Article ID: 1003－7837(2005)02,03－0132－06

Effect of MnO_2 on properties of $NiFe_2O_4$ spinel based inert anode

XI Jin-hui (席锦会), YAO Guang-chun (姚广春), LIU Yi-han (刘宜汉), ZHANG Xiao-ming(张小明)

(School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China)

Abstract: Abstract: In order to improve the properties of $NiFe_2O_4$ spinel based inert anode, some additive MnO_2 were added to raw materials. $NiFe_2O_4$ spinel with MnO_2 was made by solid-phase reaction at 1200℃ for 6 h. XRD were carried out and the effects of MnO_2 on density, conductivity and corrosion resistance were measured. XRD shows when MnO_2 was added no new phases exist and MnO_2 and $NiFe_2O_4$ formed solid solution; Mn^{4+} replaced parts of Fe^{3+} and the sample still had the structure of $NiFe_2O_4$ spinel. The crystal lattice of $NiFe_2O_4$ spinel became aberrated when MnO_2 was added, which can promote sintering, and improve density. Because Mn^{4+} replaces parts of Fe^{3+} and produces conduction electron, which can improve conductivity. The corrosion resistance of the samples was enhanced. When MnO_2 is 1.0%, the sample's corrosion rate is 1/5 of that of the sample without MnO_2. The reason is that Al_2O_3 in the melt reacts with Mn^{4+} in the sample to produce $MnAl_2O_4$. $MnAl_2O_4$ forms a dense protecting coat, which can prevent melt from eroding further. Because the key problem with inert anodes is anode corrosion, so we consider the optimal amount of MnO_2 is 1.0%.

Key words: $NiFe_2O_4$ spinel; inert anode; density; corrosion resistance; XRD

CLC number: TF777 **Document code**: A

1 Introduction

The carbon anode has been used in aluminum production for more than 100 years. But it has many shortcomings, of which the most notable problems are: (1) the consumption of anodes cause a great deal of good-quality carbon waste, and the emission of the greenhouse gases and most of the sulfurous gases will pollute environment seriously; (2) changing the anodes frequently affects the balance of heat, and cause hard work practices. Inert anodes can overcome the questions mentioned above, so researchers in the aluminum industry and in the field of materials give much attention to inert anodes[1－9].

$NiFe_2O_4$ spinel has many merits, such as high melting point, better stability, and strong resistance to molten cryolite, so it's a candidate material as inert anodes. Despite all this, it still can not fulfill the requirement for corrosion resistance to molten cryolite in the process of aluminum production.

Doping is usually adopted in preparing the functional materials[10－13]. Additive is a trace component that been added to raw materials designedly when the ceramics was prepared. Additive can change the physical-chemical property and technological property of the materials to some extent. Then the materials can get super performance by use of the right process. Additives can affect the microstructure also, so they

Received date: 2005－05－18

Biography: XI Jin-hui (born in 1977), Female, Doctor

are attached much attention in the materials research.

In this paper, some additive MnO_2 was added to raw materials—NiO and Fe_2O_3 when the inert anodes were manufactured. The effect of MnO_2 on density, and corrosion resistance was researched.

2 Experimental

2.1 Preparation of inert anodes

When synthesizing $NiFe_2O_4$, Fe_2O_3 and NiO powders were used as main raw materials, and at the same time different amount of MnO_2 was added. The powders were blended, milled, granulated, and then molded. The green bodies were sintered at 1200℃ for 6h, then the inert anodes of $NiFe_2O_4$ spinel doped with a little amount of MnO_2 were prepared.

2.2 Performance testing

The density of samples was tested by Archimedes draining method. The electrical conductivity versus temperature was measured with a standard dc four-point technique. The sample was placed in a closed tube furnace and heated from room temperature to 960℃ in air. When the sample was heated, the voltage and the current at different temperature were written down, and then the electrical conductivity was calculated by ohms law. Static corrosion experiments were carried out in the $Na_3AlF_6-5\%Al_2O_3$ molten cryolite at 960℃ for 10 h. In order to investigate the samples' microstructure, the micro-appearance and EDX analysis were carried out by scanning electron microscope.

3 Results and analysis

3.1 XRD analysis

The XRD patterns of $NiFe_2O_4$ spinel and sample with 2%MnO_2 are showed in Fig. 1 and Fig. 2 respectively. XRD shows when MnO_2 is added, no new phases exist, and MnO_2 and $NiFe_2O_4$ form solid solution. The cation Mn^{4+} go into octahedron in the structure of spinel and replace parts of Fe^{3+}, which locate 16d, Ni^{2+} still locate 8a, and O^{2-} locate 32e. The space group of Fd3m kept the same, but the lattice constant changed. The lattice constant of the sample without MnO_2 was 8.31, but lattice constant of the sample with MnO_2 was 8.341. Doping causes the lattice constant aberrant, which can promote sintering.

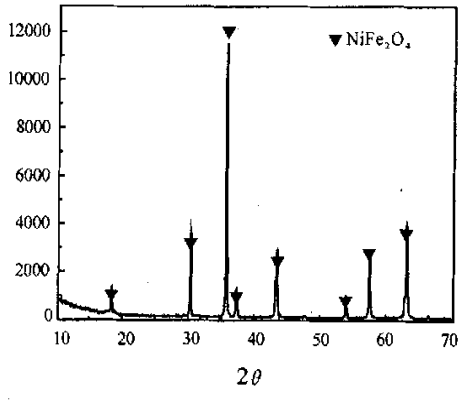

Fig. 1 XRD pattern of sample $NiFe_2O_4$ spinel

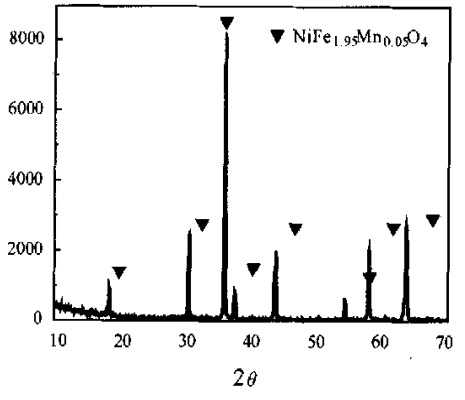

Fig. 2 XRD pattern of sample with 2%MnO_2

3.2 Effect of MnO_2 on sintering

The densities of the samples are listed in Table 1. The samples with MnO_2 have higher density, lower porosity and higher shrinkage than that of the sample without MnO_2. The sample with 1.0% MnO_2 has the maximum value of density and shrinkage, and the minimum value of porosity. This can be explained that trace MnO_2 can promote sintering.

Table 1 Density, porosity and linear shrinkage of the samples with different content of MnO_2

Amount of MnO_2/%	Density/(g·cm^{-3})	Porosity/%	Liner shinkage/%
0	3.685	30.34	8.17
0.5	3.762	28.12	9.07
1.0	4.108	20.76	11.19
1.5	4.098	20.73	11.02
2.0	4.086	21.34	10.73
2.5	4.035	23.19	10.11

The compound with spinel structure can get new physical and chemical properties after foreign ions take the ions which locate A or B in the spinel structure. Adding MnO_2 to raw materials Fe_2O_3 and NiO, the high valence ion Mn^{4+} can replace low valence ion Fe^{3+}, so it can cause the cation vacancy in the crystal lattice of $NiFe_2O_4$. The diffusion coefficient of the reactant is proportional to the concentration of lacunas in the solid-phase reaction[14]. With the diffusion coefficient increasing, the pores can be removed quickly, which is beneficial to sintering.

Solid-phase reaction is mainly dependent on the diffusion of the corpuscles of different reactants, and the temperature, atmosphere, adulterant, and lacuna and interface all can affect the diffusion. The motion of ion in the solid state matter is the course of hot activation; therefore the temperature has the especially important meaning for diffusion. Generally, the relation between diffusion coefficient and temperature can be given as formula (1):

$$D=D_0\exp\{-Q/RT\} \tag{1}$$

Temperature (T) and activation energy (Q) are two important factors to diffusion coefficient. Doping can lower diffusion activation energy, and then promote sintering.

On the other hand, the effect of temperature and adulterant on diffusion is by changing the matter's structure. Particles diffusion in solid materials is mainly by vacancy. In the crystalline material, except for hot vacancy, foreign ions can provide vacancy. In this paper, Mn^{4+} can replace Fe^{3+}, and then cation vacancy can be produced. Mn^{4+}, Fe^{3+}, Ni^{2+} can associate with vacancy V_k, and the association can diffuse quickly. But if the amount of adulterant is too much, the results will develop in the opposite direction.

3.3 Effect of MnO_2 on the electrical conductivity

The curves of conductivity—temperature are showed in Fig. 3. The conductivities of the sample with MnO_2 are all higher than that of the sample without MnO_2, so MnO_2 can promote the conductivity of the samples. Moreover, with the amount of MnO_2 increasing, the conductivity increases also. When MnO_2 is 1.0%, the conductivity is 1.168$\Omega^{-1}\cdot cm^{-1}$. When MnO_2 is 2.0%, the conductivity is 5 times of that of the sample without MnO_2. When MnO_2 is 2.5%, the conductivity lowers a little; the reason must be the conductivity is related to the density.

Adding MnO_2 to Fe_2O_3 and NiO, Mn^{4+} is the donor. According to the hole-conduction theory, when

Mn^{4+} replaces Fe^{3+} in the $NiFe_2O_4$, the conduction electron will be produced. The product of conduction electron can be beneficial to the conductivity.

The reaction is

$$3MnO_2 \xrightarrow{NiFe_2O_4} 3Mn_{Fe}^{\square} + 3e' + 4O_o^{\times} + O_2(g) \quad (2)$$

In the formula, $Mn_{Fe}^{\square}$ represents Mn^{4+} replacing the lattice point of Fe^{3+}; $O_o^{\times}$ represents O^{2-} in the normal position; e' represents conduction electron. The conductivity σ is proportional to the concentrate of quasifree electron n, so the conductivity can be expressed as follows:

$$\sigma = \sum n_i Z_i e B_i \quad (3)$$

In this formula, σ is conductivity ($\Omega^{-1} \cdot m^{-1}$); n_i represents amount of current carriers in the unit volume; Z_i represents valence number of carriers; e is the electron charge; B_i is the mobility of carriers.

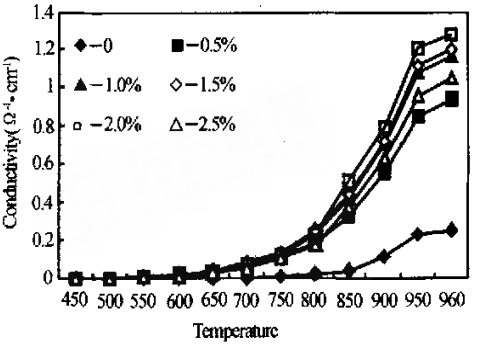

Fig. 3 Conductivity of the samples with different content of MnO_2

Conductivity is related to the amount of MnO_2, but the conductivity is not proportional to the amount of adulterant. The conductivity falls when the amount of MnO_2 keeps increasing. The reasons must be too much MnO_2 exceed the solid solubility in $NiFe_2O_4$, the electrical property will develop in the opposite direction. On the other hand, the conductivity is related to the density of materials. Pores in the materials make the electric phases discontinuous and then hinder the movement of conducting particles.

3.4 Effect of MnO_2 on corrosion rate

The corrosion rate of the samples was showed in Fig. 4. MnO_2 can improve the corrosion resistance of the samples of $NiFe_2O_4$. The corrosion rate of the sample without MnO_2 is 0.0482 $g \cdot h^{-1} \cdot cm^{-2}$. When MnO_2 is 1%, the corrosion rate is the lowest, 0.0096 $g \cdot h^{-1} \cdot cm^{-2}$; It is 1/5 of that of the sample without MnO_2.

The microstructure of the sample's surface were analysed after samples were erodes in cryolite, as shown in Fig. 5 and Fig. 6. There are many holes on the surface of the sample without MnO_2. But there are few holes on the surface of the sample with 1%MnO_2; moreover the grains are fine, so the sample is dense. In other words, MnO_2 can make grains finer, and make the sample dense, so molten salt can not erode inside further.

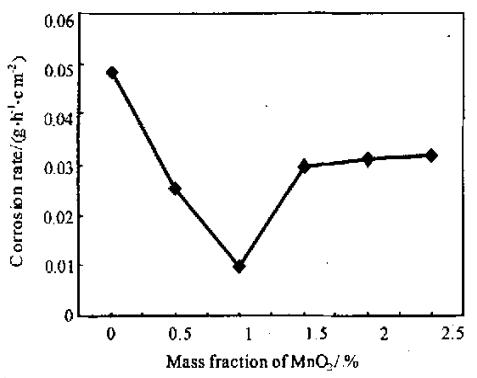

Fig. 4 Corrosion rate of the samples with different content of MnO_2

The surface of the sample eroded in cryolite was analysed by XRD. XRD patterns of sample without MnO_2 and with 1% MnO_2 are showed in Fig. 7(a) and Fig. 7 (b). The main phases on the surface of sample without MnO_2 are $NiFe_2O_4$ and solid solution $(Fe_{0.847}Al_{0.153})(Al_{1.847}Fe_{0.153})O_4$. But on the surface of the sample with 1%MnO_2, there is $MnAl_2O_4$ except for solid solution $(Fe_{0.803}Al_{0.197})(Al_{1.803}Fe_{0.197})O_4$. $MnAl_2O_4$ must be the product of Mn^{4+} and Al_2O_3 in the molten salt. $MnAl_2O_4$ forms a dense protective layer and prevents molten salt from eroding further. According to the microstructure and XRD, $MnAl_2O_4$ can improve the corrosion resistance.

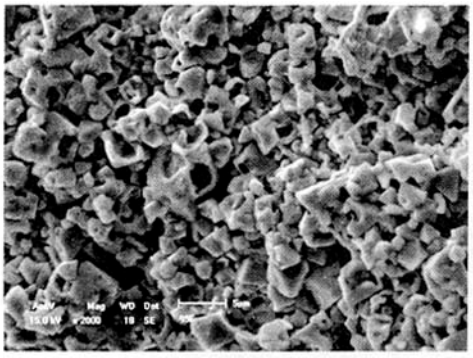

Fig. 5 SEM of $NiFe_2O_4$ sample eroded by molten salt cryolite

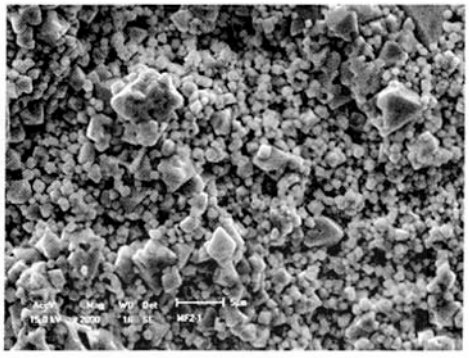

Fig. 6 EDX of sample with 1% MnO_2 eroded by molten salt cryolite

Overcoming the corrosion of inert anodes is the key problem at present. So the appropriate amount of MnO_2 is 1%.

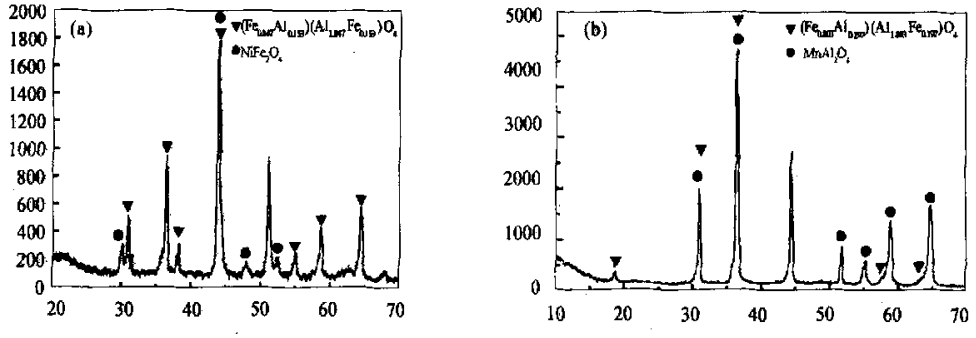

Fig. 7 XRD Pattern of samples eroded by cryolite

(a)——XRD pattern of sample without MnO_2; (b)——XRD pattern of sample with 1% MnO_2

4 Conclusions

(1) When MnO_2 is added, no new phases exist, and MnO_2 and $NiFe_2O_4$ form solid solution. Mn^{4+} replaces Fe^{3+}, and the sample still has the structure of $NiFe_2O_4$ spinel, but the crystal lattice of $NiFe_2O_4$ spinel became aberrated.

(2) MnO_2 can be beneficial to sintering and improve density.

(3) When MnO_2 is added, Mn^{4+} replaces Fe^{3+} and produces conduction electron. The product of conduction electron can be beneficial to the conductivity.

(4) The corrosion resistance of the samples was enhanced by adding MnO_2. When MnO_2 is 1.0%, the sample's corrosion rate is 1/5 of that of sample without MnO_2.

(5) The key problem on inert anodes is anode corrosion, so we consider the optimal amount of MnO_2 is 1.0%.

References

[1] Sadoway D R. Inert anodes for the Hall-Heroult cell: The ultimate materials challenge[J]. JOM, 2001, 53(5): 34—35.

[2] Benedyk J C. Status report on inert anode technology for primary aluminium[J]. Light Metal Age, 2001, 59(1—2): 36—37.

[3] Kvande H, Haupin W. Inter anodes for aluminum smelting: cnergy balances and environmental impact[J]. JOM, 2001, 53(5): 13—18.

[4] Pawlek R P. Research, development and potential[J]. Light Metal Age, 2002, 60(1—2): 50—55.

[5] Keller R, Rolseth S, Thonstad J. Mass transport considerations for the development of oxygen-evolving anodes in aluminum electrolysis[J]. Electrochim. Acta, 1996, 42(12): 1809—1917.

[6] Olsen E, Thonstad. Behaviour of Nickel ferrite cermet materials as inert anodes[A]. Light metals[C]. USA: Minerals, Metals and materials Society, 1996. 249—257.

[7] Xiao H, Hovland R, Rolseth S, *et al*. Studies on the corrosion and the behavior of inert anodes in aluminum electrolysis[J]. . Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, 1996, 27(2): 185—193.

[8] Yu X J, Qiu Z X, Jin S Z. Summary on the studies of inert anode materials of aluminium electrolysis[J]. Journal of Zibo college, 1999, 1.(1): 55—60.

[9] Thonstad J, Olsen E. Cell operation and metal purity: challenges for the use of inert anodes[J]. JOM, 2001, 5: 36—38.

[10] B. S. Skidan. The effect of additives on properties of ceramics based on zinc oxide[J]. Glass and ceramics, 2003, 60 (9—10) 339—341.

[11] Jiao W L, Zhang L, Yao G C, *et al*. Sintering process of $NiFe_2O_4$ Spinel with and without TiO_2 adding[J]. Journal of the Chinese ceramic society, 2004, 32(9): 1150—1153.

[12] Lu D S, Li W S, Liu X, Qiu S Z. Effects of doped metal elements on the structure and the electrochemical performances of spinel Lithium manganese oxide[J]. China's Manganese industry, 2002, 20(2): 30—35.

[13] Tian Z L, Lai Y Q, Duan huanan, *et al*. Effect of adding SnO_2 on electrical conductivity of nickel ferrite ceramics [J]. Conservation and utilization of mineral resource, 2004, 5: 37—40.

[14] Zeng R J. Chemistry of inorganic material[M]. Xiamen: Xiamen University press, 2001.