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PREPARATION $NiFe_2O_4$ MATRIX INERT ANODE USED IN ALUMINUM ELECTROLYSIS BY ADDING NANOPOWDER

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Abstract

Two-step sintering process was adopted to prepare $NiFe_2O_4$ matrix inert anode 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□. 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 1250□ for 6h. The effect of addition level of nanopowder on the density and porosity, bending strength and impact toughness was investigated emphatically. The results showed the addition of $NiFe_2O_4$ nanopowder had significantly increased the bending strength and impact toughness of $NiFe_2O_4$ matrix ceramic inert anode. Inert anodes had the best comprehensive properties while adding 60wt% nanopowder. The values of density and porosity were 4.62g/cm^3 and 5.2% respectively, the value of bending strength was 53.39MPa and the value of impact toughness was 3.19J/cm^2.

Introduction

In recent years, numerous works have been actively focused on the development of inert (non-consumable) anodes for replacement of consumable carbon anodes in Hall-Héroult electrolysis cells for the production of aluminum. Comparing with the consumable carbon anode used in aluminum production, the use of inert anode can bring economic and environmental enormous benefits due to the elimination of harmful emissions into atmosphere (such as carbon dioxide, sulfur compounds, fluorine, etc.) and carbon factory, decreasing the intensity of labour for anode changing consumedly, and being of acceptable cost [1, 2].

After many years' researches, there are mainly three types of inert anode for aluminum electrolysis, that is, a metal or alloy anode, a metal oxide ceramic anode, and a cermet anode [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. Among them, nickel ferrite-matrix inert anode has become the key study object for its high strength, good stability at elevated temperature, good corrosion resistance and so on [5]. Considering the high brittleness and poor thermal shock resistance 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. 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 was investigated emphatically.

Experimental Section

Materials

All of the chemical reagents were of analytical grade and were used without further purification. Double distilled, deionized water was used as a solvent. 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 $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, NaOH and dispersant sufficiently at room temperature was calcined at 800°C for 1.5h. The average particle size of the nanopowder used in this experiment is about 75nm.

Preparation Progress

Two-step sintering process was utilized to prepare $NiFe_2O_4$-matrix inert anode in this research. In the first step, a proper amount of Fe_2O_3 and NiO powders as raw materials and additives of MnO_2 and V_2O_5 were mixed in planetary muller (KQM-X4, China) for twenty-four hours using distilled water as dispersant. Following by drying, the dried mixture with 4% PVA binder was molded by cold pressing under 60MPa pressure and calcined at 1000°C in air for six hours to form the $NiFe_2O_4$ spinel matrix material. Through crushing and screening, the matrix material was separated to different size of particles, that is, 0.50mm~0.35mm, 0.21mm~0.15mm, and 0.11mm~0.08mm. Particle gradation design according to the theory of the most compact is showed in Table I. The mixtures adding different levels of nanopowder were put into glass beaker, with anhydrous alcohol as dispersant, were mixed enough under vigorous stirring and ultrasonication at room temperature. Adding with 4% PVA binder, the dried mixtures were made into 60mm×12mm×10mm blocks by cold pressing with 160MPa and sintered subsequently at 1250°C in the air atmosphere for six hours to produce $NiFe_2O_4$-matrix ceramics. The flow chart of preparation process is shown in Fig.1.

Table I Design table of particle gradation (mass fraction)

Number	Main particle 0.50mm~0.35 mm	Filling particle 0.21mm~0.15 mm	Filling particle 0.11mm~0.08 mm	Nanopowder
1	52.5%	10.5%	7%	30%
2	45%	9%	6%	40%
3	37.5%	7.5%	5%	50%
4	30%	6%	4%	60%
5	22.5%	4.5%	3%	70%

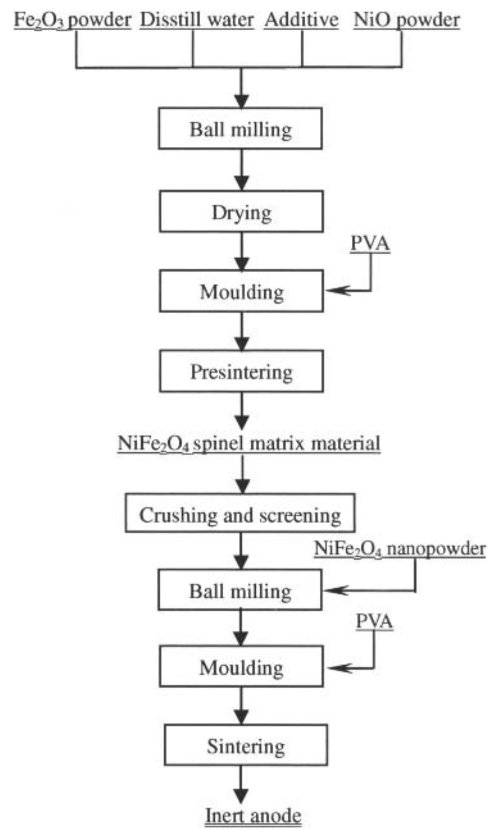

Fig.1 Flow chart of preparing $NiFe_2O_4$-matrix inert anode

Characterization

The bulk density and porosity of samples were tested by liquid displacement method in double distilled water medium using Archimedes' principle. Mechanical properties such as bending strength and impact toughness were measured by using INSTRON4206-006 electron mechanical experimental machine (USA). The fracture morphology of samples were obtained on SSX-550 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy.

Results and Discussion

Effect of nanopowder content on density and porosity

I think there is no error for this sentence using "Effect of".

The bulk density is of great importance to desirable inert anode material. Given low density, there exist lots of pores, which will lead to poor properties of the material such as poor electric conductivity, poor 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 as well as be detrimental to the corrosion resistance which decreases the used life of inert anode and the quality of as-product aluminum.

The changes of density and porosity with the content of nanopowder are shown in Fig.2. From Fig.2, it can be found that in the range of 30-60% nanopowder, the higher the nanopowder content, the higher the density and the lower porosity. However, as the content of nanopowder ranges from 60% to 70%, the changing trends of density and porosity are contrary to the former. The composite with 60% nanopowder content achieves a maximum value of density of 4.62 g/cm^3 and a minimum value of porosity of 5.2%. 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 over 60%.

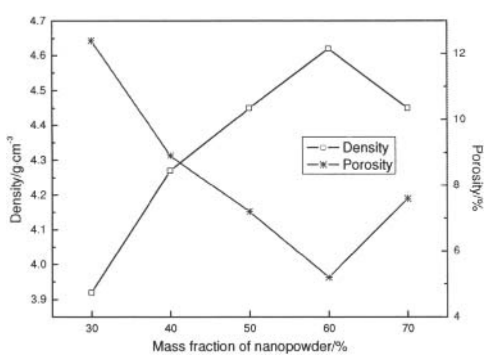

Fig.2 Effect of nanopowder on the density and porosity

Effect of nanopowder content on mechanical properties

The effect of nanopowder content on bending strength and impact toughness is showed in Fig.3, from which 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. As well as the density, the material with the content of 60% nanopowder has attained to the maximum values of bending strength and impact toughness of 53.39MPa and 3.19J/cm^2, respectively.

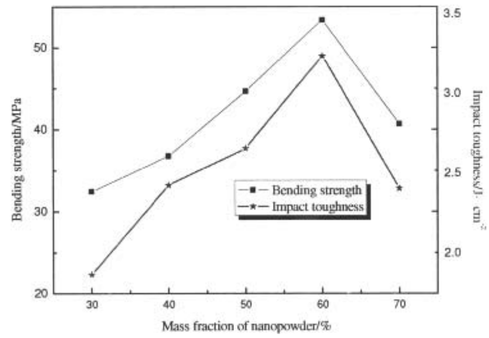

Fig. 3 Effect of nanopowder on bending strength and impact toughness

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):

$$\sigma = \sigma_0 \exp(-bP) \tag{1}$$

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, which is the lower the porosity is, the higher bending strength is.

Ceramic fracture strength versus grain size presented by Hall-Petch [10] is shown in formula (2):

$$\sigma_F = \sigma_0 + Kd^{-m} \tag{2}$$

where σ_F is intensity of ceramic; σ_0 is yield intensity; K and m are constants; and d is grain size.

The fracture micro-appearances of with various contents of nanopowder were characterized by SEM, as shown in Fig.4. From Fig.4, as the content of nanopowder increases, the grain size decreases. The average grain size decreases from 6μm to 1.5μm with the content of nanopowder increasing from 30 to 70%. The toughening of this material mainly depends on grain size. 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. Hence, with the decreasing of grain size, the crack needs more energy to extend across the increasing of grain boundary and it increases the resistance of fracture growth. When the content of nanopowder is over 60%, though the grain size is decreased, some deficiencies are produced from sintering progress, which make the impact toughness decreased slightly.

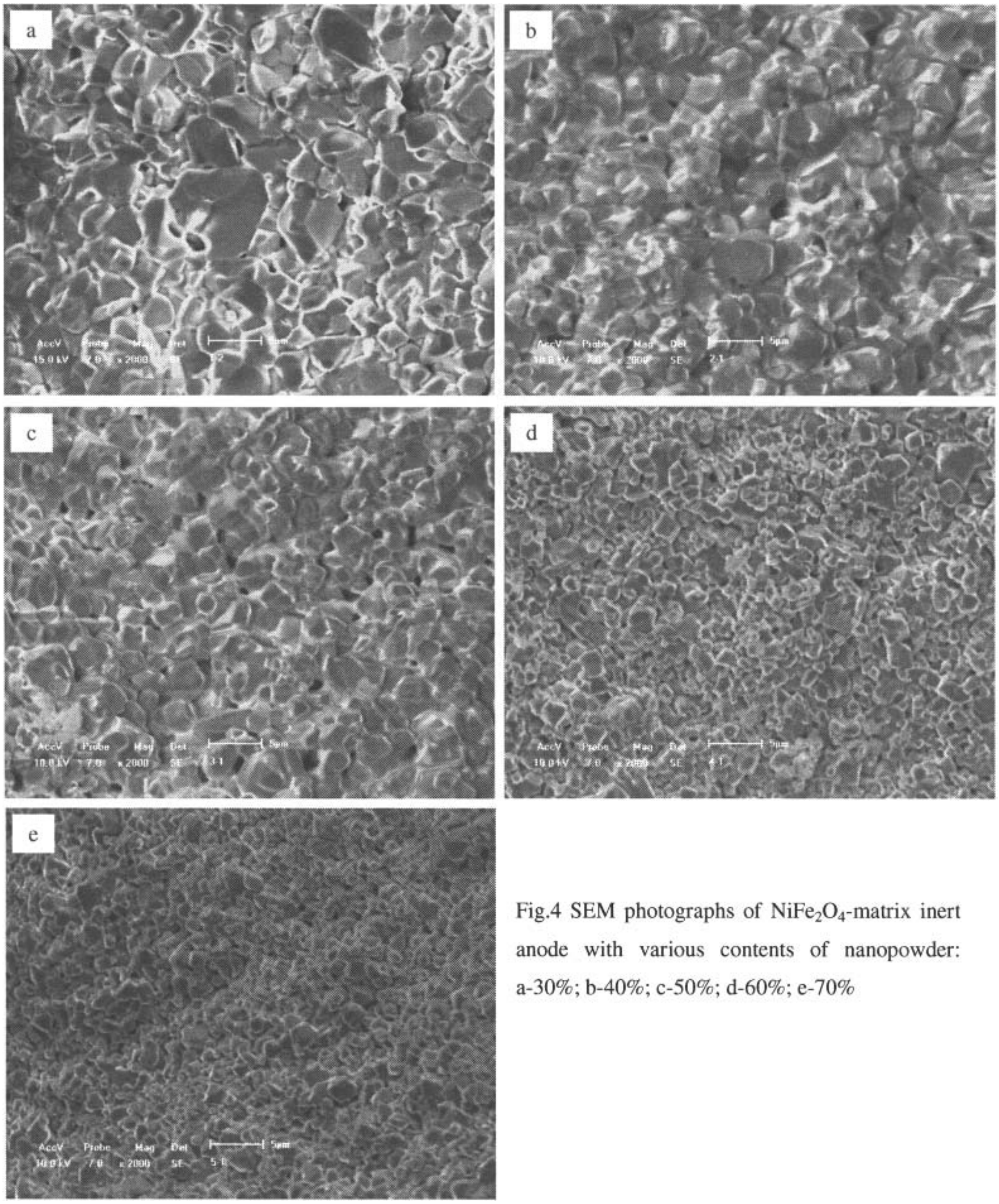

Fig.4 SEM photographs of $NiFe_2O_4$-matrix inert anode with various contents of nanopowder: a-30%; b-40%; c-50%; d-60%; e-70%

Conclusion

1) As the content of nanopowder is increased from 30 to 60%, there is a sharp change in density and porosity of $NiFe_2O_4$-matrix inert anode. A maximum density of 4.62 g/cm^3 and a minimum value of porosity of 5.2% are presented when the content of nanopowder is 60%. The density decreases and the porosity increases when the content of nanopowder is over 60%.

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 32.46MPa to 53.39MPa and impact toughness increases from 1.82 J·cm^{-2} to3.19 J·cm^{-2} with the content of nanopowder increasing from 30 to 60%. Both values of them decrease slightly when the content of nanopowder is over 60%.

Acknowledgements

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