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Study on sintering technique of $NiFe_2O_4$/SiCp used as matrix of inert anodes in aluminium electrolysis

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Abstract: In order to improve deficiencies of $NiFe_2O_4$ spinel used as matrix of inert anode in aluminium electrolysis, $NiFe_2O_4$/SiCp were prepared by the solid state reaction for the first time. Microstructural changes were observed by scanning electronic microscope and phase was determined with X-ray detector. Effect of sintering temperature and times on density, porosity and microstructure were researched, and the reasons that caused the difference were discussed deeply. At the same time the thermodynamical compatibility of $NiFe_2O_4$ and SiC was proved under 1200℃ by DTA. The results showed that the microstructure was more homogeneous when the sintering temperature reached 1180℃and the density attained their maximum about 6 h sintering. The appropriate sintering technique of $NiFe_2O_4/SiC_w$ composite materials was 1180℃×6 h.

Key words: aluminium electrolysis; inert anode; microstructure; sintering technique

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1 Introduction

Research demonstrated that $NiFe_2O_4$ spinel used as matrix of inert anode was appropriate in aluminium electrolysis[1,2]. $NiFe_2O_4$ spinel is with chemical inertness and electrochemical stability, but also is in possession of high temperature resistance, high stress and hardness[3]. But then its electro conductibility, toughness and resistance to thermal shock can't meet a demand when it is used in aluminium electrolysis, resulted in the anode cracked and the purity of the electrolytic Al bastardized as it is immersed into high temperature melting salt.

As a response to the request from the high-performance metallic and ceramic composites, SiC whiskers as a reinforcing material have become the subject of extensive research and development since the 1970s[4,5]. It is well known that SiC_w can remain thermal stability and high stress at higher temperature, at the same time it is with the stronger resistance to corrosion and oxidation, thus SiC_w as a kind of high strength fibrous material was commonly used as an effective reinforcing element to prepare composite material based metals, resins and ceramics[6,7].

The purpose of this paper is to introduce the preparation of high-performance $NiFe_2O_4/SiC_w$ composite material by research of appropriate sintering technique to improve the thermal shock resistance and toughness of $NiFe_2O_4$ spinel. The thermodynamical compatibility of $NiFe_2O_4$ and SiC_w was proved under 1200℃

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by DTA in this paper. Furthermore, effect of sintering temperature and times on density, porosity and microstructure were researched. Tests proved that the appropriate sintering technique of $NiFe_2O_4/SiC_w$ composite material was1180℃×6 h.

2 Experimental method and procedure

2.1 Preparation of $NiFe_2O_4$ samples containing SiC_w

We sintered NiO and Fe_2O_3 (mol. ratio 1:1) powder by mixing, grinding, extruding the ingredients and sintering the biscuit to be $NiFe_2O_4$ spinel at 1200℃. The Postgraduate Research Institute of Mining University of China supplied SiC_w with the length of 30—50 μm, and diameter 0.5—1 μm (as shown in Fig. 1(a)). According to the effect pH on Zeta electric potential of powder and SiC_w to control pH by NaOH and HCl liquors to disperse 5%(mass fraction) SiC_w evenly throughout $NiFe_2O_4$ powder[8,9], mixed with absolute ethyl alcohol.

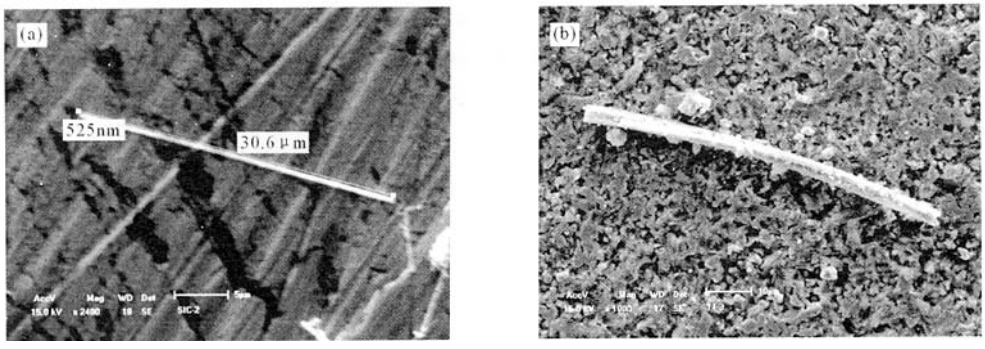

Fig. 1 Microstructures of SiC_w

(a)—before sintering; (b)—after sintering(1200℃)

2.2 Determination of the composition and measuring of the properties

The densities of samples were tested by Archimedes' draining method. The instruments used in the experiment were listed as follows:

D/max—RB X-ray diffractometer (made in Japan): CuK_α radiation; tubing pressure is 40 kV; tube current is100 mA, DT—30 thermal analyzer (made in Japan): alumina crucible; heating rate is 10℃/min in the air, SS—550 scanning electronic microscope (made in Japan).

3 The result and discussion

3.1 Effect of temperature on phase composition

The relevant reactions and free energies between 1100—1250℃ are indicated in Table 1[10]. The phase composition of complex by sintering NiO and Fe_2O_3 is shown in Fig. 2(a), it can be seen that resultant was single $NiFe_2O_4$ spinel. Figs. 2(b—d) show the phases composition of $NiFe_2O_4/SiC_w$ after sintering at 1150℃, 1200℃ and 1250℃. Except for $NiFe_2O_4$ and SiC phase, Figs. 2(b) and (c) contained SiO_2 phase that was formed with the oxidation of SiC in the air (as explained in Table1—(4) and (5)). It is well known that SiC is oxidated obviously to form into SiO_2 over 1140℃. But it can stably exist in neutral medium or reducing atmosphere under 2200℃ because generated SiO_2 can lay over the surface of SiC to hold back its further oxidation[11].

Table 1 Relevant reactions and free energies between 1100—1250℃

Possible reactions	ΔG_T/(kJ·mol^{-1})	
	1373.15 K	1523.15 K
(1) $Fe_2O_3+NiO=NiFe_2O_4$	−25.08	−25.64
(2) $6Fe_2O_3=4Fe_3O_4+O_2$	119.70	68.61
(3) $2Fe_3O_4=6FeO+O_2$	285.50	247.11
(4) $SiC+2O_2=SiO_2+CO_2$	−0.77	−0.72
(5) $SiC+1.5O_2=SiO_2+CO$	−0.77	−0.75
(6) $2FeO+SiO_2=2FeO\cdot SiO_2(s)$	−7.24	−4.08
(7) $2FeO\cdot SiO_2(s)=2FeO\cdot SiO_2(l)$	7.37	−1.88
(8) $2NiO+SiO_2=2NiO\cdot SiO_2$	−2.87	−1.49

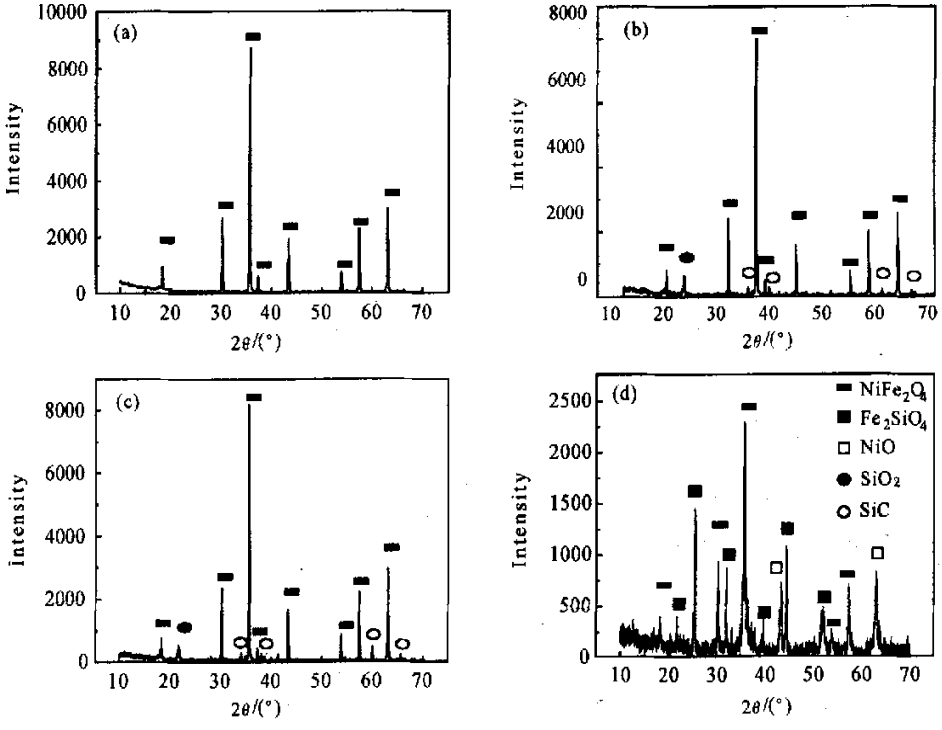

Fig. 2 XRD pattern at different temperatures

(a)—$NiFe_2O_4$; (b)—1150℃; (c)—1200℃; (d)—1250℃

The molten state and bigger porosities were observed in part of samples sintered at 1250℃, composition analysis indicated that Fe_2SiO_4 ($2FeO\cdot SiO_2$) and NiO phases accrued (as shown in Fig. 2(d)). Table1 illustrated that free energy (ΔG) was less than zero for reaction Table 1—(6) between 1100—1250℃. And the solid—liquid transformation of reaction Table 1—(7) occurred at 1219℃ ($\Delta G=0$), which led to the melting of samples. The porosities due to the oxidation of SiC_w produced bubbling. SiC phase was not seen in Fig. 2(d) and from reaction Table 1 (4)—(7).

The DTA curve showed thermodynamical compatibility of $NiFe_2O_4/SiC_w$ under 1200℃ (as shown in Fig. 3). Fig. 1(b) indicated that SiC_w can retain length diameter ratio without being sphericized under

1200℃.

3.2 Influence of sintering temperature on volume density

Fig. 4 illustrated that the density obviously increased with the rising of sintering temperature, then slightly reduced when the temperature was over 1180℃. Sintering temperature has an obvious impact on densification, the reason of which is that a series of physical processes during the sintering process relate to sintering temperature and hours[12].

Fig. 5 showed influence of sintering hours on volume density and porosity. It followed that the densities and porosities tended to stabilization when the sintering hours was more than 6 h.

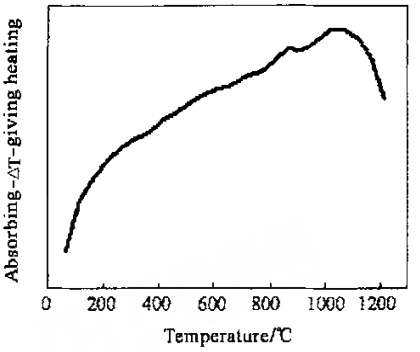

Fig. 3 DTA curves of the $NiFe_2O_4/SiC_w$ powders

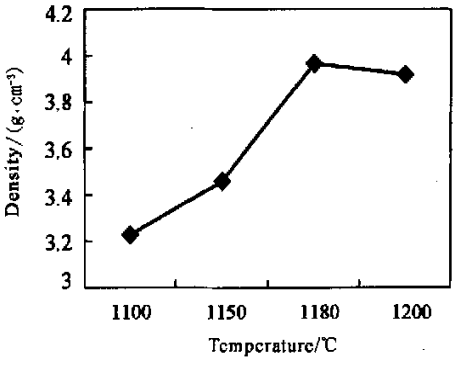

Fig. 4 Influence of sintering temperature and hours on volume

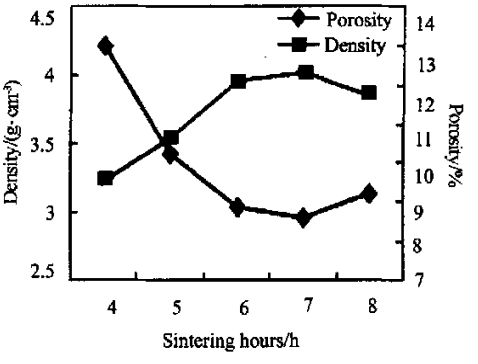

Fig. 5 Influence of sintering hours on volume density and porosity density

3.3 Effect of sintering temperature on microstructure

The microstructures of samples sintered at different temperature were shown in Fig. 6. The density was less due to much interconnected porosities (as shown in Fig. 6(a)) at 1100℃. In sintering process, the slipping and rearrangement of grains are easier with the rising of temperature, at the same time the columnar pipe changed from irregular porosities can come into being crystal boundaries, so that the density of sample sintered at 1150℃was higher than that at 1100℃. Fig. 6(c) illustrated that microstructure was more homogeneous and compact when the crystal boundary form into network. The abnormal growth of grains and excessive sintering were obvious when the temperature was 1200℃ (as shown in Fig. 6(d)). It could be seen that the tendency of the change of microstructure was in agreement with the change of density.

4 Conclusion

(1) The thermodynamical compatibility of $NiFe_2O_4$ and SiC was proved by DTA and thermodynamic calculation, and SiC_w can retain length diameter ratio without sphericizing under 1200℃.

(2) Composition analysis indicated that Fe_2SiO_4 ($2FeO \cdot SiO_2$) phases accrued when temperature was over 1220℃, so that the molten state and bigger porosities appear in regional area of samples.

(3) Microstructure was more homogeneous and compact at 1180℃, and the densities and porosities

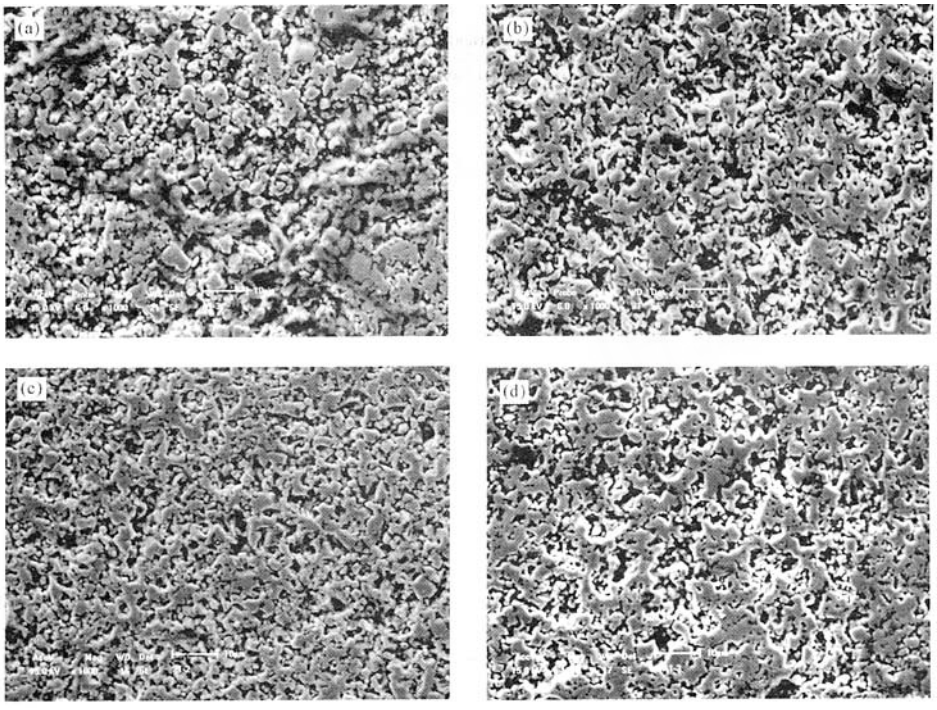

Fig. 6 Microstructures of samples
(a)—1100℃; (b)—1150℃; (c)—1180℃; (d)—1200℃

tended to stabilization when the sintering hours was more than 6h. So the appropriate sintering technique of $NiFe_2O_4/SiC_w$ composite materials was 1180℃×6 h.

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