Light Metals 2012 *Edited by: Carlos E. Suarez*
TMS (The Minerals, Metals & Materials Society), 2012

STUDY ON THE INERT ANODE FOR Al ELECTROLYSIS BASED ON THE $NiFe_2O_4$ SPINEL CERAMICS

Yihan Liu; Ming Zhao; Jing Li

Northeastern University, No. 11, Lane 3, Heping District, Shenyang City, Liaoning, 110819, China.

Keywords: Al electrolysis, Inert anode, Nickel ferrite spinel, Cermet, Carbon dioxide emission

Abstract

A kind of cermet inert anode for Al electrolysis based on $NiFe_2O_4$ had been studied in this paper. Firstly, the effect of $NiFe_2O_4$ pre-sintering temperature on properties of inert anodes was researched, and then the appropriate technological conditions were determined by the orthogonal test. The properties such as density, conductivity, corrosion rate, mechanical property and thermal shock resistance have been used as controlling parameter to obtain the optimum technological condition. The inert anode sized Φ50mm×15mm is prepared and tested as anode for 10h Al electrolysis in laboratory. This anode behaves good corrosion resistance to cryolite molten salt. The result gives that the corrosion rate of the anode was $1.5\times10^{-4}g\cdot cm^{-2}\cdot h^{-1}$ after the 8 h electrolysis, and the purity of the aluminum gained from Al electrolysis test was 92 %~93 %. The analysis shows the main contaminations in the raw aluminum are Fe, Ni and Ag.

Introduction

There are many problems in traditional aluminium electrolysis such as a great amount of energy is needed, a lot of high-quality carbon is consumed and a serious of environmental pollution is brought on. However, inert anode does not participate in electrochemical reaction in the electrolysis process and is almost non-consumable, and produce oxygen instead of carbon dioxide, so it can save a lot of resources and protecting environment. Thus, the inert anode has become the research focus in the fields of aluminum industry and materials.

The idea of using inert anodes (also called non-consumable or oxygen-producing anodes) in aluminum production is as old as the Hall-Hëroult technology, dating back to one of the inventors, Charles Martin Hall

The use of non-consumable anodes will emit oxygen and from top to bottom eliminate the consumption of anode carbon in the electrolytic process[1]. In 1990, U.S. Department of Energy carried out the electric current 120A scale test, the results were quite better, hence put forth a brilliant future for the inert anode in Al electrolysis industry [2-3]. However, the subsequent test in 1993, a 6000A current density test was not so success, it main problems were:

(1) Lower corrosion resistance of the material,
(2) The poor hot shock resistance of large-sized anodes[4]

Being funded by National Natural Science Foundation of China and National Hi-Tech Research and Development Program of China, the preparation technology and performance of large refractory-type aluminum inert anode have been investigated in this paper.

Firstly, the process of synthetizing $NiFe_2O_4$ base material with Φ100×40mm in batch has been studied. The results indicate that $NiFe_2O_4$ forms under the condition of NiO reacts with Fe_2O_3 in the air, however, Fe_2O_3 decomposes into Fe_3O_4 and O_2 in ordinary and pure argon. So air is considered as the proper sintering atmosphere to prepare $NiFe_2O_4$ material. The performance of $NiFe_2O_4$ ceramic material varies with the sintering temperature of material, and 1200 ℃ is confirmed to be the most appropriate temperature to prepare the base material in large scale.

Secondly, the electrolysis test with Φ100×20mm sized inert anode was carried out, and the result show that the cell voltage is stable in the process of electrolysis and the conductivity and the corrosion resistance of the inert anode is pretty good.

Experimental process

Preparation of $NiFe_2O_4$ spinel

We choose the Ni_2O_3 and Fe_2O_3 as primary ingredients to synthesize spinel by means of powder metallurgical methods. We studied the preparation technology and the characteristics of the cermet material at first.

After being blend、milled and granulated, the mixture is molded by press. The biscuits were sintered at the temperature of 1200℃ for 6 hours before it is synthesized as $NiFe_2O_4$ spinel doped with a little amount of TiO_2/V_2O_5. The Fig1 gives the brief flowchart of the process

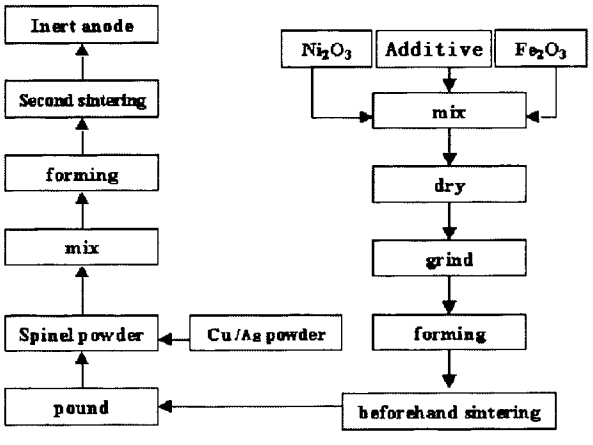

Figure 1. The brief flow chart of experiment process

Performance testing

The densitie of the samples is tested by Archimedes draining method; the pyroconductivity of the sample is tested by voltammetry; the corrosion rate of the samples in molten cryolite is tested and the condition of imitating industrial Al electrolysis. The experiment condition is the following:

(1) The ingredient of electrolyte: 90 % industrial cryolite (NaF/AlF_3-ratio is 2.2), and CaF_2 and Al_2O_3 are 5 wt% each.
(2) Experiment temperature: 960-980℃
(3) Immersion time: 30 hours (it takes only minutes until temperature gets to 960 ℃)

Furthermore, for the case of investigating the microstructure of the sample, SEM and XRD were employed.

The results and analysis

The effect of additive

The comparison microscopic structures of the samples without/with 1.5% V_2O_5 are showed as Figure 2 (a) to (d).

From Figure 2 (a) and Figure 2 (b), we can see that the spinel grains (sizing 2-7μm and shaping octahedron) accrete obviously, as 1.5% V_2O_5 being added in, this contribute to V_2O_5 can promote the grains to grow and develop perfectly.

From Figure 2 (c) and Figure 2 (d), we can see the metallic Ag (white bright point in the Fig.) is, in the pattern of reticulation, well distributed in the sample. This phenomenon comes from the adding of V_2O_5, because it can improve the interface structure between the $NiFe_2O_4$ ceramics and Ag.

The distribution of Ag as microstructure Fig.2 (d) can increase the electric conductivity of the material, for the metallic Ag which possesses better conductivity is perfectly distributed in the material. Analyzing from the view of sintering, the V_2O_5 will take the lead in becoming liquid during sintering because of its lower melting point. The melted V_2O_5 will spontaneously concentrate at the boundaries of $NiFe_2O_4$ grain and react with Fe_2O_3 and NiO to form Ni_2FeVO_6 [5]. The Ni_2FeVO_6 will change the characteristic of the boundary of grain and improve the distribution of the metallic Ag in the composite. So the electric conductivity of the samples with 15% V_2O_5 added can be obviously upgrade than the samples without V_2O_5.

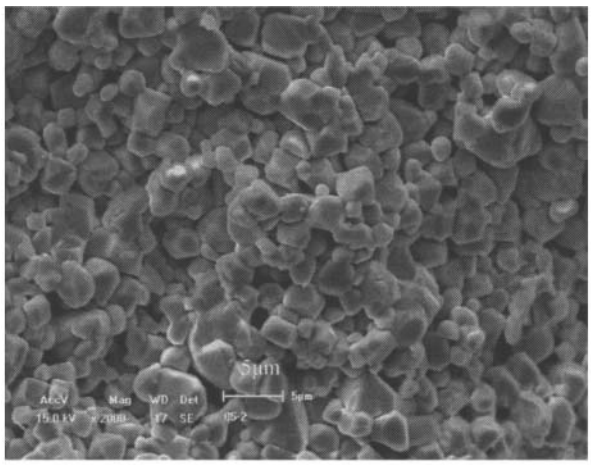

Figure 2(a) SEM of sample $NiFe_2O_4$ matrix

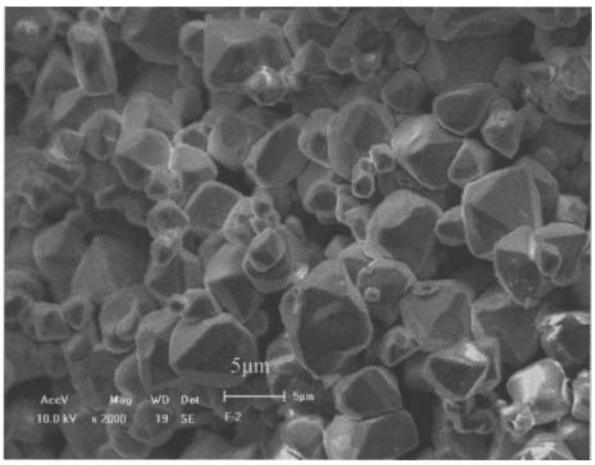

Figure 2(b) SEM of $NiFe_2O_4$ matrix with 1.5% V_2O_5

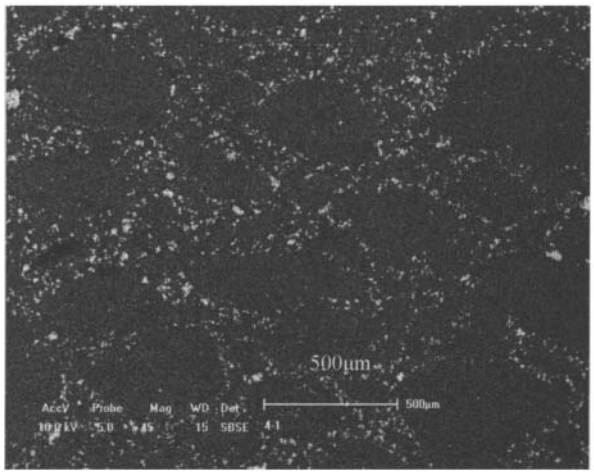

Figure 2(c) SEM photograph of sample without V_2O_5

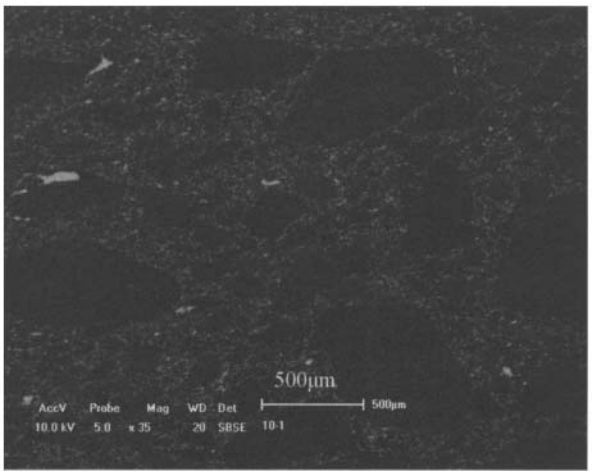

Figure 2(d) SEM photograph of sample with 1.5%V_2O_5

The fabrication of inert anode block

Table 1 shows the average porosity obtained at different sintering temperature. From the data in the Table 1, we could see, along with the sintering temperature rising, the porosity of the samples significantly decreasing. This indicates that higher sintering temperature and longer sintering time can reduce the porosity and increase compress ratio of the sintered samples; but high sintering temperature and too long sintering time easy to cause local abnormal grain growth or recrystallization, thus will reduce the thermal shock resistance and electrical conductivity of the prepared inert anode materials; so the sintering temperature for nickel ferric spinel ceramic should be enough but not be too high.

Table 1. The porosity of Samples Sintered in Different Temp.

T / ℃	Average Density g/cm^3	Average porosity %
800	3.999	25.000
900	3.863	21.994
1000	4.057	18.450
1100	4.125	15.574
1200	3.867	12.684
1300	4.271	10.457

Figure 3 (a) and (b) were SEM photography of the samples sintered at 1000 ℃ and 1200 ℃ for 6 hours.

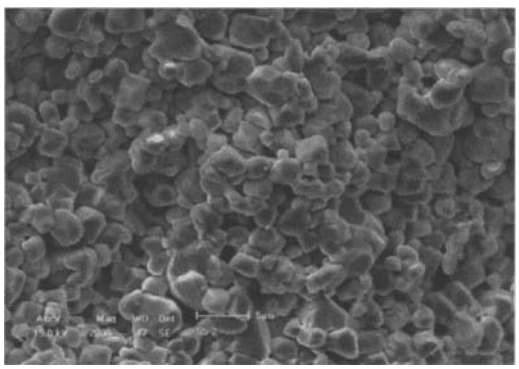

Figure 3（a）. SEM photography of samples sintered at 1000℃ for 6 hours

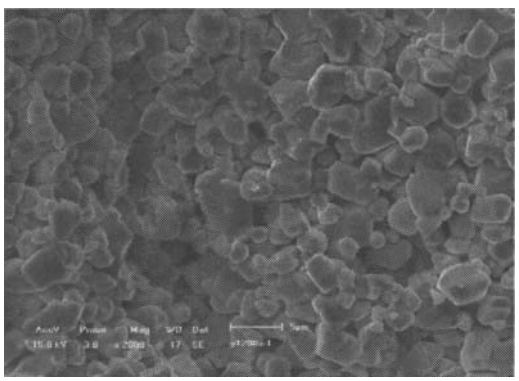

Figure 3（b）. SEM photography of samples sintered at 1200℃ for 6 hours

From Figure 3 (a) and (b), we can clearly see that the sintered sample at 1000 ℃ possess smaller grain size than the sintered sample at 1200 ℃, but these grains are not tightly joined enough and the pores among these grains are more. However, to the sintered sample at 1200 ℃, its grain growth is complete, and the combination is tight between grains.

Figure.4 is the XRD patterns of sample sintered at 1200 ℃ for 6 hours. The pattern gives us a single $NiFe_2O_4$ spinel phase according to the diffraction peak analyses, which illuminates that the solid sintering reaction of $NiFe_2O_4$ spinel almost finished after sintered at 1200 ℃ for 6 hours, and the linear shrinkage ratio is 14.3 % in this point.

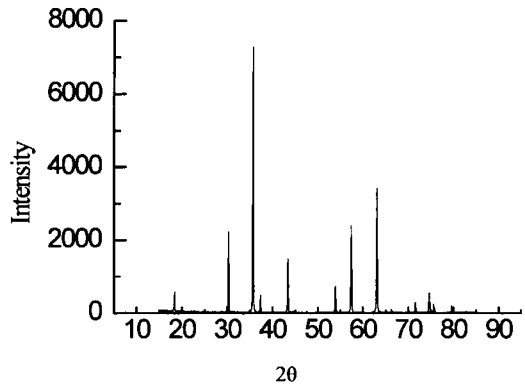

Figure 4. XRD patterns of sample sintered for 6 hours

Estimating from density, porosity and XRD investigation, we finally choose the optimum sintering temperature is 1200 ℃ and the sintering time is 6 hour.

The effect of the samples as inert anode for Al electrolysis

A small scale test of this material being used as inert anode for Al electrolysis has been studied in laboratory, Figure 5 is the facility installation.

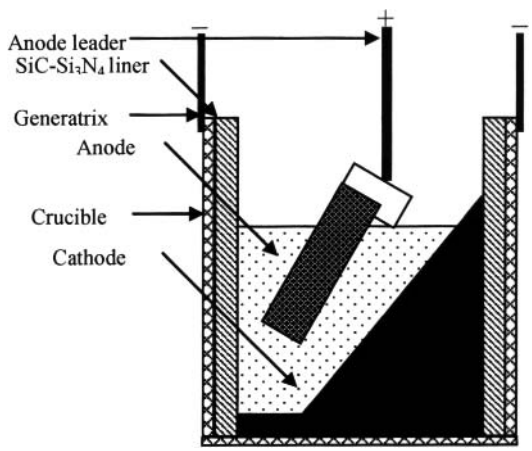

Figure 5. Schematic of electrolysis cell

The anode and the cathode were put as parallel which set at 60° oblique angle to horizon for the sake of to lead the gas removing. The electrolysis time is arranged for 8 our, and the ingredient of the electrolyte is $Na_3AlF_6 - 5\%CaF_2 - 5\%Al_2O_3$, the current density is 0.8 $A \cdot cm^{-2}$ and the distance from anode to cathode is about 5 cm. The electrolyte and the Al_2O_3 are fed up regularly during the electrolysis to maintain the electrolysis process continuous.

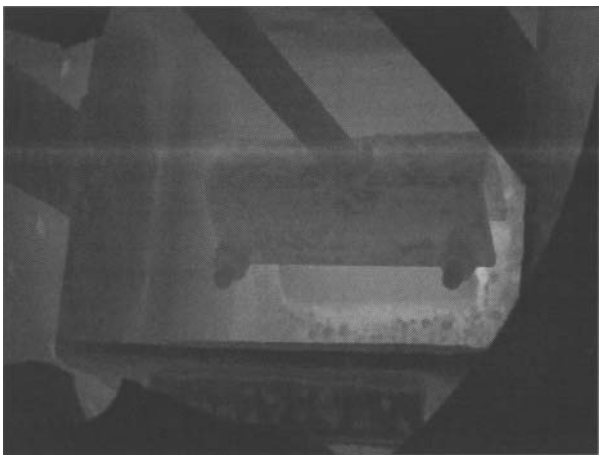

Figure 6. Schematic of electrolysis process of inert

Figure 6 is the photograph taken by camera during the electrolysis and the Figure 7 shows the voltage of the Al electrolysis cell variety during the electrolysis course. The voltage is a little high at the beginning because some cryolite has not been melted in the cell. However, the voltage goes down gradually and keeps on steadily as the electrolysis time preponderate over 1 hour.

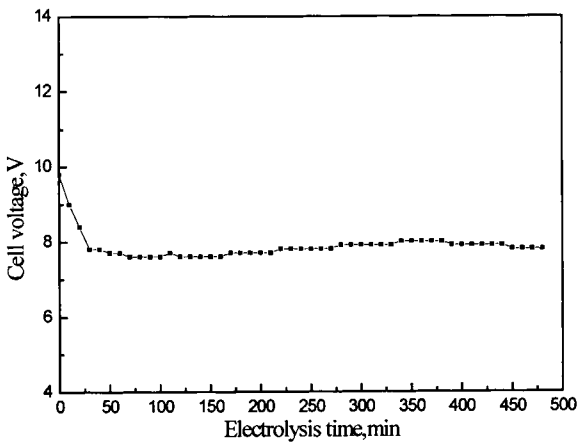

Figure 7. Variation of cell voltage with electrolysis

After electrolyzed 8 hours, the electrode was raised and cooled in the furnace. The Figure 8 is the appearance of the inert anode before and after 8 hour electrolysis. From Figure 8, we can see that the inert anode is clear and smooth on surface and there is not any crack or denudation on the sample.

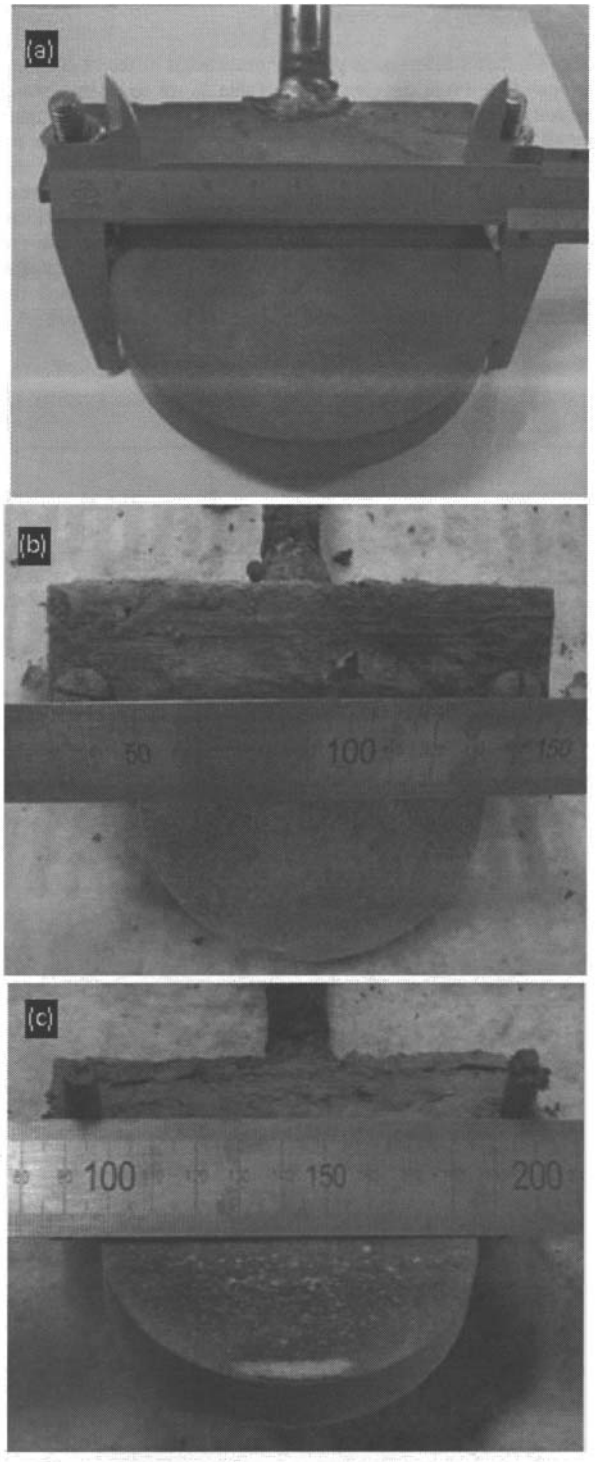

Figure 8. Appearance of anode before and after 8 hour electrolysis

(a) Before , (b) Work side, (c) Back side

The corrosion rate obtained by measuring dimension is 1.5×10^{-4} $g\cdot cm^{-2}\cdot h^{-1}$, the purity of the produced Al determined by element analysis is 93~94 mass%, and the most of the foreign impurities are identified as Fe (3.95 %), Ni (1.57 %) and Ag (0.0066).

Conclusion

(1) The additive such as TiO_2 and V_2O_5 can promote the $NiFe_2O_4$ grains to grow and develop perfectly.

(2) The additive such as TiO_2 and V_2O_5 can improve the samples' electric conductivity and corrosion resistance because it can change the component and microstructure of the $NiFe_2O_4$ grain boundary.

(3) Estimating from density, porosity and XRD investigation, the optimum sintering temperature is 1200 ℃ and the sintering time is 6 hour.

(4) The material gives a good result when it is used as inert anode for small scale aluminum electrolysis.

Reference

[1] J. Thonstad and E. Olsen. "Cell Operation and Metal Purity Challenges for the Use of Inert Anodes," *JOM*, 53 (5) (2001): 36-38.

[2] D. R. Sadoway "Inert Anodes for the Hall-Hëroult Cell: The Ultimate Materials Challenge," *JOM*, 53 (5) (2001): 34-35.

[3] H. Kvande, "Inert Electrodes in Aluminum Electrolysis Cell," *Light Metals: Proceeding of Sessions,* 128th TMS Annual Meeting & Exhibition. USA: Minerals, Metals and Materials Society, 1999.369-376.

[4] R P. Pawlek "Inter Anodes: an Update," *Light Metals: Proceedings of sessions,* 131st TMS Annual Meeting & Exhibition. USA: Minerals, Metals and Materials Society, 2002.449-456.

[5] M. Kurzawa, A. Blonska-Tabero. "Phase Equilibria in the System $NiO–V_2O_5–Fe_2O_3$ in Subsolidus Area," *Journal of Thermal Analysis and Calorimetry,* 77 (2004): 65–73.