Effect of additive BaO on corrosion resistance of xNi/10NiO-$NiFe_2O_4$ cermet inert anodes for aluminium electrolysis

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Abstract. *x*Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-*x*Ni/ (10NiO-$NiFe_2O_4$) cermet (*x*=5,10,17) inert anodes were prepared and their corrosion resistance to Na_3AlF_6-Al_2O_3 melts was studied in laboratory electrolysis. The results show that many pores are produced and electrolytes are infiltrated inside inert anodes during electrolysis based on SEM/EDS of anode. The contamination level of nickle, iron and barium in the electrolyte reach steady state after some irregular behaviour early in the tests according to XRF of electrolyte. And the wear rate of 5Ni/(10NiO-$NiFe_2O_4$), 10Ni/(10NiO-$NiFe_2O_4$), 17Ni/(10NiO-$NiFe_2O_4$), 1BaO-5Ni/(10NiO-$NiFe_2O_4$), 1BaO-10Ni/ (10NiO-$NiFe_2O_4$) and 1BaO-17Ni/ (10NiO-$NiFe_2O_4$) is 1.23 cm·year^{-1},1.42 cm·year^{-1},0.96 cm·year^{-1},3.21 cm·year^{-1},2.37 cm·year^{-1} and 3.94 cm·year^{-1}, respectively. Thus, sintering agent BaO can effectively promote the densification of *x*Ni/10NiO-$NiFe_2O_4$ cermet(*x*=5,10,17) inert anodes, but the addition of 1wt.% BaO(mass fraction) to *x*Ni/10NiO-$NiFe_2O_4$ cermet(*x*=5,10,17) inert anodes has negative effect on corrosion resistance, perhaps because additive BaO exists in the grain boundary, which accelerates the corrosion of *x*Ni/10NiO-$NiFe_2O_4$ cermet(*x*=5,10,17) inert anode.

Introduction

In recent years, $NiFe_2O_4$ 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[1-3]. Attempts have been made to replace the present day consumable carbon anode used in the Hall-Heroult process with an inert anode,the cell reaction then being,

$$2Al_2O_3 = 4Al + 3O_2 \quad (1)$$

The corrosion resistance of $NiFe_2O_4$e-based cermets, a potential inert anode material for aluminum electrolysis, are dependent on its relative density[4-6]. For Conventional sintering, the densification is usually enhanceed by increasing the sintering temperature, but the samples of grain coarsening result in low mechanical properties and electric conductivity, especailly thermal shock. Activated sintering is an effective measure to gain cermets of high relative density and close grain. Many authors have studied the impact of lowering the sintering temperature through modifying cermet composition. Some metal oxide, such as CaO[7-8] and BaO[9-10], may be the selective additive , which do not contaminate the aluminum produced.

In this paper, *x*Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-*x*Ni/(10NiO-$NiFe_2O_4$) cermet (*x*=5,10,17) were prepared by cold isostatic pressing-sintering. In order to give some available advice for the choice of anode constituent, the effect of additive BaO on the corrosion resistance of *x*Ni/10NiO-$NiFe_2O_4$ cerme were investigated . The purpose is to provide feasible cermet composition and reduce the corrosion rate of *x*Ni/10NiO-$NiFe_2O_4$ cermet.

Experimental

Preparation of sample.

*x*Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-*x*Ni/(10NiO-$NiFe_2O_4$) cermet (*x*=5,10,17) were prepared by the conventional ceramic method with reagent grade raw materials of Fe_2O_3, NiO,Ni and BaO.

Firstly, the mixture of Fe_2O_3 and NiO in the molar ratio of 1.35 were mixed and calcined in a muffle furnace for 6h at 1200℃ in static air atmosphere to form 10NiO-$NiFe_2O_4$ ceramic powder. The synthesized powder, Ni and 1wt. %.BaO powder were ground in the mediums containing dispersant and adhesive. Then, the dried mixtures were compacted at a pressure of 200MPa to get cylindrical blocks (φ20mm×45mm), bars. Finally the cermet were sintered at 1200℃ for 4h in nitrogen atmosphere of efficaciously controlled oxygen partial pressure [11].

Characterization.

Microstructure was analyzed with JSM-6360LV scanning electron microscope and EDX-GENESIS energy dispersive spectrometer. The electrolyte was prepared from reagent grade Na_3AlF_6, reagent grade AlF_3, reagent grade CaF_2 and reagent grade $A1_2O_3$ and the composition was: 5% CaF_2, 7.43% $A1_2O_3$, balance cryolite(CR=2.30). The current density of inert anode bottom was 1.0 A/cm^2. Some of electrolyte samples taken during electrolysis were dissolved by $HClO_4$ solution, and analyzed with X-ray fluorenscense spectroscopy(XRF) [12].

The annual wear rate of inert anode is calculated with the following equation,

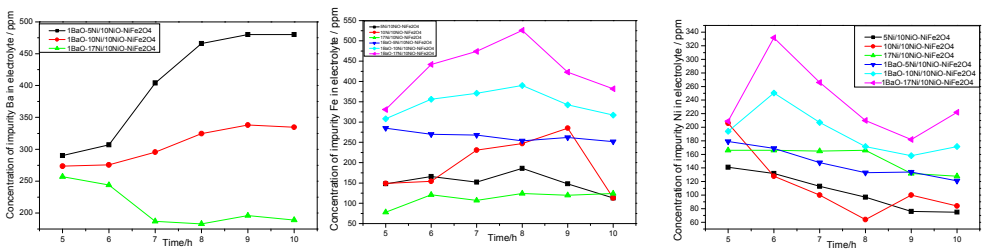
$$W_{loss}=(W_b\times C_b+W_a\times C_a)\times 10^6\times 365\times 24/(s_{anode}\times \rho_{anode}\times t) \quad (2)$$

Where W_{los} is annual wear rate of inert anode(cm·year^{-1}), 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), ρ_{anode} relative density of anode (g/cm^3),t electrolysis time(h).

Results and discussion

Electrolyte test.

As mentioned above, the bath samples taken during eletrolysis were analyzed for the concentration of anode componets and the results are plotted in Fig.1. It is clear that from 5h to 8h the Ba concentration of 1BaO-5Ni/10NiO-$NiFe_2O_4$ cermet rapidly increases in the bath and after 8h reachs the steady state 480ppm, but the Ba concentration of 1BaO-10Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-17Ni/10NiO-$NiFe_2O_4$ cermet reach the steady state 338 ppm and 190 ppm,respectively, in 7h.However, the concentration of Fe and Ni exhibit different behavior. During electrolysis,the Fe concentration rises in a similar manner as Ni and closes to its solubility.After 10h, the corresponding steady-state Fe concentration of 5Ni/10NiO-$NiFe_2O_4$, 10Ni/10NiO-$NiFe_2O_4$, 17Ni/10NiO-$NiFe_2O_4$,1BaO-5Ni/10NiO-$NiFe_2O_4$, 1BaO-10Ni/10NiO-$NiFe_2O_4$ and 1BaO-17Ni/10NiO-$NiFe_2O_4$ is 113*10^{-6}, 113*10^{-6},124*10^{-6},252*10^{-6},317*10^{-6} and 382*10^{-6}, respectively; And the corresponding steady-state Ni concentration is 75*10^{-6} ,84*10^{-6},128*10^{-6},121*10^{-6},172 *10^{-6} and 222*10^{-6}, respectively.



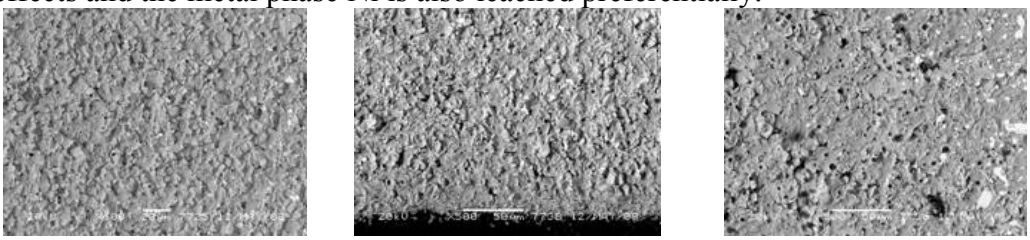
(a) (b) (c)

Fig.1. Elemental analysis of the electrolyte contamination of anode constituents versus time for the cermet electrodes: (a) impurity Ba; (b) impurity Fe; (c) impurity Ni

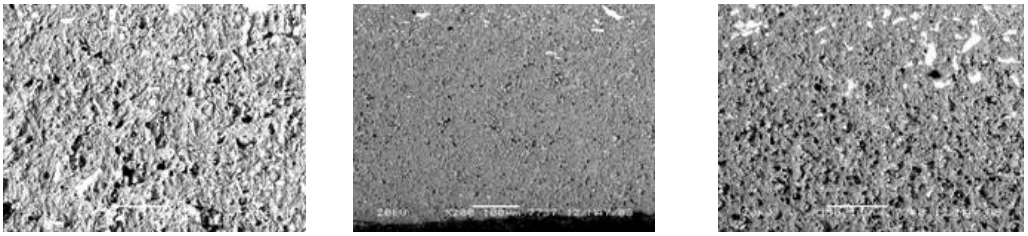
Material performance.

The inert cermet anode is sectioned and there is no any crack after electrolysis. The inert anode has been immersed in the electrolyte (Fig.2) and a corroded layer exists at the anode surface and the depth is about 400 μm at the bottom. From Fig.2(a), Fig.2(c) and Fig.2(e), the porosity of anode is very low and the metal phase Ni is leached preferentially after electrolysis, the anode could effectively hold back the bath penetration because in that 10NiO-$NiFe_2O_4$ shows good corrosion resistance to the molten cryolite during electrolysis. In Fig.2(b), Fig.2(d) and Fig.2(f), it is very

obvious that there are lots of holes and pores left and the bath penetrates into these pores by capillary effects and the metal phase Ni is also leached preferentially.



(a)5Ni/ (10NiO-$NiFe_2O_4$) (500X) (b)1BaO-5Ni/ (10NiO-$NiFe_2O_4$) (500X) (c)10Ni/ (10NiO-$NiFe_2O_4$) (500X)



(d)1BaO-10Ni/(10NiO-$NiFe_2O_4$)(500X)(e)17Ni/(10NiO-$NiFe_2O_4$)(200X)(f)1BaO-17Ni/(10NiO-$NiFe_2O_4$) (200X)

Fig.2. SEM backscattered images of the cermet inert anodes at anode bottom

As for the electrolyte penetration, it may result from two aspects. One is due to the pores left by the electrochemical dissolution of metal phase when anode is polarized, or the metal phase oxidation and the following preferential chemical dissolution, then bath penetrating into these pores by capillary effects. The other is the selective dissolution of Fe, since in the ceramic phase of the $NiFe_2O_4$ based anode, Fe has a fairly high solubility in cryolite, compared with Ni.

Anode wear rate.

According to equation (2), anode wear rate of *x*Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-*x*Ni/(10NiO-$NiFe_2O_4$) cermet (*x*=5,10,17) inert anodes were gained, as shown in Table.1 and Table.2. From Table.1 and Table.2, it is clear that the annual wear rate of 5Ni/(10NiO-$NiFe_2O_4$), 10Ni/(10NiO-$NiFe_2O_4$),17Ni/(10NiO-$NiFe_2O$), 1BaO-5Ni/(10NiO-$NiFe_2O_4$),1BaO-10Ni/(10NiO-$NiFe_2O_4$) and 1BaO-17Ni/ (10NiO-$NiFe_2O_4$) is 1.23 cm·year^{-1},1.42 cm·year^{-1},0.96 cm·year^{-1},3.21 cm·year^{-1},2.37 cm·year^{-1} and 3.94 cm·year^{-1}, respectively. Thus, the corrosion resistance of 1BaO-*x*Ni/ (10NiO-$NiFe_2O_4$) cermet (*x*=5,10,17) inert anodes is worse than that of *x*Ni/10NiO-$NiFe_2O_4$ cermet (*x*=5,10,17) inert anodes.

Table.1 corrosion resistance of *x*Ni/(10NiO-$NiFe_2O_4$) cermet

Ni content wt%	Relative density %	Imputity in electrolyte /g	Imputity in alunimun after electrolysis /g	Total imputity /g	Wear rate /cm·year^{-1}
5	95.3	0.077	0.047 Fe: 0.047; Ni:0.0	0.124	1.23
10	95.3	0.092	0.053 Fe:0.036;Ni:0.017	0.145	1.42
17	94.3	0.080	0.022 Fe:0.015;Ni:0.007	0.102	0.96

Table.2 corrosion resistance of xNi/(10NiO-NiFe2O4) cermet doped with 1%BaO

Ni content wt%	Relative density %	Imputity in electrolyte /g	Imputity in alunimun after electrolysis /g	Total imputity /g	Wear rate /cm·year^{-1}
5	96.7	0.245	0.077 Fe:0.061;Ni:0.016	0.322	3.21
10	97.3	0.254	0.012 Fe:0.012;Ni:0.0	0.266	2.37
17	95.8	0.263	0.152 Fe:0.097;Ni:0.055	0.415	3.94

Conclusions

(1)Ba concentration of 1BaO-5Ni/10NiO-$NiFe_2O_4$ cermet rapidly increases in the bath and after 8h reachs the steady state, but that of 1BaO-10Ni/10NiO-$NiFe_2O_4$ cermet and 1BaO-17Ni/ 10NiO-$NiFe_2O_4$ cermet reach the steady state in 7h. During electrolysis, the Fe concentration rises in a similar manner as Ni and closes to its solubility.

(2)The annual wear rate of 5Ni/(10NiO-$NiFe_2O_4$),10Ni/(10NiO-$NiFe_2O_4$, 17Ni/ (10NiO-$NiFe_2O_4$),1BaO-5Ni/(10NiO-$NiFe_2O_4$),1BaO-10Ni/(10NiO-$NiFe_2O_4$) and 1BaO-17Ni/ (10NiO-$NiFe_2O_4$) is 1.23 $cm\cdot year^{-1}$,1.42 $cm\cdot year^{-1}$,0.96$cm\cdot year^{-1}$,3.21 $cm\cdot year^{-1}$,2.37 $cm\cdot year^{-1}$ and 3.94 $cm\cdot year^{-1}$, respectively.

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References

[1]THONSTAD J, FELLNER P,HAARBERG G M, HIVES J,KVANDE H, STERTEN A. Aluminium.(Diisseldorf:Aluminium-Verlag, Switzerland 2001).
[2]He Han-bing, Li Zhi-you and Zhou Ke-chao. Materials Review, Vol. 21(2008):p.69-72 (in chinese).
[3]He Han-bing, Zhou Ke-chao and Li Zhi-you, Corrosion and protection, Vol.29(2008),p.359-364(in chinese).
[4] A. Ghosh, S. K. Das, J. R. Biswas, H. S. Tripathi and G. Banerjee. Ceramics International, , Vol.26(2000),p.605-608.
[5]Sarkar Ritwik, Das Samir Kumar and Banerjee Goutam. Journal of the European Ceramic Society, , Vol.22(2002),p.1243-1250.
[6]SADOWAY D R. JOM, Vol.53(2001),p. 34-35.
[7]LAI Yan-qing , ZHANG Yong , ZHANG Gang, L I J ie , HE Yue-hui, HUANG Bai-yun and LIU Ye-xiang. The Chinese Journal of Nonferrous Metals, Vol.16(2006),p.1355-1360.(in chinese)
[8]LAI Yan-qing, ZHANG Gang and ZHANG Yong. The Chinese Journal of Nonferrous Metals, Vol.16(2006),p.1608-1614. (in chinese)
[9]HE Han-bing,HUANG Bai-yun, LI Zhi-you and ZHOU Ke-chao.The Chinese Journal of Nonferrous Metals,,Vol.18（2008）,p.851-855 .(in chinese)
[10]HE Han-bing,,ZHOU Ke-chao , LI Zhi-you and HUANG Bai-yun. The Chinese Journal of Nonferrous Metals, Vol.18(2008),p.2255-2260.
[11]LAI Yan-qing, ZHANG Gang, LI Jie and LIU Ye-xiang. Journal of Central South University of Technology (Natural science), Vol.35(2004),p. 880-884.(in chinese)
[12]LAI Yan-qing,TIAN Zhonh-liang,LI Jie, YE Shao-long; LI Xin-zheng and LIU Ye-xiang.Transactions of Nonferrous Metals society of china,Vol.16（2006）,p.970-974.(in chinese)