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Effect of BaO addition on electric conductivity of xCu/10NiO-$NiFe_2O_4$ cermets

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Abstract: The effects of BaO addition on the phase composition, relative density and electric conductivity of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets were studied, which were prepared with cold isostatic pressing-sintering process. The results show that the relative densities of 5Cu/10NiO-$NiFe_2O_4$ cermet doped with 1% BaO (mass fraction) and 10Cu/10NiO-$NiFe_2O_4$ cermet doped with 1% BaO sintered at 1 473 K in nitrogen atmosphere, are increased by about 9.86% and 9.75% compared with the undoped BaO cermets, respectively. And the electric conductivities 22.79 S/cm of 5Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO and 23.10 S/cm of 10Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO are obtained, which are 2.21 times and 1.47 times of those of undoped samples, respectively. Moreover, the 10Cu/10NiO-$NiFe_2O_4$ cermets doped with 1% BaO have a maximum σ_0 of 58.91 S/cm and electric conductivity of 23.10 S/cm at 1 233 K. Maybe low melting-point phases of $BaFe_2O_4$ and $Ba_2Fe_2O_5$ have an excellent electric conductivity in xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets at 1 233 K.

Key words: Cu/10NiO-$NiFe_2O_4$ cermet; BaO; inert anode; aluminum electrolysis; electric conductivity; relative density

1 Introduction

Early candidate materials for inert anode had been concentrated on ceramic oxides, alloys and cermets[1]. Recently, cermets have received much attention due to combinative advantages of ceramic materials (low corrosion and oxidation) with metallic materials (high electric conductivity and good thermal shock resistance) [2−3]. Nickel ferrite is one of the most common compounds in a family of spinel with cubic structure. This compound offers a good combination of physical and chemical properties such as high melting-point, good resistance to chemical attack, high thermal stability, and consequently it is the preferred material as ceramics inert anode. But it is well-known that the poor electric conductivities of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets have restricted their application in the inert anode[4−5]. Sintering additive is an effective method to increase cermet densification and electric conductivity. GHOSH et al[6] obtained 99% of relative density in magnesium aluminate spinel sample with adding ZnO as additive and suggested the formation of anion vacancy in the presence of ZnO to improve density and mechanical properties. RITWIK et al[7] observed that densification temperature for magnesium aluminate spinel decreased by about 100 ℃ with addition of Cr_2O_3 up to 1%. JIAO et al[8] reported a gradual improvement in sintered density for nickel ferrite products by addition of TiO_2 up to 1%. XI et al[9] pointed out that addition of MnO_2 increased the sintering density of nickel ferrite. They also found refined grains and improved thermal shock resistance for MnO_2 containing samples. So it can be seen that sintering additive has great influence on the sintering process and microstructure of composites. XI et al[10] found that when the mass fraction of V_2O_5 was 2%, the conductivity of sample was 7 times that of sample without V_2O_5. TIAN et al[11] have gained that the addition of SnO_2 decreased the activation energy and improved its electrical conductivity. LAI et al[12] reported that when the maximum conductivity of 16.29 S/cm at 1 233 K was obtained for composites doped with 2% CaO (mass fraction), compared with 1.03 S/cm of the undoped composites. ZHANG et al[13] found that the conductivity of $NiFe_2O_4$ samples has improved significantly with addition of TiO_2.

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In this study, the effects of BaO addition on the relative density, microstructure and electric conductivity of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets were investigated.

2 Experimental

2.1 Preparation of BaO doped xCu/10NiO-$NiFe_2O_4$ composites

xCu/10NiO-$NiFe_2O_4$ (x=5, 10) and xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO were prepared by the conventional method with reagent grade raw materials of Fe_2O_3, NiO and BaO. The mixture of Fe_2O_3 and NiO in molar ratio of 1.35 was calcined in a muffle furnace at 1 200 ℃ for 6 h in air to form 10NiO-$NiFe_2O_4$ ceramic powders. X-ray diffraction results of 10NiO-$NiFe_2O_4$ ceramics are shown in Fig.1. The synthesized powders, Cu and BaO powders were ground in the mediums containing dispersant and adhesive. The dried mixture was compacted at 200 MPa to get cylindrical blocks (d 20 mm×45 mm). Then the xCu/10NiO-$NiFe_2O_4$ (x=5, 10) and xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO were sintered at 1 200 ℃ for 4 h in nitrogen atmosphere[14].

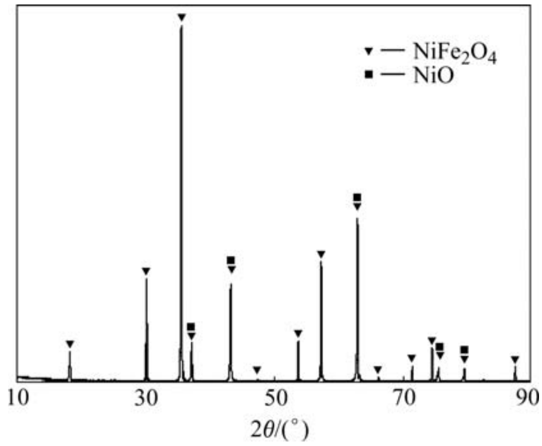

Fig.1 XRD pattern of 10NiO-$NiFe_2O_4$ composite ceramics

2.2 Characterization

The phase compositions were identified by X-ray diffraction analysis using Philips PW1390 X-ray diffractometer with Cu K_α radiation. Microstructure was analyzed with JSM-6360LV scanning electron microscope equipped with EDX-GENESIS energy dispersive spectrometer. Bulk densities were tested according to the Archimedes' method. High temperature electric conductivities based on the conventional direct current four-electrode technique were tested using experimental furnace (Fig.2)[12] by treating powder at a heating rate of 5 ℃/min in air.

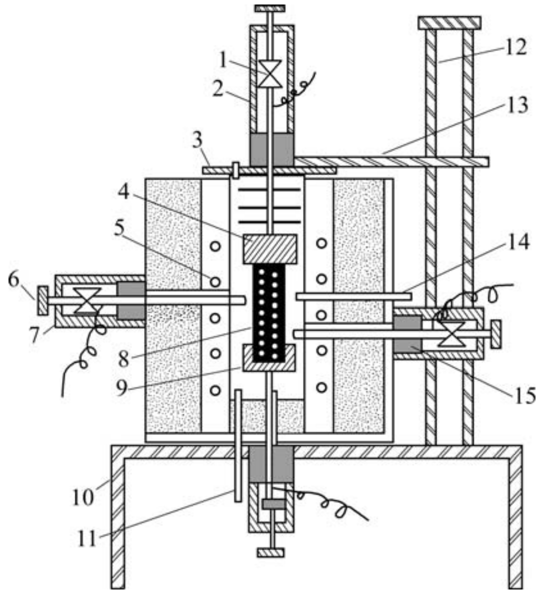

Fig.2 Drawing of experimental furnace for high temperature electric conductivity test: 1—Press sensor; 2—Super cover; 3—Sintered alumina plate; 4—Super electrode for current conduction; 5—Furnace; 6—Pressing handle; 7—Voltage measuring side electrode; 8—Specimen; 9—Bottom electrode for current conduction; 10—Steel pedestal; 11—Gas inlet; 12—Steel tram road for super cover to move; 13—Steel crossbeam for super cover to move; 14—Pt/Pt210%Rh thermocouple, with sintered alumina sheath; 15—Insulating tram road for electrode to move

3 Results and discussion

3.1 Effect of BaO addition on relative density and microstructure

The relative densities of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) and xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO are listed in Table 1. The relative densities of 5Cu/10NiO-$NiFe_2O_4$ and 10Cu/10NiO-$NiFe_2O_4$ cermets doped with 1% BaO sintered at 1 200 ℃ in nitrogen atmosphere, were increased by about 9.86% and 9.75% compared with the undoped BaO cermets, respectively. Possibly because BaO causes the presence of inherent oxygen vacancy of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets, which helps the transportation of oxygen ion, greater extent of atomic diffusion and greater mass transportation and densification results in[15].

Fig.3(a) and Fig.4(a) illustrate the SEM images of 5Cu/10NiO-$NiFe_2O_4$ and 10Cu/10NiO-$NiFe_2O_4$ cermets, respectively. It can be seen that with metallic copper contents increasing, the relative densities of samples don't change. However, the relative density of sample doped with 1% BaO has a rapid improvement according to Table 1, and sample doped with 1% BaO shows almost

Table 1 Relative density and electric conductivity of xCu-10NiO-$NiFe_2O_4$ cermets and xCu-10NiO-$NiFe_2O_4$ cermets doped with 1% BaO

w(BaO)/%	w(Cu)/%	Relative density/%	Electrical conductivity/($S\cdot cm^{-1}$)										
			303 K	373 K	473 K	573 K	673 K	773 K	873 K	973 K	1 073 K	1 173 K	1 233 K
0	5	88.35	0.593	0.847	1.326	2.607	3.632	4.710	5.015	5.690	7.621	9.102	10.30
1	5	98.21	1.904	2.414	3.855	5.710	7.546	10.03	13.55	17.59	20.79	21.63	22.79
0	10	88.44	0.715	0.969	1.903	3.542	5.368	6.494	8.218	9.150	12.11	14.39	15.63
1	10	98.19	1.676	2.404	3.675	6.528	9.121	11.98	16.10	19.84	22.97	24.89	23.10

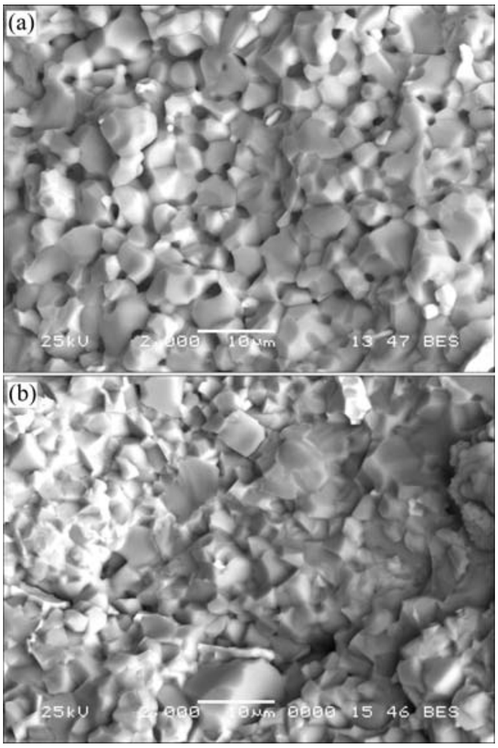

Fig.3 SEM images of cermets at 1 200 ℃: (a) 5Cu/10NiO-$NiFe_2O_4$ cermet; (b) 5Cu/10NiO-$NiFe_2O_4$ cermet doped with 1% BaO

full densification due to the tight combination of particles and removing of pores (Fig.3(b) and Fig.4(b)). Based on the thermodynamic calculation, BaO can react with $NiFe_2O_4$ at about 1 000 ℃ to generate $BaFe_2O_4$ and $Ba_2Fe_2O_5$[16]. Liquid phase appears below 1 200 ℃.

$$BaO+NiFe_2O_4 = BaFe_2O_4+NiO \tag{2}$$

$$2BaO+NiFe_2O_4 = Ba_2Fe_2O_5+NiO \tag{3}$$

So samples doped with BaO achieve densification by means of dissolution and separation of this liquid phase, which was used as transferred carrier to accelerate mass mobility and viscous flow.

3.3 Electric conductivity of BaO doped xCu/10NiO-$NiFe_2O_4$ composites

Table 1 and Fig.5 display the electric conductivities

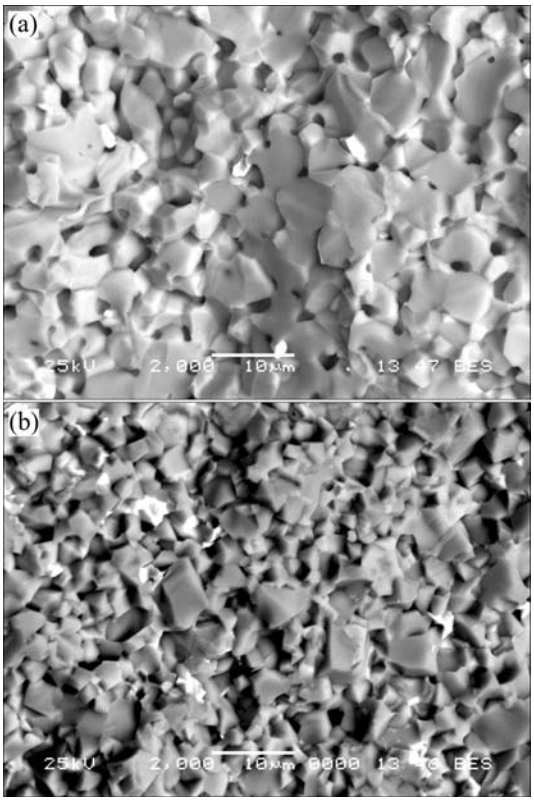

Fig.4 SEM images of cermets at 1 200 ℃: (a) 10Cu/10NiO-$NiFe_2O_4$ cermet; (b) 10Cu/10NiO-$NiFe_2O_4$ cermet doped with 1% BaO

of samples doped with 1% BaO. From Fig.5 and Table 1, the electric conductivities for samples doped with BaO are apparently higher than those of undoped samples.

This implies that addition of BaO has an active effect on electric conductivity of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets. The electric conductivities(σ) 22.79 S/cm of 5Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO and 23.10 S/cm of 10Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO are obtained, which are 2.21 times and 1.47 times those of undoped sample, respectively.

10NiO-$NiFe_2O_4$ ceramics prepared is one kind of n-type semiconductor materials containing oxygen vacancy. Thus, the function of electric conductivity σ and temperature T is described as follows:

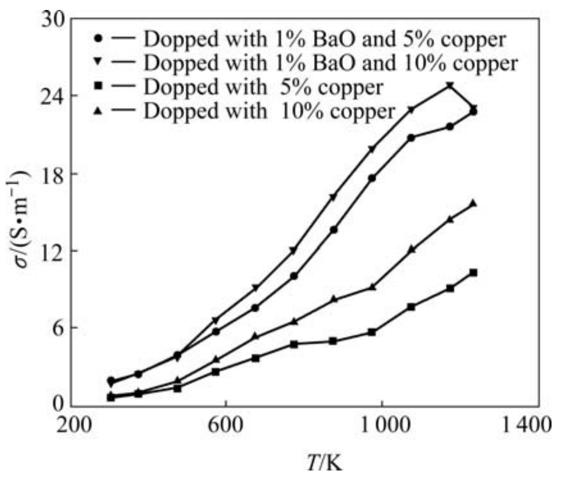

Fig.5 σ—T plots of xCu-10NiO-$NiFe_2O_4$ and xCu-10NiO-$NiFe_2O_4$ cermets doped with BaO in air

$$\sigma=\sigma_0\exp[-E/(2KT)] \tag{4}$$

where E is the electric activation energy; K is the Boltzmann constant; σ_0 is similar with one constant in the range of experimental temperature, which is determined by the following factors: concentration of current carrier N; electron quantity q, transition frequency δ, average transition distance v_0 and ambient temperature T:

$$\sigma_0=Nq^2\delta^2v_0/(kT) \tag{5}$$

The fitting results of $\ln\sigma$—T linear relations for xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets and xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO, which were sintered at 1 200 ℃, are listed in Table 2. It is observed that σ_0 of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO is higher than that of the undoped samples, and E is lower than that of undoped samples, possibly because BaO, $BaFe_2O_4$ and $Ba_2Fe_2O_5$ decrease electric activation energy and increase electric conductivity. Moreover, the 10Cu/10NiO-$NiFe_2O_4$ cermets doped with 1% BaO have a maximum σ_0 of 58.91 S/cm and electric conductivity of 23.10 S/cm at 1 233 K. Maybe low melting-point phases of $BaFe_2O_4$ and $Ba_2Fe_2O_5$ have an excellent electric conductivity in xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets at 1 233 K.

Table 2 Fitting results of $\ln\sigma$—T linear relations for xCu-10NiO-$NiFe_2O_4$ and BaO/xCu-10NiO-$NiFe_2O_4$

w(BaO)/%	w(Cu)/%	σ_0/(S·cm^{-1})	E/eV	Correlation factor	Electrical conductivity at 1 233 K/(S·cm^{-1})
0	5	21.28	0.24	98.46	10.30
1	5	46.97	0.22	97.48	22.79
0	10	37.54	0.27	98.79	15.63
1	10	58.91	0.24	98.44	23.10

4 Conclusions

1) The relative densities of 5Cu/10NiO-$NiFe_2O_4$ and 10Cu/10NiO-$NiFe_2O_4$ cermets doped with 1% BaO sintered at 1200 ℃ in nitrogen atmosphere, are increased by about 9.86% and 9.75% compared with undoped BaO cermets, respectively.

2) The electric conductivities 22.79 S/cm of 5Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO and 23.10 S/cm of 10Cu/10NiO-$NiFe_2O_4$ cermets adding 1% BaO are obtained, which are 2.21 times and 1.47 times those of undoped sample, respectively.

3) σ_0 of xCu/10NiO-$NiFe_2O_4$ (x=5, 10) cermets doped with 1% BaO is higher than that of undoped samples, and E is lower than that of undoped samples. Moreover, 10Cu/10NiO-$NiFe_2O_4$ cermets doped with 1% BaO have a maximum σ_0 of 58.91 S/cm and electric conductivity of 23.10 S/cm at 1 233 K.

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