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Effect of sintering atmosphere on phase composition and mechanical property of 5Cu/ (10NiO-$NiFe_2O_4$) cermet inert anodes for aluminum electrolysis

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Abstract

5Cu/(10NiO-$NiFe_2O_4$) cermet anodes were prepared by the cold-pressing sintering method in different atmospheres. Furthermore, their phase composition, microstructure and mechanical properties were also investigated. The results reveal that 5Cu/ (10NiO-$NiFe_2O_4$) ceramic material can be obtained by sintering in the vacuum (oxygen content is 0.02ppm) or atmospheres of Ar + air with oxygen content of 10ppm, 200ppm, 2000ppm, and 10000ppm respectively, and phase composition of the ceramics varies with oxygen content of the sintering atmosphere, greatly. Content of $NiFe_2O_4$ in the ceramic materials increases with the increase of oxygen content in the sintering atmosphere, But content of phase Cu decreases with the increase of oxygen content. When oxygen content in the atmosphere is 10ppm, the grain size of 5Cu/ (10NiO-$NiFe_2O_4$) cermet is 5.43 μm, meanwhile the bending strength reaches 80.05 MPa at the room temperature.

Introduction

The traditional industrial production of aluminum has been challenged by its high energy consumption and huge amount of greenhouse gas emission. The application of inert anode replacing carbon anode in Hall-Héroult electrolysis cells has been considered as an effective approach to solve these problems, as well as it can increase the production efficiency.

In recent years, cermet has become one of the most promising inert anode materials, because it not only has good electrical conductivity but also can resist to high temperature corrosion of molten. $NiFe_2O_4$ is often utilized as ceramic matrix for cermet inert anode because of its high melting point, excellent corrosion resistance, and stable thermal and chemical properties [1-4]. With the support by US Department of Energy, Aluminum Company of America (Alcoa) conducted a considerable work about cermet inert anode material. However, the test results of 6kA pilot cell scale showed that both the corrosion resistance and mechanical properties of $NiFe_2O_4$ cermet could not meet the requirements [5].

As well known, the mechanical properties and corrosion resistance of ceramic which are closely related to its phase composition and microstructure are affected by the sintering atmosphere of the preparation process.. Therefore, to improve the properties of $NiFe_2O_4$ cermet, the materials were prepared in different sintering atmospheres. The results showed that ceramic phase of $NiFe_2O_4$ would be probably decomposed if the material was prepared in vacuum or a reductive atmosphere. While the utilization of inert atmosphere not only improves the densification of material but also obtains the expected material. [6-10].

Nevertheless, investigations of mechanical property of $NiFe_2O_4$ cermet inert anodes for aluminum reduction in sintering atmosphere were few. In this paper, 5Cu/(10NiO-$NiFe_2O_4$) cermet was prepared in the vacuum (vacuum degree is 1.0×10^{-2}Pa,and oxygen content is 0.02ppm) and atmospheres of Ar + air with oxygen content of 10ppm, 200ppm, 2000ppm, and 10000ppm (to make the results easy to discussion, the above atmospheres were expressed by G_0, G_1, G_2, G_3 and G_4 respectively), and then, the phase composition, microstructure and mechanical property were studied. This paper aims to provide technical guidance for optimization of preparation process of $NiFe_2O_4$ based ceramic materials.

Experimental

Fabrication of anodes

A mixture of Fe_2O_3 and NiO with the molar ratio of 1.35 was prepared, and then calcined in a muffle furnace at 1200℃ for 6h in a static air atmosphere to form $10NiO\text{-}NiFe_2O_4$ ceramic powder. The synthesized powder and Cu powder were ground in a medium containing dispersant and adhesive. Finally, the mixed ceramic-metal powder was dried and was statically pressed into some bars (6mm × 5mm × 42mm) under 2×10^8Pa. Then they were sintered at 1350℃ for 4h in different atmospheres.

Measurement methods

Phase composition of ceramic material was analyzed by Rigaku3014 X-ray diffraction system, and microstructure was analyzed by JSM-6360LV scanning electron microscope. In addition, the phase composition was measured for three times to insure the reliability of the results.

Three-point-bending strength of the sintered specimen was evaluated with a CSS-44100 electrical universal testing machine by using a span of 30mm and a cross-head speed of 0.5mm/min. Each bending strength data was achieved by the average value with testing for five bars.

Result and discussion

Phase and microstructure

The XRD phase and its quantitative analysis results of $5Cu/(10NiO\text{-}NiFe_2O_4)$ cermet sintered in different atmospheres (G_0, G_1, G_2, G_3 and G_4) are shown in Fig.1and table 1, respectively. From the fig. 1,it is found that all the samples obtained in five different sintering atmospheres contain phases of Cu, $NiFe_2O_4$ and NiO. Table 1 reveals that phase contents of $NiFe_2O_4$ and Cu vary with the changing of O_2 content in the sintering atmosphere, which is also found in literatures [11-12]. Moreover, content of phase $NiFe_2O_4$ in the cermet sintered in atmosphere (G_3 or G_4) is higher than that in the cermet obtained in other atmospheres. It is also noted that content of phase $NiFe_2O_4$ is lowest with 64.9%, while content of Cu is highest with 9% in G_0. Moreover, in G_3, content of phase $NiFe_2O_4$ is 71%, the highest of all, but content of Cu is only 6.2 %, which is lower.

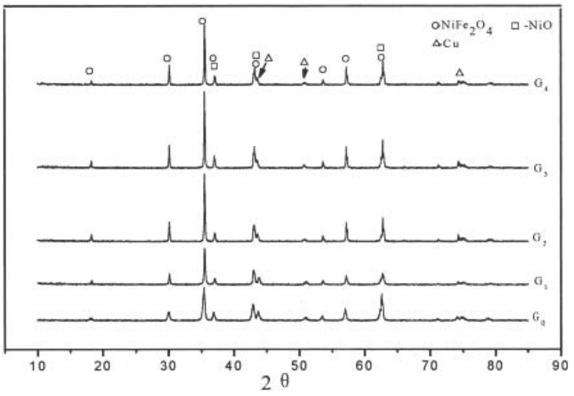


Fig.1 The X-ray diffraction patterns of qualitative analysis of $5Cu/(10NiO\text{-}NiFe_2O_4)$
(G_0, G_1, G_2, G_3 and G_4 in the figure repress samples obtained in different atmosphere)

Table 1 Relative content of phases by XRD quantitative analysis in $5Cu/(10NiO\text{-}NiFe_2O_4)$ cermet

Phase species	Relative content of phases (%)				
	G_0	G_1	G_2	G_3	G_4
$NiFe_2O_4$	64.9	66.3	68.5	71	69.1
NiO	26	26.1	24.3	22.7	25.3
Cu	9	7.6	7.2	6.2	5.6

(G_0, G_1, G_2, G_3 and G_4 repress samples obtained in different atmosphere. Data of phase content was the average value of three repeated experiments under the same condition.)

The reason of the above results can be expressed by the following reaction (1),

$$NiFe_2O_4 \leftrightarrow NiFe_2O_{4-x} + \frac{x}{2}O_2 \qquad (1)$$

It needs to point out that the stoichiometric compound $NiFe_2O_4$ and the nonstoichiometric compound $NiFe_2O_{4-x}$ cannot be distinguished in the XRD analysis. Fe in $NiFe_2O_{4-x}$ has two forms of Fe^{2+} and Fe^{3+}. When oxygen content in the atmosphere increases, Fe^{2+} is oxidized to Fe^{3+}, then Fe^{3+} together with NiO transforms to $NiFe_2O_4$, as a result, phase content of $NiFe_2O_4$ increases.

Furthermore, table 1shows that phase content of NiO in G_0 or

G_1 is higher than that in G_2, G_3, and G_4. The variation of phase content of NiO among G_2, G_3 and G_4 are very small. The reason is that $NiFe_2O_4$ phase will decompose partly in G_0 and G_1, which can be expressed by the following reaction (2).

$$NiFe_2O_4 \leftrightarrow NiO + Fe_2O_3 \qquad (2)$$

Content of phase NiO is related with not only quantity of raw material, but also oxygen content in atmosphere. When oxygen content in atmosphere is higher, such as G_2, G_3 and G_4 $NiFe_2O_4$ phase will decompose no longer. Thus the variation of phase content of NiO from G_2 to G_4 is very small.

In addition, phase content of Cu decreases with the increase of oxygen content in atmosphere. That is probably because that Cu phase is oxidized more easily in atmosphere with high oxygen content. Cu reacts with O_2, and forms Cu_2O or CuO, which can be expressed by reactions (3) and (4) as follow.

$$Cu + \frac{1}{2}O_2 \leftrightarrow CuO \qquad (3)$$

$$2Cu + \frac{1}{2}O_2 \leftrightarrow Cu_2O \qquad (4)$$

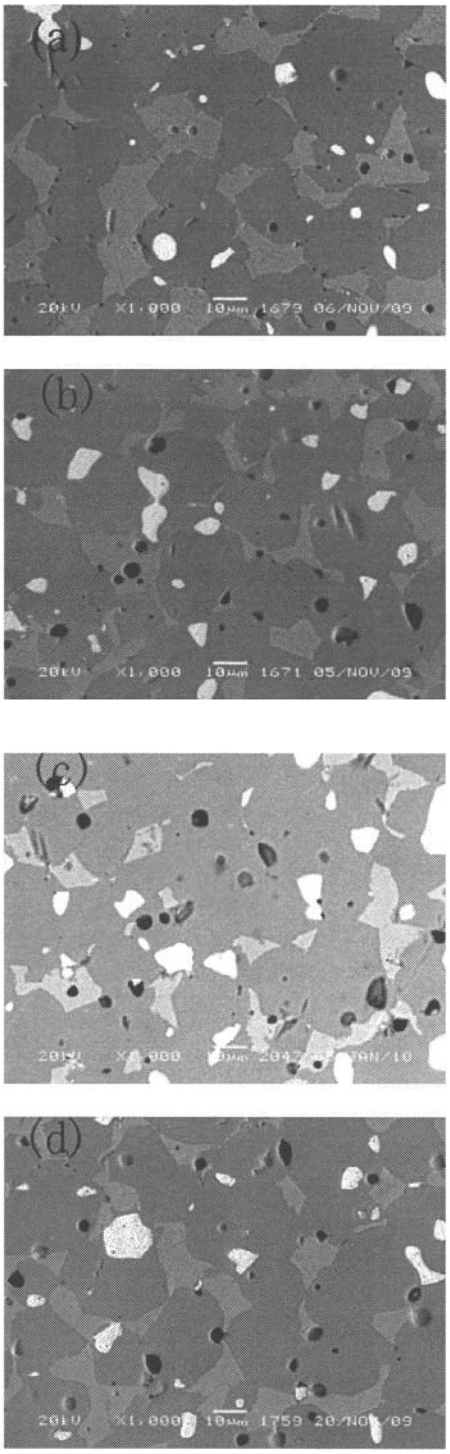
.Table 2 Oxygen partial pressure of different reaction by thermodynamic calculation at 1350℃

Code name of reaction	Oxygen partial pressure /Pa	Oxygen content in atmosphere /ppm
(3)	1428	2856
(4)	49	100

(Oxygen partial pressure was obtained by thermodynamic calculation, and oxygen content in atmosphere was transformed from oxygen partial pressure.)

Oxygen partial pressure of reaction (3) and (4) at 1350℃ are shown in table 2. It reveals that Cu will be partly oxidized to Cu_2O when oxygen content in atmosphere is between 100ppm and 2856ppm. When oxygen content in atmosphere is higher than 2856ppm, Cu phase will be partly oxidized, and form both Cu_2O and CuO.

The microstructures of samples obtained in different atmospheres are illustrated in Fig.2. The dark-gray region, light-gray region and white region represent $NiFe_2O_4$, NiO and Cu respectively. It shows that metallic phase of Cu and NiO in 5Cu/ (10NiO-$NiFe_2O_4$) cermet present polygon graphic, and distribute in phase $NiFe_2O_4$, independently. This phenomenon was also reported in literatures [13-15]. Moreover, metallic phase Cu in 5Cu/ (10NiO-$NiFe_2O_4$) cermet is well distributed when oxygen content in atmosphere is less than 2000ppm. Moreover, phase of Cu almost disappears in the outer layer of the cermet, and layered phenomenon takes place in the cermet when O_2 content in the atmosphere is 10000ppm.



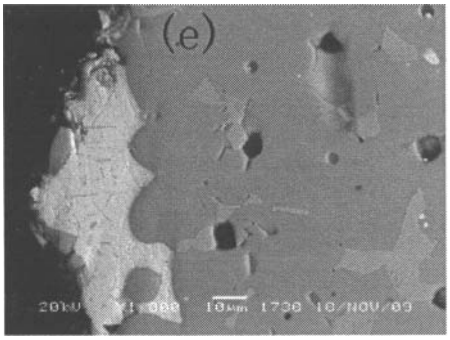


Fig.2 SEM images of 5Cu/(10NiO-$NiFe_2O_4$) cermet in different sintering atmosphere
((a), (b), (c), (d) and (e) represent samples obtained in G_0, G_1, G_2, G_3 and G_4, respectively)

Bending strength

As is shown in table 3, the shrinkage of ceramic material obtained in G_0 is the largest (12.8%), but the shrinkage variation of material obtained in G_1, G_2, G_3 and G_4 are very small. The result also reveals that grain sizes obtained in G_0 (5.76μm), and G_1 (5.43μm) are larger than that obtained in other atmospheres. Meanwhile gain sizes of cermet sintered in G_2, G_3 and G_4 almost have no change. Therefore, oxygen content in atmosphere hardly influenced shrinkage and grain size of ceramic material. That is because that liquid phase sintering is used to prepare 5Cu/ (10NiO-$NiFe_2O_4$) ceramic materials in the study.

Table 3 Shrinkage, grain size and bending strength of 5Cu/(10NiO-$NiFe_2O_4$) cermet

Performance test	Sintering atmosphere				
	G_0	G_1	G_2	G_3	G_4
Shrinkage /%	12.8	11.65	11.9	11.35	11.35
Average grain diameter /μm	5.76	5.43	4.74	4.78	4.77
Bending strength /MPa	72.84	80.05	73.96	65.02	61.87

(G_0, G_1, G_2, G_3 and G_4 repress samples obtained in different atmosphere. Each test in table 3 was reproduced for five times. Data in table 3 was the average value of these five repeated experiments.)

The bending strength decreases with the increase of oxygen content in atmosphere. And bending strength of 5Cu/(10NiO-$NiFe_2O_4$) obtained in G_0 is highest with a value of 80.05MPa. It is could be interpreted by the mixing rule as follow. Generally speaking, there are many factors affected on the bending strength, such as material grain size. Relative density and phase content. And the relation of all the factors can be expressed in the mixing rule[16],

$$\sigma_f = \sigma_r + (\sigma_m - \sigma_r)V_m \qquad (5)$$

$$V_r + V_m = 1 \qquad (6)$$

σ_f - Material bending strength, MPa
σ_m - Bending strength of matrix phase, MPa
σ_γ - Bending strength of strengthening phase, MPa
V_m- Volume fraction of matrix phase, %
V_γ - Volume fraction of strengthening phase, %

The bending strength decreases obviously with increase of O_2 content in the atmosphere, though shrinkage and average grain of ceramic materials obtained in different sintering atmosphere vary inconspicuous. It is the result of comprehensive influence of metallic phase （σ_m）, hard phase （σ_γ） and grain size etc.

Conclusion

Ceramic materials containing the promising phase can be obtained in sintering atmospheres with oxygen content of 10ppm, 200ppm, 2000ppm and 10000ppm, respectively. Phase content of $NiFe_2O_4$ and Cu are affected greatly by the sintering atmosphere. In a word, Ceramic materials tend to have higher phase content of $NiFe_2O_4$ sintered under atmosphere with higher oxygen content, and higher phase content of Cu sintered under atmosphere with lower oxygen content. When oxygen content in atmosphere is 2000ppm or 10000ppm, content of phase $NiFe_2O_4$ is higher. Phase content of Cu is the highest when sintering atmosphere is the vacuum.

With the increase of oxygen content in sintering atmosphere, the bending strength decreases significantly, but both the shrinkage and grain size of 5Cu/ (10NiO-$NiFe_2O_4$) almost have no changes. Results of the above experiments show that when oxygen content in the atmosphere is 10ppm, 5Cu/(10NiO-$NiFe_2O_4$) ceramic material presents the good mechanical property, and the bending strength reaches the highest (80.05MPa).

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