# Effect of Additive BaO on corrosion resistance of 10NiO-$NiFe_2O_4$ Composite Ceramic anodes

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**Abstract.**The laboratory-scale performance of aluminum electrolysis show that the 10NiO-$NiFe_2O_4$ composite ceramics doped with 0.5%-1.0%BaO exhibit good general performances during electrolysis testing in a laboratory-scale cell conducted in cryolite electrolyte at 1233K with anode current densities of 1.0A/$cm^2$, which lasted for 10 hours.Moreover, the wear rate of 10NiO-$NiFe_2O_4$, 0.5BaO/(10NiO-$NiFe_2O_4$), 1BaO /(10NiO-$NiFe_2O_4$), 2BaO/(10NiO-$NiFe_2O_4$) and 4BaO/(10NiO-$NiFe_2O_4$) is 5.90 cm·$year^{-1}$,4.27cm·$year^{-1}$,3.66 cm·$year^{-1}$,4.06cm·$year^{-1}$ and 4.57 cm·$year^{-1}$,respectively. Thus the addition of BaO to 10NiO-$NiFe_2O_4$ cermet is advantageous, but excessive BaO is adverse to corrosion resistance of 10NiO-$NiFe_2O_4$ cermet.

## Introduction

In recent years, the cermet has become one of the most promising inert anode materials due to its high ceramic corrosion resistance and metallic electric conductivity. $NiFe_2O_4$ is the first choice as ceramic matrix for cermet inert anode because of its good performance including high melt point, good corrosive resistance, stably thermal and chemical property. The aluminum electrolysis generally happen in cryolite molten salt at 960℃, so the inert anode should have high densification, high electric conductivity, strong corrosive resistance, thermal stability, and low overvoltage for oxygen evolution[1-3]. The pilot scale of 6000A experiment [4], with the support by US Department of Energy, exposed the low relative density, unsatisfied electrical conductivity and high wear rate. Hence, it is important to improve its corrosive resistance and other properties.

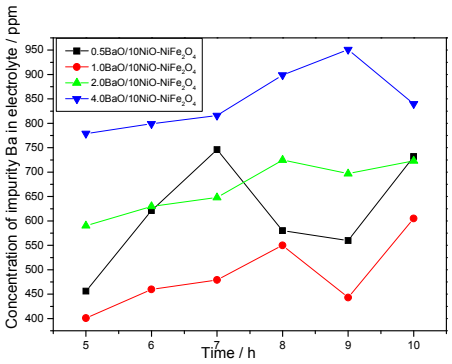
The corrosion resistance of $NiFe_2O_4$-based cermet, a potential inert anode material for aluminum electrolysis, is dependent on its relative density. Conventional sintering enhances the densification usually by increasing the sintering temperature, but the samples of grain coarsening result in low mechanical performances and electrical conductivity. Activated sintering is an effective measure to gain cermet of high relative density and close grain. Some metal oxide, such as BaO[5-8] and CaO[9-10] , may be the selective additive , which do not contaminate the aluminum produced.

In this paper, 10NiO-$NiFe_2O_4$ composites doped with BaO were prepared by cold isostatic pressing-sintering. In order to give some available advice for the choice of inert anode, the effect of BaO content on the corrosion resistance of 10NiO- $NiFe_2O_4$ composite ceramics were investigated.

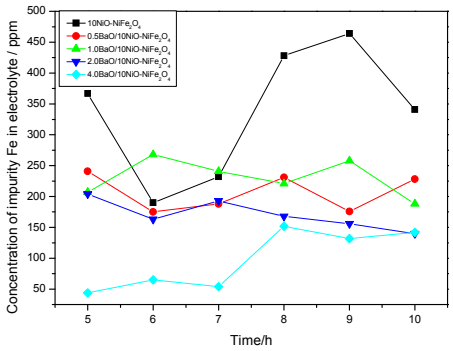
## Results and discussion

**Impurities concentration in bath during electrolysis.**From Fig.1, it is clear that the different ceramic composition showed a varying dissolution degree of anode components. For the 10NiO-$NiFe_2O_4$ ceramic anode, the steady state of impurities Ni and Fe is reached and the average concentrations are 68ppm and 353ppm, respectively, when the electrolysis ends. Compared with the solubility of impurities Ni and Fe mentioned by DeYoung (bath ratio 1.1, melt with 6.5 wt% $Al_2O_3$, 1000℃)[11], the values are far below the solubility (90ppm for impurity Ni, 580ppm for impurity Fe). However, for the ceramic anode which are studied and contain the oxide BaO as modifying

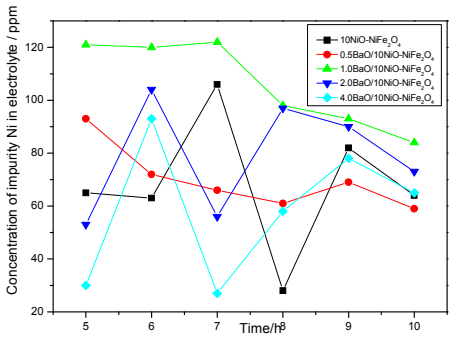
agent, the concentration of impurities in the electrolyte increases. For example, for the investigated ceramic anodes, which the content of the oxide BaO is 0.5%, 1.0%, 2.0% and 4.0%, the average concentration of impurity Ni in the bath are 70ppm, 106ppm, 78ppm and 59ppm, respectively; the average concentrations of impurity Fe are 206ppm, 230ppm, 142ppm and 78ppm, respectively; the average concentrations of impurity Ba are 615ppm, 490ppm, 668ppm and 847ppm respectively at the end of electrolysis testing. From the concentration of impurities in the bath during electrolysis, it indicates that addition of the oxide BaO to ceramic anode as modifying agent is advantage for anti-corrosion to reduce the Fe concentration in molten cryolite, but the corrosion degree of ceramic anode deteriorates with the content of BaO increases.




(a) impurity Ba versus time




(b) impurity Fe versus time




(c) impurity Ni versus time

Fig.1 Elemental analyses of the electrolyte contamination of anode constituents versus time for the ceramic electrodes

**Anode Wear rate.**

The equation of annual corrosion rate of inert anode,

$$W_{loss} = (W_b \times C_b + W_a \times C_a) \times 10^{-6} \times 365 \times 24 / (s_{anode} \times \rho_{anode} \times t) \quad (1)$$

Where $W_{loss}$ is annual corrosion rate of inert anode(cm/a), $W_b$ total quality of electrolyte(g), $C_b$ impurity concentration of electrolyte($10^{-6}$), $W_a$ total quality of aluminum after electrolysis(g), $C_a$ impurity concentration of aluminum after electrolysis ($10^{-6}$), $S_{anode}$ total anode area immersed in electrolyte($cm^2$), $\rho_{anode}$ relative density of anode ($g/cm^3$),t electrolysis time(h)

From Table.1 and Table 2, The total impurities (Fe and Ni) from 1BaO/(10NiO-$NiFe_2O_4$) composite ceramic anode is the lowest in test. Moreover, the wear rate of 10NiO-$NiFe_2O_4$, 0.5BaO/(10NiO-$NiFe_2O_4$), 1BaO/(10NiO-$NiFe_2O_4$), 2BaO/(10NiO-$NiFe_2O_4$) and 4BaO/(10NiO-$NiFe_2O_4$) is 5.90 $cm \cdot year^{-1}$,4.27$cm \cdot year^{-1}$,3.66 $cm \cdot year^{-1}$,4.06$cm \cdot year^{-1}$ and 4.57 $cm \cdot year^{-1}$, respectively. The addition of BaO to 10NiO-$NiFe_2O_4$ composite cermic is advantageous, but excessive BaO is adverse to corrosion resistance of 10NiO-$NiFe_2O_4$ cermet. Possibly because BaO can effectively promote relative density of 10NiO-$NiFe_2O_4$ composite ceramic and thus improve its corrosion resistance.

Table 1 net increment of elements from anode distributed in electrolyte and aluminum cathode

| sample | increment in electrolyte /g | | | increment in cathode /g | | |
|---|---|---|---|---|---|---|
| | Ba | Fe | Ni | Ba | Fe | Ni |
| $NiFe_2O_4$-10NiO | — | 0.11 | 0.02 | — | 0.21 | 0.24 |
| 0.5BaO-($NiFe_2O_4$-10NiO) | 0.18 | 0.06 | 0.02 | <0.006 | 0.13 | 0.03 |
| 1.0BaO-($NiFe_2O_4$-10NiO) | 0.15 | 0.07 | 0.03 | <0.006 | 0.08 | 0.03 |
| 2.0BaO-($NiFe_2O_4$-10NiO) | 0.20 | 0.05 | 0.02 | <0.006 | 0.10 | 0.03 |
| 4.0BaO-($NiFe_2O_4$-10NiO) | 0.25 | 0.03 | 0.02 | <0.006 | 0.12 | 0.03 |

Table 2 total impurity increment and wear rate of xBaO/$NiFe_2O_4$-10NiO composite ceramics after electrolysis

| Doping content of BaO/wt% | Increment in electrolyte/g | Increment in aluminum/g | Total increment/g | Wear rate /cm/a |
|---|---|---|---|---|
| 0 | 0.13 | 0.45 | 0.58 | 5.90 |
| 0.5 | 0.26 | 0.16 | 0.42 | 4.27 |
| 1 | 0.25 | 0.11 | 0.36 | 3.66 |
| 2 | 0.27 | 0.13 | 0.40 | 4.06 |
| 4 | 0.30 | 0.15 | 0.45 | 4.57 |

Generally speaking, the composite ceramic anodes investigated may deteriorate in operating Hall cells by a number of possible mechanisms such as chemical dissolution, electrochemical dissolution, reduction by dissolved metal aluminum, electrolyte penetration, and grain boundary attack[12]. Under the current electrolysis conditions, chemical dissolution, electrolyte penetration and grain boundary attack serve as three major corrosion mechanisms.

There were several possible reactions during electrolysis:

$$2AlF3\,(l) + 3\,FeO\,(s) = 3FeF2\,(l) + 3/2O2\,(g) + 2Al\,(l) \quad (2)$$

$$2AlF3\,(l) + Fe2O3\,(s) = 2FeF3\,(l) + 3/2O2\,(g) + 2Al\,(l) \quad (3)$$

$$2AlF3\,(l) + 3NiO\,(s) = 3NiF2\,(l) + 3/2O2\,(g) + 2Al\,(l) \quad (4)$$

$$2AlF3\,(l) + 3BaO\,(s) = 3BaF2\,(l) + 3/2O2\,(g) + 2Al\,(l) \quad (5)$$

In all, for the composite ceramic anode doped with 0.5%-1.0%BaO, the corrosion mainly is affected by the chemical dissolution and grain boundary attack, which implies the composite ceramic anode is corroded at stoichiometric ratio and peeled off layer by layer. Thus, the stability of ceramic anode 0.5%-1.0%BaO can be maintained during electrolysis and it shows good corrosion resistance.

## Conclusions

(1)Addition of oxide BaO to ceramic anode as modifying agent is advantageous for anti-corrosion to reduce the Fe concentration in molten cryolite. Thus, the stability of ceramic anode 0.5%-1.0%BaO can be maintained during electrolysis and it shows good corrosion resistance.

(2)Ceramic anode is corroded badly by electrolyte penetration. Possibly because the reaction between bath and composite ceramic anode components (NiO, $NiFe_2O_4$) is limited, but the corrosion of composite ceramic anode doped with BaO is mainly affected by the reaction between bath and the additive BaO.

(3)The wear rate of 10NiO-$NiFe_2O_4$, 0.5BaO/(10NiO-$NiFe_2O_4$), 1BaO/(10NiO-$NiFe_2O_4$), 2BaO/(10NiO-$NiFe_2O_4$) and 4BaO/(10NiO-$NiFe_2O_4$) is 5.90 cm • $year^{-1}$,4.27cm • $year^{-1}$,3.66 cm •$year^{-1}$,4.06cm •$year^{-1}$ and 4.57 cm •$year^{-1}$,respectively. The addition of BaO to 10NiO-$NiFe_2O_4$ composite ceramic is advantageous, but excessive BaO is adverse to corrosion resistance of 10NiO-$NiFe_2O_4$ cermet.

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