fracture toughness and thermal shock resistance were studied. X-ray diffraction analysis indicates the coexistence of (Cu-Ni), NiO and NiFe₂O₄ phases in the cermets. Within the content range of metallic phase from 0% to 20% (mass fraction), the maximal bending strength (176.4 MPa) and the minimal porosity (3.9%) of composite appear at the metallic phase content of 5%. The fracture toughness increases and Vickers' hardness decreases with increasing metal content. When the thermal shock temperature difference (Δt) is below 200 °C, the loss rate of residual strength for 10NiO-NiFe₂O₄ ceramic is only 8%, but about 40% for (85Cu-15Ni)/(10NiO-NiFe₂O₄) cermets. As Δt is above 200 °C, the residual strength sharply decreases for sample CN0 and falls slowly for samples CN5–CN20.

Key words: NiFe₂O₄; cermet inert anode; aluminum electrolysis; metallic phase; fracture toughness; thermal shock resistance

1 Introduction

The use of inert or non-consumable anodes and wettable cathodes for replacement of consumable carbon anodes and cathodes in Hall-Heroult electrolysis cells for the production of aluminum has been a technical and commercial goal for many decades[1–3]. During electrowinning in the novel cells with inert anodes, the specific criteria that an inert anode material used in aluminum electrolysis are[4]: 1) acceptable electric conductivity comparable to carbon anodes at operating temperature; 2) low reactivity with bath and oxygen when being anodic-polarized; 3) adequate mechanical strength; 4) ability to be fabricated into large shapes; 5) stable electrical connection with metal rod; 6) relatively low cost and ready availability, and 7) ability to produce commercial purity aluminum.

The current research on cermet for inert anode mainly focuses on the properties of electrolysis corrosion and conductivity, but only few studies are about its mechanical characteristics. Since 1980, Aluminum

Company of America (Alcoa) has conducted[5], supported by US Department of Energy, a considerable work about cermets inert anodes. One of the major successes was to determine 17Cu-18NiO-NiFe₂O₄ cermet to be the promising material because of its high electric conductivity and good corrosion resistance during electrolysis. Thereafter, an intensive and extensive work was concentrated on the electric conductivity and corrosion behavior of this material. However, the work of the mechanical characteristics was almost neglected. Only a few investigations had studied the bending strength of 17Cu-18NiO-NiFe₂O₄[5]. The pilot scale experiments[2,5–6] exhibited that the inert anode samples chipped in the electrolysis process due to their poor mechanical properties, though the samples showed favorable corrosion resistance and conductivity. So the poor mechanical properties have become a main technical obstacle to development of cermet inert anodes. The previous work[7] showed that the cermets with 10NiO-NiFe₂O₄ as ceramic matrix appeared high relative density and favorable corrosion resistance. For metal composition, Cu is one of favorable choices because of

its combination of the advantages of perfect conductivity and corrosion resistance. However, during sintering process, its low melting point and poor wettability with NiFe_2O_4 affected the mechanical properties of materials because of its sweating out and inhomogeneous dispersion in cermets[8]. The previous research[9] indicated that Ni could improve the wettability between Cu and NiFe_2O_4 and promote the sintering process.

In this study, Cu-Ni/(10NiO-NiFe₂O₄) cermets, using Ni and Cu as metallic phase and 10NiO-NiFe₂O₄ as ceramic phase, were fabricated by cold pressing and sintering. The effects of content of metallic phase on the mechanical properties of (85Cu-15Ni)/(10NiO-NiFe₂O₄) cermet inert anode were investigated.

2 Experimental

(85Cu-15Ni)/(10NiO-NiFe₂O₄) cermet composites were fabricated with conventional cold pressing and sintering process with reagent grade raw materials of Ni, Cu, NiO and Fe₂O₃. A proper amount of NiO and Fe₂O₃ (the excess content of NiO, compared with that of the stoichiometric NiFe_2O_4 , in the ceramic phase is 10%, mass fraction) were mixed by ball milling and then calcined in a muffle furnace at 1 200 °C for 6 h at static air atmosphere to obtain 10NiO-NiFe₂O₄ ceramic powders. The X-ray diffraction pattern of the synthesized ceramic powder is illustrated in Fig.1. The calcined powders were mixed with metal powders (85Cu-15Ni) by ball milling again and then compressed to form cylindrical blocks (20 mm in diameter and 45 mm in thickness) at a pressure of 200 MPa. The electrodes were sintered at 1 250 °C for 4 h in nitrogen atmosphere of efficaciously controlled oxygen partial pressure[9–10]. The compositions and theoretical densities of samples are listed in Table 1. The mass fractions of metallic phases with Cu and Ni were 85% and 15% (mass fraction), respectively. With respect to CN0, CN5, CN10, CN15 and CN20, the mass fractions of metal phase were 0%, 5%, 10%, 15%, 20% (mass fraction), respectively.

Bulk density and apparent porosity of samples were tested according to the Archimedes' method. Phase

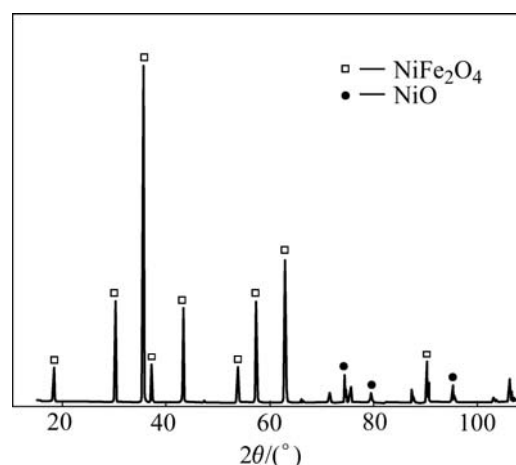


Fig.1 XRD patterns of 10NiO-NiFe₂O₄ ceramic

composition of the composite was identified by X-ray diffraction analysis using Philips PW1390 X-ray diffractometer with CuK_α radiation. Microstructure was analyzed with JSM-5600LV scanning electron microscope and XJP-6A metallurgical microscope. Three-point-bending strength of the sintered specimens (3 mm × 4 mm × 36 mm) was evaluated with a CSS-44100 electrical universal testing machine using span of 30 mm and cross-head speed of 0.5 mm/min. Bending strength data were achieved by average value with testing for six bars. Fracture toughness and hardness were measured with indentation strength(IS) method based on the equation given by GUAN et al[11] using a AKASHI(AVK-A) Vickers' hardness tester at 98 N with a load time of 10 s.

3 Results and discussion

3.1 Phase composition of cermet samples

The X-ray diffraction patterns of the prepared cermets samples are shown in Fig.2. The major peaks detected include those of (Cu, Ni), NiO and NiFe_2O_4 . Compared with the diffraction peak of Cu[12], the peak position of Cu corresponds to that of (Cu-Ni), and the difference is just a decrease of crystal face spacing of (Cu-Ni) due to solid solution from Ni to Cu.

Table 1 Compounds and theoretical densities of samples

Sample	Composition(mass fraction)/%				Theoretical density/ (g·cm ⁻³)
	Cu	Ni	NiO	NiFe ₂ O ₄	
CN0	0	5.515	10.0	90.0	5.515
CN5	4.25	5.685	9.5	85.5	5.685
CN10	8.50	5.855	9.0	81.0	5.855
CN15	12.75	6.025	8.5	76.5	6.025
CN20	17.00	6.196	8.0	72.0	6.196

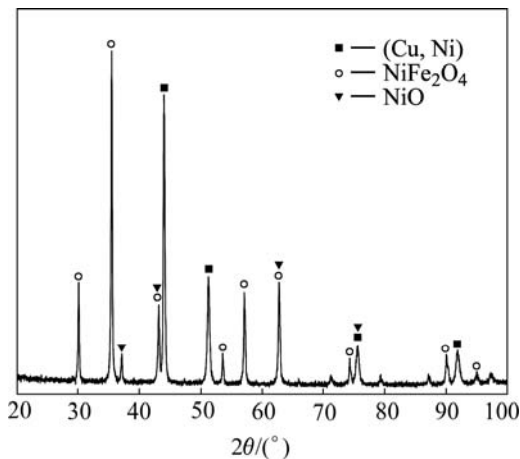


Fig.2 XRD patterns of (85Cu-15Ni)/10NiO-NiFe₂O₄ cermets

3.2 Effect of metallic phase content on bending strength

The mechanical property is of great importance to desirable inert anode material. Generally speaking, proper metal will improve the mechanical property of cermet. Given low metallic content, it is hard for cermet to exhibit the advantage of metallic strengthening. 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. The bending strength and porosity of composites are displayed in Fig.3. As the content of Cu-Ni increases from 0 to 5%, the bending strength increases and the porosity decreases. However, as the metallic content ranges from 5% to 20%, the changing trends of bending strength and porosity are contrary to the former. The composite with 5% metallic content achieves a maximum value of bending strength of 176.4 MPa and a minimum value of porosity of 3.9%, respectively. Besides,

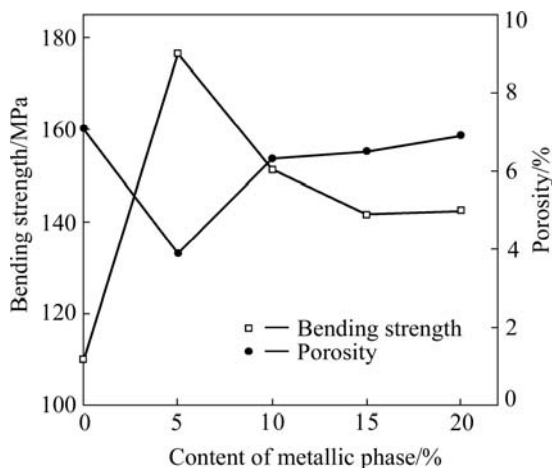


Fig.3 Relationship between room temperature bending strength, porosity and content of metal phase of (85Cu-15Ni)/10NiO-NiFe₂O₄ cermets

the changes of bending strength and porosity of cermets are not apparent when the metallic content ranges from 10% to 20%.

In general, the bending strength of cermets is related to several factors such as ceramic grain size[11], porosity [13], metallic phase dispersion, binding strength between ceramic phases and metallic phases[14]. Eqns.(1) and (2) illustrate that decreasing grain size and porosity can increase material strength:

$$\sigma = \sigma_0 + Kd^{-1/2} \quad (1)$$

$$\tau = \tau_0 \exp(-bp) \quad (2)$$

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

As showed in Fig.4, there is no obvious change on ceramic grain size (10–20 μm) for the composites (CN5–CN20) with various metallic contents. Though the composite CN0 has smaller grain size (5–10 μm) than others, the strength decreases reversely due to large porosity. Fig.3 shows that the porosity obviously increases when the metallic content is above 5%. In this study, the sintering temperature (1 250 $^{\circ}\text{C}$) is higher than the melt point of 85Cu-15Ni alloy (1 175 $^{\circ}\text{C}$), so these cermet composites are treated in liquid sintering process. From Fig.4, the wettability between metal phase (Cu-Ni) and ceramic phase (NiO-NiFe₂O₄) is not improved and particles are contacted with each other to form continuous framework, which are isolated by the liquid outside. Increasing sintering temperature or holding time can produce strong conglutination and capillarity of particles, which may cause the metal to be squeezed out from ceramic matrix. This trend will be enhanced with increase of metallic content. In this research, it can be found that the metal is overflowed on the surface of sample when metallic content is over 10%. The effect of metallic toughing weakened is related with the decrease of metallic content and the strength declined is related to the increase of porosity and the decrease of densification. These results are coincident with conclusions from Fig.4. In addition, Eqn.(3) suggests that high interfacial energy and small wetting angle are propitious to increased interfacial binding strength:

$$W = \sigma_{LV}(1 + \cos\theta) \quad (3)$$

where W is interfacial binding strength; σ_{LV} is interfacial energy; θ is wetting angle.

Generally, the homogeneous dispersion of metal phase can improve interfacial contact between ceramic and metal and promote function of metallic toughening. However, as seen from Fig.4, metallic particles most locate in the isolated pores with unexpected aggregation, thus the strength is not determined by metal but by

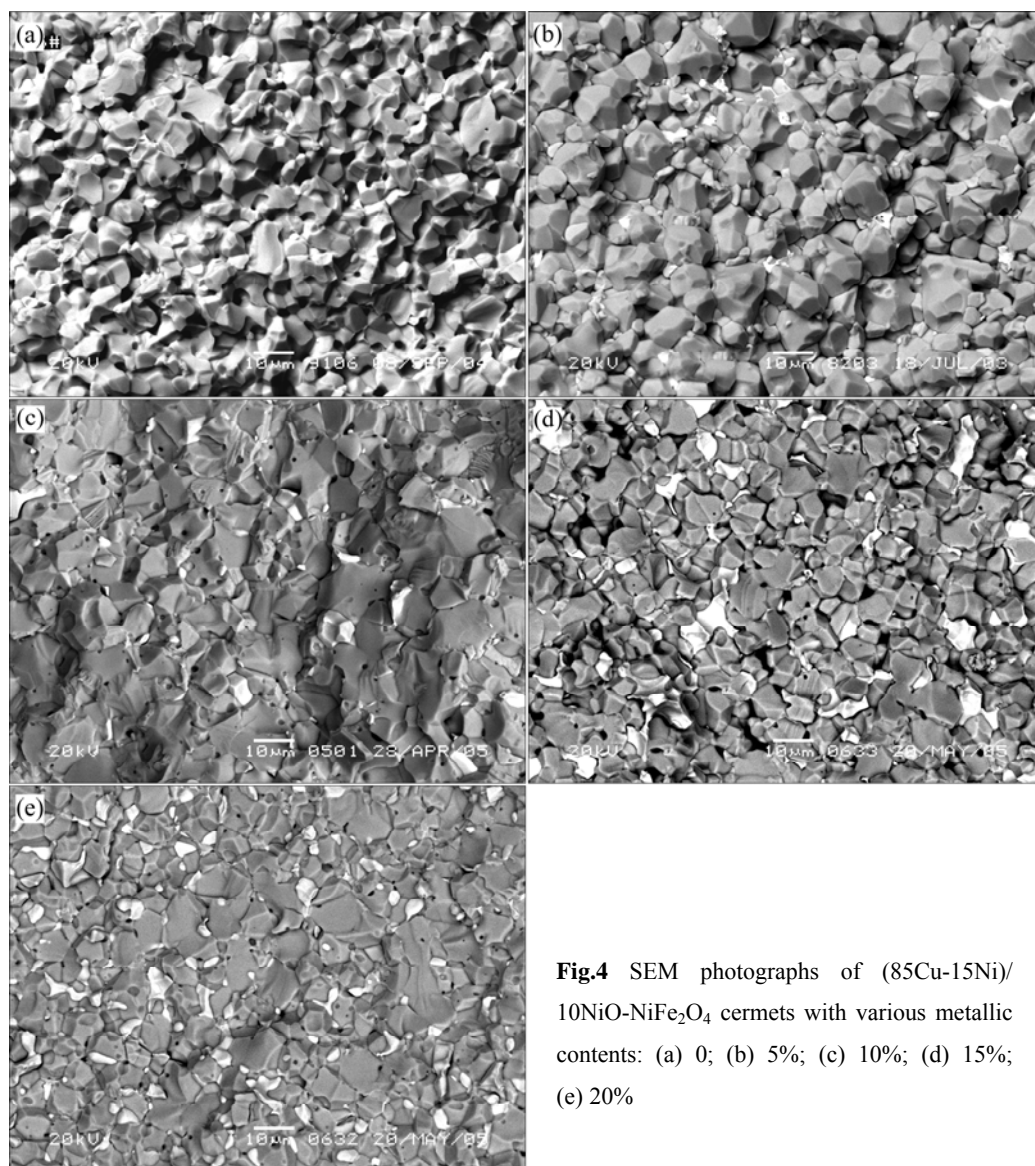


Fig.4 SEM photographs of (85Cu-15Ni)/10NiO-NiFe₂O₄ cermets with various metallic contents: (a) 0; (b) 5%; (c) 10%; (d) 15%; (e) 20%

ceramic. So increasing metallic content may result in an increase of metallic aggregation and decrease of metallic toughening.

3.3 Effect of metallic phase content on fracture toughness

From Fig.5, as metallic content increases, the hardness is decreased and the fracture toughness is increased. The hardness decreases from 4 972.3 MPa to 3 809.2 MPa and the fracture toughness increases from 1.22 MPa·m^{1/2} to 2.80 MPa·m^{1/2} with increasing metallic content from 0 to 20%.

The toughening of cermet mainly depends on metallic particle[15]. The crack always extends through the way with low energy. It is difficult 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. Hence, This increases the

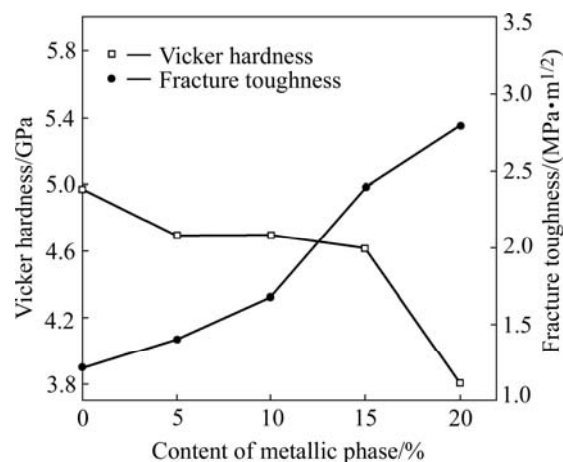


Fig.5 Vicker hardness and fracture toughness of (85Cu-15Ni)/10NiO-NiFe₂O₄ cermets with various metallic contents

extending distance and resistance of fracture growth and strengthens the function of the bridging toughening and

crack deflection toughening simultaneously.

3.4 Effect of metallic phase content on thermal shock resistance

The cermets exhibit various abilities of thermal shock resistance in process of thermal shock experiments. Fig.6 shows the residual strength of specimens quenched at different thermal shock temperature differences. The results suggest that the decline of residual strength is apparent for samples CN5–CN0 but unobvious for samples CN0 quenched at thermal shock temperature difference(Δt) below 200 °C. As Δt is above 200 °C, the residual strength sharply decreases for sample CN0, but falls slowly for samples CN5–CN20.

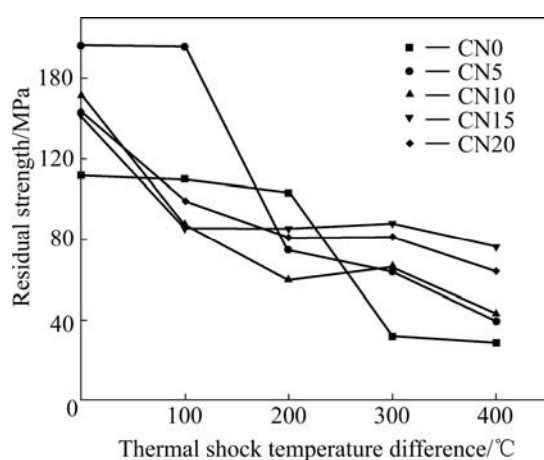


Fig.6 Plot of retained flexural strength vs temperature difference for (85Cu-15Ni)/10NiO-NiFe₂O₄ cermets

According to the theory of thermal shock resistance by HASSELMAN[16], on condition of thermal shock, the presence and spread of crack are related with elastic strain energy and fracture surface energy deposited in composite. Small elastic strain energy and high fracture surface energy can decrease the possibility of spread of crack and increase the ability of thermal shock resistance of composite. In current work, when Δt is between 0 and 200 °C, the ceramic (CN0) shows the promising thermal shock resistance property compared with that of cermets (CN5–CN20), which is related with much pore and other defects in the ceramic (CN0). These defects are not propitious to increasing strength, but improving the capability to resist the spread of catastrophic crack. In the other word, the existence of these defects provides a certain space to relax the stress and cause a decrease of the elastic strain energy and an increase of fracture surface energy. Besides, fine grain particle also benefits to improving the thermal shock resistance of composite. It is generally thought that metallic addition will improve the thermal shock resistance of cermets. But at high temperature, a sharp decline of strength is attributed to the oxidation of metallic phase. Furthermore, the aggregation of metal also weakens the effect of metallic

toughening. When the thermal shock temperature change is between 200 °C and 400 °C, the cermet composites CN5–CN20 show better thermal shock properties than ceramic composite CN0. Although the full densification of cermets composites are not achieved, the relative densities are all exceeded 92%, so metal on the surface of composite is oxidized and compact film is formed to postpone or prevent the further oxidation during heating process[17]. Consequently, the effect of metallic toughening can be exhibited with the increase of thermal shock temperature difference and the crack is either passivated or deflected by the metal inclusions.

4 Conclusions

1) As metallic content is increased from 0 to 20%, there is a sharp change in bending strength and porosity of (85Cu-15Ni)/(10NiO-NiFe₂O₄) composites. A maximum strength of 176.4 MPa and a minimum porosity of 3.9% are presented when the metallic phase content is 5%. Increasing the metallic content from 5% to 20%, the strength decreases and the porosity increases, but the change is not obvious when the metallic content is over 10%.

2) The hardness decreases and the fracture toughness increases with an increase of metallic content. The fracture toughness increases from 1.22 MPa·m^{1/2} to 2.80 MPa·m^{1/2} and hardness decreases from 4 972.3 MPa to 3 809.2 MPa with the metallic content increasing from 0 to 20%.

3) As the thermal shock temperature difference (Δt) is below 200 °C, a change of strength of 10NiO-NiFe₂O₄ ceramic is not apparent, but (85Cu-15Ni)/10NiO-NiFe₂O₄ cermet shows obvious change with a decrease ratio of about 40%. As Δt is above 200 °C, the strength of ceramic distinctly falls and decrease ratio of strength is more than 70%. While the residual strengths of cermets remain at the same level and decrease ratios of residual strengths fall with increasing metallic content.

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