

## The Metal Phase Selection of 10NiO-NiFe<sub>2</sub>O<sub>4</sub>-Based Cermet Anodes for Aluminum Electrolysis

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### Abstract

$x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet,  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet ( $x=5,10,17$ ) were prepared for aluminum electro-winning and their corrosion resistance into a classical electrolyte was studied in laboratory electrolysis. The results show that preferential corrosion of Ni metal was observed and electrolytes are penetrated into the anode during electrolysis. Nevertheless, this corrosion mechanism was not necessary observed in the cases of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. Moreover, the thickness of the depleted metal zone of cermet inert anode with 20Ni-Cu is thinner than that of Ni and Cu ( $x=5,10,17$ ). According to Gibbs free energy change and wear rate calculations, the corrosion resistance of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is better than that of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. Because of the higher electrical conductivity and the better wettability with ceramic matrix, we observed that nickel addition improves relative density of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and copper enhances the electrical conductivity of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. Thus, the corrosion resistance of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet was found better than both  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet

### 1 Introduction

Oxygen-evolving cermet inert anode is an alternative to the conventional consumable carbon anode for production of aluminum. Copper or nickel is the main metallic constituent in the nickel ferrite cermet investigated in the present work. Odd-Arne Lorentsen [1] studied the nickel ferrite cermet anodes containing 17wt.% copper metal added and the electrolysis tests were run for 48 hours at 960°C. They observed that copper was depleted in the outer zone of the anode. Chin et al [2] dissolved nickel oxide, iron oxide and elemental copper, frequent constituents of inert anodes, in alumina-saturated cryolite melts. They observed that the transfer of these elements from the fluoride melt into the aluminum was complete and that nickel, iron and copper were reduced and alloyed into aluminum in non-electrolytic experiments.

Blinov et al [3] obtained the best results with an inert anode composition of 65wt.% NiFe<sub>2</sub>O<sub>4</sub>-18wt.% NiO-17wt.% Cu, giving a corrosion rate at 800°C of 1.4 cm per year. The mechanisms and kinetics involved in the transfer of inert anode components between the anode and the cathode were investigated by Olsen and Thonstad [4], who developed a cell with

good convection and no concentration gradients.

Special care has to be taken to avoid solid deposits at the cathode.

$x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$ ,  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermets ( $x=5,10,17$ ) were prepared by cold isostatic pressing-sintering, and the corrosion resistance and corrosion mechanism of cermet inert anodes above mentioned were investigated.

### 2 Experimental

#### 2.1 Preparation of samples

$x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermets,  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermets and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  ( $x=5,10,17$ ) cermets were prepared by the conventional ceramic method with raw materials of Fe<sub>2</sub>O<sub>3</sub>, NiO, Cu and Ni reagent grade [5].

#### 2.2 Characterization

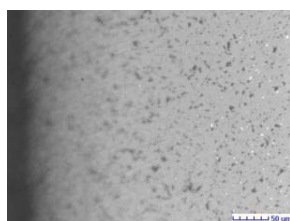
Microstructure was analyzed with JSM-6360LV scanning electron microscope. Bulk densities were calculated by the Archimede's method. Some of electrolyte samples taken during electrolysis were analyzed with X-ray fluorescence spectroscopy (XRF).

### 3 Results and discussion

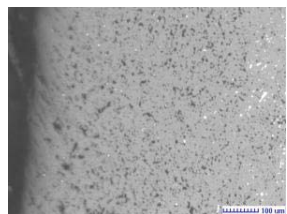
#### 3.1 Material performance

##### 3.1.1 $x\text{Ni}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$ cermet

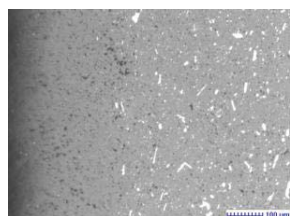
After electrolysis, a depleted metal zone is observed on the surface of the anode and the thickness of the depleted metal zone is about 200-400  $\mu\text{m}$  from the surface that had been immersed in the electrolyte. As observed on Fig 1, the porosity of anode is very high and the metal phase Ni was preferentially leached out during electrolysis. Moreover, many holes were left after electrolysis, which suggested the anode couldn't effectively retain bath penetration. So that, corrosion of  $x\text{Ni}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  cermet anode is mainly due to the corrosion of Ni and the reaction between bath and composite ceramic anode components ( $\text{NiO}$ ,  $\text{NiFe}_2\text{O}_4$ ). It seems that oxygen diffuses into the anode surface to oxidize Ni metallic phase and some electrolyte penetrates into the inert anode. This phenomenon was also found and supported by STRACHAN[6].



(a) 5Ni (100X)



(b) 10Ni (100X)

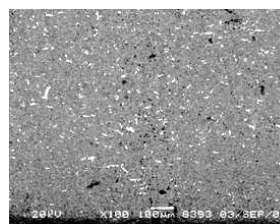


(c) 17Ni (100X)

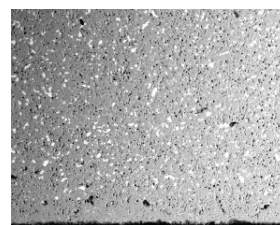
Fig.1 metallographic images of  $x\text{Ni}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  cermet inert anodes at anode bottom

##### 3.1.2 $x\text{Cu}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$ cermet

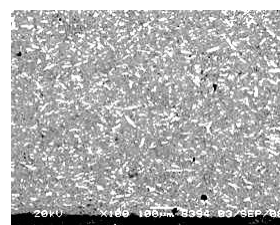
The SEM images are shown in Fig.2. The Cu metallic phase on the anode surface seems not preferentially corroded and the porosity of anode remains low. From Figure 2, we observed that Cu disappeared completely from the surface layer of  $5\text{Cu}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$ ,  $10\text{Cu}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  and  $17\text{Cu}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  cermet anode. The metal-depleted layers are about 50  $\mu\text{m}$ , 40  $\mu\text{m}$  and 30  $\mu\text{m}$ , respectively. Therefore, we concluded that the thickness of the depleted metal zone of the cermet containing Cu is thinner than the one with Ni.



(a) 5Cu (100X)



(b) 10Cu (100X)



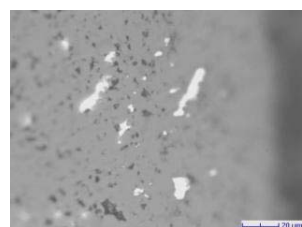
(c) 17Cu (100X)

Fig.2 SEM images of  $x\text{Cu}/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  cermet inert anodes at anode bottom

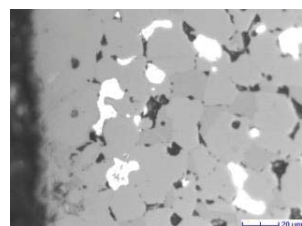
##### 3.1.3 $x(20\text{Ni}-\text{Cu})/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$ cermet

Metallographic images of immersed anode side of  $x(20\text{Ni}-\text{Cu})/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  ( $x=5,10,17$ ) cermets are given in Fig.3. It shows that the porosity of  $x(20\text{Ni}-\text{Cu})/(10\text{NiO}-\text{NiFe}_2\text{O}_4)$  cermet anodes is very low after electrolysis and the thickness of the depleted metal Cu-Ni zone on the surface layer are about 30  $\mu\text{m}$ , 20  $\mu\text{m}$  and 20  $\mu\text{m}$  respectively. This porosity may

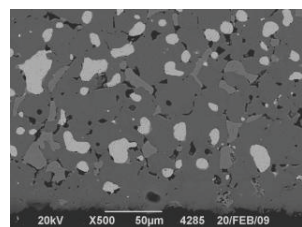
result of the electrochemical dissolution of metal phase when the anode is polarized, or of the metal phase oxidation followed by a preferential chemical dissolution. In all cases, the thickness of the depleted metal zone of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is thinner than in the cases of the  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and of the  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet .



(a) 5(20Ni-Cu) (500X)



(b) 10(20Ni-Cu) (500X)



(c) 17(20Ni-Cu) (500X)

Fig.3 metallographic images of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet inert anodes at anode bottom

### 3.2 Anode Wear rate

From Table 1, we can see that the relative density of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is lower than that of  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. Anode wear rate of  $x\text{Ni}/10\text{NiO-NiFe}_2\text{O}_4$  cermet,  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet ( $x=5,10,17$ ) inert anodes were calculated according to the content of impurities in the electrolyte and aluminum gained from electrolysis. As we can see from Table 1, the annual wear rates of 5Ni/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet, 10Ni/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet, 17Ni/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet are 4.88 cm.a<sup>-1</sup>, 4.70 cm.a<sup>-1</sup> and 4.48 cm.a<sup>-1</sup>,

respectively. The annual wear rate of 5Cu/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet, 10Cu/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet and 17Cu/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet are 1.23 cm.a<sup>-1</sup>, 1.42.cm.a<sup>-1</sup> and 0.96 cm.a<sup>-1</sup>, respectively. Moreover, the annual wear rate of 5(20Ni-Cu)/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet, 10(20Ni-Cu)/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet and 17(20Ni-Cu)/(10NiO-NiFe<sub>2</sub>O<sub>4</sub>) cermet is 0.70 cm.a<sup>-1</sup>, 0.82 cm.a<sup>-1</sup> and 0.65 cm.a<sup>-1</sup>, respectively. Possible causes can be because Cu increases electrical conductivity and nickel has a better wettability with ceramic matrix, which improve corrosion resistance of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet ( $x=5,10,17$ ) inert anode[7].

Table 1 corrosion resistance of  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$ ,  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet

Ni or/and Cu content/wt%	Relative density/%	Total impurity/g	Wear rate/cm a <sup>-1</sup>
5Ni	98.2	0.48	4.88
10Ni	98.1	0.48	4.70
17Ni	96.1	0.47	4.48
5Cu	95.3	0.124	1.23
10Cu	95.3	0.145	1.42
17Cu	94.3	0.102	0.96
5(20Ni-Cu)	98.1	0.08	0.70
10(20Ni-Cu)	98.9	0.10	0.82
17(20Ni-Cu)	98.8	0.07	0.65

### 3.3 Corrosion mechanism

The Gibbs free energy calculations of some reactions at 1273 K are listed in Table 2. From Table 2, the NiO formation Gibbs free energy change is -130.64 KJ.mol<sup>-1</sup>, which is lower than that CuO -41.49 KJ.mol<sup>-1</sup> or Cu<sub>2</sub>O -77.18 KJ.mol<sup>-1</sup>. This implies that the formation of NiO is favored compared to CuO and Cu<sub>2</sub>O. Moreover, the Gibbs free energy change of metal Ni formed NiF<sub>2</sub> is -496.51 KJ.mol<sup>-1</sup>, which is lower than that of metal Cu formed CuF<sub>2</sub> -370.89 KJ.mol<sup>-1</sup>. The results imply that the tendency of metal Ni to form NiF<sub>2</sub> is larger than the formation of CuF<sub>2</sub>

from Cu. Thus, the calculation result of Gibbs free energy change assesses that the corrosion resistance of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is better than that of  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. Copper has a better electrical conductivity and nickel has a better wettability with ceramic matrix, so that, we observed that the mixture of these two metals provided an improvement of their respective properties when mixed with  $(10\text{NiO-NiFe}_2\text{O}_4)$ . Thus, both by experiments and calculation, we concluded that the corrosion resistance of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet was better than  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet in the same conditions.

Table 2 the electrode potential of some reaction at 1273 K

number	reaction equation	Gibbs free energy change (KJ mol <sup>-1</sup> )
1	NiO/Ni	-130.64
2	CuO/Cu	-41.49
3	Cu <sub>2</sub> O/Cu	-77.18
4	NiF <sub>2</sub> /Ni	-496.51
5	CuF <sub>2</sub> /Cu	-370.89

The Gibbs free energy calculations for the reactions of decomposition of NiFe<sub>2</sub>O<sub>4</sub> in NiFe<sub>2</sub>O<sub>4</sub>-based oxides in Table 3 is -138.55 KJ.mol<sup>-1</sup>, which suggest that NiFe<sub>2</sub>O<sub>4</sub> has a tendency to produce NiO and FeO. Moreover, the Gibbs free energy of the

reduction reaction between aluminum and oxides (FeO, Fe<sub>2</sub>O<sub>3</sub>, NiO and CuO) are -771.11 KJ.mol<sup>-1</sup>, -781.81 KJ.mol<sup>-1</sup>, -894.86 KJ.mol<sup>-1</sup> and -523.69 KJ.mol<sup>-1</sup>, respectively, which imply that the tendency of reduction reaction is NiO > Fe<sub>2</sub>O<sub>3</sub> > FeO > CuO. Furthermore, the Gibbs free energy change of reaction between AlF<sub>3</sub> and oxides (FeO, Fe<sub>2</sub>O<sub>3</sub>, NiO and CuO) in Table 3 are 61.52 KJ.mol<sup>-1</sup>, 137.57 KJ.mol<sup>-1</sup>, 81.29 KJ.mol<sup>-1</sup> and 286.26 KJ.mol<sup>-1</sup>, respectively, which imply that the tendency of reduction reaction is FeO > NiO > Fe<sub>2</sub>O<sub>3</sub> > CuO. Due to the lower solubility of Ni compared to Fe and Cu the impurity level in primary aluminum is ordinarily Fe > Ni > Cu.

According to the results mentioned above,  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet,  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet anodes may deteriorate in operating Hall-Heroult cells by different mechanisms such as chemical dissolution, electrochemical dissolution, reduction by Al dissolved in electrolyte, electrolyte penetration, and grain boundary preferential corrosion. According to our experimental observations and calculation results, we concluded that chemical dissolution, electrochemical dissolution and electrolyte penetration serve as three major corrosion mechanisms under the present electrolysis conditions.

Table 3 the Gibbs free energy change of some reaction at 1200 K

number	Reaction equation	Gibbs free energy change (KJ mol <sup>-1</sup> )
6	NiFe <sub>2</sub> O <sub>4</sub> → NiO + 2FeO + 1/2O <sub>2</sub> + 2e	-138.55
7	3FeO(s) + 2Al(l) = 3Fe(s) + Al <sub>2</sub> O <sub>3</sub> (s)	-771.11
8	Fe <sub>2</sub> O <sub>3</sub> (s) + 2Al(l) = 2Fe(s) + Al <sub>2</sub> O <sub>3</sub> (s)	-781.81
9	3NiO(s) + 2Al(l) = 3Ni(s) + Al <sub>2</sub> O <sub>3</sub> (s)	-894.86
10	3CuO(s) + 2Al(l) = 3Cu(s) + Al <sub>2</sub> O <sub>3</sub> (s)	-523.69
11	3FeO(s) + 2AlF <sub>3</sub> (l) = 3FeF <sub>2</sub> (s) + Al <sub>2</sub> O <sub>3</sub> (s)	61.52
12	Fe <sub>2</sub> O <sub>3</sub> (s) + 2AlF <sub>3</sub> (l) = 2FeF <sub>3</sub> (s) + Al <sub>2</sub> O <sub>3</sub> (s)	137.57
13	3NiO(s) + 2AlF <sub>3</sub> (l) = 3NiF <sub>2</sub> (s) + Al <sub>2</sub> O <sub>3</sub> (s)	81.29
14	3CuO(s) + 2AlF <sub>3</sub> (l) = 3CuF <sub>2</sub> (s) + Al <sub>2</sub> O <sub>3</sub> (s)	286.26

#### 4 Conclusions

The thickness of the depleted metal zone of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is thinner than that of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet ( $x=5,10,17$ ). The corrosion resistance of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is better than that of  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. The corrosion resistance of  $x(20\text{Ni-Cu})/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet is better than that of  $x\text{Cu}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet and  $x\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$  cermet. The tendency of reduction reaction is  $\text{NiO} > \text{Fe}_2\text{O}_3 > \text{FeO} > \text{CuO}$ , and the impurity level in primary aluminum is ordinarily  $\text{Fe} > \text{Ni} > \text{Cu}$ . Chemical dissolution, electrochemical dissolution and electrolyte penetration serve as three major corrosion mechanisms under the present electrolysis conditions

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