Preparation and Corrosion Resistance of $NiFe_2O_4$-$NiCr_2O_4$ Composite Ceramic-Based Inert Anodes

Jing Li[1], Shengzhong Bao[2], Menghan Shi[3], Changlin Li[4] and Lifen Luo[5]
1, 3. Intermediate Engineers
5. Senior Engineer
2, 4. Professor level Senior Engineers
Zhengzhou Non-ferrous Metals Research Institute of Chalco (ZRI), Zhengzhou, China
Corresponding author: sz_bao@chinalco.com.cn
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Abstract

The new aluminum electrolysis technology with inert anodes and TiB_2 wettable cathodes is one of the important pathways for the aluminum electrolysis industry to achieve its carbon neutrality goals. The $NiFe_2O_4$-based cermet inert anodes have obvious comprehensive performance advantages. However, improving its corrosion resistance while balancing electrical conductivity and thermal shock resistance remains one of the main research directions at present. In this paper, Cr_2O_3 was introduced to prepare a $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic, which was then fabricated into a cermet inert anode. Subsequently, static corrosion tests and 20 A electrolysis tests were conducted. The results showed that the corrosion resistance of the $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic inert anode has significantly improved compared with the cermet inert anode based on traditional pure $NiFe_2O_4$ ceramic. Moreover, a stable and protective film layer could be formed during the electrolysis process under powered conditions.

Keywords: Inert anode, $NiFe_2O_4$-$NiCr_2O_4$ composite ceramics, $NiFe_2O_4$-based cermet, Corrosion resistance.

1. Introduction

Aluminum electrolysis technology with inert anodes can fundamentally address the issue of the release of CO_2, PFC, and CO_2 gases from the consumption of traditional carbon anodes during electrolysis. Particularly, $NiFe_2O_4$-based cermet integrates the corrosion resistance of the ceramic phase and the electrical conductivity of the metallic phase based on spinel-type ceramic materials by incorporating the metallic phase to improve the brittleness and electrical conductivity. In recent years, $NiFe_2O_4$-based cermet has been recognized as the most promising inert electrode material system. However, under the molten salt electrolysis conditions in the aluminum electrolysis (960 °C, Na_3AlF_6-Al_2O_3 molten salt), gradual corrosion of the anode materials and selective dissolution of some metallic elements are still critical problems limiting its life [1].

In recent years, significant progress has been made in the research of inert electrode materials for aluminum electrolysis, and material preparation has also scaled up from small-scale laboratory research to medium- and large-scale industrial application research [2–5]. Since Alcoa announced that a 17 % Cu-42.91 % NiO-40.09 % Fe_2O_3 inert anode (referred to as 5324-17Cu) features good electrical conductivity and corrosion resistance [6], M/$NiFe_2O_4$-based cermet has been regarded as the most promising inert anode material. Cermet with a ceramic phase of $NiFe_2O_4$ + 10NiO and a metallic phase M of binary or ternary alloy primarily composed of Cu, Ni, and Fe has been extensively studied. Research on cermet-based anode materials mainly focuses on the following aspects: first, enhancing the density of the material by optimizing sintering preparation processes; second, enhancing the corrosion resistance and electrical conductivity of the material by optimizing ceramic phase and metallic phase; third, conducting theoretical research from aspects such as electrical conductivity and corrosion mechanisms. With respect to optimization of ceramic phase, the primary research direction involves introducing a secondary ceramic phase or oxide addition and conducting electrolytic corrosion test to investigate the changes in the phase structure and composition of the material and evaluate their effects on sintering densification, strength, microstructure, electrical conductivity, corrosion resistance, thermal shock resistance, etc., so as to identify the optimal secondary ceramic phase or added oxides and their content. NiO, TiN, ZrB_2, REO, CoO, MnO, SnO_2, V_2O_5, ZrO_2 and the like have all been used as additives [7–16].

Cr, characterized by excellent corrosion resistance, can form a thin and dense oxide film in an oxidation environment, with self-repairability. This study focuses on the ceramic phase. By introducing the secondary ceramic phase $NiCr_2O_4$ into the traditional $NiFe_2O_4$, the original $NiFe_2O_4$ single-phase ceramic is optimized into a $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic. In addition, the influence of this optimization on the corrosion resistance of anode material is investigated. The experiment adopted a two-step sintering process to prepare $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic, and a cold-pressing sintering process to prepare the inert anode materials required for the experiment to investigate the influence of the introduction of the secondary phase $NiCr_2O_4$ on the sintering performance, microstructure and film-forming property under electrolysis in low-temperature bath of (Cu-Ni-Fe)-$NiFe_2O_4$-based cermet, with the aim of improving the performance of inert anode materials for aluminum electrolysis.

2. Methodology

2.1 Sample Preparation

Raw materials used in the experiment: NiO, Fe_2O_3, Cu, Ni, and Cr_2O_3 were analytically pure. A two-step sintering process was adopted for the preparation of $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic. First, $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic raw material powder was pre-synthesized via a high-temperature solid-phase synthesis method. The synthesized powder was mixed with a binder, ball-milled, dried, molded under pressure, and then sintered into bulk materials for use in static chemical corrosion and electrolysis experiments. First, NiO, Fe_2O_3, and Cr_2O_3 were weighed in a molar ratio of 1:0.8:0.2, respectively, and mixed uniformly using a ball mill, with deionized water as the grinding medium. The mixture was dried in an oven, crushed, and sieved. After the obtained mixed powder was placed in a corundum crucible and calcined at 1000 °C under an air atmosphere for 6 hours in a muffle furnace, 80 %$NiFe_2O_4$-20 %$NiCr_2O_4$ceramic powder was obtained. The synthesized powder was crushed, mixed with deionized water as a dispersant, 1.5 % PVA as a binder, and ball-milled. The dried powder was molded into ⌀ 45 mm × 0.5 mm circular green blocks on the four-column hydraulic press under a pressure of 200 MPa. The green blocks were sintered at 1250 °C under an air atmosphere for 4 h. The sintered samples were subject to performance testing and static corrosion experiments. The synthesized metal powder and the composite ceramic product were mixed in a mass fraction of 3:7 to prepare the (Cu52Ni30Fe18) and (80 % $NiFe_2O_4$-20 % $NiCr_2O_4$-10NiO) cermet mixed powder, mixed with deionized water as a dispersant, and 1.5 %PVA as a binder, and ball-milled. The dried powder was molded into 75 × 48 ×10 mm green blocks under a pressure of 200 MPa. The green blocks were sintered at 1250 °C under N_2 atmosphere for 4 h to obtain electrolysis experiment samples. The sintered samples were subject to performance testing and 20 A electrolysis experiment for corrosion resistance testing. Simultaneously, pure $NiFe_2O_4$ and 30(Cu52Ni30Fe18)-70$NiFe_2O_4$ samples were prepared for contrast experiments.

2.2 Static Chemical Corrosion Experiment

The chemical corrosion experiment used a low-temperature electrolyte mainly composed of NaF-KF-AlF_3. The experimental temperature was set at 800 °C. Circular sintered samples were immersed in the electrolyte which was placed in an alumina crucible with fixed capacity for 24 h bath penetration into the bulk layer, indicating that the formed film layer has a certain protective effect.

Overall: $NiFe_2O_4$-$NiCr_2O_4$ composite cermet can form a protective film layer in the bath, resulting from in-situ oxidation and expansion of the ceramic phase and the metallic phase. The corrosion layer formed by penetration of a small amount of electrolyte and the bulk layer without corrosion of electrolyte indicates that although a film layer has been formed, it is required to improve and enhance the resistance to corrosion of electrolyte and molten salt for the $NiFe_2O_4$-$NiCr_2O_4$ composite cermet under powered conditions.

4. Conclusion

(1) $NiFe_2O_4$-$NiCr_2O_4$ composite ceramic powder with high purity can be synthesized by mixing NiO, Fe_2O_3 and Cr_2O_3 in a molar ratio of 1:0.8:0.2 and holding the mixture at 1000 °C for 6 hours under an air atmosphere.

(2) The incorporation of $NiCr_2O_4$ phase in the ceramic phase can enhance the static corrosion resistance of $NiFe_2O_4$-based anode materials in the NaF-KF-AlF_3 low-temperature bath system, as the film layer formed on its surface is relatively dense.

(3) After the electrolysis test of $NiFe_2O_4$-$NiCr_2O_4$ composite cermet, although a complete film layer can be formed in terms of microstructure, it is necessary to improve the resistance to bath corrosion of the film layer.

5. References

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