

Effect of sintering atmosphere on phase composition and mechanical properties of 5Ni/(10NiO–NiFe₂O₄)

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Abstract: 5Ni/(10NiO–NiFe₂O₄) cermet materials were prepared by cold pressing sintering method in different atmospheres. The phase compositions were studied by XRD, microstructure was studied by SEM and mechanical properties were studied by three-point-bending strength and heat cycle. The results show that Ni/(NiO–NiFe₂O₄) cermet can be obtained by sintering in vacuum or atmospheres with oxygen content of 2×10^{-5} , 2×10^{-4} and 2×10^{-3} , respectively, but the phase composition of the ceramics varies greatly with oxygen content of the sintering atmosphere. The cermet tends to have a high content of NiO when sintered in vacuum. The content of NiFe₂O₄ and Ni in the cermet materials respectively increases and decreases with increasing oxygen in the sintering atmosphere. In the vacuum, cermet has an average grain size of 3.90 μm and bending strength of 138.59 MPa, which is able to withstand thermal shock tests 6.67 times in average.

Key words: nickel ferrite; cermet; mechanical property; sintering atmosphere

1 Introduction

Consumable carbon anodes have been used in aluminum smelting for more than 100 years. However, some problems such as mass superior carbon consumption and green house gas generation still exist. Inert anodes are not consumed during electrolysis. So, it is hopeful to solve the problems mentioned above. The application of inert anodes is significant to aluminum electrolysis energy saving and environmental protection [1, 2].

In recent years, cermet has become one of the most promising inert anode materials, because of its good electrical conductivity and resistance to high temperature corrosion in molten salts during aluminum electrolysis. NiFe₂O₄ is often studied as ceramic matrix for cermet inert anode because of its high melting point, excellent corrosion resistance and stable thermal and chemical properties. Aluminum Company of America (Alcoa) has conducted considerable study about cermet inert anode materials. However, the test results of 6 kA pilot cell show that both the mechanical properties and corrosion resistance of NiFe₂O₄ cermet could not meet requirements of thermal shock resistance and corrosion

resistance [3].

As well known, good mechanical properties and corrosion resistance of ceramic materials are depended upon its phase composition and microstructure which are affected by the sintering atmosphere of the preparation process. In order to obtain NiFe₂O₄ cermet inert anode with desirable phase composition, ceramic inert anodes are prepared in different sintering atmospheres [4–6], and it is reported that ceramic phase of NiFe₂O₄ would be decomposed in vacuum. When the sintering is conducted in the inert atmosphere, not only the improved densification but also the expected composition of the material is obtained. TIAN et al [7] investigated the effects of sintering temperature, composition and dispersion of the metal phase among ceramic matrixes on the high temperature electrical resistivity of the NiFe₂O₄-based cermet.

The high temperature mechanical properties and corrosion resistance of inert anode are critical for the successful application on aluminum reduction. Nevertheless, few works on mechanical properties of NiFe₂O₄ cermet inert anodes in sintering atmosphere are found. In this work, 5Ni/(10NiO–NiFe₂O₄) cermet was prepared and the phase composition, microstructure and mechanical properties were studied.

2 Experimental

2.1 Fabrication of anodes

A mixture of Fe_2O_3 and NiO with molar ratio of 1.35:1 was prepared. $10\text{NiO-NiFe}_2\text{O}_4$ ceramic powder was fabricated by calcining the above mixture in a muffle furnace at $1200\text{ }^\circ\text{C}$ for 6 h in air. The synthesized powder and Ni powder were ground in a medium containing dispersant and adhesive. Then, the mixed ceramic-metal powder was dried and statically pressed into cubic with size of $5\text{ mm}\times 5\text{ mm}\times 36\text{ mm}$ or cylinder specimen with size of $d20\text{ mm}\times 10\text{ mm}$ under pressure of $2\times 10^8\text{ Pa}$. Finally, the specimens were sintered at $1350\text{ }^\circ\text{C}$ for 4 h in the vacuum ($1.0\times 10^{-2}\text{ Pa}$) and atmospheres of Ar and air with oxygen content of 2×10^{-5} , 2×10^{-4} and 2×10^{-3} , respectively. To make it easy to discuss, the above atmospheres were expressed as A_0 , A_1 , A_2 and A_3 , respectively).

2.2 Characterization techniques

The phase composition of ceramic materials (powder) was analyzed by Rigaku3014 X-ray diffraction system and the microstructure was analyzed by JSM-6360LV scanning electron microscope. The sample preparation includes cutting, inlaying and polishing. The three-point-bending strength of the sintered specimen was evaluated with a CSS-44100 electrical universal testing machine with span of 30 mm at cross-head speed of 0.5 mm/min. Bending strength data were recorded by calculating the average value of 5 samples. Also, thermal shock resistance was tested with heat cycle. The sample was placed in the electric furnace at $960\text{ }^\circ\text{C}$ for 30 min, and then taken out in air to room temperature. This operation was repeated until the sample burst. In addition, the phase composition and thermal shock resistance were measured three times to ensure the reliability of the results.

3 Results and discussion

3.1 Phase and microstructure

The XRD analysis results of $5\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$ cermet sintered in different atmospheres (A_0 , A_1 , A_2 and A_3) are shown in Fig. 1. It is found that all the samples obtained in the four different sintering atmospheres contain Ni , NiFe_2O_4 and NiO phases. The phase quantitative analysis results (Table 1) reveal that all the phase contents vary with the oxygen content in atmosphere. With the increase of oxygen content, NiFe_2O_4 in the cermet increases at the beginning and then decreases, while NiO appears a contrary trend, and Ni decreases gradually, which has the same experiment

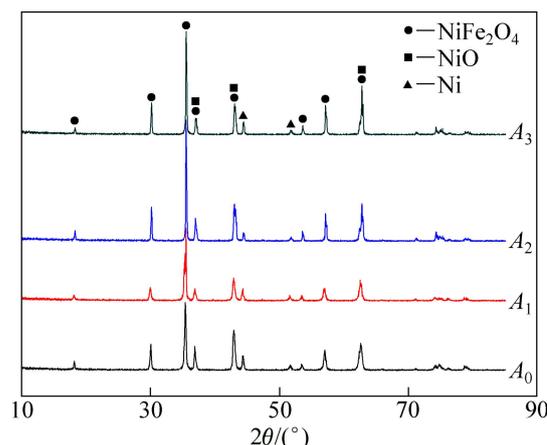


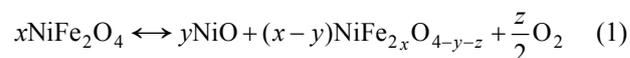
Fig. 1 X-ray diffraction patterns of $5\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$

Table 1 Relative content of phases by XRD quantitative analysis in $5\text{Ni}/(10\text{NiO-NiFe}_2\text{O}_4)$ cermet

Atmosphere	Relative content/%		
	NiFe_2O_4	NiO	Ni
A_0	60.6	30.9	8.5
A_1	66.5	27.0	6.8
A_2	70.7	23.8	5.5
A_3	66.1	30.5	3.4

results as Refs. [9, 10]. It must be pointed out that NiFe_2O_4 content of 60.6% is the lowest, while Ni content of 8.5% is the highest in the atmosphere A_0 . While the sample is sintered in the atmosphere A_2 , NiFe_2O_4 content is 70.7% which is the highest of all, NiO content is 23.8% which is the lowest.

The reasons for the variation of different phase content in the ceramics can be expressed as



Under vacuum condition, reaction (1) moves to the right and reaction (2) moves to the left, therefore, the content of Ni in A_0 is higher than that in other atmospheres, and the content of NiFe_2O_4 is the lowest. Moreover, it needs to point out that the stoichiometric compound NiFe_2O_4 and the nonstoichiometric compound $\text{NiFe}_{2x}\text{O}_{4-y-z}$ cannot be distinguished in the XRD analysis. There are two forms of elemental Fe in $\text{NiFe}_{2x}\text{O}_{4-y-z}$, Fe^{2+} and Fe^{3+} . When the oxygen content in the atmosphere increases, Fe^{2+} in $\text{NiFe}_{2x}\text{O}_{4-y-z}$ is oxidized to Fe^{3+} , then Fe^{3+} together with NiO transforms to NiFe_2O_4 . As a result, NiFe_2O_4 content increases. The change of NiO content is caused by both reactions (1) and (2), when the samples are sintered under atmospheres A_1 and A_2 , the reaction rate of metal Ni oxidated to NiO is slower than

that of NiO reacted to NiFe₂O₄. Consequently, the variation of phase content of NiO is getting less. When the sintering process is conducted in A₃, reaction (2) takes place mainly. Therefore, the content of NiO appears a rising trend, while the content of Ni phase presents a downward trend.

The microstructures of samples obtained in different atmospheres are illustrated in Fig. 2. Through EDAX, the dark-gray region, light-gray region and white region represent NiFe₂O₄, NiO and Ni, respectively. This shows that the change of porosity in 5Ni/(10NiO–NiFe₂O₄) materials is not obvious with the increase of oxygen content. Moreover, metal Ni in nickel ferrite-based cermet most appears spheroidal or long chain-shaped, and forms forked structure, which was also found by ZHANG [10]. It also reveals that Ni appears cross linking to some extent when the oxygen concentration is less than 2×10^{-4} , and the grain size of metal Ni is bigger than that obtained in other atmospheres. While in A₂ and A₃, the distribution of Ni is relatively uniform in nickel ferrite-based cermet.

3.2 Bending strength

As shown in Table 2, the result indicates that the shrinkage of cermet material decreases from 11.95% to 10.75% with the increase of oxygen content from 0 to 2×10^{-4} , and the grain size ranges from 3.9 to 3.28 μm. NiFe₂O₄ is a type of stoichiometric compound with anti-structure defect which makes the grains of NiFe₂O₄ vary in different oxygen contents. When the oxygen content in atmosphere is lower, the oxygen defect concentration of NiFe₂O₄ lattice increases conspicuously, which accelerates the atomic diffusion and makes the grains grow [11–13].

Table 2 Properties of 5Ni/(10NiO–NiFe₂O₄) cermet under different atmospheres

Atmosphere	Shrinkage/%	Average grain diameter/μm	Bending strength/MPa
A ₀	11.95	3.90	138.59
A ₁	11.45	3.61	115.70
A ₂	10.95	3.58	122.30
A ₃	10.75	3.28	123.60

Generally speaking, there are many factors affect the bending strength, such as material grain size, relative density and phase content [14–16]. The relation of all the factors can be expressed in the mixing rule as [17]

$$\sigma_f = \sigma_r + (\sigma_m - \sigma_r)V_m \quad (2)$$

$$V_r + V_m = 1 \quad (3)$$

where σ_f is the material bending strength, MPa; σ_m is the bending strength of matrix phase, MPa; σ_r is the bending strength of strengthening phase, MPa; V_m is the volume fraction of matrix phase, %; and V_r is the volume fraction of strengthening phase, %.

Although the shrinkage and average grain size of the ceramic materials obtained in different sintering atmospheres vary inconspicuously, the bending strength decreases obviously with the increase of O₂ content in the atmosphere. It is the result of comprehensive influence of metallic phase (σ_m), strengthening phase (σ_r) and grain size, etc. From Table 2, it is observed that the highest bending strength of NiFe₂O₄-based cermet of 138.59 MPa can be obtained in A₀ atmosphere. The main reason is that the density of the materials is the highest, and both the contents of strengthening phase and Ni are higher, which can enhance the bending strength to some

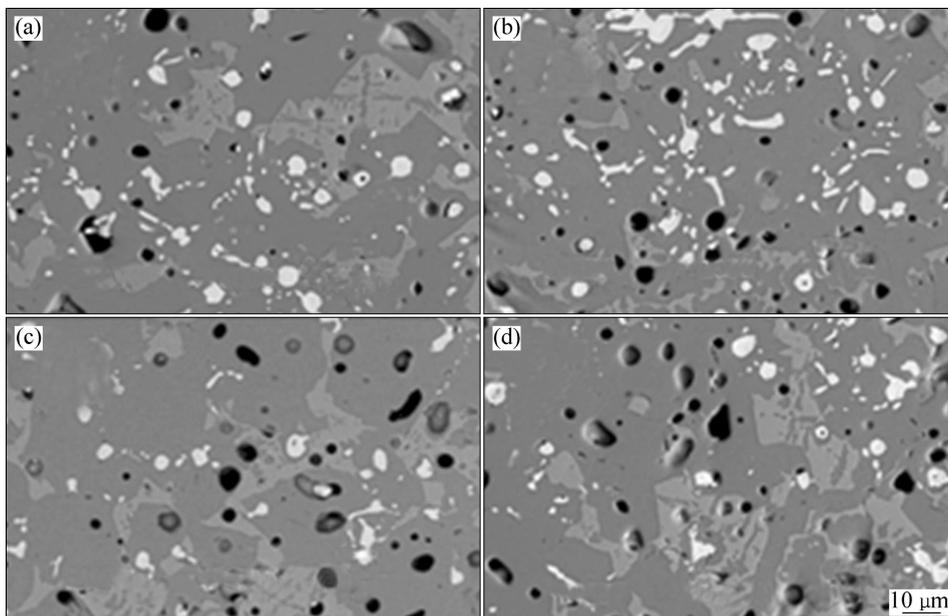


Fig. 2 SEM images of 5Ni/(10NiO–NiFe₂O₄) cermet in different sintering atmospheres: (a) A₀; (b) A₁; (c) A₂; (d) A₃

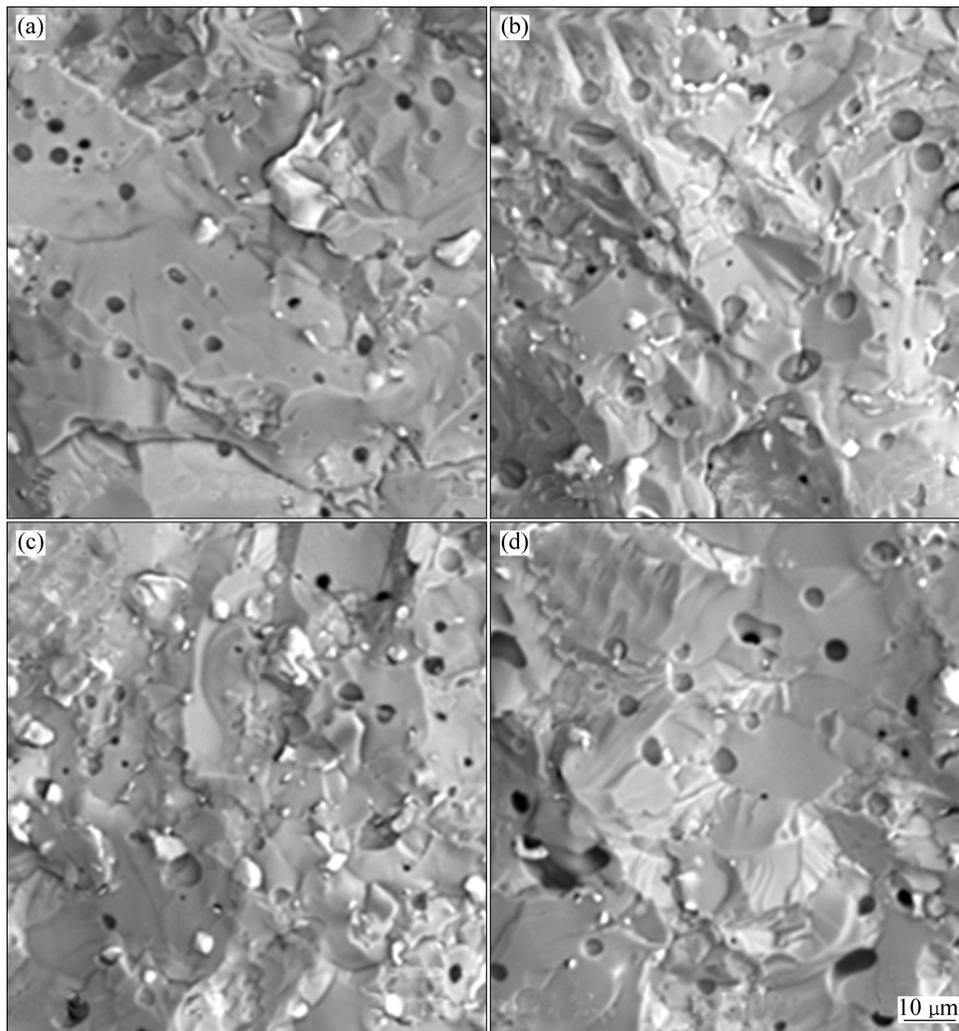


Fig. 3 Fracture surface images of 5Ni/(10NiO–NiFe₂O₄) cermet in different sintering atmospheres: (a) A₀; (b) A₁; (c) A₂; (d) A₃

extent. However, the bending strength of 5Ni/(10NiO–NiFe₂O₄) materials increases with the increase of oxygen content in atmosphere. This is because the strengthening phase (NiO) in 5Ni/(10NiO–NiFe₂O₄) cermet increases with the increase of oxygen content, as seen in Table 1.

As shown in Fig. 3, the fracture of material appears crystalloid, so the fracture is brittle rupture. The fracture shows ice-sugar shape as traditional intercrystalline fracture, and the grains cannot be found obviously. Therefore, the main fracture mechanism of the materials obtained in four atmospheres is transgranular fracture. This illustrates that the bond strength of grain boundary is good.

3.3 Thermal shock resistance

The results of the thermal shock resistant test of the materials are listed in Table 3. The results reveal that 5Ni/(10NiO–NiFe₂O₄) cermet has better thermal shock resistance in A₀ and A₁ than that in A₂ and A₃. The reason for the above phenomenon can be attributed to the high

content of metal phase, which contributes to restrain crack propagation [18, 19]. Moreover, the density has certain influence on the materials thermal expansion, the higher the density of materials is, the smaller interstice of grain is.

Table 3 Thermal shock resistance of 5Ni/(10NiO–NiFe₂O₄)

Sintering atmosphere	Thermal shock cyclic number
A ₀	6.67
A ₁	4.67
A ₂	2
A ₃	2

4 Conclusions

1) 5Ni/(10NiO–NiFe₂O₄) cermet inert anode can be obtained in vacuum or atmospheres with oxygen content of 2×10^{-5} , 2×10^{-4} and 2×10^{-3} , respectively. But the sintering atmosphere has a great influence on the phase content. With the increase of oxygen content in sintering atmosphere, NiFe₂O₄ content increases at the beginning

and then decreases, while NiO content appears the contrary trend and Ni phase content decreases gradually.

2) With the increase of oxygen content in sintering atmosphere, both the shrinkage and the average grain size of 5Ni/(10NiO–NiFe₂O₄) decrease gradually. In vacuum atmosphere, 5Ni/(10NiO–NiFe₂O₄) cermet has an average grain size of 3.90 μm and bending strength of 138.59 MPa, which are able to withstand thermal shock tests averaged 6.67 times.

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烧结气氛对 5Ni/(10NiO–NiFe₂O₄)金属陶瓷物相组成及力学性能的影响

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摘要: 在不同烧结气氛下采用冷压烧结法制备 5Ni/(10NiO–NiFe₂O₄)金属陶瓷, 通过 XRD 研究其物相组成, SEM 研究其显微结构, 并用三点抗弯测试和抗热震实验检测其力学性能。结果表明: 在真空气氛及氧含量分别为 2×10^{-5} 、 2×10^{-4} 和 2×10^{-3} 的气氛中均可获得 Ni/(10NiO–NiFe₂O₄)金属陶瓷, 但气氛中氧含量对物相含量影响较大。在真空气氛中 NiO 含量相对较高。材料中 NiFe₂O₄ 和 Ni 的含量分别随着气氛中氧含量的上升而增加和减小; 在真空烧结气氛中, 可获得晶粒尺寸为 3.90 μm 的 5Ni/(10NiO–NiFe₂O₄)金属陶瓷, 其抗弯强度可达 138.59 MPa, 且在 960 °C 实验条件下平均抗热震循环次数可达 6.67 次, 具有相对较好的力学性能。

关键词: NiFe₂O₄; 金属陶瓷; 力学性能; 烧结气氛