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Effect of sintering atmosphere on corrosion resistance of Ni/(NiFe₂O₄-10NiO) cermet inert anode for aluminum electrolysis

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Abstract: A comparative study on the corrosion resistance of $17\text{Ni}/(\text{NiFe}_2\text{O}_4-10\text{NiO})$ cermet inert anode prepared in different sintering atmospheres was conducted in Na₃AlF₆-Al₂O₃ melt. The results indicate that the corrosion rates of NiFe₂O₄-based cermet anodes prepared in the vacuum and the atmosphere with oxygen content of 2×10^{-3} (volume fraction) are 6.46 and 2.71 cm/a, respectively. Though there is a transition layer with lots of holes or pores, a densified layer is formed on the surface of anode due to some reactions producing aluminates. For the anode prepared in the atmosphere with oxygen content of 2×10^{-3} , the thickness of the densification layer (about 50 µm) is thicker than that (about 30 µm) formed on the surface of anode prepared in the vacuum. The contents of NiO and Fe(II) in NiFe_{2x}O_{4-y-z} increase with the decrease of oxygen content in sintering atmosphere, which reduces the corrosion resistance of the material.

Key words: sintering atmosphere; corrosion resistance; NiFe₂O₄-based cermet; inert anode; aluminum electrolysis

1 Introduction

For almost 120 years, aluminum has been produced electrochemically by the Hall–Héroult process. This technology uses carbon anode and liquid aluminum cathode to decompose alumina dissolved in the molten cryolite [1]. The use of inert anode instead of carbon eliminates the generation of the greenhouse gas CO_2 when the oxygen liberated from the dissociation of alumina reacts with anode carbon. It also reduces perfluorocarbon(PFC) byproducts and other polluting emissions such as PAHs. So, the development of inert anode is a long standing dream of researchers [2,3].

However, the development of viable non-carbon anodes is very challenging due to numerous restrictive requirements for inert anode material in the highly aggressive environment of Al electrolysis cell. After plenty of research efforts from Al producers and academic laboratories, though some materials such as alloy, cermet and oxide ceramic were regarded as promising candidates, no acceptable inert anode material has yet been found for long-term use in industrial aluminum electrolysis [1,4–8]. In recent years, the oxide ceramic is abandoned gradually because of its low electrical conductivity, high brittleness and other problems such as being difficult to connect the metal rod [2]. The cermet anodes are ranked as one of the most appropriate candidates because of their combination of high corrosion resistance of ceramic and high electrical conductivity of metal [9–11]. NiFe₂O₄ is often utilized as ceramic matrix for cermet inert anode because of its high melting point, excellent corrosion resistance, stable thermal and chemical properties [2,5,7,12].

To improve the mechanical properties of ceramic material, modifying agent or sintering assistant was used during the preparation process, and some progress was made [13]. The effects of sintering atmosphere on the mechanical properties of NiFe₂O₄-based cermets were also studied in our previous studies, and the results showed that the alteration of oxygen content in the sintering atmosphere could affect the microstructure and mechanical properties of NiFe₂O₄-based cermets [14]. However, it is known to all that the corrosion resistance of material is the most important performance for inert anodes, it is not only related to the life of inert anode, but also affects the quality of metal Al.

In this work, $17Ni/(NiFe_2O_4-10NiO)$ cermet inert anodes were prepared in different sintering atmospheres by cold pressing-sintering process. And the influence of

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oxygen content in the sintering atmosphere on its corrosion resistance to $Na_3AlF_6-Al_2O_3$ melt was studied. The purpose is to explore the impact of the sintering atmosphere on the corrosion resistance of Ni/(NiFe₂O₄-10NiO) cermet inert anode.

2 Experimental

2.1 Fabrication of anodes

The raw materials, metal Ni powder, NiO and Fe₂O₃ were all of reagent grade. The samples of 17Ni/ (NiFe₂O₄-10NiO) cermet were prepared by the same process as Ref.[14]. A proper amount of Fe₂O₃ and 10% (mass fraction) excess NiO, compared with that of the stoichiometric NiFe₂O₄, were mixed by using a ball mill, and then calcined in a muffle furnace at 1200 °C for 6 h to obtain NiFe₂O₄-10NiO ceramic powder. The calcined ceramic powder was mixed again with metal Ni powder by ball milling in the media containing dispersant and adhesive that were organic to avoid the metal oxidation. Finally, the mixed ceramic-metal powder was dried and pressed into cylindrical blocks ($d20 \text{ mm} \times 40 \text{ mm}$), which were sintered at 1350 °C for 4 h in the vacuum or an atmosphere with the oxygen content of 2×10^{-3} (volume fraction) respectively to get the desired Ni/(NiFe₂O₄-10NiO) cermet inert anode samples.

2.2 Chemical and bath preparation

The bath was made up of raw materials Na₃AlF₆, AlF₃, CaF₂ and Al₂O₃. Among them, Na₃AlF₆, CaF₂ and Al₂O₃ were reagent grade. AlF₃ was purified by sublimation three times and its purity was above 99.5%. All the components were dried at 150 °C for at least 48 h in the vacuum oven to remove the water before being used. The mole ratio of NaF to AlF₃ ($n(NaF)/n(AlF_3)$) in Na₃AlF₆–AlF₃–CaF₂–Al₂O₃ melt was 2.3:1, and the contents of CaF₂ and Al₂O₃ were both 5.0% (mass fraction). The powder components were mixed and the initial mass of electrolyte was 800 g.

2.3 Cell design and electrolysis procedure

A sketch of the experimental cell is presented in Fig. 1. A hole was drilled at the bottom of graphite crucible and some metal aluminum (about 90 g, the purity was 99.5% and obtained from Yunnan Aluminum Co., Ltd.) was added. Thus, a steady cathode surface could be obtained during electrolysis. Alumina sleeve was set in the graphite crucible and about 800 g electrolyte was contained. Under the operating conditions of the laboratory test, the cell could not be thermally self-sustaining. It was necessary to provide extra heat by placing the experimental cell with the anode together in a vertical laboratory furnace and the furnace was heated to the desired temperature.



Fig. 1 Sketch of experimental cell for electrolysis (A — Stainless steel anode rod; B — Alumina cover; C — NiFe₂O₄-based cermet inert anode; D — Metal aluminum cathode; E—Alumina tube; F—Alumina crucible; G—Graphite crucible; H—Electrolyte; I—Graphite mechanical support)

Metal aluminum was added prior to electrolysis. The cell with NiFe₂O₄-based cermet inert anode was heated to the required temperature of 960 °C and kept for 2 h before immersing the anode and electrifying 20 min afterwards. The electrolysis temperature was maintained at 960 °C during testing. The temperature of Na₃AlF₆–AlF₃–CaF₂–Al₂O₃ melt was measured with Pt/Pt–10%Rh thermocouple once 1 h and maintained below a range of ± 3 °C during testing. The temperature accuracy of the furnace was controlled to ± 1 °C by TCE–II programmable temperature control unit.

The anode-bath contacting area was controlled by the immersion depth of anode, which was 1.0 cm. The current and the cell voltage were supplied and monitored by a multi-purpose potentiostat/galvanostat (model 273A/10, Perkin-Elmer Instruments). The current density of anode bottom was 1 A/cm² and the current was kept constant throughout the experiment. Al₂O₃ was supplied once every 15 min and its content could be kept constant during the experiment.

After electrolysis, the anode was raised out of the bath while maintaining polarization so as to prevent reduction of the anode material by dissolved metal aluminum. The cell was left to cool with the anode resting above the electrolyte. The metal aluminum recovered was also analyzed by X-ray fluorescence spectrum (Philips 8424 TW2424) (analytic error lower than 5%) for getting the contents of Ni and Fe. The anodes tested were sectioned, mounted, polished, and analyzed by XRMA (JSM–5600LV) using a quantitative energy dispersive spectrometer (EDS) connected to the SEM. The phase composition of NiFe₂O₄-based cermet inert anode before electrolysis was also analyzed by Rigaku3014 X-ray diffractometer.

3 Results and discussion

3.1 Material performance

The results from our previous studies indicated that it took approximately 4–6 h for stoichiometric $NiFe_2O_4$ in $Na_3AlF_6-AlF_3-Al_2O_3$ melt to reach a steady-state content, which was regarded as the solubility [15]. The study carried out by OLSEN and THONSTAD [16] also confirmed this. Therefore, the electrolysis experiments lasted for 10 h here.

After testing, the contents of Ni and Fe in the metal aluminum recovered at the cathode were analyzed by XRF. The increments of impurities Ni and Fe are listed in Table 1. As can be seen, for test No. 1, the increment of impurity Ni in aluminum is 0.222 g, while for test No. 2, the value is only 0.094 g. It can be calculated that the increment of Ni is decreased significantly (by 57.7%) due to the change of sintering atmosphere during preparation. The same is true for the impurity Fe, although its increment is decreased by only 36.8%. It can be concluded that the alteration of oxygen content in the sintering atmosphere is helpful for improving the quality of the metal aluminum.

 Table 1 Increment of impurities Ni and Fe and corrosion rate of anode

Test No.	Sintering atmosphere	Increment of impurities in aluminum/g		Corrosion
		Ni	Fe	rate/(cm·a ')
1	Vacuum	0.222	0.462	6.46
2	Oxygen content of 2×10^{-3}	0.094	0.292	2.71

Generally speaking, the corrosion rate of anode is nearly the same as the deposition rate of impurity into the aluminum cathode after the corrosion reaches a steady-state. Therefore, the corrosion rate of inert anode can be calculated according to the deposition rate of some kinds of impurities at the cathode [17]. As for $17\text{Ni}/(\text{NiFe}_2\text{O}_4-10\text{NiO})$ cermet inert anode, its corrosion rate can be obtained by the change of Ni content in the metal aluminum recovered at the cathode based on the following equation [17]:

$$v_{\rm c} = \frac{\Delta m_{\rm Ni(Al)}}{w_{\rm Ni(cer)} \rho S \tau} \times 365 \times 24 \tag{1}$$

where v_c (cm/a) is the corrosion rate of anode, $\Delta m_{Ni(Al)}(g)$ is the increment of Ni in the metal aluminum at the cathode, $w_{Ni(cer)}$ (%) is content (mass fraction) of Ni in the anode, ρ (g/cm³) is the density of anode, $S(cm^2)$ is the area of the anode surface immersed in the bath, and τ (h) is the time of electrolysis.

The corrosion rate based on Eq. (1) is calculated to be 6.46 cm/a for $17\text{Ni}/(\text{NiFe}_2\text{O}_4-10\text{NiO})$ cermet inert anode prepared in the vacuum. However, for the inert anode prepared in the atmosphere with the oxygen content of 2×10^{-3} , its corrosion rate is 2.71 cm/a. This indicates that the corrosion resistance of Ni/(NiFe₂O₄-10NiO) cermet to Na₃AlF₆-AlF₃-Al₂O₃ melt can be improved by changing the oxygen content of sintering atmosphere.

3.2 Microstructure analysis

The XRD analysis results of $17\text{Ni}/(\text{NiFe}_2\text{O}_4-10\text{NiO})$ cermet prepared in different atmospheres are shown in Fig. 2. It is found that both the samples obtained in the vacuum and the atmosphere with oxygen content of 2×10^{-3} contain the phases Ni, NiFe₂O₄ and NiO, and no other impurity appears. But the characteristic peak of NiFe₂O₄ is more obvious for the anode prepared in the atmosphere with oxygen content of 2×10^{-3} than that for the anode prepared in the vacuum.



Fig. 2 XRD patterns of 17Ni/(NiFe₂O₄-10NiO)

With the change of oxygen content in the sintering atmosphere, the following reaction may occur:

$$NiFe_2O_4 \longrightarrow NiFe_{2x}O_{4-y-z} + NiO + O_2 \uparrow$$
(2)

Thus, the ceramic NiFe₂O₄, which is one of the components of anodes tested, will be decomposed into NiFe_{2x}O_{4-y-z} and NiO if the oxygen content in the atmosphere decreases. Although the stoichiometric compound NiFe₂O_{4-y-z} cannot be distinguished by XRD, there are two forms for the element Fe in NiFe_{2x}O_{4-y-z}, which are Fe(II) and Fe(III). When the oxygen content in the sintering atmosphere decreases, Fe(III) in NiFe_{2x}O_{4-y-z} is reduced to Fe(II) and the content of Fe(II) increases. In Na₃AlF₆–AlF₃–Al₂O₃ melt, lower valence state Fe(II) in NiFe_{2x}O_{4-y-z} may dissolve more easily than higher valence state Fe(III) [11]. Therefore, the corrosion resistance of 17Ni/(NiFe₂O₄–10NiO) cermet prepared in

the vacuum decreases.

At the same time, Reaction (2) also indicates that the content of NiO decreases and the content of NiFe₂O₄ increases if the anode is sintered at high oxygen content. The results from the XRD also show that the mass fractions of phases NiFe₂O₄ and NiO are 71.5% and 17.8% respectively for the anode prepared in the atmosphere with the oxygen content of 2×10^{-3} . If the anode is prepared in the vacuum, the mass fractions of phases NiFe₂O₄ and NiO are 64.4% and 20.4%, respectively. The results of Ref. [18] show that the corrosion resistance of NiFe₂O₄ is better than that of NiO. So, if the cermet inert anode is prepared in the atmosphere with the oxygen content of 2×10^{-3} , its corrosion resistance is better than that prepared in the vacuum.

To obtain more information, SEM images of cross-sections of the anode surfaces after electrolysis are obtained and shown in Fig. 3. There are some visible structural changes for the anodes sintered in different atmospheres when going from the unchanged interior of the electrode to the surface. A distinct densification layer is formed on the surface of anode. The results from EDS analysis of the densification layer show that there is element Al, which is not added to the anode during the preparation process, existing after electrolysis besides elements Ni, Fe and O. This phenomenon may appear via some reactions forming aluminates such as NiFe₂O₄, NiAl₂O₄ and FeAl₂O₄ [16]. Further studies should be

Fig. 3 SEM images of anodes after electrolysis: (a) Anode prepared in atmosphere with oxygen content of 2×10^{-3} ; (b) Anode prepared in vacuum

conducted to reveal the reason that the densification layer forms.

For the anodes prepared in different atmospheres, another point which should be noted is that there is a porous layer between the surface and the interior of anode after electrolysis. And in this layer, which is called "transition layer" here, the metal phase Ni disappears and there are some holes or pores left. The amounts of holes or pores in the transition layer are more than those in the anode material itself. The elements of Ni, Fe, Al, Na, O and F were detected. And the thickness of the transition layer for both the anodes prepared in different atmospheres is almost the same, which is about 500 μ m. This may be due to the electrochemical reaction (Reaction (3)) between the metal Ni and the electrolyte infiltrated into the anode, which causes the preferential dissolution of the metal Ni during electrolysis [19].

$$3Ni+2AlF_3=3NiF_2+2Al$$
 (3)

It is very obvious for the anodes prepared in different atmospheres that the thickness of the densification layer on the surface is different. The densification layer with thickness of about 50 µm is formed for the anode prepared in the atmosphere with the oxygen content of 2×10^{-3} after electrolysis for 10 h. However, the thickness is only about 30 µm for the anode prepared in the vacuum. Since the surface layer of this anode is denser than the anode material itself which contains some pores due to its poor sintering characteristics, it is helpful for NiFe2O4-based cermet inert anode to improve its corrosion resistance against Na₃AlF₆-AlF₃-Al₂O₃ melt. Therefore, the corrosion rate of the anode prepared in the atmosphere with the oxygen content of 2×10^{-3} is lower than that prepared in the vacuum.

4 Conclusions

1) The corrosion rate of $17\text{Ni}/(\text{NiFe}_2\text{O}_4-10\text{NiO})$ cermet during electrolysis can be reduced by properly improving the oxygen content of sintering atmosphere. Based on the change of Ni in the metal aluminum recovered at the cathode, the corrosion rate of anode prepared in the atmosphere with the oxygen content of 2×10^{-3} is 2.71 cm/a. However, for the anode prepared in the vacuum, its corrosion rate is 6.46 cm/a.

2) The decrease of the oxygen content in the sintering atmosphere will cause the increase of the content of Fe(II) in NiFe_{2x}O_{4-y-z}, which may dissolve more easily than that of Fe(III). Meanwhile, the content of NiO also increases. It is adverse to improve the corrosion resistance of the anode during electrolysis.

3) A distinct densification layer is formed on the surface, and a transition layer with lots of holes or pores also comes into being between the surface and the interior. The thicknesses of the densification layer for the anodes prepared in the atmosphere with oxygen content of 2×10^{-3} and in the vacuum are about 50 and 30 µm, respectively. Further studies should be conducted to reveal the reason that the distinct layer forms.

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烧结气氛对铝电解 Ni/(NiFe₂O₄-10NiO)金属 陶瓷惰性阳极耐腐蚀性能的影响

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摘 要:对比研究了不同烧结气氛条件下制备的 17Ni/(NiFe₂O₄-10NiO)金属陶瓷惰性阳极在 Na₃AlF₆-Al₂O₃ 熔体 中的耐腐蚀性能。研究结果表明,在真空和氧含量为 2×10⁻³(体积分数)气氛下制备的 NiFe₂O₄ 基金属陶瓷阳极电 解腐蚀率分别为 6.46 和 2.71 cm/a。尽管电解后阳极过渡层中出现了许多孔洞,但在反应新生成的铝酸盐作用下, 阳极表面形成了一层致密层。对于氧含量为 2×10⁻³ 气氛下制备的阳极,其表面电解后生成的致密层厚度(约为 50 μm)大于真空条件下阳极表面所生成的致密层厚度(约为 30 μm)。随着烧结气氛中氧含量的降低,所获材料中 NiO 和 NiFe_{2x}O_{4-y-z}中 Fe(II)的含量均增加,材料的抗腐蚀能力降低。

关键词: 烧结气氛; 耐腐蚀性能; NiFe₂O₄基金属陶瓷; 惰性阳极; 铝电解