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Densification of Ni-$NiFe_2O_4$ cermets for aluminum electrolysis①

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Abstract: The density of cermet inert anodes in aluminum electrolysis is of great importance. Ni-$NiFe_2O_4$ cermets were studied with respect to their densification affected by ball milling time, particle size of raw powders, contents of metallic phase, sintering atmosphere and temperature. The results show that, prolonging ball milling time will increase the density with the optimum value of 150 min; cermets containing 0-15% Ni(mass fraction) have high relative density ranging from 94% to 96%, but with Ni content increasing, the density slightly decreases; weak reductive atmosphere is favorable to densification; the relative density increases from 80.38% to 96.85% with the sintering temperature increasing from 1 100 ℃ to 1 300 ℃ while it decreases at 1 400 ℃, which may be due to crystal grain coarsening. So the sintering temperature of Ni-$NiFe_2O_4$ cermets in current work should be controlled at 1 300 ℃, where the relative density is 96.85%.

Key words: Ni-$NiFe_2O_4$ cermets; densification; inert anode; aluminum electrolysis
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1 INTRODUCTION

Aluminum electrolysis consumes enormous energy and resources, and the consumption will be considerably decreased by introduction of inert anode and wettable cathode. However, under the tough working condition of aluminum electrolysis, i. e. highly corrosive Na_3AlF_6-Al_2O_3 molten salts at high temperature (940-960 ℃), the inert anodes necessary for the successful production of aluminum might have the following properties: be insoluble in a fluoride melt, be resistant towards anode oxygen, have good electrical conductivity, possess adequate strength at high temperature and be resistant to thermal shock and creep rupture[1, 2].

Cermets and self-passivating alloy are two kinds of candidate inert anode materials, which are intensively studied and seem to be most prospective. The so-called cermets are supposed to contain the advantages of both ceramic materials, i. e. low corrosion and oxidation, and metallic materials, i. e. good electrical conductivity and high thermal shock resistance. The typical cermets compose spinel oxide and metal, i. e. ceramic phases of $Ni_xFe_{3-x}O_4$, $Ni_yFe_{1-y}O$, $NiFe_2O_4$+ NiO, $ZnFe_2O_4$ + ZnO, or $Ni_xFe_{2y}Zn_zO_{(3y+x+z\pm\delta)}$, and metal phases of Cu, Ni, Cu-Ni, Ni-Fe, Cu-Cr, or Cu-Ag. The densification of cermets is of great importance, because high relative density will reduce corrosion rate, lower electronic resistance, improve mechanical strength, avoid oxidation of metal phase and creep rupture because of electrolyte penetration[2-4]. Therefore, based on our previous work to avoid metal bleeding or cluster, in this paper, the effects of ball milling time of raw powder of Ni and $NiFe_2O_4$, contents of metal Ni, sintering atmosphere and sintering temperature on the density of Ni-$NiFe_2O_4$ cermets were studied and the relevant mechanisms were also discussed.

2 EXPERIMENTAL

Raw materials, nickel powder, NiO and Fe_2O_3 were all reagent grade. Ni-$NiFe_2O_4$ cermet samples were prepared with a conventional cold pressing-sintering technique. Proper amount of NiO and Fe_2O_3 were mixed by ball milling and calcined at 1 150 ℃ for 6 h under air to get the stoichiometric $NiFe_2O_4$ powder[5]. The $NiFe_2O_4$ powders and Ni were mixed and micronized by ball milling in the mediums containing dispersant and adhesive in planet ball mill. Finally the dried powders were pressed into cylindrical shape specimens (d20 mm × 40 mm) at the biaxial pressure of 200 MPa and sintered at 1 100-1 400 ℃ for 4 h in con-

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trolled atmosphere to get the desired cermet samples[6].

Particle size distribution analysis was conducted with a laser particle size analyzer(LS601, Zhuhai, China). The relative density, porosity of the cermet samples were tested with the ASTM Archimedes Method C373-88(1999). Phase composition examination was performed with X-ray diffraction analysis in a Rigaku 3014 X-ray diffractometer. Microstructure and composition analysis were carried out using an XJP-6A optical microscope and a scanning electron microscope(JSM-5600LV).

3 RESULTS AND DISCUSSION

3.1 Effect of ball milling time for raw powders of Ni and $NiFe_2O_4$

In the current work the effects of different ball milling time ranging from 0 to 600 min, on the mean particle size and the relative densities were studied. The sintering was conducted at 1 200 ℃ for 4 h and the rotating rate of ball milling was kept at 240 r/min. The results are listed in Table 1.

As listed in Table 1, the relative densities of green samples and sintered samples increase with prolonging ball milling time when the time is less than 150 min; and the trend is on the contrary when the time is more than 150 min. This indicates that the powder activity affecting the pressing and sintering densification, can be enhanced to some extent by prolonging ball milling time. The powder activity includes powder surface activity and lattice activity. The former depends on powder size and shape and the latter depends on lattice size, lattice defects, internal stress, and so on. The longer ball milling time, on one hand, makes the powder shape more irregular, the grain smaller, rusulting in increase of both activities; and on the other hand, brings about more lattice defects, enhancing sintering driving force, accelerating sintering densification[5-8]. After 150 min, however, the mixed powders begin to assemble and become large, decreasing their activity. Though the sample green density increases because of granulation effect, the sintering density decreases. Therefore, the optimum ball milling time is 150 min for Ni-$NiFe_2O_4$ in current work.

3.2 Effect of metal contents

Nickel is a good sintering aid for many compounds in sintering process[6]. Former studies[9-11] have found that relative densities of Ni-$NiFe_2O_4$ are higher than those of Cu-$NiFe_2O_4$ in the same condition, and much higher than those of $NiFe_2O_4$ sintered in air. So we deduce that nickel probably is beneficial to $NiFe_2O_4$ sintering. In this work, Ni-$NiFe_2O_4$ cermets with different Ni contents were sintered at 1 200 ℃ for 4 h in weak reductive atmosphere to investigate the effect of contents of Ni on Ni-$NiFe_2O_4$ sintering densification.

As listed in Table 2, the relative densities of Ni-$NiFe_2O_4$ cermets are constantly high with the Ni content varying in 0 - 15% (mass fraction). Compared with stoichiometric $NiFe_2O_4$ ceramics, relative densities of Ni-$NiFe_2O_4$ cermets are not improved. This may lie in two reasons. First, metal nickel has no function as sintering aids during Ni-$NiFe_2O_4$ cermet sintering. Second, its effect is probably the same as that of weak reductive atmosphere, i.e. they both bring about oxygen deficiencies, which can speed atomic diffusion and strengthen the sintering process, so the effect as sintering aids of sintering atmosphere probably overshadows that of Ni[12-14]. The effect of sintering atmosphere will be further discussed.

Also from Table 2, rather than what we have expected, when metal content is more than 5% (mass fraction), with the Ni content increasing, the relative densities slightly decreases. Although nickel is compatible with $NiFe_2O_4$ matrix, excessive Ni powder may lead to two bad effects. First, big metal grains form in 15%Ni-$NiFe_2O_4$ as shown in Fig. 1, which causes steric hindrance and retards the samples densification when they locate at the boundary of $NiFe_2O_4$ grains[12, 13]. Second, they induce too many oxygen deficiencies which assemble to pores, increasing pores in crystals, so impairing Ni-$NiFe_2O_4$ densification[15].

Table 1 Change of physical properties of cermets with ball milling time

Ball milling time/min	Mean particle size/μm	Relative density of green sample/%	Relative density of sintered sample/%
0	95.55	55.08	86.00
30	8.97	56.39	90.60
150	5.09	61.02	94.38
210	6.02	61.56	92.73
600	6.54	61.71	91.39

Table 2 Effect of Ni content on relative density of Ni-$NiFe_2O_4$ cermets

Nickel content (mass fraction)/%	Relative density/%	Apparent porosity/%
0	94.22	5.78
1	93.98	6.02
2	94.15	5.85
3	94.19	5.81
5	94.68	5.32
10	93.55	6.45
15	93.07	6.97

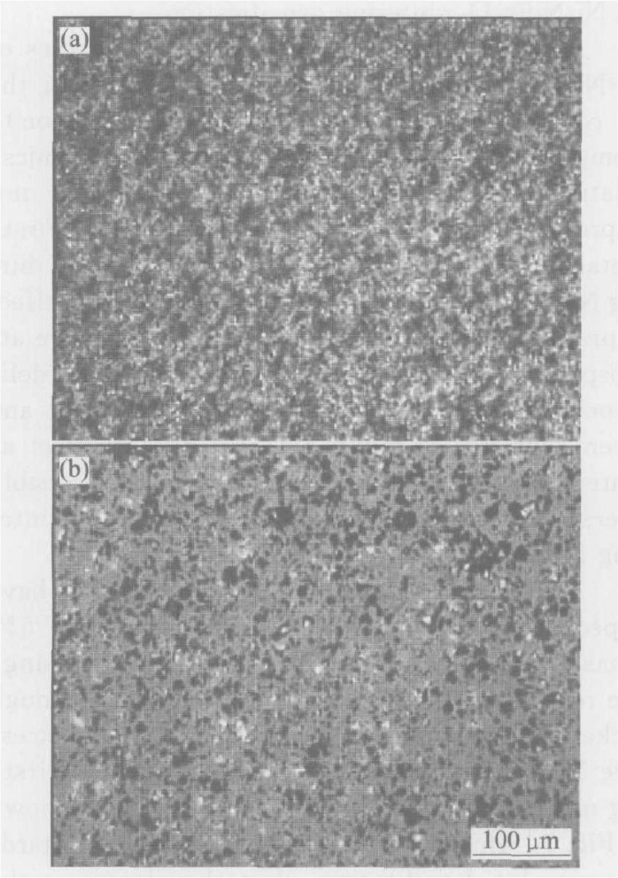

Fig. 1 Microstructures of Ni-$NiFe_2O_4$ cermets
(a) —5% Ni/$NiFe_2O_4$; (b) —15% Ni/$NiFe_2O_4$

3.3 Effect of sintering atmosphere

Previous works[9-11] investigated the controlling of sintering atmosphere, and its effect on the micro-composition of the cermets. In order to eliminate the effect of metal phase on the micro-composition and the densification process and to guide the densification of $NiFe_2O_4$ based cermets, the current work studies and compares the relative densities of stoichiometric $NiFe_2O_4$ ceramic sintered in different atmosphere. The results are summarized in Table 3.

In Table 3, the oxygen partial pressures of weak reductive atmosphere A and B are lower than the equilibrium oxygen pressure of the oxidation reaction for Ni or the decomposition reduction for NiO, and the former's is lower than that of latter. As listed in Table 3, the relative density of $NiFe_2O_4$ ceramic sintered in weak reductive atmosphere is 15% greater than that of $NiFe_2O_4$ ceramic sintered in air at 1 200 ℃, and is close to that of $NiFe_2O_4$ ceramic sintered in air at 1 400 ℃. $NiFe_2O_4$ is a kind of dislocable deficient compounds, so the larger relative density might result from the fact that weak reductive atmosphere can introduce oxygen deficiencies, which brings about lattice distortion, activation of sintering and increase of ceramic densification[14, 16, 17].

Table 3 Effect of sintering atmosphere on relative density of $NiFe_2O_4$

Sintering temperature/℃	Sintering atmosphere	Bulk density/(g•cm^{-3})	Relative density/%
1 200	Weak reductive A	5.07	94.36
1 200	Weak reductive B	5.05	94.12
1 200	Air	4.26	79.33
1 400	Air	5.06	94.52

Fig. 2 shows the X-ray diffraction patterns of $NiFe_2O_4$ sintered in weak reductive atmosphere A, B, and in air, and the former two are very similar to the last one, except for several $FeNi_3$ peaks. Semi-quantitative analysis shows that the samples sintered in weak reductive A and B contain approximately 4% and 1% $FeNi_3$ (mass fraction), respectively, resulting from oxygen deficiencies increase induced by the weak reductive atmosphere. Because little $FeNi_3$ phase hardly influences the corrosive resistance of cermets, eligible cermets inert anodes can be sintered in weak reductive atmosphere to get large densification.

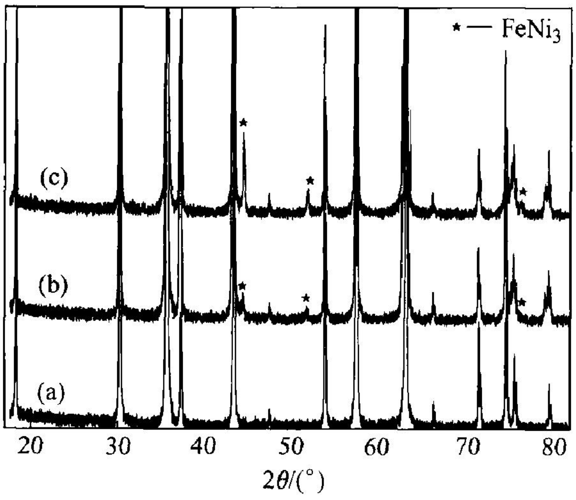

Fig. 2 XRD patterns of $NiFe_2O_4$ ceramics sintered in different atmospheres
(a) —Air; (b) —Weak reductive atmosphere A;
(c) —Weak reductive atmosphere B

3.4 Effect of sintering temperature

Sintering temperature schedule is crucial to the densification of cermets. Previous works[10, 11] showed that nickel effuses from the cermets when sintered at the temperature above the melting point of Ni, i. e. 1 453 ℃, which is harmful to samples' properties such as electric conductivity and corrosion resistance. In present study, 5% Ni-$NiFe_2O_4$ were sintered at different temperatures below Nickel's melting point, and held for the same period of 4 h in weak reductive atmosphere.

As summarized in Table 4, when the sintering temperature increases from 1 100 ℃ to 1 200 ℃, the relative density increases greatly from 80.38% to 94.51%, and the apparent porosity correspondingly decreases from 19.62% to 5.49%. Further increase in sintering temperature has little effect on the densification and sintering temperature higher than 1 300 ℃, i. e. 1 400 ℃; on the contrary, leads to lower relative density.

Table 4 Effect of sintering temperature on relative densities of 5% Ni-$NiFe_2O_4$ samples

Sintering temperature/ ℃	Relative density/ %	Apparent porosity/ %
1 100	80.38	19.62
1 200	94.51	5.49
1 300	96.85	3.15
1 400	95.23	4.77

In the solid-state sintering, Ni-$NiFe_2O_4$ sintering process at high temperature can be described as following steps. Firstly, in the relatively low temperature stage, with the sintering temperature increasing, sintering necks shrink, distance between grains is shortened, grains grow, open pores disappear and green samples shrink, which results in the increase of density and strength. Higher temperature can considerably accelerate this process, therefore, cermets density remarkably increases with the sintering temperature increasing. Secondly, when the relative density reaches about 90%, most of open pores become close; sintering process comes into the stage of close pore spheroidization, shrinkage, or disappearance. Increasing temperature can also increase the activation energies of material transport, strengthen sintering driving force, reduce pore surface and accelerate pore shrinkage and disappearance, but the effects on densification in this stage are much less than those in the first one[7, 8]. When the relative density is higher than 95%, temperature increasing might bring about anti-densification, as listed in Table 4, resulting in the phenomenon that the relative density of the sample sintered at 1 400 ℃ is lower than that of samples sintered at 1 300 ℃.

There might be several reasons leading to the anti-densification process. Firstly, the gas is insolvable to the cermets, thus the gas pressure in close pores quickly rises with the temperature increasing, and the shrinkage stops when the pressure is greater than the pore surface tension force. Secondly, higher temperature leads to further particle growth, which is detrimental to the densification process. Fig. 3 shows that the grain size of sample sintered at 1 200 ℃ is about 10 μm; whereas that of samples sintered at 1 400 ℃ is about 15 μm. Thirdly, too higher temperature induces Kirkendall effect of material (atom, ion, or deficiency), which has adverse impact on densification[6, 7].

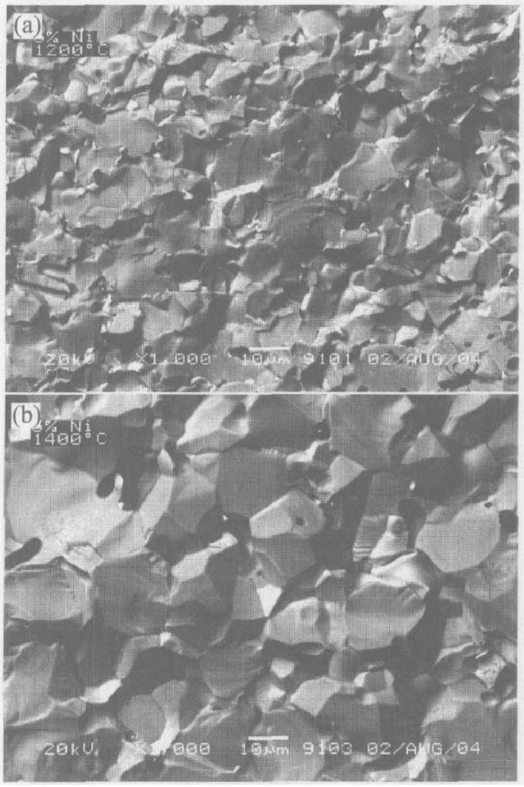

Fig. 3 SEM images of 5% Ni-$NiFe_2O_4$ sintered at different temperatures
(a) —1 200 ℃; (b) —1 400 ℃

Therefore the optimum sintering temperature for Ni-$NiFe_2O_4$ cermets is 1 300 ℃, resulting in the highest relative density. From the analysis above, the temperature at first stage of sintering should be elevated slowly to decelerate the early densification and reduce the formation of close pores. And the sintering temperature should not be too high; the holding time should not be too long.

4 CONCLUSIONS

1) At the rotating rate of 240 r/min under present condition, the proper ball milling time is

150 min, with which the mean diameter of mixed Ni-$NiFe_2O_4$ powders is 5.09 μm and the density of sintered cermets is 94.38%.

2) Cermets containing 0 − 15% Ni have high relative density ranging from 94% to 96%, but with the Ni content increasing, the density slightly decreases because of metallic grains growth. Nickel powders probably have no function as sintering aids or this function is concealed by the effect of weak reductive sintering atmosphere.

3) Sintering atmosphere is vital to densification of Ni-$NiFe_2O_4$ cermets. Weak reductive sintering atmosphere induces more oxygen deficiencies which reinforce the sintering process and accelerate the densification.

4) Sintering temperature greatly influences densification of Ni-$NiFe_2O_4$ cermets. Properly high temperature is of benefit to densification. The relative density of Ni-$NiFe_2O_4$ cermets increases from 80.38% to 96.85% with the sintering temperature increasing from 1 100 ℃ to 1 300 ℃; while it decreases at 1 400 ℃, which may be due to crystal grain coarsening. Furthermore, too high temperature also brings about irregular lattice growth, and the mean grain size of cermets sintered at 1 200 ℃ is about 10 μm, whereas that of sample sintered at 1 400 ℃ is about 15 μm.

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