The behavior of the additive Yb$_2$O$_3$ doped in the anodes during electrolysis

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Abstract: Investigation of the behavior of additive Yb$_2$O$_3$ in the anode during electrolysis is an important method for improving the corrosion resistance of the grain boundary to high-temperature molten salt electrolyte. The author examined the Yb content of cermets after both sintering and electrolysis and the experimental results showed that a dense layer of NiFe$_2$O$_4$-NiAl$_2$O$_4$-FeAl$_2$O$_4$ ceramic favorably formed on the surface of the anodes only if the electrolysis time was greater than 10 hours. Moreover, NiFe$_2$O$_4$, NiAl$_2$O$_4$ and FeAl$_2$O$_4$ were produced and dissolved continuously as a result of the chemical and electrochemical corrosion that took place after the formation of the dense layer. As the electrolysis time was extended, Yb$_2$O$_3$ or YbFeO$_3$ gradually dissolved into the electrolyte and primary aluminum as an impurity substance.

Key words: behavior; grain boundary; dense layer; Yb$_2$O$_3$; YbFeO$_3$

1. Introduction

NiFe$_2$O$_4$-NiO-based cermets are one of the most promising inert anode materials for aluminum electrolysis because of their good corrosion resistance and high electrical conductivity in high-temperature molten salt 1-6. However, due to the differences in corrosion between the metal phase and ceramic phase in cermets, the preferential corrosion of the metal phase causes some problems such as electrolyte permeability, swelling and cracking 7-10. Thus, it is necessary to take effective measures to improve the corrosion resistance of the metal phase to high-temperature molten salt electrolyte. At present, adding additives to strengthen the grain boundary and forming a dense ceramic spinel layer on the surface of NiFe$_2$O$_4$-based cermets inert anodes are the important way to accomplish this.

XI et al. 11 pointed out that the addition of MnO$_2$ increases the relative density of nickel ferrite, refines the grain and improves the thermal shock resistance of samples containing MnO$_2$. XI 12 also reported that V$_2$O$_5$ can improve corrosion resistance, and distribute Ni$_2$FeVO$_6$ along the grain boundary, which can control the chemical dissolution of the ceramic anode. The reinforced grain boundary can then control the grain boundary corrosion rate.

TAO et al. 13 reported that the grains coarsen after doping with Yb$_2$O$_3$, and the reaction product phase is distributed along the NiFe$_2$O$_4$ grain boundary in the way of point and line. Moreover, the reaction product of Y$_2$O$_3$ and the ceramic phase is distributed in the NiO and along the NiFe$_2$O$_4$ grain boundary.

However, little work has been reported on the behavior of additives on the grain boundary during electrolysis. To the best of the author’s knowledge, the additive Yb$_2$O$_3$ is advantageous for the relative density, corrosion resistance and electrical conductivity of cermets 14, but very few studies have evaluated the behavior of Yb$_2$O$_3$ on the grain boundary during electrolysis, especially during the formation of a NiFe$_2$O$_4$-NiAl$_2$O$_4$-FeAl$_2$O$_4$ dense layer on the surface of inert anodes.

2. Experimental

2.1 Preparation of cermets

xYb$_2$O$_3$-15(20Ni-Cu)/(85-x)(NiFe$_2$O$_4$-10NiO)(x=0, 0.25, 0.5, 0.75 and 1.0) cermets were prepared from reagent-grade nickel powder (99.9 wt%, Tianjing, China), copper powder (99.9 wt%, Tianjing, China), nickel oxide (99 wt%, Jinchuan, China) and iron oxide (99 wt%, Qidong, China) using an isostatic pressing-sintering process. The raw materials were Fe$_2$O$_3$ and NiO, ball-milled in distilled water for 2 hours, dried for 12 hours at 90°C and then calcinated in air at 1200°C for 4 hours. Yb$_2$O$_3$ and 20Ni-Cu powder were added to the calcinated powder, and the mixture was uniaxially compacted.

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to form cylindrical blocks (about 20 mm in diameter and 40 mm thick) at 200 MPa and sintered at 1300°C for 4 hours in a nitrogen atmosphere with an original oxygen partial pressure of 100 ppm.

### 2.2 Characterization

The electrolyte used consisted of Na₃AlF₆ (99 wt%, Shanghai, China), AlF₃ (98 wt%, Shanghai, China), CaF₂ (98.5 wt%, Tianjing, China) and Al₂O₃ (98 wt%, Tianjing, China). The composition was 5% CaF₂, 7.43% Al₂O₃ and the balance cryolite (NaF/AlF₃=2.3). A 3-cm distance was used between anode and cathode, and the current density was 1.0 A/cm². Al₂O₃ was added at 15-min intervals based on the electrolytic consumption rate at 80% cathode current efficiency.

The anode was analyzed with XRD and SEM/EDS. The phase composition of the electrolyte and cermet was identified by X-ray diffraction analysis using a Philips PW1390 X-ray diffractometer with Cu-Kα radiation. The microstructure was analyzed with a JSM25600LV scanning electron microscope and XJP26A metallographic microscope.

### 3. Results and Discussion

Fig. 1 shows the metallographic images of the surfaces of the 15(20Ni-Cu)/(10NiO-NiFe₂O₄) and 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) anodes after sintering at 1300°C for 4 hours, and Fig. 2 presents the metallographic images of the 15(20Ni-Cu)/(10NiO-NiFe₂O₄) and 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) polished anodes after electrolysis for 10 hours. The images show a very clear interface between the anode components and the relative density is high. A metal-depleted dense layer formed on the surface of the cermets after electrolysis for 10 hours in high-temperature molten salt regardless of whether the Yb₂O₃ was doped or undoped in the cermets, and the thickness of the metal-depleted dense layer was about 20-50 µm. This suggests that a dense layer of NiFe₂O₄-NiAl₂O₄-FeAl₂O₄ ceramic favorably formed on the surface of the anodes during electrolysis.

Fig. 1 shows the metallographic images of the surfaces of the 15(20Ni-Cu)/(10NiO-NiFe₂O₄) and 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) anodes after sintering at 1300°C for 4 hours.
Fig. 2 presents the SEM images and EDX analysis of the surface 0.5Yb$_2$O$_3$-15(20Ni-Cu)/(10NiO-NiFe$_2$O$_4$) polished anodes after sintering at 1300°C for 4 hours, and Fig. 4 shows the SEM images and EDX analysis of the 0.5Yb$_2$O$_3$-15(20Ni-Cu)/(10NiO-NiFe$_2$O$_4$) polished anodes after electrolysis for 20 hours. Every interface is very clear, and the results of the EDX analysis show that the white particles in Fig. 3 are Yb$_2$O$_3$. Fig. 3 (b), (c) and (d) indicate that the Yb content was 10.74 at%, 16.70 at% and 12.13 at%, respectively.

Fig. 3. the SEM image and EDX analysis of the surface 0.5Yb$_2$O$_3$-15(20Ni-Cu)/(10NiO-NiFe$_2$O$_4$) polished anodes after sintering at 1300°C for 4 hours
A metal-depleted dense layer was produced on the surface of the 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) anode after electrolysis for 20 hours, and its thickness was 20 µm. According to the EDX analysis in Fig. 4 (b), (c) and (d), the Yb content was 12.13 at%, 15.40 at% and 8.43 at%, respectively, which was a little lower than the sample after sintering. These results indicate that the Yb₂O₃ or YbFeO₃ was corroded by the high-temperature molten salt electrolyte during electrolysis, and the Yb element gradually entered the electrolyte and the primary aluminum.

The formation law of the dense NiFe₂O₄-Ni₃A₂O₄-FeAl₂O₄ ceramic layer has been investigated previously. The progression of mutual diffusion, volume expansion and interaction took place during the formation of the dense layer, indicating that Yb₂O₃ or YbFeO₃ was involved in this process and also took part in the mutual reaction, which is a part of the dense NiFe₂O₄-Ni₃A₂O₄-FeAl₂O₄ ceramic layer.

To survey the differences in corrosion resistance between Yb₂O₃ or YbFeO₃ and NiFe₂O₄-Ni₃A₂O₄-FeAl₂O₄, electrolysis was carried out over an extended time in the lab-scale electrolytic tank. Figures 5, 6, 7 and 8, respectively, show the SEM images of the bottom of the anodes and EDX analysis of the 15(20Ni-Cu)/(10NiO-NiFe₂O₄), 0.25Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄), 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) and 0.75Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) cermets after electrolysis for 100 hours with an alumina concentration of 7.43%. The compact layer was about 50 µm, 30 µm, 30 µm and 100 µm thick at the bottom of the anode, respectively. Unfortunately, there are some fractures on the 1.0Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) anode during electrolysis so the thickness of the compact layer was not measurable, revealing that the excess Yb₂O₃ was disadvantageous to the corrosion resistance of the anode. In addition, on the basis of the EDX analysis in Figs. 5–8, the Yb element was not found, indicating that the Ni, Fe and Cu elements were corroded during the dynamic corrosion balance of the dense layer on the surface of the anodes. At the same time,
either corrosion of the Yb element or preferential corrosion of the Yb element had taken place.

(a) SEM image             (b) EDX analysis of point seven

<table>
<thead>
<tr>
<th>Element</th>
<th>At%</th>
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<tr>
<td>O K</td>
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<tr>
<td>Al K</td>
<td>1.31</td>
</tr>
<tr>
<td>Fe K</td>
<td>29.91</td>
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<tr>
<td>Ni K</td>
<td>14.40</td>
</tr>
<tr>
<td>Cu K</td>
<td>0.45</td>
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</tbody>
</table>

(c) EDX analysis of point eight  
(d) EDX analysis of point nine

Fig. 5 the SEM images of the bottom of the anodes and EDX analysis of the 15(20Ni-Cu)/(10NiO-NiFe2O4) cermets after electrolysis for 100 hours with an alumina concentration of 7.43%
Fig. 6 the SEM images of the bottom of the anodes and EDX analysis of the 0.25Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) cerments after electrolysis for 100 hours with an alumina concentration of 7.43%

(c) EDX analysis of point eleven

Fig. 7 the SEM images of the bottom of the anodes and EDX analysis of the 0.5Yb₂O₃-15(20Ni-Cu)/(10NiO-NiFe₂O₄) cerments after electrolysis for 100 hours with an alumina concentration of 7.43%

(a) SEM image
(b) EDX analysis of point twelve
(c) EDX analysis of point thirteen
(d) EDX analysis of point fourteen
The dense ceramic layer can prevent the molten salt electrolyte from penetrating into the anode due to its high density and excellent corrosion resistance. Therefore, during the dynamic corrosion balance of the dense layer, several reactions may occur, as shown in equations 1 to 9. The NiFe$_2$O$_4$, NiA$_2$O$_4$ and FeAl$_2$O$_4$ formed and dissolved continuously during electrolysis because of chemical and electrochemical corrosion. Meanwhile, the Yb$_2$O$_3$ or YbFeO$_3$ gradually dissolved into the electrolyte and the primary aluminum as the impurity substance.

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\begin{align*}
\text{Al}_2\text{O}_3 + \text{NiO} &= \text{NiAl}_2\text{O}_4 \\
\text{FeO} + \text{Al}_2\text{O}_3 &= \text{FeAl}_2\text{O}_4 \\
\text{FeO} + \text{NiO} + \text{O}_2 &= \text{NiFe}_2\text{O}_4 \\
3\text{NiAl}_2\text{O}_4 + 2\text{AlF}_3 &= 3\text{NiF}_2 + 4\text{Al}_2\text{O}_3 \\
3\text{FeAl}_2\text{O}_4 + 2\text{AlF}_3 &= 3\text{FeF}_2 + 4\text{Al}_2\text{O}_3 \\
3\text{NiFe}_2\text{O}_4 + 12\text{AlF}_3 &= 3\text{NiF}_2 + 6\text{FeF}_2 + 4\text{Al}_2\text{O}_3 \\
\text{Yb}_2\text{O}_3 + 2\text{AlF}_3 &= 2\text{YbF}_3 + \text{Al}_2\text{O}_3 \\
\text{YbFeO}_3 + 2\text{AlF}_3 &= \text{YbF}_3 + \text{FeF}_2 + \text{Al}_2\text{O}_3 \\
2\text{NiO} + 4\text{FeO} + \text{O}_2 &= 2\text{NiFe}_2\text{O}_4
\end{align*}
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4. Conclusions

1. A dense layer of NiFe$_2$O$_4$-NiAl$_2$O$_4$-FeAl$_2$O$_4$ ceramic is favorably formed on the surface of anodes only if the electrolysis time is greater than 10 hours.

2. The Yb$_2$O$_3$ or YbFeO$_3$ is gradually corroded by the high-temperature molten salt electrolyte during electrolysis.

3. The NiFe$_2$O$_4$, NiA$_2$O$_4$ and FeAl$_2$O$_4$ are formed and dissolved continuously during
electrolysis because of chemical and electrochemical corrosion. Meanwhile, Yb$_2$O$_3$ or YbFeO$_3$ is gradually dissolved into the electrolyte and the primary aluminum as the impurity substance.

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