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Effect of additive on corrosion resistance of $NiFe_2O_4$ ceramics as inert anodes

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Abstract: In order to improve the corrosion resistance of $NiFe_2O_4$ ceramics as inert anode, additive V_2O_5 was added to raw materials NiO and Fe_2O_3. The inert anodes of nickel-ferrite ceramics were prepared by powder metallurgic method and the static corrosion rate in Na_3AlF_6-Al_2O_3 was determined by mass loss measurement. The effect of V_2O_5 on sintering property and corrosion resistance was studied. The results show that V_2O_5 can promote the grain to develop completely and improve sintering property. EDS results show the reaction product Ni_2FeVO_6 distributes along the grain boundary. The corrosion tests show that V_2O_5 is beneficial to improving corrosion resistance remarkably. The reasons that V_2O_5 can improve the corrosion resistance must be V_2O_5 promoting the gains to develop completely and Ni_2FeVO_6 distributes along the grain boundary. The stable structure can control the chemical dissolution of ceramics anode and the reinforced grain boundary can control the grain-boundary corrosion rate.

Key words: $NiFe_2O_4$; inert anode; additive; corrosion resistance

1 Introduction

In conventional aluminium electrolysis, the major cell reaction is

$$1/2Al_2O_3+3/4C=Al+3/4CO_2 \tag{1}$$

Thus, using carbon anodes has many disadvantage, such as the consumption of anode carbon and the emission of carbon dioxide and fluorocarbon. With an inert anode, the reaction[1] is

$$1/2Al_2O_3=Al+3/4O_2 \tag{2}$$

The introduction of inert anodes will evolve oxygen [2−3], being friendlily to environment, which makes the use of inert anode commercially attractive. Re- searches have been done in order to find the appropriate material for inert anodes in aluminum production.

However, the inert anode must meet some basic requirements[4]: to exhibit a low corrosion rate in the high-temperature melts and environment of high oxidizability; not to contaminate the produced metal Al; to be economically feasible and to be a good electric conductor. A lot of research work has been carried out, which can be divided into three classes, namely, metals [5−6], ceramic oxides[7−8], and cermets[9−10], but no material has been found to satisfy all these requirements. One of the formidable challenges is the corrosion property.

The major corrosion mechanisms of inert anodes in electrolyte are chemical dissolution, electrolyte penetration as well as electrochemical dissolution.

As discussed by RAY[11], the cermets anode material may be corroded via several mechanisms such as oxidation, chemical dissolution (fluorination), electrochemical dissolution, reduction by dissolved metal Al, electrolyte penetration, and grain boundary attack. Under conventional electrolysis conditions, chemical dissolution and electrolyte penetration serve as two major corrosion mechanisms[12−13].

For the chemical dissolution, the reasons are the dissociation of $NiFe_2O_4$ ceramics and the following reactions with electrolyte[14]:

$$2AlF_3(s)+3FeO(s)=3FeF_2(s)+3/2O_2(g)+2Al(l) \tag{3}$$

$$2AlF_3(s)+Fe_2O_3(s)=2FeF_3(s)+3/2O_2(g)+2Al(l) \tag{4}$$

$$2AlF_3(s)+3NiO(s)=3NiF_2(s)+3/2O_2(g)+2Al(l) \tag{5}$$

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As for the electrolyte penetration, LI et al[14] thought it may result from two reasons. The first one is due to pores left by the electrochemical dissolution of metal phase when anodes are polarized, or by the metal phase oxidation and the following preferential chemical dissolution. Bath penetrates into these pores by capillary effects. The second one is the selective dissolution of Fe. In the ceramic phase of the $NiFe_2O_4$-based anode, Fe has a fairly high solubility in cryolite, compared with Ni. So improving the density of ceramics matrix and strengthening the grain boundary are very important.

In this work, the $NiFe_2O_4$ ceramics with little amounts of V_2O_5 (0−2.0%, mass fraction) were prepared. By determining the density and corrosion rate of anodes and analyzing anode by EDS connected to the SEM, we expected to see how V_2O_5 affects the sintering property and corrosion resistance.

2 Experimental

2.1 Preparation of $NiFe_2O_4$ ceramics

The raw materials, NiO, Fe_2O_3 and V_2O_5 were all in reagent grade. $NiFe_2O_4$ ceramics samples with V_2O_5 were prepared by cold pressing-sintering process. NiO and Fe_2O_3 and a proper amount of V_2O_5 (0%, 0.5%, 1.0%, 1.5%, 2.0%, respectively) were mixed by ball milling and then the mixed powders were cold pressed into rectangular blocks (70 mm×18 mm×(10−11) mm) at the pressure of 100 GPa and sintered at 1 200 ℃ for 6 h.

2.2 Performance tests

The density was tested by Archimedes draining method. Samples with V_2O_5 were prepared for characterization by DSC (SDT Q600), DTA (SDT22960) and X-ray diffraction (XRD) (RigakuD/max-RB) to investigate if there are foreign phases produce.

The samples were immerged in molten cryolite, with temperature maintained at 960 ℃ for 10 h, to determine the static state corrosion rate. The electrolyte was made up of reagent grade CaF_2 and AlF_3, technical grade NaF and Al_2O_3. The CR (molar ratio of NaF to AlF_3) was kept to be 2.2, and the concentrations of CaF_2 and Al_2O_3 were both kept to be 5% (mass fraction). The eroded samples were washed in 30%$AlCl_3$ solution at 100 ℃ to remove the adhering melt. The corrosion rate was determined by mass loss measurement.

Some anodes were analyzed by scanning electron microscope(SEM) (SSM550) and energy dispersive spectrometer(EDS) connected to the SEM.

3 Results and analysis

3.1 Effect of V_2O_5 content on ceramics density

The changes of density and volume shrinkage with the content of V_2O_5 are shown in Fig.1. From Fig.1, it can be found that in the range of 0−2.0% V_2O_5, the higher the V_2O_5 content, the higher the density and the larger the volume shrinkage, especially when the content of V_2O_5 is more than 1%. The fact shows that V_2O_5 can promote sintering property.

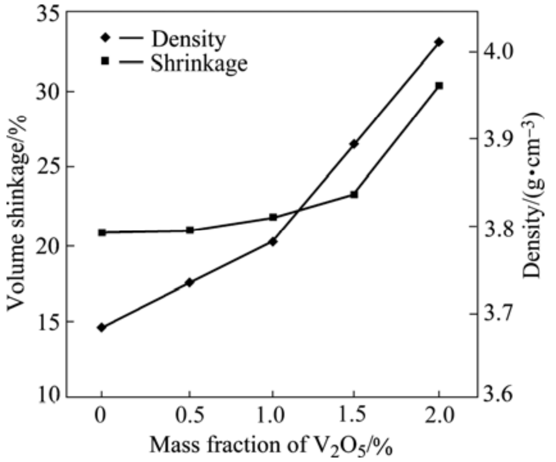

Fig.1 Effect of V_2O_5 on density and volume shrinkage

The microstructures of samples without V_2O_5 and with 1.5%V_2O_5 are shown in Fig.2(a) and Fig.2(b) respectively. The grain size in the sample without V_2O_5 is small and uniform, being 2−4 μm commonly, and the grains are granulose. But when 1.5%V_2O_5 is added, the grain size accretes obviously. Furthermore, the grain size is non-uniform, being 2−8 μm, and big grain is octahedron. This shows that V_2O_5 can promote the grain

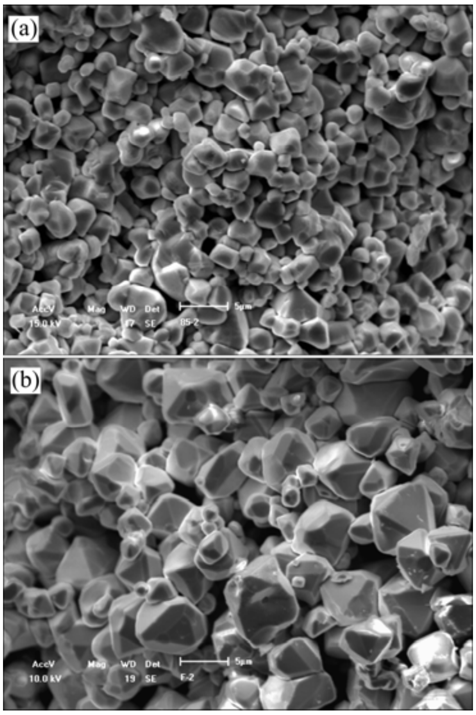

Fig.2 SEM photographs of samples: (a) Without additive; (b) With 2.0%V_2O_5

to grow and develop completely.

In order to analyze the effect of V_2O_5 on sintering, the distribution of elements such as Ni, Fe, V and O on the polished surface of $NiFe_2O_4$ with 2.0% V_2O_5 was analyzed by scanning electron microscopy, as shown in Fig.3. It can be seen that the element V distributes along the grain boundary.

Ternary phase diagram of the system NiO-V_2O_5-Fe_2O_3[15] is shown in Fig.4. The reaction products of the compositions of NiO-Fe_2O_3-2%V_2O_5 in this work lies in the XI section. The phase compositions in this section are Ni_2FeVO_6, NiO and $NiFe_2O_4$.

In order to study if there are new phases produce, the DSC was carried out on the Fe_2O_3-NiO-2%V_2O_5 system, and the curve is shown in Fig.5(a). There is a small exothermic peak at 625−650 ℃. It can be determined that a chemical reaction arises at 625−650 ℃. Due to the fact that the amount of V_2O_5 is too little, the exothermic peak is not obvious. Then the DTA was carried out on the Fe_2O_3-NiO-30%V_2O_5 system, and the curve is shown in Fig.5(b). A exothermic peak exists from 625.07 ℃ to 651.64 ℃. It is same as the former. In order to study the new phase, XRD analysis was carried out. Fig.6 shows the XRD pattern of sample with 2.0%V_2O_5. It can be seen that the new phase is Ni_2FeVO_6. The peak is probably associated with the produce of Ni_2FeVO_6. Combining with Fig.3, we can know Ni_2FeVO_6 concentrates at the grain boundary. According to Ref.[15], the melting point of Ni_2FeVO_6 is low. At the sintering temperature adopted in this work, Ni_2FeVO_6 becomes liquid. The sintering of the system (Fe_2O_3-NiO-2%V_2O_5) is liquid-phase sintering, so in this process, the densification was gotten through mass transfer of liquid phase. The small grains dissolve, and the big grains grow bigger, so the grain sizes are non-uniform. And the liquid can promote the grains to grow and develop completely with the regular octahedron shape. With the amount of V_2O_5 increasing, the amount of liquid increases, so the character of liquid improving sintering is more obvious.

3.2 Effect of V_2O_5 content on corrosion resistance

The effect of V_2O_5 content on corrosion rate is shown in Fig.7, from which it is obvious that adding V_2O_5 can dramatically lower the corrosion rate. Corrosion rate of sample without V_2O_5 is 0.048 2 $g\cdot cm^{-2}\cdot h^{-1}$. The

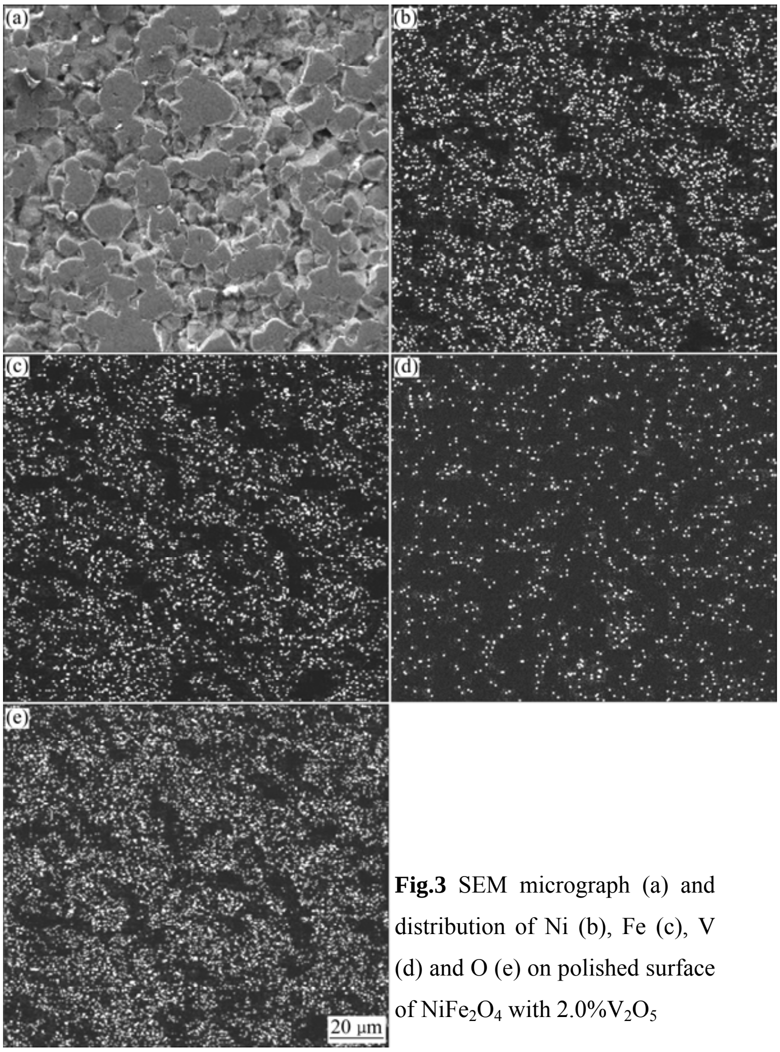

Fig.3 SEM micrograph (a) and distribution of Ni (b), Fe (c), V (d) and O (e) on polished surface of $NiFe_2O_4$ with 2.0%V_2O_5

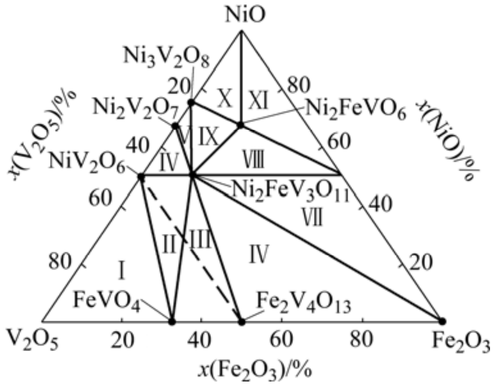

Fig.4 Ternary phase diagram of $NiO\text{-}V_2O_5\text{-}Fe_2O_3$

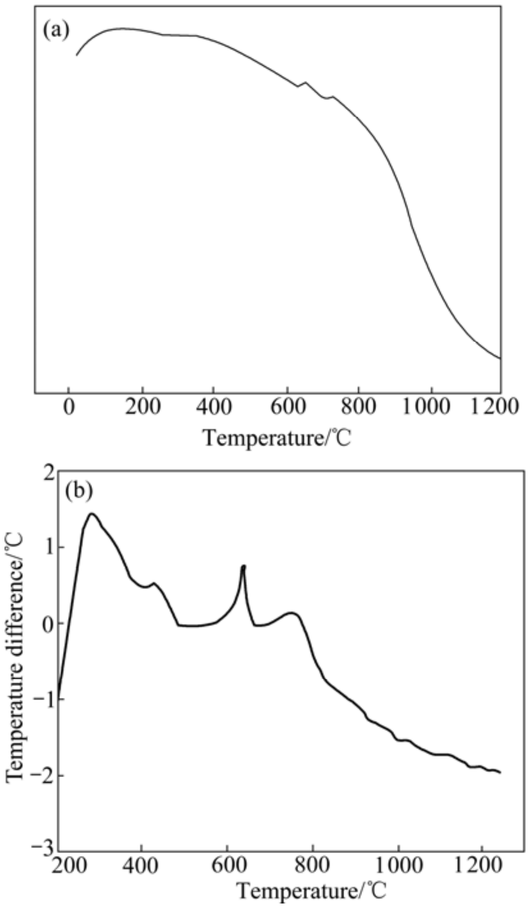

Fig.5 DSC curve of $Fe_2O_3\text{-}NiO\text{-}2\%V_2O_3$ (a) and DTA curve of $Fe_2O_3\text{-}NiO\text{-}30\%V_2O_5$ system (b)

corrosion rate of sample with $0.5\%V_2O_5$ is 0.011 $g\cdot cm^{-2}\cdot h^{-1}$, 1/4 of that of sample without V_2O_5. The corrosion rate of sample with $1.5\%V_2O_5$ is the lowest, being 0.001 05 $g\cdot cm^{-2}\cdot h^{-1}$, 1/46 of that of sample without additive.

After being eroded in molten salt, the two samples are all in good condition, no crack or tumescence. But the sample without V_2O_5 is not smooth, many visible pits on it. On the contrary, the sample with $1.5\%V_2O_5$ is smooth and no visible pits appear.

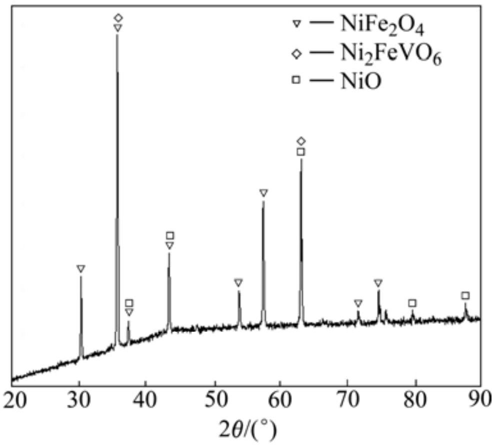

Fig.6 XRD pattern of sample with $2.0\%V_2O_5$

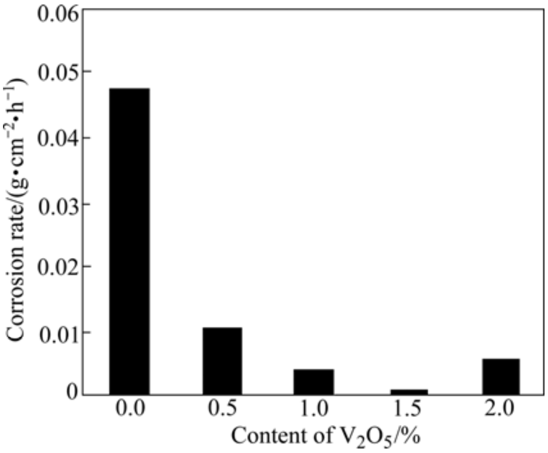

Fig.7 Corrosion rate of samples with different contents of V_2O_5

The eroded surfaces were characterized by SEM, as shown in Fig.8. From Fig.8(a), it can be found that many big holes on the grains and the grains become loosen because the grain boundary is attacked by molten cryolite. From Fig.8(b), it can be seen that the sample is eroded slightly then its surface is flat. There are only the fewer and smaller holes on the grains and grains bind closely. So the grain and grain boundary all have good corrosion resistance to melt and could effectively hold back the melt penetration.

The surface of sample with V_2O_5 is eroded slightly, which is coincident with the result of the samples' corrosion rate.

The reasons that V_2O_5 can improve the corrosion resistance must be V_2O_5 promoting the gains to develop completely with the octahedron shape and Ni_2FeVO_6 concentrating at grain boundary. The stable structure could control the chemical dissolution of ceramics anode, which is beneficial to improving the corrosion resistance of sample in molten cryolite. Moreover the reaction product Ni_2FeVO_6 concentrates at grain boundary and it has good corrosion resistance, so can reinforce the corrosion resistance of the grain boundary. As the candidate materials of inert anodes, the requirement to corrosion rate is rigorous. Improving the corrosion resistance is the key problem that researchers are making great efforts to solve. In this work, adding V_2O_5 can increase the corrosion resistance of sample remarkably, so V_2O_5 is an interesting additive for $NiFe_2O_4$ ceramics.

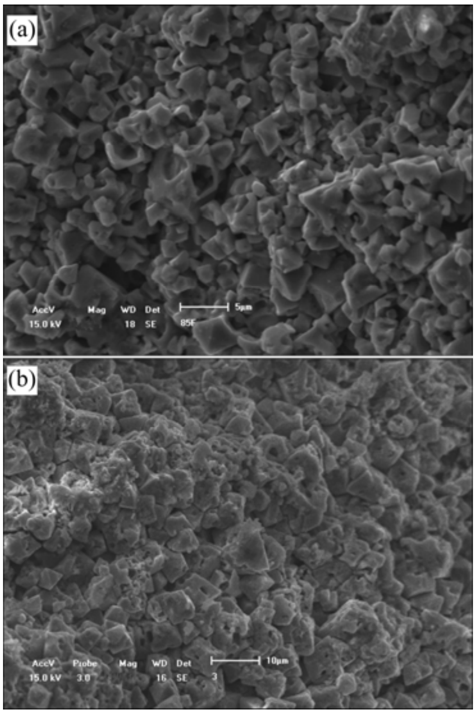

Fig.8 SEM photographs of samples eroded by molten cryolite: (a) Without additive; (b) With 1.5%V_2O_5

4 Conclusions

1) When V_2O_5 is added to NiO, Fe_2O_3 and Ni_2FeVO_6 are produced, which has lower melting-point. During sintering, it becomes liquid and then promotes sintering property.

2) V_2O_5 can improve the corrosion resistance of samples in molten cryolite remarkably. After being eroded for 10 h, the sample with 1.5%V_2O_5 is in good condition and the corrosion rate of the sample is 1/46 of that of sample without additive.

3) The reasons that V_2O_5 can improve the corrosion resistance are that liquid promotes the grain to develop completely and Ni_2FeVO_6 concentrates at grain boundary. The stable structure could control the chemical dissolution of ceramics anode. Ni_2FeVO_6 has better corrosion resistance than $NiFe_2O_4$, so Ni_2FeVO_6 controls the grain-boundary corrosion rate.

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