Available online at www.sciencedirect.com
SCIENCE DIRECT
Trans. Nonferrous Met. Soc. China 16(2006) 970−974
Transactions of Nonferrous Metals Society of China
www.csu.edu.cn/ysxb/

Results from 100 h electrolysis testing of $NiFe_2O_4$ based cermet as inert anode in aluminum reduction

LAI Yan-qing(赖延清), TIAN Zhong-liang(田忠良), LI Jie(李 劼),
YE Shao-long(叶绍龙), LI Xin-zheng(李新征), LIU Ye-xiang(刘业翔)

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

Received 7 December 2005; accepted 6 March 2006

Abstract: A 100 mm diameter cup-shaped inert anode for aluminum electrolysis consisting of cermet 17Ni/83(10NiO-90$NiFe_2O_4$) was prepared and the operating performance was evaluated in a laboratory cell with the electrolyte CR2.3 and Al_2O_3 concentration 7.43% (mass fraction). The results indicate that no major operational difficulties are encountered during the testing which lasts for 101.5 h and the inert anode exhibits good general performances. The steady-state average concentration of impurity Ni in the bath is close to the solubility, however, the Fe concentration is lower than its solubility. The contents of the main contaminants for aluminum produced are Ni 0.128 8%, Fe 1.007 4%. The corrosion rate of inert anode under electrolysis conditions based on the content of impurity Ni in metal aluminum is approximately 8.51 mm/a.

Key words: aluminum electrolysis; inert anode; cermet; $NiFe_2O_4$

1 Introduction

Since the Hall-Héroult process was applied in aluminum production, an inert anode was always the target that the aluminum industry was seeking for in the new technology field[1]. Some selection criteria have been defined in order to identify materials for the use as inert anodes[2,3]. Over the years, many materials have been tested in laboratory. Research on inert anodes was focused on ceramic inert anodes, especially SnO_2-based [4−6] and metallic inert anodes [7, 8], as well as cermet inert anodes[9−11]. Compared with metals and oxides, which can only meet one or two of selection criteria and miss the others, the cermets seem, in this sense, more promising to become the bulk material for the inert anode.

Since 1980, supported by the US Department of Energy, Aluminum Company of America(Alcoa) conducted significant work on the use of ferrites. They developed a new cermet material consisting of a nickel ferrite-nickel oxide substrate containing Cu as a metal phase to provide acceptable electrical conductivity[12]. The work was continued by Battelle Pacific Northwest Laboratories, but they were not able to reproduce the best results obtained by Alcoa.

In previous work, we have tested the $NiFe_2O_4$ based cermet and determined the optimum composition in Na_3AlF_6-Al_2O_3 melts. In this paper, the operating performance of a 100 mm diameter cup-shaped inert anode of cermet, which consisted of 17% (mass fraction) metal Ni and 83% ceramic (10NiO-90$NiFe_2O_4$), was evaluated in a laboratory electrolysis cell. It was the first time that a large anode had been produced. Therefore, the purpose of this test is to determine whether the electrolysis testing with large anode yields results similar to those from the laboratory test with small anodes.

2 Experimental

2.1 Preparation of sample

The raw materials, nickel powder, NiO and Fe_2O_3 were all reagent grade. $NiFe_2O_4$ based cermet samples were prepared by an isostatic pressing-sintering process [13]. A proper amount of Fe_2O_3 and 10% excess NiO, compared with that of the stoichiometric $NiFe_2O_4$, were mixed by ball milling in a stainless steel ball mill. The mixture was dried and then calcined to form the 10NiO-

Foundation item: Project(2005CB623703) supported by the National Basic Research Program of China; Project(50474051) supported by the National Natural Science Foundation of China; Project(03JJY3080) supported by the Natural Science Foundation of Hunan Province, China
Corresponding author: LAI Yan-qing; Tel: +86-731-8830474; E-mail: 13975808172@126.com

$90NiFe_2O_4$ ceramic powder. It was proved by the X-ray diffraction patterns that the calcined powders had $NiFe_2O_4$ and NiO phases. Metal nickel powder of 17% was added to the calcined powder and the mixture was again ball milled. During milling, organic solvent and dispersant were used rather than water because water may cause oxidation of the metal particles. Finally, the mixture were isostaticly pressed into cylindrical blocks and sintered at 1 350 ℃ for 4 h in an atmosphere of efficaciously controlled oxygen partial pressure to get the desired cermet samples.

The diameters of the cup-shaped anode were 102.24 mm at the top, 102.20 mm at the mid-section, and 102.22 mm at the bottom and the height was 117.38 mm. The relative density of samples was 93.52%.

Some kind of transition material was used to connect the anode and the anode rod. A thermocoulpe was located adjacent to the joint point and was insulated with alumina sleeve. This protective sleeve protruded above the cell liner to a cooler zone outside of the furnace. The anode cup was then filled with metallurgical grade alumina.

2.2 Cell design

Under the operating conditions of laboratory test, the cell would not be thermally self-sustaining; it was necessary to provide extra heat by placing the cell in a vertical furnace. The furnace had a minimum cross-sectional dimension of 300 mm diameter. The major components of the cell are shown in Fig.1.

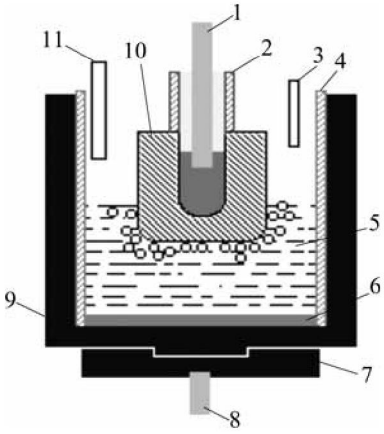

Fig.1 Sketch of electrolysis cell: 1 Anode rod; 2 Alumina sleeve; 3 Bath withdrawing tube; 4 Alumina liner; 5 Electrolyte; 6 Metal aluminum; 7 Graphite mechanical support; 8 Cathode rod; 9 Graphite crucible; 10 Inert anode; 11 Alumina feed tube

The graphite crucible had an outside diameter of 280 mm and an inner diameter of 210 mm. The alumina liner was 200 mm in inner diameter with a wall thickness of 3 mm. This liner extended from the lower crucible edge upward for 300 mm. It contained both the metal cathode pool and the cell electrolyte. The upper liner prevented oxygen generated at the anode from coming into contact with the graphite crucible or the furnace interior. It also defined the current path from the anode to the metal pool and not directly to the sidewall. Two stainless steel rods (diameter 25 mm) were used for electrical connection to the anode and cathode crucible. The anode rod was insulated from the anode support bar by an insulating ring. In addition to supporting the anode assembly, this bar was used to raise and lower the anode to assure a proper distance between the anode and cathode during electrolysis. The cathode rod was connected to the bottom of the graphite crucible and insulated from the furnace. The volume above the upper edge of the crucible and extending to the furnace wall was filled with insulating materials such as silica boards and light mass and high insulating fire brick.

2.3 Electrolysis operation

The electrolyte was prepared from reagent grade Na_3AlF_6, technical grade AlF_3, reagent grade CaF_2 and technical grade Al_2O_3 and the composition was: 5% CaF_2, 7.43% Al_2O_3, balance cryolite(CR=2.30). All compositions were dried at 120 ℃ for 48 h to remove the water before using. The crucible contained a total of 6 200 g electrolyte. Metal aluminum (1 785 g) was added prior to electrolysis. The cell with inert anode was heated to the required temperature 960 ℃ and kept for 2 h before immersing the anode and electrifying 20 min later. The immersion depth of anode was approximately 30 mm.

During the first 42 h, the current was kept at 90 A. Subsequently, it was changed to 60 A. The current density of inert anode bottom was respectively 1.10 and 0.73 A/cm^2. During electrolysis, Al_2O_3 was added at 15 min intervals in amounts based on the electrolytic consumption rate at 70% cathodic current efficiency. Electrolyte (CR=2.1) was supplied to offset the losing caused by volatilization. The cell voltage and reference voltage between inert anode and aluminum electrode were measured. Bath samples were taken just before the addition of alumina and further analyzed to determine the level of anode constituents in the melt. To investigate the thermal shock resistance of anode, two tests were carried out during electrolysis by removing the alumina board above the cell.

After the test, the anode was raised out of the melt while maintaining polarization so as to prevent reduction of the anode material by dissolved metal. The cell was left to cool with the anode resting above the electrolyte. Some of electrolyte samples taken during electrolysis were dissolved by $HClO_4$ solution, and analyzed with X-ray fluorenscense spectroscopy(XRF). The precision

of the analyses was approximately 10% for the measured values below 100×10^{-6}, 5% for values between $(100-1\ 000)\times10^{-6}$ and 3% above $1\ 000\times10^{-6}$. The anode was sectioned, polished and analyzed with SEM/EDS.

3 Results and discussion

3.1 Electrolyte test

During electrolysis, the cell voltage is relatively steady and there is no any sharp fluctuation. The average cell voltage is the 5.592 V when the current is 90 A, and is 4.312 V when the current is 60 A.

An interesting observation of the cermet inert anode is that gas bubbles, almost like a froth with 0.5−1 mm diameter, evolve at the anode surface. The voltage fluctuations due to bubble evolution for anode is shown in Fig.2. The most value of reference voltage variation at anode is 49 mV caused by small bubbles. It is smaller than the 135 mV caused by the graphite anode[2].

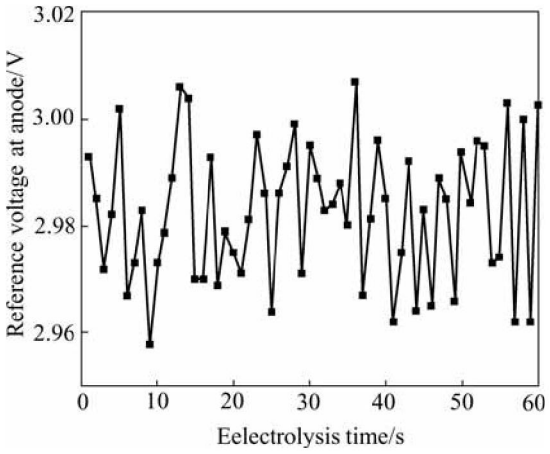

Fig.2 Voltage fluctuation due to bubble formation on anode surface

As mentioned above, the bath samples taken during electrolysis were analyzed for the concentration of anode components and the results are plotted in Fig.3. It is clear that the concentration of Ni rapidly increases in the bath at the beginning and reaches the steady state. The steady-state concentration is 77.83×10^{-6} and fairly close to the solubility measured by DEYOUNG[14] and LAI et al[15]. However, the Fe content exhibits different behaviour, as shown in Fig.3. During the first 3.5 h of electrolysis, the Fe concentration rises in a similar manner as Ni and closes to its solubility. After this initial period, the Fe content falls and reaches steady-state value. When the current is 90 A and 60 A, the corresponding steady-state concentration is 480×10^{-6} and 364×10^{-6}, respectively. The results differ from the previous conclusion of LAI et al[16]. It may be the corrosion mechanisms change under different anode current densities.

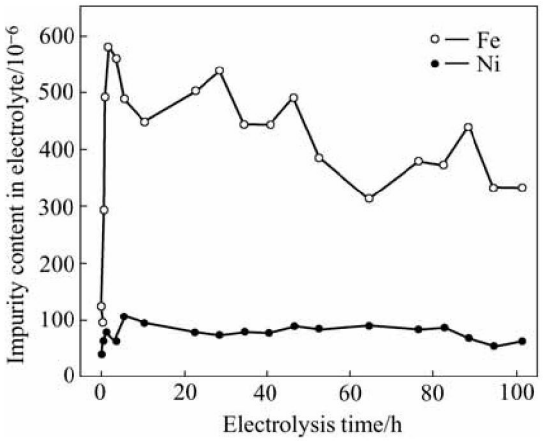

Fig.3 Elemental analyses of electrolyte contamination of anode constituents vs electrolysis time for cermet electrodes

After electrolysis, the current efficiency calculated based on the metal aluminum recovered at cathode is 60.81%. In the cell, the electrolyte is agitated strongly by the oxygen gas bubbles produced at the anode surface. When the gas bubbles move to the cathode surface, they will react with aluminum. In addition, Al_4C_3 is produced at the cathode. All these factors decrease the current efficiency. From Table 1, the iron content is high and can not meet the level of remelting aluminum. The cause is that some Fe enters the electrolyte and further aluminum in the operation such as adding alumina, removing the agglomeration of electrolyte during electrolysis. The anode corrosion rate obtained by the Ni content in recovered metal aluminum is 8.51 mm/a.

Table 1 Impurity content of anode constituents in metal aluminum

Ni	Fe
0.128 8	1.007 4

3.2 Material performance

After electrolysis, there is a black layer of about 1 mm thickness which can be separated easily from the anode surface. It is proved that the layer has single-phase of $NiFe_2O_4$ spinel structure as the X-ray diffraction pattern shown in Fig.4.

The inert cermet anode is sectioned and there is no any crack though twice thermal shock resistance tests are carried out during electrolysis. A corroded layer exists at the anode surface and the depth is about 5 mm at the bottom that has been immersed in the electrolyte (Fig.5). It seems that oxygen diffuses into the anode surface to oxidize the metal phase and some electrolyte infiltrates into the inert anode. This phenomenon was also found by STRACHAN[17].

The SEM images of anode bottom before and after electrolysis are shown in Fig.6. It is obvious that the

metal phase Ni is leached preferentially, there are a lot of holes and pores and the density of the anode surface decreases. The X-ray mapping images near the inert cermet anode bottom surface show that a lot of electrolyte has penetrated into the anode and filled in the pores.

During electrolysis, the decomposition voltage of reaction (1) with unit activity alumina at 1 238 K is 2.240 V (assuming the activity of AlF_3 is 1.5×10^{-3})[18]. Normally, a thin oxide coating will be always present on the anode surface. However, under electrolysis condi-

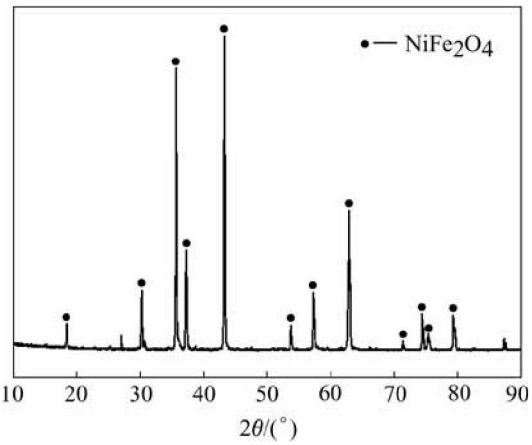

Fig.4 XRD pattern of separated layer

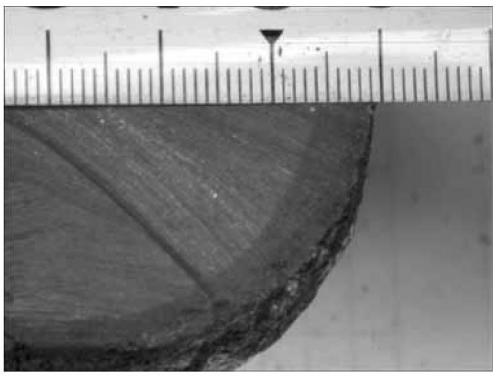

Fig.5 Corroded layer at anode surface

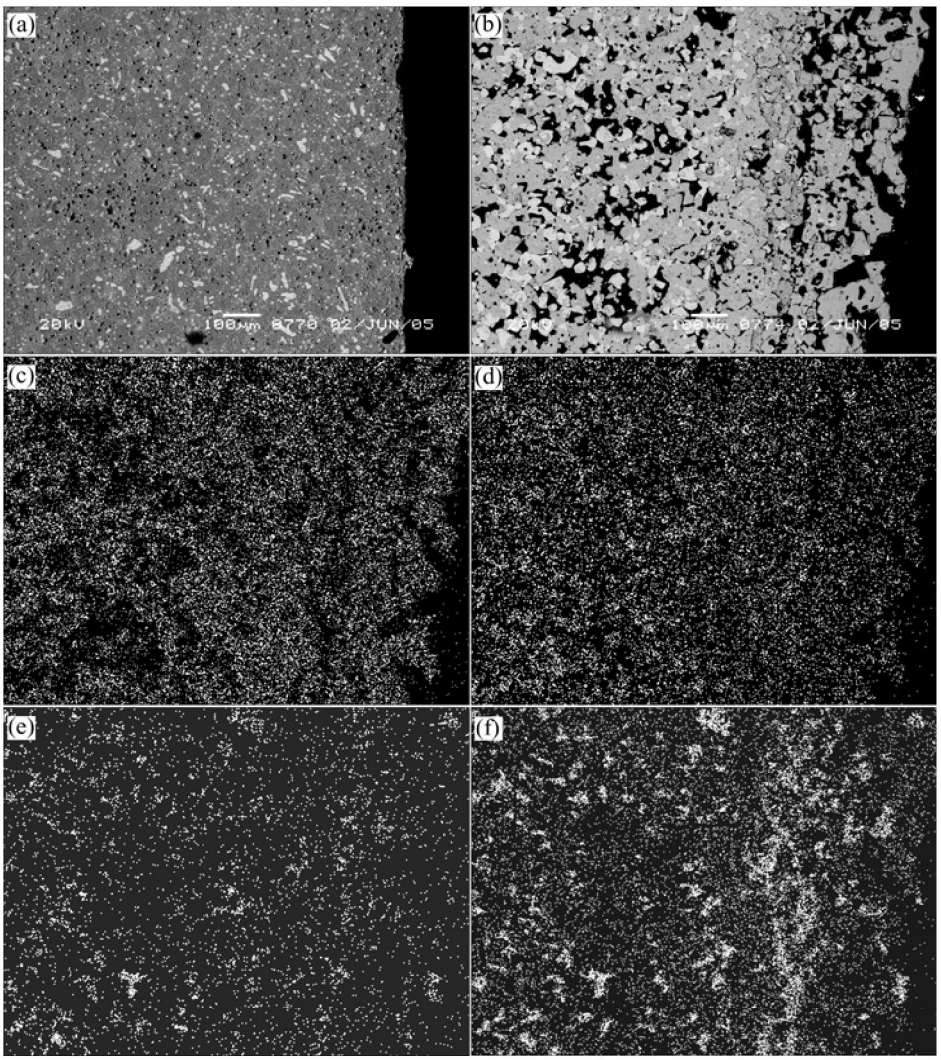

Fig.6 SEM images of anode before and after electrolysis and mapping images for Fe, Ni, Al, F from area near bottom surface: (a) Before electrolysis; (b) After electrolysis; (c) Fe mapping for Fig.6(b); (d) Ni mapping for Fig.6(b); (e) Na mapping for Fig.6(b); (f) F mapping for Fig.6(b)

tion, it should be further noted that the Ni metal present in the anode may fluorinate at 1.912 V, which is lower than that for oxygen production.

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

As for the electrolyte penetration, it may result from two aspects. The first 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 second one 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. In the present work, the relative density of anode is low (only 93.52%) and the metal Ni content is high (17%). To restrain or eliminate effectively the above-mentioned factors, which is adverse to resistance corrosion of inert anode, it is necessary to improve the relative density and decrease the content of metal to enhance the performance of anode resistance corrosion further.

4 Conclusions

1) The $NiFe_2O_4$ based cermet inert anode presents good general performances during electrolysis testing in molten cryolite at 960 ℃. The corrosion rate is 8.51 mm/a based on the Ni content in metal aluminum.

2) The current efficiency is around 60.81% based on the recovered aluminum at cathode. The contents of the main contaminatnts for aluminum produced is Ni 0.128 8%, Fe 1.007 4% and does not reach the comer- cial requirement.

3) From the post-examination with SEM/EDS of the anode, the metal Ni is found to be corroded preferentially and produce many pores during electrolysis.

References

[1] THONSTAD J, FELLNER P, HAARBERG G M, HÍVEŠ J, KVANDE H, STERTEN Å. Aluminium (3rd edition) [M]. Düsseldorf: Aluminium-Verlag, 2001. 328−338.

[2] PETERSON R D, RICHARDS N E, TABEREAUX A T. Results of 100 hour electrolysis test of a cermet anode: operational results and industry perspective [A]. CHRISTIAN M B. Light Metals 1990 [C]. Warrendale, PA: TMS, 1990. 385−393.

[3] MCLEOD A D, LIHRMAN J M, HAGGERTY J S SADOWAY D R. Selection and testing of inert anode materials for Hall cells [A]. ZABREZNIK R D. Light Metals 1987 [C]. Warrendale, PA: TMS, 1987. 357−365.

[4] WANG H, THONSTAD J. The behaviour of inert anodes as a function of some operating parameters [A]. CAMPBELL P G. Light Metals 1989 [C]. Warrendale, PA: TMS, 1989. 283−290.

[5] YANG Jian-hong, LIU Ye-xiang, WANG Hua-zhang. The behaviour and improvement of SnO_2-based inert anodes in aluminium electrolysis [A]. DAS S K. Light Metals 1993 [C]. Warrendale, PA: TMS, 1993. 493−495.

[6] XIAO H. On the Corrosion and the Behavior of Inert Anodes in Aluminium Electrolysis [D]. Trodheim, Norway: Norwegian Institute of Technology, 1993.

[7] WINDISCH C F Jr, MARSCHMAN S C. Electrochemical polarization studies on Cu and Cu-containing cermet anodes for the aluminium industry [A]. ZABREZNIK R D. Light Metals 1987 [C]. Warrendale, PA: TMS, 1987. 351−355.

[8] HRYN J N, SADOWAY D R. Cell testing of metal anodes for the aluminium electrolysis [A]. DAS S K. Light Metals 1993 [C]. Warrendale, PA: TMS, 1993. 475−483.

[9] RAY S P. Inert anodes for hall cells [A]. MILLER R E. Light Metals 1986 [C]. Warrendale, PA: TMS, 1986. 287−298.

[10] OLSEN E, THONSTAD J. Nickel ferrite as inert anodes in aluminium electrolysis (part Ⅰ): Material fabrication and preliminary testing [J]. Journal of Applied Electrochemistry, 1999, 29: 293−299.

[11] TARCY G P. Corrosion and passivation of cermet inert anodes in cryolite-type electrolytes [A]. MILLER R E. Light Metals 1986 [C]. Warrendale, PA: TMS, 1986.309−320.

[12] WEYAND J D, DEYOUNG D H, RAY S P, TARCY G P, BAKER F W. Inert anodes for alulminum smelting, final repore [R]. PA 15069, Washington DC: Aluminum Company of America, February, 1986.

[13] ZHANG Gang, LAI Yan-qing, TIAN Zhong-liang, QIN Qing-wei, LI Jie, LI Wen-xian. Preparation of nickel ferrite based cermets for aluminum electrolysis [J]. Journal of Material Science and Engineering, 2003, 21(4). 44−47. (in Chinese)

[14] DEYOUNG D H. Solubilities of oxides for inert anodes in cryolite-based melts [A]. MILLER R E. Light Metals 1986 [C]. Warrendale, PA: TMS, 1986. 299−307.

[15] LAI Yan-qing, TIAN Zhong-liang, QIN Qing-wei, ZHANG Gang, LI Jie. Solubility of composite oxide ceramics in Na_3AlF_6-Al_2O_3 melts [J]. Journal of Central South University of Technology, 2003, 34(3): 245−248.(in Chinese)

[16] LAI Yan-qing, DUAN Hua-nan, LI Jie, SUN Xiao-gang, LIU Ye-xiang. On the corrosion behaviour of Ni-NiO-$NiFe_2O_4$ cermets as inert anodes in aluminum electrolysis [A]. KVANDE H. Light Metals 2005 [C]. Warrendale, PA: TMS, 2005. 529−534.

[17] STRACHAN D M, KOSKI O H, MORGAN L G, WESTERMAN R E, PETERSON R D, RICHARDS N E, TABEREAUX A T. Results from a 100-hour electrolysis test of a cermet anode: material aspects [A]. CHRISTIAN M B. Light Metals 1990 [C]. Warrendale, PA: TMS, 1990. 395-401.

[18] RAY S P. Effect of cell operating parameters on performance of inert anodes in Hall-H Héroult cells [A]. ZABREZNIK R D. Light Metals 1987 [C]. Warrendale, PA: TMS, 1987. 367−380.

(Edited by YUAN Sai-qian)