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Effect of doping Al on the microstructure of Cu-Ni-NiFe$_2$O$_4$-NiO cermets

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Abstract

Cu-Ni-NiFe$_2$O$_4$-NiO cermets doped with Al (0, 0.8, 2, 3.2 wt%) were prepared by a powder metallurgy process. The effect of Al content, Al adding method and sintering temperature on the microstructure of the cermets were studied using XRD, SEM/EDS, and DSC. The results show that NiO and NiFe$_2$O$_4$ phase are partly reduced to Ni by adding Al at the sintering temperature. The Al element is mainly distributed in the NiFe$_2$O$_4$ phase, and the doping of Al is not conducive to the densification of cermet. The density of the cermet decreases with increasing Al content. The morphology of the metallic phase is related to the Al adding method. Specimens prepared by pre-alloying of Al show smaller metallic particle size than that by mixing of Al. However, the Al adding methods have little effect on the densification and the phase composition. The sintering temperature around the solid phase line of the metallic phase is beneficial to the densification.

1. Introduction

Currently, the aluminum electrolysis process is carried out in Hall—Héroult cell, where the anode is carbon materials and highly corrosive cryolite is adopted as the electrolyte. Consumable carbon anode reacts with oxygen and electrolyte to generate CO$_2$, CF$_3$, and other greenhouse gases in the electrolysis process. To produce 1 ton Al, about 2 ton CO$_2$ will be generated because of the anode consumption. Researchers have been looking for an anode material that is economical and nonconsumable (inert anodes) since the invention of the Hall—Héroult process. The inert anode should have good electrical conductivity, mechanical properties and corrosion resistance. The annual corrosion rate of the inert anode should be less than 1 cm, and the conductivity should be in the level of carbon anode [1]. At present, the most studied materials are Cu-based alloy [2–4], Ni-based alloy [5], NiFe$_2$O$_4$-based cermet [6], and SnO$_2$-based ceramics [7].

Surface characterization is the key for inert anodes remaining inert in Hall—Héroult cells. In 1999, a concept of dynamic inert anode of which the dissolution and formation of oxide film on the anode surface were dynamic equilibrium was put forward by Hryn and Pellin [8]. It is desired to form a dense, corrosion resistant and conductive ceramic layer on the anode surface, which could inhibit the electrochemical corrosion of the metallic phase and ensure the good electrical conductivity of the anode. The surface of these alloy anodes was composed of a mixture of NiFe$_2$O$_4$ which has excellent corrosion resistance in cryolite and other oxides. For example, when the Cu$_{65}$Ni$_{20}$Fe$_{15}$ alloy anode was electrolyzed at 700 $^\circ$C, an oxide film composed of CuO/Cu$_2$O/NiO/Fe$_2$O$_3$/NiFe$_2$O$_4$ was formed [9]. The oxide film was formed mainly by the oxidation of the metallic phase. Because of the volume change during oxidation, internal stress was easily generated in the film or at the film—alloy interface, resulting in delamination, cracking, and shedding of the film. A dense metal-free ceramic surface layer was also found in NiFe$_2$O$_4$-based cermets after 50 h electrolysis, which could prevent preferential corrosion of the metallic phase [10]. Therefore, keeping the stability and reliability of the ceramic surface layer is the main focus of inert anode research.

To better control the structure of the anode surface layer, the formation mechanism of the surface ceramic layer was studied. For alloy anodes, the surface layer was mainly formed through the oxidation of the anode components and the reactions between the oxidation products and the electrolyte [9]. For cermet anodes, the...
formation of the dense ceramic surface layer was caused by the oxidation of the metallic phase, the conversion of NiO to NiFe$_2$O$_4$, and the formation of aluminate generated by the reaction of Al$_2$O$_3$ with the ceramic phase [11–13]. The electrolysis process was also tailored to obtain a dense and stable ceramic surface layer, such as the current density should be in an appropriate range that the corrosion rate and formation rate of the ceramic layer were similar [14, 15]. On the other hand, optimizing the anode composition was a major way. A coherent ceramic surface layer just could be formed in the alloy anode with a suitable Ni/Fe ratio [16, 17] and Cu content [2]. Fe$_2$O$_3$ [18] and NiO [19] of the main composition to be NiFe$_2$O$_4$ was added into Cu-Ni-Fe alloy and Ni-Fe alloy, respectively. The results confirmed that the addition of NiO and Fe$_2$O$_3$ was beneficial to the formation of NiFe$_2$O$_4$ ceramic layer on the anode surface. Ascribe to the addition of Fe in the metallic phase, a dense protective oxide film was also formed on the surface of Cu-Ni-Fe-NiFe$_2$O$_4$ cermets with a metallic phase content of 40 wt% during the electrolysis process through the reaction of newly generated NiO and the Fe-rich NiFe$_2$O$_4$ [4, 20]. Most inert anode forms a protective oxide film generally contained Ni and Fe elements, but Ni and Fe elements were detrimental to the Al quality [21]. Reducing the Ni, Fe content in cathode Al became another research object. Al was added to Cu [9] and Cu-Ni-Fe alloy [3, 22], and the preferential oxidation of Al and the formation of aluminate on the anode surface contributed to the formation of a corrosion resistant surface layer. Some researchers used Al$_2$O$_3$ [23, 24] or NiAl$_2$O$_4$ [25] instead of NiFe$_2$O$_4$ to prepare Al$_2$O$_3$-based or NiAl$_2$O$_4$-based cermets. It is hard to form a dynamic protective film for the complexities of Al$_2$O$_3$ dissolution and aluminate formation.

Al element doped in inert anode would not affect the Al quality and probably be beneficial to the formation of a corrosion resistance surface layer. Until recently, to the best of our knowledge, there is very little literature about the studies on adding Al to NiFe$_2$O$_4$-NiO-Cu-Ni cermet inert anodes. In this paper, the effects of Al content, Al adding method, and the sintering temperature on the microstructure of NiFe$_2$O$_4$-NiO-Cu-Ni cermets were studied.

2. Experimental procedure

2.1. Specimen preparation

Cu-Ni-Al-NiFe$_2$O$_4$-NiO cermets were prepared by powder metallurgy process, similar to the previously reported work [11]. NiFe$_2$O$_4$-NiO ceramic powder with 90% NiFe$_2$O$_4$/10% NiO (wt%) was prepared by high temperature solid phase synthesis. NiO (77.64 wt% Ni, Jinchuan Group Ltd., China) and Fe$_2$O$_3$ (99.60 wt%, 0.75 μm, JFE Chemical Co., Japan) powders were ball milled in a mass ratio of 1 to 1.6 and then calcined in air at 1200 °C for 6 h. Ni (99.9 wt%, 200 mesh, Tianjin Kemilou Chemical Reagent Co., Ltd.), Cu (99.5 wt%, 9.86 μm, Gripm Advance Materials Co., Beijing, China), Al (99.7 wt%, 8–9 μm, Hunan Goldsky Aluminum High-tech Co., Ltd., Hunan, China) powders were mixed using a blender. The mass ratio of Ni/Cu was 1 to 1. The Al content was 0, 2, 5, 8 wt%, respectively. Part of the metallic powder mixture was pre-alkoyed at 900 °C under H$_2$ atmosphere. The synthetic ceramic powder was ball milled respectively with the metallic powder mixture and then calcined in air at 1200 °C for 6 h. NiFe$_2$O$_4$-NiO-Cu-Ni cermet inert anodes were sintered by a heating rate of 10 °C/min and cooling rate of 4 °C/min. The sintered cermets using metallic powder mixture and pre-alkoyed powder as raw material were respectively denoted as MA-x, AA-x, in which x was the theoretical mass fraction of Al in the cermets.

2.2. Characterization

The bulk densities of the sintered specimens were tested using the Archimedes method. Three pieces of same as-sintered samples were taken to measure the bulk density. The theoretical densities of the specimens were calculated using the rule of mixtures calculations. Then, the relative density was equal to the quotient of the bulk density to the theoretical density. The sintered cermets were cut with a diamond cutting machine, and then ground and polished for microstructure characterization. The cross-sectional microstructures of the specimens were examined by scanning electron microscopy (SEM) (Quanta FEG 250, FEI Company, Eindhoven, Netherlands). The element contents and distribution in different phases were analyzed by X-ray energy-dispersive spectroscopy (EDS) (INCA X-MAX50, Oxford, UK). The phase compositions were identified by X-ray diffraction (XRD) (D8 ADVANCE, Brucker AXS, German) with Cu K$_\alpha$ radiation (λ = 0.15406 nm) at a scanning rate of 6° min$^{-1}$ and the specimens were ground into powder with agate before XRD analysis. Differential scanning calorimetry (DSC) (NETZSCH STA 449F3, Selb, Germany) was used to study the thermal reaction of the metallic powder mixture and cermet powder mixture in the heating process in flowing N$_2$ atmosphere with a gas flow rate of 20 ml min$^{-1}$, and a heating rate of 10 °C min$^{-1}$. 

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3. Results

3.1. Microstructure of the specimens

3.1.1. Different Al dopant contents

The specimens were sintered at 1300 °C. The metallic phase was partly exuded on the specimen surface when the Al content was 0.8 wt% or less, and no metallic exudate was found when the Al content was up to 2 wt%. Figure 1 shows the relative densities of the specimens with different Al content. The specimen without Al dopant had the highest relative density of 98%, which was close to the value of 97% reported by Xiong [26]. The relative density decreased slowly as the increase of Al content when the Al content was below 0.8 wt%. When the Al content was above 0.8 wt%, the density dropped sharply, and the relative density of the specimen with 3.2 wt% Al was only 75%.

Figure 2 shows the XRD patterns of the specimens without Al dopant and with 2 wt % Al dopant, respectively. Both specimens were mainly composed of NiFe₂O₄ and NiCu phases. There may be NiO phase, whose diffraction peaks are very close to the NiFe₂O₄ phase. The diffraction peak at 2θ = 37.382° for the specimen without Al was stronger than that doped with 2 wt% Al. Additionally, after doping 2 wt% Al, the diffraction peaks of the NiFe₂O₄ phase shifted slightly towards the diffraction peaks of the Fe₃O₄ phase (PDF75–0449).

Figure 3 shows the micrographs of the specimens doped with different Al content. With increasing the Al content, the number of pores increased obviously. The pore size and the agglomeration of the metallic phase also increased. The NiO phase content decreased and very little NiO phase could be found when the Al content increased to 3.2 wt%.

Table 1 shows the EDS results of the metallic phase and NiFe₂O₄ phase in figures 3(a) and (c). The metallic phase in both specimens was mainly composed of Cu and Ni elements. After doping 2 wt% Al, the Cu/Ni atomic ratio in the metallic phase dropped from 0.95 to 0.70 and the Fe/Ni atomic ratio in NiFe₂O₄ phase increased from 3.04 to 3.19 as compared with that of the specimen without Al dopant. It is indicated the Ni content increased in the metallic phase and decreased in NiFe₂O₄ phase after doping Al. Al content in the metallic phase of the specimen with 2 wt% Al dopant was only 0.04 at%, much lower than the theoretical value of 10.63 at%. Moreover, about 2.33 at% Al was detected in NiFe₂O₄ phase.

3.1.2. Different Al adding methods

The AA-2 and MA-2 specimens were sintered at 1350 °C, and their relative densities were 83.62% and 81.24%, respectively. The relative density of the AA-2 was slightly higher than that of the MA-2. The number of extruded metallic particles on the surface of the MA-2 was less but the particle size was larger than that of the AA-2.

Figure 4 shows the micrographs of the AA-2 and MA-2 specimens. Both specimens had irregular pores. The number and size of the pores in MA-2 were slightly more and larger than that of AA-2. Metallic particles in MA-2 had larger size and more obvious network structure than those in AA-2.

Table 2 shows the EDS results of the metallic phase and NiFe₂O₄ phase in figure 4. The phase compositions of the two specimens were similar. Al was not found in the metallic phase and was mainly distributed in the...
Figure 2. XRD patterns of the specimens sintered at 1300 °C without Al dopant (a) and with 2 wt% Al dopant (b).

Figure 3. SEM images of the specimens with different Al content sintered at 1300 °C: (a) 0 wt%; (b) 0.8 wt%; (c) 2 wt%; (d) 3.2 wt%.
NiFe$_2$O$_4$ phase. It indicated that the adding method of Al mainly affected the micromorphology of the metallic phase and had little influence on the composition of the specimen.

3.1.3. Different Al dopant contents

The MA-2 compacts were sintered at different temperatures. The metallic phase was partly extruded when sintered at above 1300 °C. Figure 5 shows the relative densities of the specimens sintered at different temperatures. With increasing the sintering temperature, the relative density quickly increased first, and then the increase slowed down. When the sintering temperature was higher than 1300 °C, the relative density declined sharply.

Figure 6 shows the SEM images of MA-2 specimens sintered at different temperatures. There were two sizes of metallic particles in the specimen sintered at 1250 °C. The large particles were irregular and the long direction was up to 50 μm, while the small particles were about 10 μm or less. Some large irregular pores also existed. The contrast of NiFe$_2$O$_4$ phase was not uniform. A little dark grey phase was found, especially on the surround of pores. Compared with the specimen sintered at 1250 °C, the number of fine metallic particles in the specimen sintered at 1300 °C decreased sharply. The metallic particles became coarse, and the worm-like morphology of the large metallic particles was much obvious. The number of pore was significantly reduced, and the contrast of NiFe$_2$O$_4$ phase became much uniform, as shown in figure 6(b). However, the number of pores increased again as sintered at 1350 °C.

Table 3 shows the EDS results of the metallic phase and NiFe$_2$O$_4$ phase in figures 6(b) and (c). The Cu/Ni atomic ratios of the metallic phase in the specimens sintered at 1300 °C and 1350 °C were similar, about 0.71, which was less than the theoretical value of 0.99. Al was also found in the NiFe$_2$O$_4$ phase and no Al element was found in the metallic phase. The Fe/Ni atomic ratio in the NiFe$_2$O$_4$ phase in the specimens sintered at 1300 °C and 1350 °C was 3.19 and 3.26 respectively.

Figure 7 shows the elements distribution of the specimen sintered at 1350 °C. The distribution of Cu, Ni elements in the metallic phase and Fe, Ni, O elements in the ceramic phase was uniform, while the distribution of

| Specimen     | Region | Ni      | Fe      | Cu     | O     | Al    |
|--------------|--------|---------|---------|--------|-------|-------|
| Without Al dopant | Point 1 | 48.81   | 1.89    | 46.61  | 2.69  |       |
|              | Point 2 | 9.27    | 28.15   | 0.30   | 62.28 |       |
| MA-2         | Point 3 | 55.68   | 1.76    | 39.20  | 3.37  | 0.04  |
|              | Point 4 | 8.37    | 26.72   | 0.34   | 62.23 | 2.33  |

| Specimen | Region | Ni      | Fe      | Cu     | O     | Al    |
|----------|--------|---------|---------|--------|-------|-------|
| MA-2     | point 1 | 59.24   | 3.95    | 32.94  | 3.87  |       |
|          | point 2 | 7.39    | 23.69   | 0.10   | 64.39 | 4.42  |
| AA-2     | point 3 | 59.54   | 3.09    | 33.75  | 3.62  |       |
|          | point 4 | 7.20    | 22.20   | 0.12   | 64.51 | 5.98  |
Al element in NiFe$_2$O$_4$ phase was inhomogeneous. The Al content in the dark grey region of NiFe$_2$O$_4$ phase was slightly higher than that in the light grey region.

### 3.2. DSC

Figure 8 shows the DSC curves of Cu-47.5Ni-5Al metallic powder mixture, and MA-2 and AA-2 mixed powders. Cu-47.5Ni-5Al mixture had an obvious exothermic peak at 640°C. A small endothermic peak existed at 1250°C, and no endothermic peak of Al melting was found. For the MA-2 mixture, there was an obvious endothermic peak at 657°C, and a wider exothermic peak at 945°C, and a smaller endothermic peak at 1092°C.

| Sintering temperature | Region | Ni   | Fe  | Cu   | O    | Al  |
|-----------------------|--------|------|-----|------|------|-----|
| 1300 °C               | point 1| 55.47| 1.92| 39.05| 3.56 |     |
|                       | point 2| 7.81 | 24.89| 0.63 | 62.34| 4.33|
| 1350 °C               | point 3| 55.35| 0.77 | 39.19| 4.69 |     |
|                       | point 4| 7.45 | 24.33| 0.24 | 63.05| 4.93|

Al element in NiFe$_2$O$_4$ phase was inhomogeneous. The Al content in the dark grey region of NiFe$_2$O$_4$ phase was slightly higher than that in the light grey region.
For the AA-2 mixed powders, only a small exothermic peak appeared at 1052 °C, followed by a small endothermic peak at 1065 °C.

4. Discussions

According to the calculation of thermodynamic data [27], the Gibbs free energy change of reaction formulas (1), (2), (3), and (4) at 1300 °C are $-868.91 \text{ kJ}$, $-16.40 \text{ kJ}$, $-815.28 \text{ kJ}$ and $-124.89 \text{ kJ}$, respectively. It indicates that the four reactions occur at 1300 °C, and reaction (1) is the easiest to conduct. Therefore, NiO and NiFe$_2$O$_4$ phases could be reduced by the adding Al at 1300 °C, resulting in the decrease of NiO content in the specimen and an increase of Ni content in the metallic phase. Although Al could also react with Ni to form intermetallic compounds at 529 °C [28], NiAl intermetallic compounds would be oxidized through the preferential oxidation of Al at high temperature [29]. Al element would be dissociated from the metallic phase and reacted with NiO and NiFe$_2$O$_4$ to produce Al$_2$O$_3$ and FeAl$_2$O$_4$. Then the Al$^{3+}$ in Al$_2$O$_3$ replaced Fe$^{3+}$ in the octahedral position of NiFe$_2$O$_4$ [30]. Additionally, FeAl$_2$O$_4$ and NiFe$_2$O$_4$ are partially dissolved [12]. Therefore, the Al element is mainly distributed in the NiFe$_2$O$_4$ phase.

Figure 7. Element distribution of MA-2 specimen sintered at 1350 °C.

Figure 8. DSC curves of Cu-47.5Ni-5Al mixture (a), MA-2 mixed powder (b) and AA-2 mixed powder (c).
When increasing the Al content, more NiO phase and NiFe2O4 phase were reduced, resulting in the reduction of NiO phase content and the increase of Ni content in the metallic phase. According to the Cu-Ni binary alloy phase diagram [31], the melting point of Cu-Ni alloy increases as the Ni content increases. With the increase of Al content, the liquid phase sintering temperature increased. In the solid sintering process, the densification was primarily controlled by the diffusion of NiFe2O4. Fe was partly dissolved in NiO phase [32], which could increase the vacancy concentration of NiFe2O4 and promote the densification of NiFe2O4. The volume is reduced by 13.24% for reaction (1). Therefore, the reduction of NiO caused by Al was not convenient for the densification of the cermets.

The Cu/Ni atomic ratio in the metallic phase of the MA-2 sintered specimen was 0.7 as shown in table 3, whose solidus and liquidus temperatures were 1301 °C and 1343 °C, respectively. When the sintering temperature was below 1300 °C, the densification of the cermets was depended on the diffusion which related to the sintering temperature. Generally, the higher the sintering temperature is, the higher density of the specimen is. When the cermets were sintered at 1300 °C, around the solidus temperatures, small amount of liquid metal could be formed because of the fluctuation of furnace temperature and the unevenness of the metallic phase composition. Then the transient liquid phase sintering occurred, which promotes the densification. However, much more liquid metal would form as the sintering temperature rose further, then the liquid metal was extruded and formed large pores due to the low wettability between Cu-Ni and NiFe2O4. Then the relative density decreased.

During the heating process, Al would react with Ni to form intermetallic compounds [33]. As shown in figure 8(a), the reaction temperature was 640 °C for Cu-47.5Ni-5Al mixed powder. When Al was added in a mixture, most Al particles were separated from Ni particles by Cu and ceramics particles. The Al was melted firstly, and then reacted with Ni at 945°C (figure 8(b)) as the flowing of liquid Al. At this moment, the sintering of the ceramic phase did not begin. The metal particles grow very quickly during the alloying process, resulting in a large metallic particle and a net morphology. Due to the different diffusion coefficients of Ni and Al, volume expansion occurred during the alloying process, and some large pores were formed [34, 35]. These large pores were hard to be eliminated in the later sintering process [36]. Therefore, the sintered specimen had many large pores.

When Al was added in the form of pre-alloy, in which Al reacted with Ni to form Ni3Al and other intermetallic compounds, and the pores generated by the reaction of Ni and Al could be eliminated before sintering. Therefore, the specimen with alloyed Al had a higher relative density than that of the specimen with mixing Al. According to figure 8(a), the melting point of Cu-47.5Ni-5Al was 1250 °C. Therefore, the specimen with alloyed Al was mainly obtained by solid phase sintering at temperature below 1250 °C. During the heating process, the ceramic phase was gradually densified, and the pore channels between the ceramics grains became smaller. Part of the metal particles has been isolated by the ceramic particles when the metallic phase was melted. The growth of the metallic phase was inhibited, resulting in fine metallic grains. Although the Al was pre-alloyed, the activity of Al was still very high. Al could reduce the ceramic phase at high temperature, leading to an increase of Ni content in the metallic phase.

5. Conclusions

In this work, a cermet with Cu-Ni-Al of 40 wt% and NiFe2O4-NiO of 60 wt% was prepared by sintering at 1200 °C – 1350 °C. The effects of Al content, Al adding method, and sintering temperature on the microstructure of the cermets were studied. The following conclusions are obtained:

1. For the specimen with 2 wt% Al, 1300 °C is a suitable sintering temperature for the cermet. The relative density first increases with increasing sintering temperature. However, the relative density decreases sharply when the sintering temperature is higher than the solidus temperature (1301 °C).

2. The addition of Al is not conducive to the densification of the cermets because of the reaction between Al and the ceramic phase, while the relative density decreases as the increase of Al content.

3. Al added in both mixture and pre-alloy can reduce the content of NiO and NiFe2O4 at sintering temperature, and Al element primarily exists in NiFe2O4 phase.
(4) The morphology of the metallic phase is related to the Al adding method. Specimens with pre-alloyed Al have smaller metallic particle size than that of the mixture sample. Al adding method shows little effect on the densification and the phase composition.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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