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EFFECT OF NANOPOWDER CONTENT ON PROPERTIES OF $NiFe_2O_4$ MATRIX INERT ANODE FOR ALUMINUM ELECTROLYSIS

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Abstract

Two-step sintering process was adopted to prepare $NiFe_2O_4$ matrix inert anode for aluminum electrolysis in this research. In the process of synthesizing $NiFe_2O_4$ spinel, Fe_2O_3 and NiO powders as raw materials added additives were synthesized at 1000 ℃ for 6h. Through crushing and screening, adding $NiFe_2O_4$ nanopowder, particle gradation and compression molding, the nickel ferrite matrix ceramic inert anode was sintered secondarily at 1300 ℃ for 6h. The effect of $NiFe_2O_4$ nanopowder content on the density and porosity, bending strength and impact toughness was investigated in details. The results showed the addition of $NiFe_2O_4$ nanopowder had considerable influence on the properties of $NiFe_2O_4$ matrix ceramic inert anode. Inert anodes had the best comprehensive properties while adding 30 wt% nanopowder. The values of density and porosity were 4.86 g/cm^3 and 3.5% respectively, the value of bending strength was 42.47 MPa and the value of impact toughness was 3.31 J/cm^2.

Introduction

Since Hall-Héroult process for the industrial production of aluminum was invented in 1886, despite obtaining much progress, there were still many shortcomings such as great energy consumption, serious environmental pollution and unstable production as well. Comparing with the consumable carbon anode used in aluminum production now, the use of inert anode can bring economic and environmental enormous benefits due to the elimination of harmful emissions into atmosphere and carbon factory, decreasing the intensity of labor for anode changing consumedly, and being of acceptable cost [1-2].

However, the inert anode must be: physically stable at service temperature, resistant to attack by molten fluoride electrolyte, resistant to attack by pure oxygen, electrochemically stable, electronically conductive, resistant to thermal shock and economically feasible [3]. A lot of research work has been carried out, which can be divided into three classes, namely, metal alloys, ceramic oxides, and cermets, but no material has been found to satisfy all these requirements[3]. Alloy anode is good at ductility and conductivity, but bad at the thermal stability and corrosion resistance [4], while ceramic anode is bad at brittleness and conductivity, but good at the refractoriness and corrosion resistance. Nickel ferrite is one of the most common compounds in a family of spinel with cubic structure. This compound offers a good combination of physical and chemical properties such as high melting-point, good resistance to chemical attack, high thermal stability, and consequently it is the preferred material as ceramics inert anode [5].

Considering the high brittleness of $NiFe_2O_4$-matrix ceramic inert anode, it has not been used in electrolytic production of aluminum for it doesn't meet the requirements of aluminum electrolysis process. So, toughening the ceramic becomes a strategic point. There are many ways to toughen ceramic materials such as particle reinforcing, fiber reinforcing and so on. Nickel ferrite spinel nanopowder was added to improve the mechanical properties of inert anode in this research.

In this paper, $NiFe_2O_4$-matrix inert anodes were prepared by cold-pressing and sintering progress adding nickel ferrite spinel nanopowder. The effect of addition level of nanopowder on the density and porosity, bending strength and impact toughness were investigated emphatically.

Experimental

Materials

All of the chemical reagents were of analytical grade and were used without further purification. Manipulations and reactions were carried out in air without the protection of nitrogen or inert gas. Nickel ferrite spinel nanopowder was synthesized via solid-state reactions at low temperature based on my own previous work [6]. The precursor, prepared by rubbing $FeSO_4•7H_2O$, $NiSO_4•6H_2O$, NaOH and dispersant sufficiently at room temperature, was calcined at 800 ℃ for 1.5h. The average particle size of the nanopowder used in this experiment is about 75nm, as shown in Figure 1.

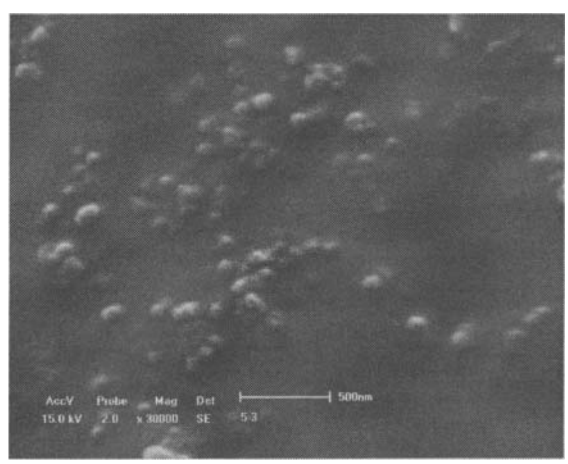


Figure 1. SEM image of $NiFe_2O_4$ spinel nanopowder.

Preparation Progress

In this study, two-step sintering process was utilized to prepare $NiFe_2O_4$-matrix inert anode. In the first step, a proper amount of

Fe_2O_3 and NiO powders as raw materials and MnO_2 and V_2O_5 powders as additives were mixed in planetary muller (KQM-X4, China) for twenty-four hours using distilled water as dispersant. Following by drying, the dried mixtures with 4 % PVA binder were molded by cold pressing under 60 MPa pressure and calcined in a muffle furnace at 1000 ℃ for 6h in a static air atmosphere to form the $NiFe_2O_4$ spinel matrix material. Through crushing and screening, the matrix materials were separated to different size of particles, namely, 0.50 mm - 0.35 mm, 0.105 mm - 0.074 mm, and <0.074 mm. Particle gradation design is showed in Table I, according to the theory of the most compact.

The mixtures, with different contents of nanopowder, were put into glass beaker, using anhydrous alcohol as dispersant, and mixed enough under vigorous mechanical rabbling and ultrasonication at room temperature. Adding with 4 % PVA binder, the dried mixtures were made into 60mm×12mm×10mm compacts by cold pressing under 200 MPa and sintered subsequently at 1300 ℃ in the air atmosphere for 6 h to produce $NiFe_2O_4$-matrix ceramics. The flow chart of preparation process is shown in Figure 2.

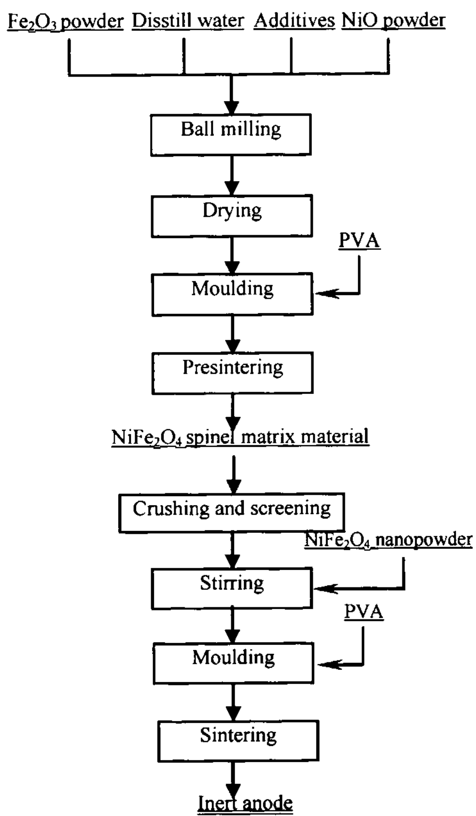


Figure 2. Flowing chart of preparing $NiFe_2O_4$-matrix inert anode.

Characterization

The bulk density and porosity of the sintered bulks were determined using Archimedes' method with deionized water as the immersion medium. Mechanical properties such as bending strength and impact toughness were measured by using INSTRON4206-006 electron mechanical experimental machine (USA). The fracture morphologies of samples were obtained on SSX-550 scanning electron microscopy (SEM).

Table I. Design of Particle Gradation

Main particle (500~355μm)	Filling particle (105~74μm)	Filling particle (<74μm)	Nanopowder (<100nm)
42%	18%	40%	0
		30%	10%
		20%	20%
		10%	30%
		0	40%

Results and Discussion

Effect of Nanopowder Content on Bulk Density and Porosity

Generally speaking, the undesirable pores in the materials play a key role in properties. The more the cores are, the worse the properties are. The pores can decrease electric conductivity, mechanical properties and corrosion resistance and so on. With the poor electric conductivity, it will result in great anode ohmic voltage drop, high cell voltage and energy consumption. The low corrosion resistance would decrease the used life of inert anode and the quality of as-product aluminum.

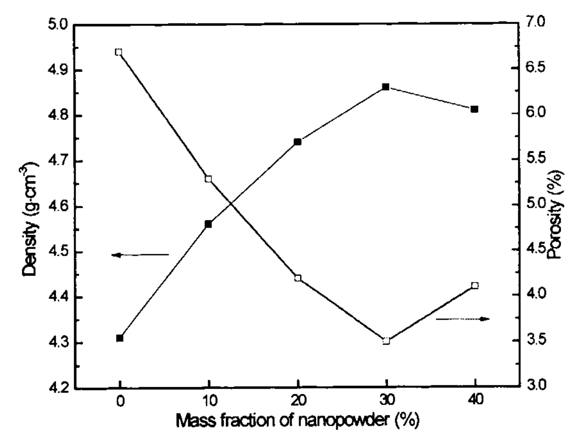


Figure 3. Effect of nanopowder on the density and porosity.

The variations in density and porosity with the content of nanopowder are sketched in Figure 3. Seen from Figure 3, it can be found that in the range of 0-30 % nanopowder, the higher the nanopowder content, the higher the density and the lower porosity. However, as the content of nanopowder ranges from 30 % to 40 %, the changing trends of density and porosity are contrary to the former. The composite with 30 % nanopowder content achieves a maximum value of density of 4.86 g/cm^3 and a minimum value of porosity of 3.5 %.

In the particle gradation, with the increase of nanopowder content, large particles reduced result in fewer pores which were filled by nanopowder fully. So the bulks were more compact after cold-pressing. What's more, more nanopowder in a proper range provided greater sintering force due to higher Gibbs free energy for large specific surface area. That promoted the gains to develop completely and made the bulk more compact as the nanopowder content increasing. Whereas, greater volume shrinkage made the materials cracked easily while the content of nanopowder was over 30 %.

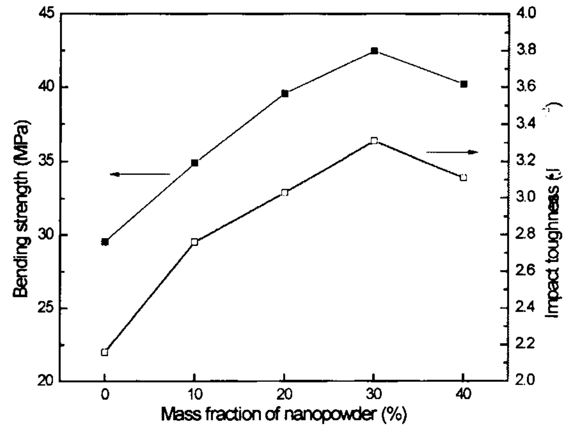
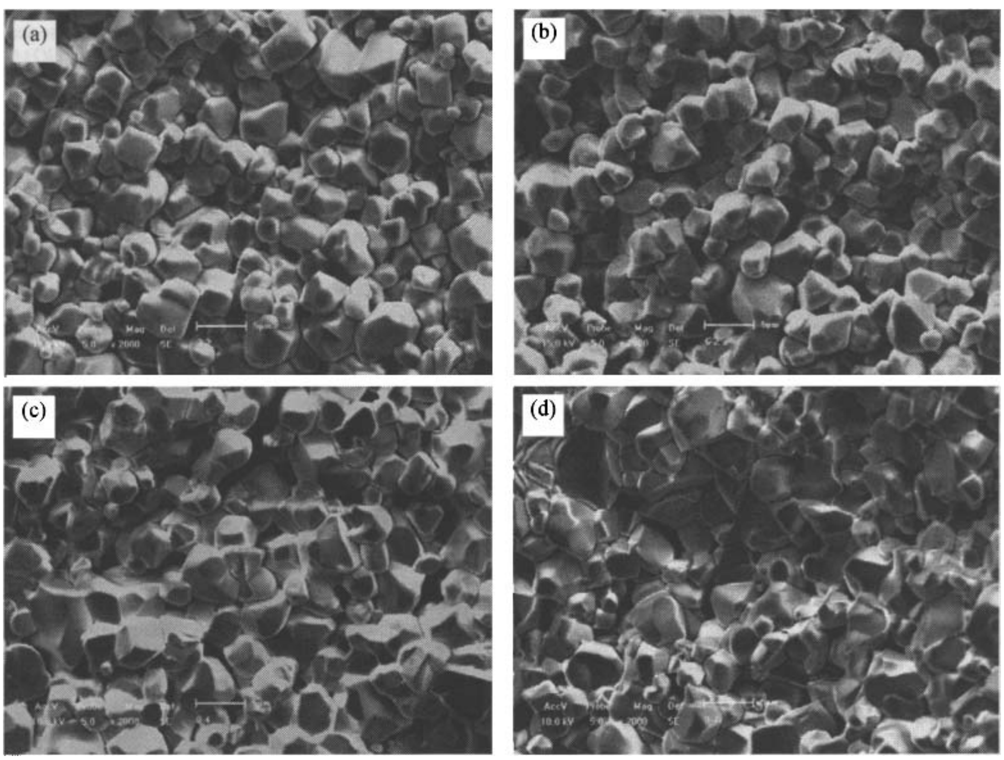


Figure 4. Effect of nanopowder on bending strength and impact toughness.

Effect of Nanopowder Content on Mechanical Properties

The changes of bending strength and impact toughness with nanopowder content are plotted in Figure 4. It is obvious that the changing trend of bending strength and impact toughness is consistent with the density's and contrary to the porosity's, indicating that the pores are undesired in materials. As the same as the density, when the nanopowder content is 30 %, the materials have attained to the maximum values of bending strength and impact toughness of 42.47 MPa and 3.31 J/cm^2, respectively.



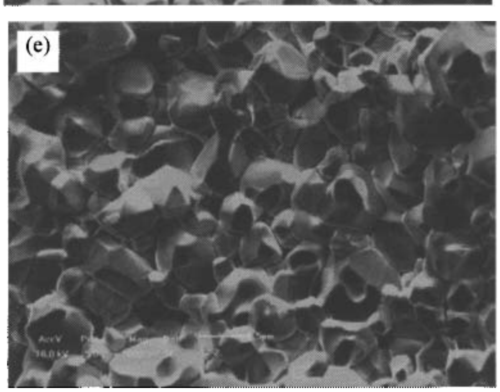


Figure 5. SEM photographs of $NiFe_2O_4$-matrix inert anodes with various contents of nanopowder: (a)-0%, (b)-10 %, (c)-20 %, (d)-30 %, and (e)- 40 % (mass fraction).

In general, the bending strength of ceramic is related to several factors such as ceramic grain size [7] and porosity [8]. W. Duchworth [9] presented the relation between ceramic fracture strength and porosity as shown in formula (1):

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

where P is porosity; σ is strength for sample with porosity of P; σ_0 is strength for sample without pores; and b is a constant. From formula (1), the significant inverse relation is found between porosity and bending strength.

Figure 5 depicts the fracture surfaces of specimens prepared with different nanopowder content, determined by SEM. The very prominent feature in SEM figures is the intergranular fracture which is the common element of all the specimens.

As the nanopowder content increases, more nanopowder is filled in the interspaces between larger granules. So the compacts denser after cold-pressing, which is favorable to densification in the sintering process. Additionally, the high surface area of nanopowder supplies a substantial sintering driving force. Therefore, in the same sintering temperature and dwell time, the samples with higher nanopowder content are sintered more adequately, where the binding force between grains are stronger. In Figure 5(a), most grains seems to be independent each other, implying weak bond. With the nanopowder content increases, the grains draw close and interspaces eliminate, showing strong bond. As well-known, the crack always extends through the way with low energy. It is difficult for crack to extend through the complete grain but easy to extend across the interface between grains due to the relatively low fracture energy. In certain extent of research, the smaller the grain size is, the more the grain boundary is. Additionally, more energy is consumed in the fracture process resulting from the strong bond. Hence, with the nanopowder content increases, the crack needs more energy to extend across the grain boundary and it increases the resistance of fracture growth. When the content of nanopowder is over 30 %, some deficiencies are produced from sintering progress (as shown in Figure 5(e)), which make the impact toughness decreased slightly.

Conclusions

1) As the content of nanopowder is increased from 0 to 30 %, there is a sharp change in density and porosity of $NiFe_2O_4$-matrix inert anode. A maximum density of 4.86 g/cm^3 and a minimum value of porosity of 3.5 % are presented when the content of nanopowder is 30 %. The density decreases and the porosity increases when the content of nanopowder is over 30%.

2) The changing trend of bending strength and impact toughness is consistent with the density's and contrary to the porosity's. The bending strength increases from 29.54 MPa to 42.47 MPa and impact toughness increases from 2.16 $J\bullet cm^{-2}$ to 3.31 $J\bullet cm^{-2}$ with the content of nanopowder increasing from 0 to 30%. Both values of them decrease slightly when the content of nanopowder is over 30 %.

Acknowledgements

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