

## EFFECTS OF THE ADDITIVE $ZrO_2$ ON PROPERTIES OF NICKEL FERRITE CERMET INERT ANODE

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### Abstract

The objective of this paper is to study a new attempt on preparing Cu-Ni-NiO-NiFe<sub>2</sub>O<sub>4</sub> ceramic inert anodes by adding ZrO<sub>2</sub> (0~1.50wt %), carrying out high temperature solid-state process. NiFe<sub>2</sub>O<sub>4</sub> spinel, the matrix material, was prepared firstly with extra 18wt% NiO and Fe<sub>2</sub>O<sub>3</sub> as the raw materials. The product was crushed to fines, and then mixed uniformly with Cu-Ni and ZrO<sub>2</sub> powders to prepare Cu-Ni-NiO-NiFe<sub>2</sub>O<sub>4</sub> ceramic inert anodes by cold-pressing sintering method. The impact of ZrO<sub>2</sub> addition on the relative density, the bend strength and the corrosion resistance of Cu-Ni-NiO-NiFe<sub>2</sub>O<sub>4</sub> ceramic inert anodes was investigated. The results show that, with the addition of 0.5wt% ZrO<sub>2</sub>, the relative density slightly increases and the corrosion resistance decreases a little while the bending strength improves remarkably from 55.50MPa of the sample without ZrO<sub>2</sub> additive to 105.26Mpa.

### Introduction

In conventional aluminum electrolysis, using carbon anodes has many disadvantages such as the consumption of carbon anode and the emission of carbon dioxide and fluorocarbon. So the appearance of inert anodes draws people's attention [1].

The electrolyzing inert anodes will release oxygen [2, 3], being friendly to environment, which makes the use of inert anodes commercially attractive. Numerous researches have been done on finding the appropriate material for inert anodes in aluminum production. Nowadays inert anodes can't still meet some basic requirements [4]. For example, inert anodes exhibit a high corrosion rate in the high-temperature cryolite melts, low conductivity and environment of high oxidizability. The purity

of the produced metal Al can not be guaranteed and more importantly, the use of inert anodes is not economically feasible. More recently, Aluminum Company of America (Alcoa) conducted, with support by US Department of Energy, having arrived at a new cermet material consisting of 17Cu-42.91NiO-40.09Fe<sub>2</sub>O<sub>3</sub> to provide acceptable electrical conductivity combined with good corrosion resistance [5]. Steven C. Marschman applied for a U.S. Patent 4,871,437 in 1989, having arrived at a new cermet material consisting of a nickel ferrite-nickel oxide ceramic containing copper and nickel as metals phase to provide a stable electrode to have significantly improved electrical conductivity [6]. A U.S. Patent 5,794,112 applied by Siba P. Ray in 1998, describes the sintering atmosphere preparation of cermet. The gaseous atmosphere has an oxygen content that is controlled at about 5-3000 ppm, preferably about 5-700 ppm and more preferably about 10-350 ppm in order to obtain a desired composition in the resulting composite [7]. The former studies mainly focused on the conductivity and corrosion resistance of cermet but little on the additive and mechanical properties. In this article, we use ZrO<sub>2</sub> as additive to improve the bending strength of inert anodes and to study various properties of inert anodes by the experiment.

### Experimental

#### Preparation of the matrix material

The matrix material NiFe<sub>2</sub>O<sub>4</sub> spinel was prepared using NiO with excessive content of 18wt% and Fe<sub>2</sub>O<sub>3</sub> as the raw materials. The two oxides were firstly cold compacted to produce billets to the pressure of 60MPa. Secondly the billets were sintered with the temperature of 1000°C for 6 h.

Preparation of Cu-Ni-NiO-NiFe<sub>2</sub>O<sub>4</sub> ceramics

NiFe<sub>2</sub>O<sub>4</sub> spinel was grinded to fines particles. Subsequently the granular spinel was uniformly mixed with Cu-Ni (17wt.%) and the additive of ZrO<sub>2</sub> with different contents. The contents of ZrO<sub>2</sub> were 0.0 wt.%, 0.5 wt.%, 1.0 wt.% and 1.5wt.% respectively. Finally the mixed powders were cold compacted using uni-axial compaction to the pressure of 200MPa. The Cu-Ni-NiO-NiFe<sub>2</sub>O<sub>4</sub> ceramic inert anodes were made through the sintering process at the temperature of 1200°C for 6 h. The final products were rectangular billets (60 mm×12 mm×8 mm).

Performance tests

The density was measured by Archimedes' principle. The crystal structure of samples doped with ZrO<sub>2</sub> were identified by powder X-ray diffraction (XRD, PW3040/60, Holland) with CuKα radiation, 2θ in the range of 10°~90° with a step of 0.04°. The fractured surfaces were examined by scanning electron microscopy (SEM, SSX-550, Japan). The samples were immersed in molten cryolite with the temperature of 960□ for 10 h to determine the static state corrosion rate. The electrolyte was made up of reagent grade CaF<sub>2</sub> and AlF<sub>3</sub>, technical grade NaF and Al<sub>2</sub>O<sub>3</sub>. The CR (molar ratio of NaF to AlF<sub>3</sub>) was kept to be 2.8, and the concentrations of CaF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were both kept to be 5wt.%. The eroded samples were washed in 30wt% AlCl<sub>3</sub> solution at 100 □ to remove the adhering melt. The corrosion rate was determined by mass loss measurement [8].

**Results and analysis**

Effect of ZrO<sub>2</sub> content on ceramics relative density

Table.I Effect of ZrO<sub>2</sub> on relative density and porosity of samples.

the content of ZrO <sub>2</sub> /%	relative density/%	porosity /%
0.0	99.37	0.63
0.5	99.63	0.37
1.0	99.50	0.50
1.5	99.56	0.44

The changes of relative density and porosity with the content of ZrO<sub>2</sub> are shown in Table.I. It can be seen from Table.I that the relative density decreases to some extent while the porosity gradually goes up in the range of 0.5–1.5wt.% ZrO<sub>2</sub>. The rules of the changes were not obvious, however, it can be determined that the additive of ZrO<sub>2</sub> is favorable for increase of anodes' relative density and decline of their porosity.

Effect of ZrO<sub>2</sub> content on ceramics bending strength

The effect of ZrO<sub>2</sub> content on bending strength is shown in Fig.1. It is obvious that bending strength is dramatically enhanced by adding ZrO<sub>2</sub>. Bending strength of samples without ZrO<sub>2</sub> is 55.5MPa while the bending strength of sample with 0.5wt.% ZrO<sub>2</sub> is 105.26MPa which is 1.897 times as much as that of sample without ZrO<sub>2</sub>. And it is the highest bending strength of all the samples.

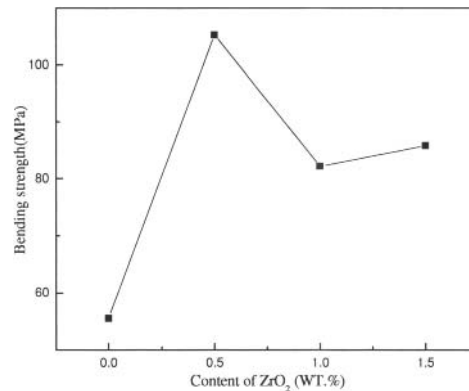


Fig.1 Effect of ZrO<sub>2</sub> on bending strength of samples.

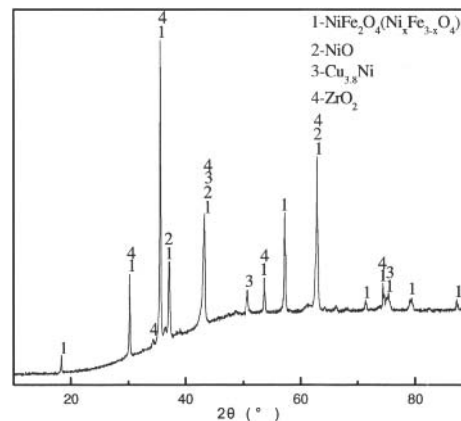


Fig.2 XRD pattern of the sample with ZrO<sub>2</sub>.

Fig.2 shows the XRD pattern of the sample with ZrO<sub>2</sub>.

It is clear from Fig.2 that ZrO<sub>2</sub> does not enter into the matrix material, and the crystal transformation is taken by itself.

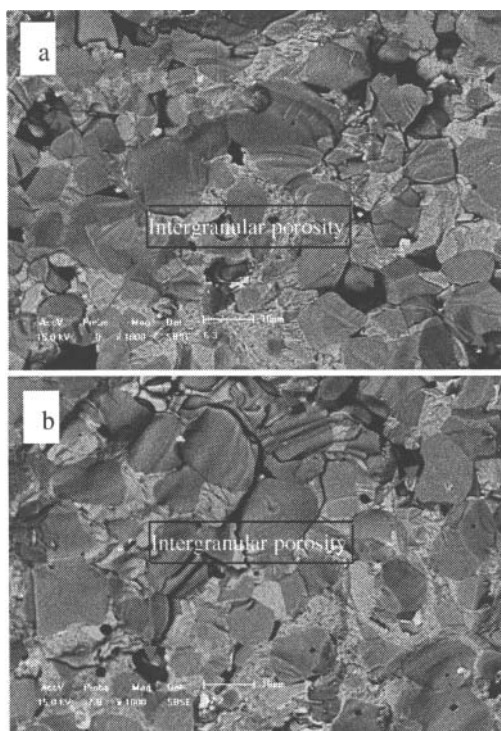


Fig.3 SEM photographs of the sample containing ZrO<sub>2</sub> with (a) 0.0wt.% and (b) 0.5wt.%.

The microstructures of samples without and with 0.5wt.% ZrO<sub>2</sub> are shown in Fig.3 (a) and (b) respectively. The grain sizes with different samples are analogous to each other. However, the intergranular porosity of the sample without ZrO<sub>2</sub> is much greater than that of the sample with 0.5wt.% ZrO<sub>2</sub>, as marked by the arrows in Fig.3. The ZrO<sub>2</sub> particles are mainly distributed at intercrystalline.

As is well known, the melting point of ZrO<sub>2</sub> is 2715 °C and ZrO<sub>2</sub> has three different crystal types including cubic crystal system, tetragonal crystal system and monoclinic crystal system. Monoclinic crystal system of ZrO<sub>2</sub> at ambient pressure is converted into tetragonal crystal system at 1170°C and tetragonal crystal system to cubic crystal system at 2370°C.

ZrO<sub>2</sub> crystal converts to and fro between monoclinic crystal system and tetragonal crystal system as the sintering temperature is 1200°C, which is lower than that of tetragonal

crystal system.

The furnace temperature gradually goes down after the completion of the sintering progress. Volume expansion of ZrO<sub>2</sub> is made impossible due to the compacted matrix material. Therefore, a part of ZrO<sub>2</sub> can be preserved in the matrix material as tetragonal crystal system. It can be concluded that part of ZrO<sub>2</sub> at room temperature still belongs to tetragonal crystal system.

The bending strength is improved mainly due to ZrO<sub>2</sub> having tetragonal crystal system. The crack begins to appear as the sample containing tetragonal crystal ZrO<sub>2</sub> is stressed. It can be sure that conversion of ZrO<sub>2</sub> from tetragonal crystal system to monoclinic crystal system is inevitable due to appearance of the crack. The phase transformation of ZrO<sub>2</sub> results in the expansion of ZrO<sub>2</sub> and the extension of crack is effectively prevented. A greater force is employed to destroy the sample. Nevertheless, the content of ZrO<sub>2</sub> of the sample is finite. The sample would be destroyed due to excessive volume expansion of ZrO<sub>2</sub> particle if the content of ZrO<sub>2</sub> exceeds the upper limit. The optimum content of ZrO<sub>2</sub> is 0.5wt.%.

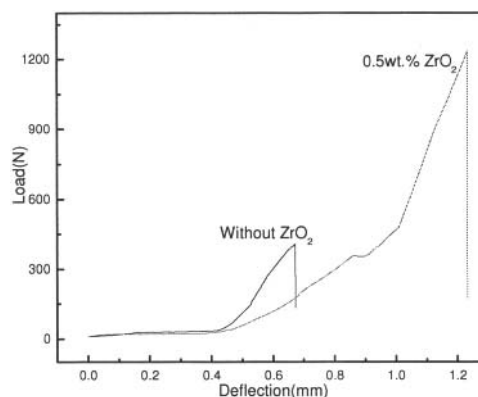


Fig.4 Three-point bending curves of samples.

The three-point bending curves of samples without ZrO<sub>2</sub> and with 0.5wt.% ZrO<sub>2</sub> are shown in Fig.4. Under the force, the sample without ZrO<sub>2</sub> begin to crack under the force while a platform on the three-point bending curve of the sample with 0.5wt.% ZrO<sub>2</sub> is visible. Volume expansion of ZrO<sub>2</sub> particle starts to be taken due to the transformation from tetragonal crystal system to monoclinic crystal system. The sample with 0.5wt.% ZrO<sub>2</sub> can undertake a much greater force.

#### Effect of ZrO<sub>2</sub> content on corrosion resistance

The samples with different content of  $ZrO_2$  eroded by molten salt are shown in Fig.5. And the effect of  $ZrO_2$  content on corrosion rate is shown in Fig.6. It is obvious that the corrosion resistance can be degraded by adding  $ZrO_2$ . The corrosion rate of the sample without  $ZrO_2$  is  $0.015g\cdot cm^{-2}\cdot h^{-1}$ . The corrosion rate of the sample with 0.5wt.%  $ZrO_2$  is  $0.028 g\cdot cm^{-2}\cdot h^{-1}$  and with 1.5wt.%  $ZrO_2$  is  $0.040g\cdot cm^{-2}\cdot h^{-1}$ . And the higher the  $ZrO_2$  content, the higher the corrosion rate. As the content of  $ZrO_2$  is 1.5wt.%, the corrosion rate is the highest.

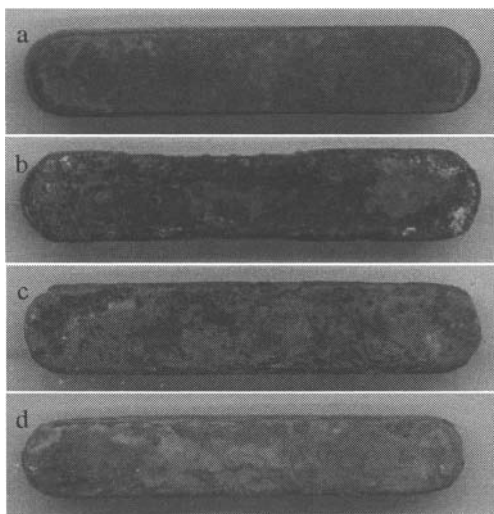


Fig.5 Photographs of the samples eroded by molten salt containing  $ZrO_2$  with the content of (a) 0.0wt.%, (b) 0.5wt.%, (c) 1.0wt.% and (d) 1.5wt.%.

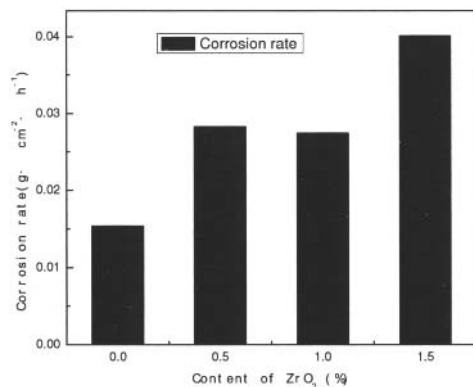


Fig.6 Corrosion rate of the samples with different content of  $ZrO_2$ .

The volume expansion of  $ZrO_2$  particle is the reasons for the

increase of the corrosion rate having  $ZrO_2$ .  $ZrO_2$  particle has enough space to change from tetragonal crystal system to monoclinic crystal system as the corrosion of the matrix material result in the extension of crack. Meanwhile the  $ZrO_2$  particle starts volume expansion lead to more matrix materials crack. Thus corrosion rate of the sample apparently increases.

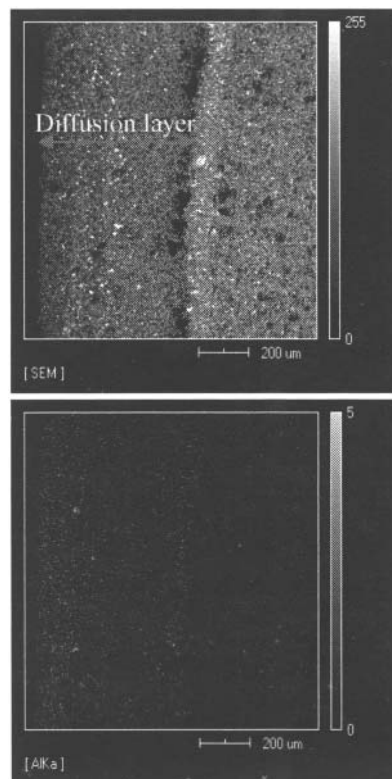


Fig.7 SEM micrograph of the distribution on the polished section of  $NiFe_2O_4$  without  $ZrO_2$  eroded by molten salt.

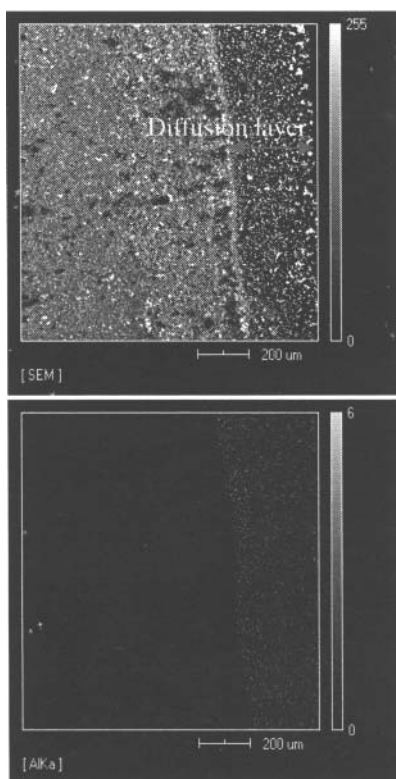


Fig.8 SEM micrograph of the distribution on the polished section of  $\text{NiFe}_2\text{O}_4$  with 1.5wt.% $\text{ZrO}_2$  eroded by molten salt. The SEM micrographs of the distribution on the polished section of  $\text{NiFe}_2\text{O}_4$  without  $\text{ZrO}_2$  and with 1.5wt.%  $\text{ZrO}_2$  are shown in Fig.7 and Fig.8 respectively. As seen from the two figures, the diffused layer is dramatically reduced by adding  $\text{ZrO}_2$ . The diffused layer has fine corrosion resistance. The diffused layer is the destroyed by volume expansion of  $\text{ZrO}_2$  particle. The corrosion resistance decrease resulting from  $\text{ZrO}_2$ .

### Conclusions

- 1) The relative density of the sample with  $\text{ZrO}_2$  decreases to some extent while the porosity is on the contrary. The relative density of the sample with 0.5wt.%  $\text{ZrO}_2$  may arrive at 99.67%.
- 2) The bending strength is dramatically enhanced by adding  $\text{ZrO}_2$ . Bending strength of sample without  $\text{ZrO}_2$  is 55.5MPa. The bending strength of sample with 0.5wt.%  $\text{ZrO}_2$  is up to 105.26MPa and is 1.897 times as much as that of sample without  $\text{ZrO}_2$ .
- 3) The corrosion resistance is not significantly improved by adding  $\text{ZrO}_2$ . The corrosion rates of the samples containing  $\text{ZrO}_2$  with the content of 0.0wt.%, 0.5wt.% and 1.5wt.% is are  $0.015\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ ,  $0.028\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$  and  $0.040\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$

respectively. The higher the  $\text{ZrO}_2$  content, the higher the corrosion rate is.

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### References

- [1] E. Olsen, J. Thonstad, "Behaviour of Nickel ferrite cermet materials as inert anode," (Light metals proceeding of sessions, TMS Annual Meeting, USA, The Minerals, Metals and Materials Society, 1996), 249-257.
- [2] R. P. PAWLEK, "Inert anodes: An update," (Light metals proceeding of sessions, TMS Annual Meeting, USA, The Minerals, Metals and Materials Society, 2002), 449-456.
- [3] D. R. SADOWY, "Inert anode for the Hall-Héroult cell: The ultimate materials challenge," *JOM*, 2001, 53(5), 34-35
- [4] E. Olsen, J. Thonstad, "Nickel ferrite as inert anodes in aluminium electrolysis (Part I): Material fabrication and preliminary testing," *Journal of Applied Electrochemistry*, 1999, 29(3), 293-299.
- [5] J. D. Weyand, D. H. DeYoung, S. P. Ray, G. P. Tarcy and F. W. Baker, "Inert Anodes for Aluminium Smelting, Final Report," (Aluminium Company of America, Alcoa Laboratories, Alcoa Center, 1986), DOE No. DOE/CS/40158-20, Department of energy, Idaho operations office, Idaho Falls, ID (1986)

[6] C. S. Marschman, C N. Davis, "Cermets anode with continuously dispersed alloy phase and process for making," US Patent, 4871437, 1989.

[7] S P. Ray, R W Woods, Controlled atmosphere for fabrication of cermet electrodes, US Patent, 5794112, 1998.

[8] J. H. Xi, Y. J. Xie, G. C. Yao, Y. H. Liu, "Effect of additive on corrosion resistance of  $\text{NiFe}_2\text{O}_4$  ceramics as inert anodes," *Transactions of Nonferrous Metals Society of China*, 18 (2) (2008), 356-360.