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Effect of additive V_2O_5 on sintering mechanism and properties of inert anodes of $NiFe_2O_4$ spinel

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Abstract: In order to improve the properties of inert anode of $NiFe_2O_4$ spinel, some additive V_2O_5 was added to raw materials-powders of NiO and Fe_2O_3. The powders of NiO, Fe_2O_3 were mixed with slight amount of V_2O_5, then they are moulded and sintered at 1200℃ for 6h. The sintering mechanism of powders of NiO and Fe_2O_3 with some additive V_2O_5 was researched. The effect of V_2O_5 on density, electrical conductivity and corrosion resistance of inert anode of $NiFe_2O_4$ spinel was studied at the same time. The results show that the sintering mechanism for powders of NiO and Fe_2O_3 with some additive V_2O_5 is liquid-phase sintering. Additive V_2O_5 can increase the density of the samples, especially it improves the corrosion resistance of the samples remarkably. When the amount of V_2O_5 is 1.5%, the sample's corrosion rate is 1/80 of that of sample without V_2O_5. But the electrical conductivity of the samples with V_2O_5 is lower than that of the sample without V_2O_5.

Key words: V_2O_5; $NiFe_2O_4$ spinel; inert anode; density; electrical conductivity; corrosion resistance
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1 Introduction

The idea of using inert anodes (also called non-consumable or oxygen-producing anodes) in aluminum production is as old as the Hall-Heroult process, dating back to one of the inventors, Charles Martin Hall. An inert anode is intended to replace a consumable carbon anode, the cell reaction is

$$Al_2O_3 + 3/2C = 2Al + 3/2CO_2 \tag{1}$$

The requirements for low energy consumption, low production investment and reducing the emission of greenhouse gas speed the research for inert anodes in aluminum production. With an inert anode, the cell reaction will be

$$Al_2O_3 = 2Al + 3/2O_2 \tag{2}$$

The use of non-consumable anodes will emit oxygen and eliminate the consumption of anode carbon in the electrolytic process and, with it, the emission of the greenhouse gases CO_2, CO, CF_4, C_2F_6, and most of the sulfurous gases (SO_2, COS, CS_2, H_2S). Since the use of the Hall-Heroult process, the research for inert anodes in aluminum production has been an extensive topic[1-3]. Investigators have carried out a lot of research work and trials in order to seek the appropriate materials for inert anodes in aluminum production[4-7].

S. P. Ray applied the patent of inert anodes of $NiFe_2O_4$ spinel-based composite oxides. Henceforth the

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research for inert anodes of $NiFe_2O_4$ spinel is very positive[8-10]. In 1990, U.S. Department of Energy carried out the benchscale research, the current being 120 A. The results of this test were better. In 1993, the industrial test—the current being 6000 A was carried out. The test was failed, and it exposed the main problems, that were: (1) poor corrosion resistance; anode was eroded then affected the quality of aluminum; (2) poor thermal shock resistance of large-sized anodes, when the anodes were put into the cryolite-based melt at high temperature, the anodes cracked due to being heated rapidly. At present, the key problem with inert anodes is anode corrosion[11,12].

In this paper, the inert anodes of $NiFe_2O_4$ spinel with 15% excess NiO and little amount of V_2O_5 were synthesized. The effects of V_2O_5 on sintering and the properties of electrical conductivity、corrosion resistance were studied.

2 Experimental

2.1 Preparation of $NiFe_2O_4$ with small amount of V_2O_5

When synthesizing $NiFe_2O_4$ with 15% excess NiO, Fe_2O_3 and NiO powders were used as main raw materials, at the same time different amount of V_2O_5 was added. The powders were blended, milled and granulated, then molded. The biscuits were sintered at 1200℃ for 6 h, then the inert anode of $NiFe_2O_4$ spinel doped with little amount of V_2O_5 was prepared.

2.2 Performance testing

The samples' densities were tested by Archimedes draining method. The pyroconductivity was tested by voltammetry. The samples' static state corrosion rates in molten cryolite were tested in loss in weight technique. 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 Sintering mechanism

The curves of the samples' density and volume shrinkage are showed in Fig. 1. The samples' density and volume shrinkage increase with the content of V_2O_5. The fact shows that V_2O_5 can promote sintering, especially when the content of V_2O_5 is more than 1%.

The melting point of V_2O_5 is low, about at 650－750℃[13]. The sintering temperature in this test was 1200℃, So when the V_2O_5 was added, the course of sintering was liquid-phase sintering. During sintering, liquid phase accrued. The liquid phase scattered on the surface of NiO and Fe_2O_3, so, the surface tension of the liquid phase made the solid grains contact and then promote sintering. The characteristic of liquid-phase sintering was more obvious with the amount of liquid phase. On the other hand, V_2O_5 could dissolve part of Fe_2O_3 and NiO, and the process of dissolving and depositing promoted the grains growth completely. The phenomena could be seen in Fig. 3.

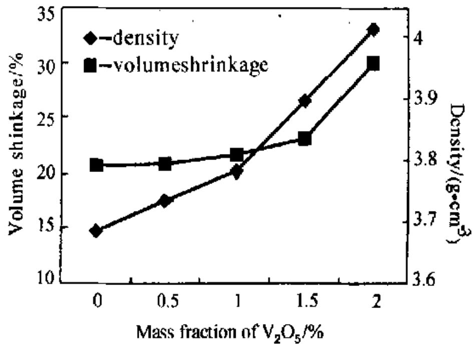

Fig. 1 Effect of V_2O_5 on density and volume shrinkage of the sample

In Fig. 1 we also can see the samples' density and volume shrinkage increase rapidly with the content of

V_2O_5, especially when the amount of V_2O_5 is 1.5%. The phenomena show that the amount of V_2O_5 increases, the amount of liquid phase increases too, and the characteristic of liquid-phase sintering is more obvious.

The driving force of densification of liquid-phase sintering is the liquid's capillary force between fine grains. This force produces the pressure between grains, and it makes the grains glide easily and realign. At the same time, the capillary force made the solid grains dissolve and deposit, which made the contact sites become flat, then the biscuits shrinked. Further more due to the liquid phase, the cervix growth of the solid grains quickened. The liquid-phase sintering can make the samples densification through the several processes[14].

3.2 Microstructure of samples with V_2O_5

The microstructures of samples without V_2O_5 and with 1.5% V_2O_5 are showed in Fig. 2 and Fig. 3 respectively. The grain size in the sample without V_2O_5 is uniformity, being 2−4 μm commonly, and the grains are granulose. But when 1.5% V_2O_5 was added, the grain size accretes obviously. Further more, the grain size is nonuniform, being 2−7 μm, and the big grain is octahedron. It shows that V_2O_5 can promote the grain to grow and develop completely. During sintering, liquid-phase occurred in the system ($Fe_2O_3 - NiO - V_2O_5$), so the densification was got through mass transfer in liquid phase. The small grains dissolved, and the big grains grew big, so the grains sizes are nonuniform.

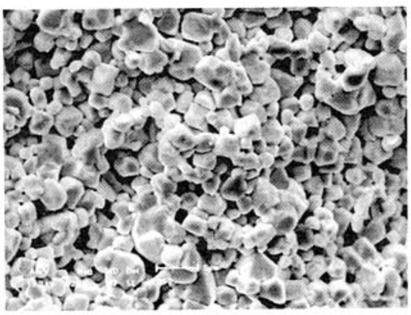

Fig. 2 SEM of sample without V_2O_5

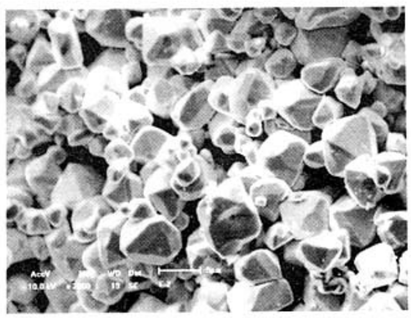

Fig. 3 SEM of sample with 1.5% V_2O_5

3.3 Effect of V_2O_5 on the sample's conductivity

The curves of conductivity of the samples with different content of V_2O_5 are given in Fig. 4. The conductivity increases with the account of V_2O_5, but the conductivity is lower than that of the samples without V_2O_5. The result shows that V_2O_5 restrains the conductivity of $NiFe_2O_4$ spinel. The phenomena can be explained by reaction product when V_2O_5 is added.

Ternary phase diagram of the system $NiO-V_2O_5-Fe_2O_3$[15] is showed in Fig. 5. The reaction products of the compositions of the system $NiO-V_2O_5-Fe_2O_3$ in this paper lies in the XI section. The phase compositions in this section are $Ni_2FeVO_6-NiO-NiFe_2O_4$. In the process of sintering, V_2O_5 becomes liquid, and the liquid concentrates at the grain boundaries.

The reaction product of V_2O_5 and Fe_2O_3, NiO is Ni_2FeVO_6, and the conductivity of Ni_2FeVO_6 is poorer than that of $NiFe_2O_4$. Ni_2FeVO_6 makes the barrier potential of grain boundaries increase. In the semiconductor ceramics, the barrier potential of grain boundaries has great effect on the materials' properties. So the samples' conductivity with V_2O_5 is lower than that of the samples without V_2O_5. But the samples' conductivity increases with the amount of V_2O_5. The reason is that the samples' conductivity is not only re-

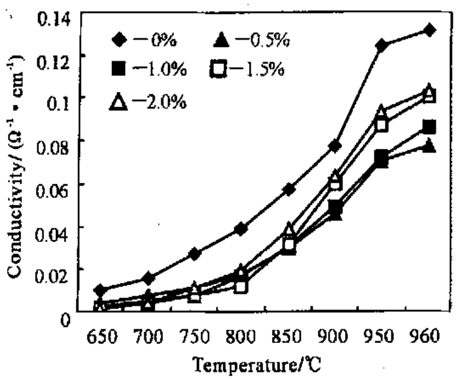

Fig. 4 Conductivity of the samples with different content of V_2O_5 at different temperature

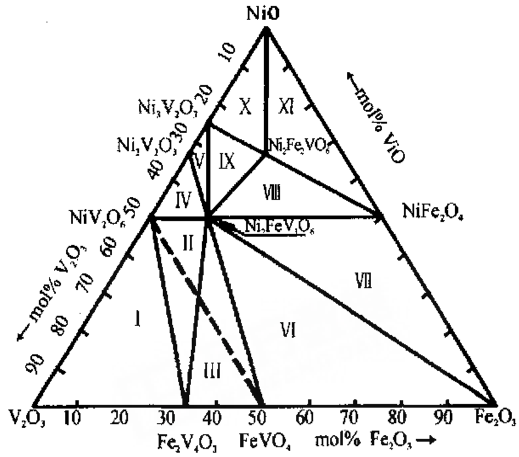

Fig. 5 Ternary phase diagram of $NiO\text{-}V_2O_5\text{-}Fe_2O_3$

lated to additive, but also related to density of the samples.

3.4 Effect of V_2O_5 on the sample's corrosion rate

The samples' corrosion rates are showed in Fig. 6. In Fig. 6, we can see the corrosion rates of the samples with V_2O_5 are much lower than that of the samples without V_2O_5. The corrosion rate of the samples without V_2O_5 is $0.07302\ g\cdot h^{-1}\cdot cm^{-2}$, but the samples with 0.5% V_2O_5 is $0.010998\ g\cdot h^{-1}\cdot cm^{-2}$. The sample's corrosion rate is 1/5 of that of the sample without V_2O_5. When the addition level is 1.0%, the corrosion rate is $0.004441\ g\cdot h^{-1}\cdot cm^{-2}$, 1/15 of that of the sample without V_2O_5. The minimum of the corrosion rate of the sample is that with 1.5% V_2O_5. The corrosion rate is $0.000592\ g\cdot h^{-1}\cdot cm^{-2}$, about 1/80 of that of the sample without V_2O_5. V_2O_5 can improve the samples' corrosion resistance greatly, so it is a good additive for improving the corrosion resistance. As a candidate material for inert anodes, corrosion resistance of $NiFe_2O_4$ spinel is demanded rigorously. So V_2O_5 has great significance for improving corrosion resistance.

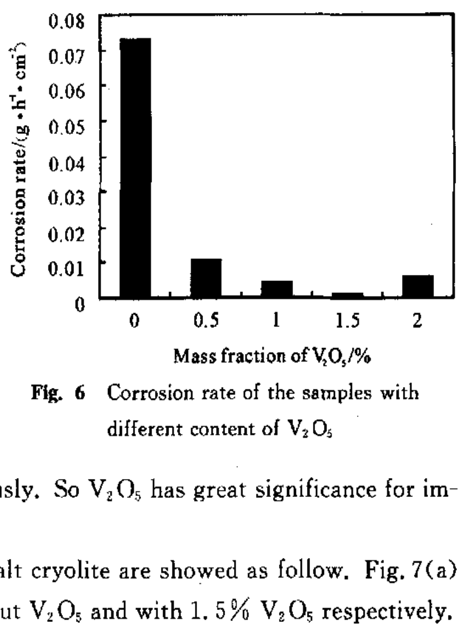

Fig. 6 Corrosion rate of the samples with different content of V_2O_5

The SEM and EDX analysis of samples eroded by molten salt cryolite are showed as follow. Fig. 7(a) and Fig. 8(a) are the microstructure of the eroded samples without V_2O_5 and with 1.5% V_2O_5 respectively. The grains of the samples eroded by molten salt cryolite have some holes. Comparing the Fig. 8 and Fig. 7, we can find that the holes on the grains of the samples with 1.5% V_2O_5 are fewer than that of the sample without V_2O_5. This is coincident with the result of the samples' corrosion rate.

Fig. 7(b) and Fig. 8(b) are the EDX analysis of the eroded samples without V_2O_5 and with 1.5% V_2O_5 respectively. Comparing Fig. 8(b) with Fig. 7(b), we can see that the amount of Fe in the sample with V_2O_5 is more than that of the sample without V_2O_5. The element V also can be found in the sample. The eroded by molten salt cryolite

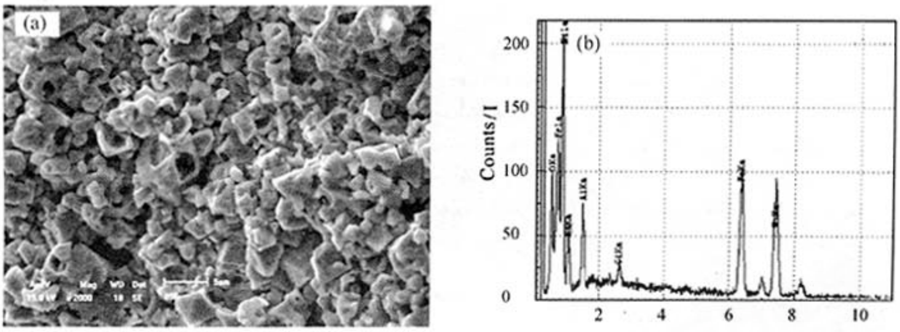

Fig. 7 SEM photography (a) and EDX analysis (b) of the sample of $NiFe_2O_4$

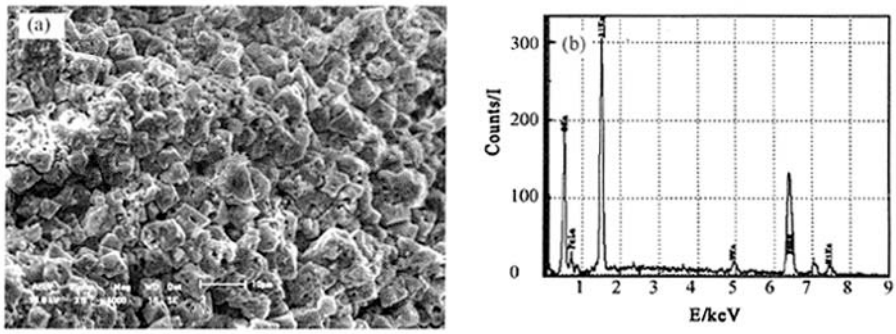

Fig. 8 SEM photography (a) and EDX analysis (b) of sample with 1.5% V_2O_5

reason maybe the reaction product Ni_2FeVO_6 lies in the grain boundaries, and Ni_2FeVO_6 has good corrosion resistance. Ni_2FeVO_6 increases the stability of the grain boundaries, so the sample's corrosion resistance can be promoted.

After analyzing the effect of V_2O_5 on the samples' properties, we confirm the optimal amount of V_2O_5 is 1.5%.

4 Conclusion

V_2O_5 can promote sintering, improve the samples' density and shrinkage. Further more, it can improve the samples' corrosion resistance remarkably. But the conductivity of the samples falls.

Improving the corrosion resistance of the materials used for inert anodes is the key question that must be solved urgently. In this paper, V_2O_5 can improve the samples' corrosion resistance remarkably, so it's an interesting additive. Although it reduces the conductivity, we can improve the conductivity by adding some metals. This question will be researched further.

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