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Electrical resistivity of $NiFe_2O_4$ ceramic and $NiFe_2O_4$ based cermets①

TIAN Zhong-liang(田忠良), LAI Yan-qing(赖延清), LI Jie(李 劼),
ZHANG Gang(张 刚), LIU Ye-xiang(刘业翔)
(School of Metallurgical Science and Engineering, Center South University, Changsha 410083, China)

Abstract: $NiFe_2O_4$ ceramic and $NiFe_2O_4$ based cermets, expected to be used as the inert anodes in aluminum electrolysis, were prepared and their electrical resistivities were measured at different temperatures. The effects of temperature and composition on their electrical resistivities were investigated. The results indicate that the electrical resistivities of $NiFe_2O_4$ based cermets mainly depend on temperature, resistivity of ceramic matrix, composition and dispersion of the metal phase among ceramic matrix. The electrical resistivity of $NiFe_2O_4$ ceramic decreases from 10.094 Ω·cm to 0.475 Ω·cm with increasing temperature from 573 K to 1 233 K. The electrical resistivities of $NiFe_2O_4$ based cermets are greatly lowered, but decrease with increasing the temperature with similar trend compared to that of $NiFe_2O_4$ ceramic. The resistivities of $NiFe_2O_4$ based cermets containing 5% Ni, 5% Cu and 5% Cu-Ni alloy are 0.046 8, 0.066 8 and 0.0532 Ω·cm at 1 233 K, respectively, which are all acceptable as inert anode materials compared to that of the current carbon anode used for aluminum electrolysis.

Key words: $NiFe_2O_4$; cermet; electrical resistivity; inert anode; aluminum electrolysis
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1 INTRODUCTION

The development of inert anodes (non-consumable anodes) is a long-standing dream of researchers as a replacement for the consumable carbon anode, which is used in the Hall-Héroult process[1]. In conventional aluminium electrolysis, the major cell reaction is

$$1/2Al_2O_3 + 3/4C = Al + 3/4CO_2 \quad (1)$$

With an inert anode, the reaction is[2]

$$1/2Al_2O_3 = Al + 3/4O_2 \quad (2)$$

Thus, the introduction of inert anodes will eliminate anode carbon consumption and reduce environmental problems such as the emission of carbon dioxide, perfluorocarbon and evolve oxygen[3, 4], which makes the use of inert anode be commercially attractive. As an inert anode material, the anodic ohmic voltage drop caused by its resistance should be comparable with that of current carbon anode used in aluminium electrolysis, otherwise the purpose for decreasing cell voltage, improving current efficiency and saving energy cannot be realized. So inert anode materials need not only good corrosion resistance to the molten salts and high stability with respect to oxidizing gases such as oxygen, but also good electrical conductivity[5-8].

A number of materials examined, especially ceramic oxides, eg nickel ferrite spinel, were found to have very low solubility at high temperature in the molten cryolite[9-11]. But generally speaking, the ceramic oxides have very poor electrical conductivity even at high temperature[5, 12-14]. On the contrary, metals have excellent electrical conductivity but exhibit low resistance to the molten cryolite and are unstable with respect to oxygen expect for noble metals, eg platinum. Therefore, a so-called cermet material has been proposed and constructed, which is prepared by dispersing metal powders in ceramic oxide matrix. The intention is to have the inert anode material possessing the desirable properties of metallic material as well as those of the ceramic.

According to recent studies[3], nickel ferrite spinel is one of the most promising ceramic oxide matrixes of cermet inert anodes with respect to the corrosion resistance to melts. In this paper, $NiFe_2O_4$ ceramic and $NiFe_2O_4$ based cermets were prepared and their electrical resistivities were measured at different temperatures. The effects of temperature and composition of metal phase on the electrical resistivities of $NiFe_2O_4$ based cermets were studied.

2 EXPERIMENTAL

Reagent grade raw materials of NiO and Fe_2O_3

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Correspondence: TIAN Zhong-liang, PhD; Tel: +86-731-8830474; E-mail: tianzhongliang@126.com

were mixed according to the mole ratio of $x(\mathrm{Ni}) : x(\mathrm{Fe}) : x(\mathrm{O}) = 1 : 2 : 4$. The mixed oxides were calcined in a furnace at 1 473 K for 6 h in air. It is proved that the calcined powders have single-phase of $NiFe_2O_4$ spinel structure with the X-ray diffraction patterns shown in Fig. 1. Then, a series of samples of $NiFe_2O_4$ ceramic and $NiFe_2O_4$ based cermets were prepared with gauge of d20 mm × 40 mm using the cold isostatic pressing process. The sample of $NiFe_2O_4$ ceramic was sintered at 1 673 K for 4 h in air. The green cylinders of $NiFe_2O_4$ based cermet were sintered at a certain temperature at 1 393 - 1 673 K for 4 h in an atmosphere of efficiently controlled oxygen partial pressure. High density, low porosity and uniform dispersion of metal phase among ceramic phase were desirable.

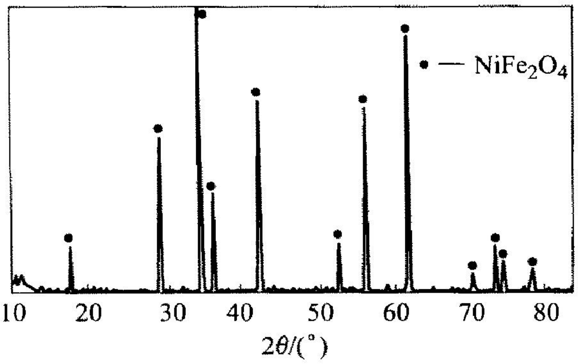

Fig. 1 XRD pattern of calcined powder

High temperature electrical resistivities of the ceramic and cermet samples were determined with a direct current quadripole electrodes measuring apparatus[15], in which an EG & G Model 273A Potentiostat/Galvanostat was used as the direct current source and signal detectors of current and voltage. The resistance capacity of apparatus is 10^{-4} - 10^{4} Ω at 298 - 1 373 K in air, inert, reductive or oxidative atmosphere. In this paper, test was carried out in an atmosphere of efficiently controlled oxygen partial pressure to avoid the oxidization of metal. The electrical resistivity ρ is determined by the following equation:

$$\rho = \frac{\pi r^2}{l} \times \frac{U}{J} \qquad (3)$$

where r is the radius of cylinder sample; l and U are the interval and voltage drop between two electrodes, respectively; J is the current density through the sample.

After the completion of measurement, some samples were mounted and examined by optical microscopy.

3 RESULTS AND DISCUSSION

3.1 Effect of temperature on electrical resistivity of $NiFe_2O_4$ ceramic and Ni-containing $NiFe_2O_4$ cermet

The changes of electrical resisitivities ρ of $NiFe_2O_4$ ceramic and 2% Ni-containing cermet with temperature are illustrated in Fig. 2.

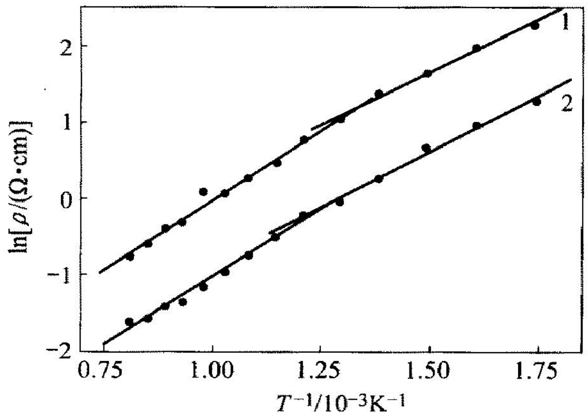

Fig. 2 Effect of temperature on electrical resistivity for $NiFe_2O_4$ ceramic and cermet
1 —$NiFe_2O_4$ ceramic; 2 —2% Ni-containing $NiFe_2O_4$ cermet

From Fig. 2, the resistivity of $NiFe_2O_4$ ceramic sintered at 1 673 K, whose relative density is 93.10%, decreases from 10.094 Ω·cm to 0.475 Ω·cm with increasing the temperature from 573 K to 1233 K. This could be attributed to the increase in the drift mobility of electric charge carriers, which was thermally activated on increasing the temperature. It is seen that the straight line is broken. One possible reason is that the ferromagnetic materials transform to paramagnetic ones at the Curie temperature as reported in Ref. [12].

In fact, this decrease in ρ with increasing temperature is the normal behavior for semiconductors which is controlled by the following Arrhenius relation[12, 16]:

$$\rho = \rho_0 \exp[E/kT] \qquad (4)$$

where ρ_0 is the pre-exponential constant or resistivity at infinitely high temperatures, E is the activation energy released by electron from one level to the neighboring one, k is the Boltzmann's constant and T is absolute temperature.

For nickel ferrite, the presence of Ni ions on octahedral-(B) sites, Fe ions on tetrahedral-(A) sites and B-sites favor the ion exchange interactions expressed as Eqn. (5)

$$Ni^{2+} + Fe^{3+} = Ni^{3+} + Fe^{2+} \qquad (5)$$

Thus the conduction mechanism for the N-type semiconductor is predominantly due to the hopping of electrons from Fe^{2+} to Fe^{3+} ions; while that for the P-type semiconductor is due to the holes transfer from Ni^{3+} to Ni^{2+} ions. It seems that the present sample has both types of charge carriers, which participate in the conduction process, and the conductivity is the sum of conductivity for both types.

Fig. 2 indicates that the electrical resistivity of 2% Ni-containing cermet sintered at 1 673 K, whose relative density is 96.49%, decreases with increasing temperature. The material exhibits the characteristic of semiconductors, too. There is also the Curie temperature where a change in the slope of the straight line appears. There are similar slopes of straight lines at line 1 and line 2.

3.2 Effect of composition of metal phase on electrical resistivity of $NiFe_2O_4$ based cermets

The electrical resistivities of other cermets were measured at different temperatures besides $NiFe_2O_4$ ceramic and 2% Ni-containing cermet. The results are shown in Table 1 and Fig. 3.

From the data illustrated in Table 1, although the content of metals added to ceramic is only 5%, their resistivities both at 873 K and 1 233 K are much lower than that of nickel ferrite ceramic. There is difference of about 10 times between the ceramic and cermets. For example, at 1 233 K, the electrical resistivities of $NiFe_2O_4$ ceramic and 5% Cu-containing cermet are 0.475 Ω·cm and 0.066 8 Ω·cm, respectively. The data also show that the electrical resistivities of cermets change with various metals added. The resistivities of $NiFe_2O_4$ based cermets containing 5% Ni, 5% Cu and 4.25% Cu+ 0.75% Ni at 1 233 K are 0.048 6, 0.066 8 and 0.053 2 Ω·cm, respectively.

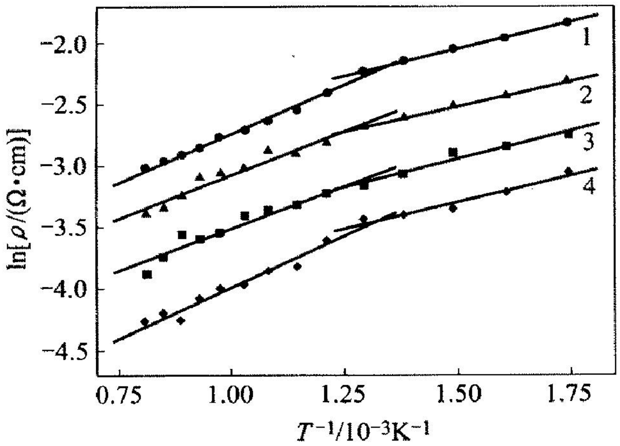

Fig. 3 Effect of temperature on electrical resistivity for $NiFe_2O_4$ based cermets
1 —5% Ni-containing $NiFe_2O_4$ cermet;
2 —10% Ni-containing $NiFe_2O_4$ cermet;
3 —15% Ni-containing $NiFe_2O_4$ cermet;
4 —20% Ni-containing $NiFe_2O_4$ cermet

The effect of content of metal nickel on the electrical resistivity of nickel ferrite based cermet at different temperatures is illustrated in Fig. 3. It is very clear that increase in the content of metal nickel would greatly enhance the electrical conductivity of material examined. At 1 233 K, the resistivity of ceramic is 0.475 Ω·cm and that of 5% Ni-containing cermet is 0.048 6 Ω·cm. The descent of the value of resistivity is one level of magnitude. And when the content of metal is added up to 20%, the resistivity of cermet falls to 0.017 6 Ω·cm. Though their electrical resistivities are high compared to that of the current carbon anode used in aluminium electrolysis, which is 0.005 5 Ω·cm[13], it is acceptable as inert anode material.

Usually the oxide may conduct electricity by three different mechanisms individually or in combination: metallic conductivity, ionic conductivity, as semiconductors through excess electrons (N-type) or holes (P-type)[13].

For cermet, the following theory model may explain the factors that affect its resistivity. For this, a block of metal and a block of ceramic are assumed as cylinders and the radius of the cross-section of both blocks are equal to r. As shown in Fig. 4, the lengths of metal and ceramic cylinders are l_M and l_C, respectively. Thus,

$$\rho_M = \frac{\pi r^2}{l_M} R_M \tag{6}$$

$$\rho_C = \frac{\pi r^2}{l_C} R_C \tag{7}$$

where ρ_M and ρ_C are the resistivity of the metal and ceramic, respectively; r is their radius; R_M and R_C are their resistance, respectively.

If the total resistance and the resistivity are R and ρ, respectively, then

$$R = R_M + R_C = \frac{\rho_M l_M + \rho_C l_C}{\pi r^2}$$

Therefore,

$$\rho = \frac{\pi r^2}{l} R = \frac{\rho_M l_M + \rho_C l_C}{l_M + l_C} \tag{8}$$

Table 1 Electrical resistivity of various cermets

Cermet	Sintering condition		Relative density/ %	Electrical resistivity/ (Ω·[illegible])	
	Sintering temperature/ k	Holding time/ h		873 K	1 233 K
$NiFe_2O_4$ ceramic	1 673	4	93.10	1.637 0	0.475 0
5% Ni-containing cermet	1 673	4	96.53	0.079 8	0.048 6
5% Cu-containing cermet	1 398	4	93.25	0.122 2	0.066 8
5% Cu-Ni-containing cermet	1 473	4	94.27	0.096 7	0.053 2

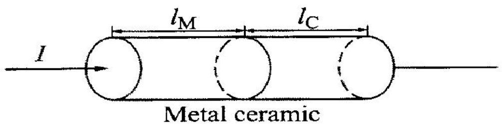

Fig. 4 Resistivity model of cermet

Set $\frac{l_M}{l_M + l_C} = x$

Thus $\rho = \rho_M x + \rho_C(1 - x)$ (9)

Because of $\rho_M \ll \rho_C$ (the difference is roughly four orders of magnitude), so

$\rho = \rho_C(1 - x)$ (10)

where x is defined as the fraction of the effective transfer distance of electric charges of metal phases in the cermet. Clearly, x is related to the content of the metal and the dispersion of the metal phase among oxide phase.

Eqn. (10) shows that ρ is only affected by ρ_C and x, not by ρ_M.

For the effect of temperature on the electrical resistivity of 2% Ni-containing cermet (Fig. 2), it can be considered that the activation energy E of the ceramic matrix controls the electrical resistivity of either the cermet or oxide, and E is not related to the resistivity of the metal. It is a good agreement with Eqn. (10).

It is well known that the copper metal has lower resistivity than the nickel has. However, 5% Cu-containing cermet has higher resistivity than $NiFe_2O_4$ based cermet containing 5% Ni and 4.25% Cu + 0.75% Ni has. It seems that the resistivity of cermets is independent of the resistivity of the metals added.

In Eqn. (10), x is related to the content of the metal and the dispersion of the metal phase among oxide phase matrix. A fine dispersion of metal among the oxide ceramic phases greatly increases the value x, thus the electrical resistivity ρ of cermet falls significantly. The resistivity of 5% Cu-containing cermet is higher than that of 5% Ni-containing cermet, because copper dispersion among ceramic phase is more poor than that of nickel. Fig. 5 shows the micrograph of Ni-containing cermet, in which bright area is the nickel metal phase, and the grey area is the nickel ferrite ceramic phase. It is clear that the metal phase is interwoven with the ceramic phase. Such interwoven phases are certainly favorable to decrease of the resistivity. But the Cu-containing cermet has not such interwoven structure. There is a lot of copper in the microvoids existed in cermet. Fig. 6 obviously shows that some spherical copper particles located in the voids. In this structure, metal dispersion is very unfavored to conductivity. So, the copper cannot obviously act an important role in the conducting electricity. That is attributed to the poor wettability between the copper phase and the ceramic phase in the cermet. Due to that the copper metal melting point is only 1 356 K, the cermet sintering process is a liquid phase sintering process. Generally, the liquid phase sintering should be favorable to increasing the density, however, the liquid copper particles, in this case, tend to aggregation because of poor wettability and then move into the microvoids existed in the cermet. Thus, the copper phase dispersion among the ceramic phase in cermet is decreased greatly, even the copper forms a block filling up nearby voids and sometimes flows out of the sample.

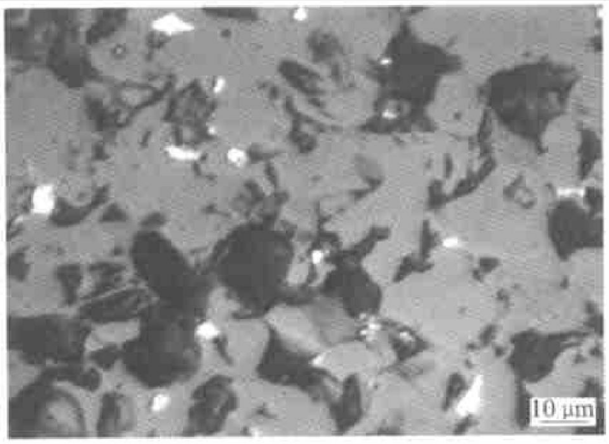

Fig. 5 Micrograph of Ni-containing cermet

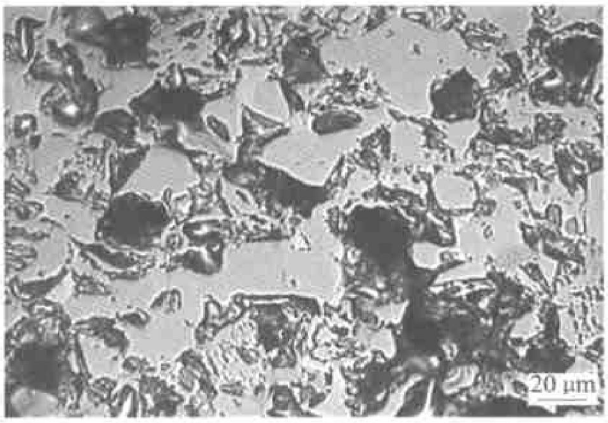

Fig. 6 Micrograph of Cu-containing cermet

However, the wettability may be improved by adding other metals, such as nickel. When nickel was added to Cu-containing cermet, the wettability between the metal phase and ceramic phase is improved (Fig. 7). The electrical resistivity of cermet is also decreased from 0.066 8 Ω·cm to 0.0532 Ω·cm, which contains only 0.75% nickel metal.

According to Eqn. (10), when the content of metal increases, x will increase, and the electrical resistivity of cermet will greatly fall. This is accordant

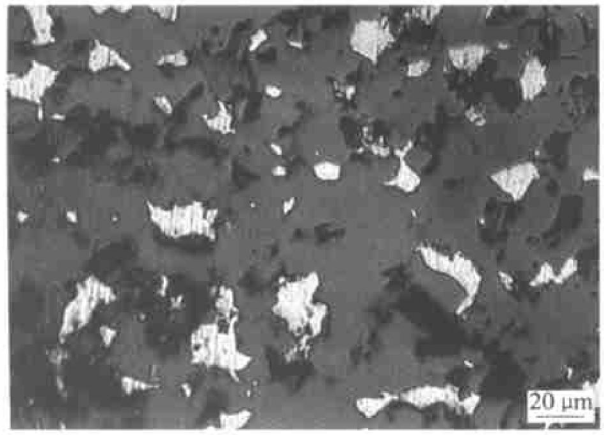

Fig. 7 Micrograph of Cu/Ni-containing cermet

with experimental results illustrated in Fig. 3.

4 CONCLUSIONS

1) The nickel ferrite ceramic exhibits the characteristic of semiconductor, and its electrical resistivity remarkably decreases from 10.094 Ω • cm to 0.475 Ω•cm with increasing temperature from 573 K to 1 233 K.

2) The electrical resistivities of $NiFe_2O_4$ based cermets mainly depend on temperature, resistivity of ceramic matrix, composition and dispersion of the metal phase among ceramic matrix. The change trends of the electrical resistivities of cermets and with that of $NiFe_2O_4$ ceramic. Although the content of metal added is only 5%, the electrical resistivities of $NiFe_2O_4$ based cermets greatly decrease, compared to that of $NiFe_2O_4$ ceramic. The resistivities of $NiFe_2O_4$ based cermets containing 5% Ni, 5% Cu and 5% Cu-Ni alloy are 0.046 8, 0.066 8 and 0.053 2 Ω •cm at 1 233 K, respectively, which are all acceptable for inert anodes.

3) Though the electrical resistivities of cermets are greatly lowered, it is higher than that of carbon anode currently used in aluminium electrolysis. To enhance the electrical conductivity of cermet further, it is necessary to improve the wettability between ceramic matrix and added metals.

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