

EFFECT OF MnO₂ ADDITION ON EARLY-STAGE SINTERING BEHAVIOR AND PROPERTIES OF NiFe₂O₄ CERAMICS

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Abstract

The samples with small amounts of MnO₂ (0, 0.5, 1.0, 2.5 wt%, respectively) were prepared via ball-milling process and two-step sintering process from commercial powders (i.e. Fe₂O₃, NiO and MnO₂). Microstructure features, phase transformation, the early-stage sintering behavior and mechanical properties of Mn-doped NiFe₂O₄ samples have been investigated. Results indicate that the reduction of MnO₂ into Mn₂O₃ and following the reduction of Mn₂O₃ into MnO existed in sintering process. No new phases are detected in the matrix, the crystalline structures of ceramic matrix are still NiFe₂O₄ spinel structure. MnO₂ addition can promote the sintering process. The temperature for 1 wt% MnO₂-doped samples to reach the maximum shrinkage rate is 59 °C lower than that of un-doped samples.

Introduction

Much attention has been paid on novel techniques of inert anodes in aluminum electrolysis area for many years [1]. With development of green anode materials for aluminum production, the current efficiency of aluminum electrolysis is as high as 96 % now, but consumable carbon anodes are used, the anode product being CO₂ and CO, also with fluorocarbons in the electrolysis process [2].

Up to now, various researches have been carried out to find a kind of appropriate materials as inert anodes, which would solve numerous ecological and economical problems through releasing environment-friendly O₂ during electrolysis. A patent applied by S. P. Ray in 1998 brought NiFe₂O₄ into researchers' view [3-5]. NiFe₂O₄ based cermets are one of the most promising candidate inert anodes materials for aluminum electrolysis production, which have the desirable properties of metallic materials as well as those of ceramics and possess a better corrosion resistance and a higher thermal shock resistance in the molten cryolite-alumina bath [6-8]. For low reactivity of solid substance in the preparation of ceramic matrix for the intensive bonding force among the solid particles, it is hard to obtain high density target products at lower temperatures. Preparing ultra-fine powder or using sintering promoters has been exploited [9-11] mostly to obtain target products. The latter one is more economical and directly to improve sintering ability for large-scale industrial fabrication. MnO₂ introduction can improve relative density of CeO₂ from 68% for un-doped samples to 94 % for 1 wt% MnO₂-doped samples sintered at 1300 °C for 1 h [12-14]. The densities of alumina samples containing 3.0 % MnO₂ and 0.5 %TiO₂ sintered at 1250 °C for 1 h are up to 98.2 % of the theoretical density

(T.D.) [15]. It can be seen that MnO₂ is an effective sintering promoter for certain ceramic materials mentioned above.

In this paper, a two-step sintering process was applied to prepare MnO₂-doped NiFe₂O₄ ceramics. Effect of MnO₂ introduction on early-stage sintering behavior, microstructures, mechanical properties and promoting sintering mechanism was presented.

Experimental Procedure

Synthesis

The molar ratio of NiO to Fe₂O₃ was 1.87:1 in mixture of NiO and Fe₂O₃ commercial powders. Ceramic bodies were fabricated from high purity reagents [Fe₂O₃: 99.3 %, NiO: 99.9 % and MnO₂: 97.5% (Guoyao, China)]. Raw materials were ground in distilled water via a ball-milling for 24 h and dried at 120 °C, then ground with 4 vol% polyvinyl alcohol (PVA) binder and pressed into cylinder blocks. The blocks were calcined at 1000 °C for 6 h to produce NiFe₂O₄ ceramic matrix.

The matrix products were crushed and ball-milled with MnO₂ in the same way, then the mixture of calcined matrix and MnO₂ additive were dried thoroughly. Adding 4 vol% PVA binders, the dried mixture was fabricated into cylinder bars (70 mm×15 mm×8 mm) by cold pressing at a pressure of 200 MPa and pressure holding time 5 min.

Sintering Experiment

Sintering studies for the green blocks (Φ 8.5 mm × 9.5 mm) were performed in air in a vertical dilatometer (SETSYS18 EV-24, France). The samples were heated at a constant rate (10 K/min) to a desired temperature to observe axial shrinkage and then cooled down to ambient temperature.

Characterization and Performance Test

Fracture surface was characterized by scanning electron microscope (SEM) (SSX-550, Japan). Crystalline phases were identified by X-ray diffractometer (Japan) with Cu K α radiation, pip voltage 40 kV, current 100 mA. The samples for measurements of relative density and mechanical property were sintered at 1200 °C in air for 6 h, then cooled down to room temperature. The porosity and bending strength of samples were tested by Archimedes drainage and three-point method on INSTRON4206-006 electron mechanical experimental machine (USA), respectively.

Results and Discussion

Phase Identification

Phase analysis using X-ray diffraction patterns (XRD) was performed, as shown in Figure 1, which confirms the formation of cubic spinel structure. It indicates no new phases formed in the sintered samples with the introduction of MnO₂ into ceramic matrix. It may be contributed to the entrance of Mn ions into the lattice of NiFe₂O₄. And the calculated lattice constants for undoped and 1 wt% MnO₂ doped samples are 8.31 Å and 8.34 Å, which leads to lattice distortion of NiFe₂O₄ spinel. It is beneficial for sintering process.

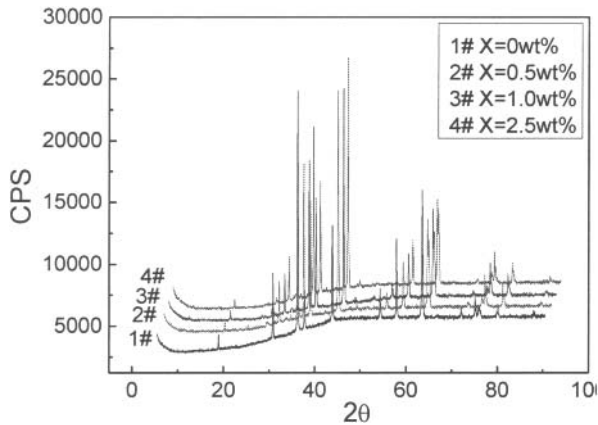


Figure 1. XRD patterns of the samples with different amounts of MnO₂ addition.

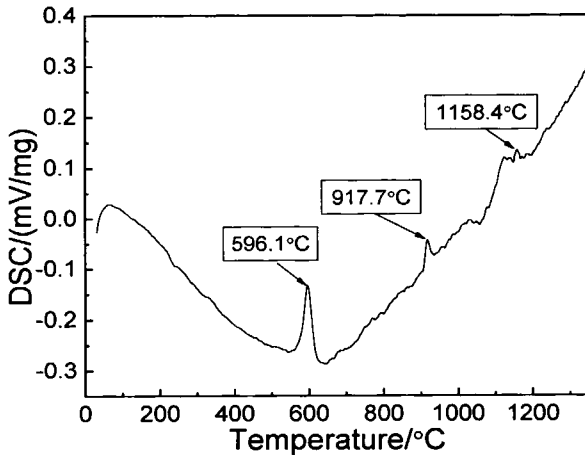
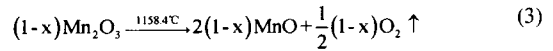
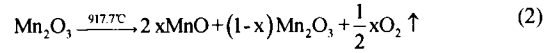
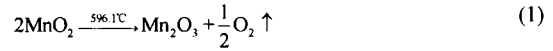


Figure 2. DTA curve of the sample with 2 wt% MnO₂ addition..

Results from DTA curve for 2 wt% MnO₂-doped samples, as shown in Figure 2, indicates that there are three exothermic peaks at 596.1 °C, 917.7 °C and 1158.4 °C, respectively. It is somewhat different from MnO₂-CeO₂ system [12]. Zhang et al. [14] found that three reduction peaks of MnO₂ occurred at 650 °C, 1000 °C and 1200 °C, respectively.

It seems that the reduction of MnO₂ in our case follows the same way as presented in literature [14], the decomposition temperature of each step is lower than that in their case, i.e.:



Characterization and Mechanical Properties

Results from measurements of relative densities and bending strengths are listed in Table 1. It can be seen that un-doped samples have a lower relative density (~ 90.84 %) and poorer bending strength (~ 19.03 MPa) than those without MnO₂ addition. As the MnO₂ addition increases from 0 to 1 wt%, the values of the densities and the bending strengths increase and reach a maximum at x = 1.0 wt%, which are about 93.6 % and 38.75 MPa, respectively.

Table 1 Relative Densities and Bending Strengths of the Samples Sintered at 1200 °C for 6 h with different amounts of MnO₂

MnO ₂ content (wt%)	Relative density (%)	Bending strength (MPa)
0	90.84	19.03
0.5	91.98	24.76
1.0	93.63	38.75
1.5	93.24	34.11
2.0	93.12	30.24
2.5	92.71	21.34

The selected microstructures of un-doped, 0.5, 1.0 and 2.5 wt% MnO₂-doped samples sintered in air at 1200 °C for 6h are shown in Figure 3. It can be seen that un-doped samples have a looser structure with grain size 2~ 4 μm. When 0.5 wt% MnO₂ added, the apparent sintering trajectories were detected. Solid-solution phenomenon and smaller grain size can be detected in 1 wt% MnO₂-doped samples. When the doping amount is up to 2.5 wt%, the local positions are riddled with pores and non-uniform particles.

It suggests MnO₂ additive can enhance the densification in the doping level from 0 to 1.0 wt%. When MnO₂ addition is over 1.0 wt% (for instance, 2.5 wt% in this paper), it is against the densification process in the samples. It may be attributed to MnO₂ doping exceeds its solubility in the ceramic matrix, which could result in accumulation of MnO₂ addition at boundaries, so that increase diffusion activation energy. It is unfavorable for the sintering process.

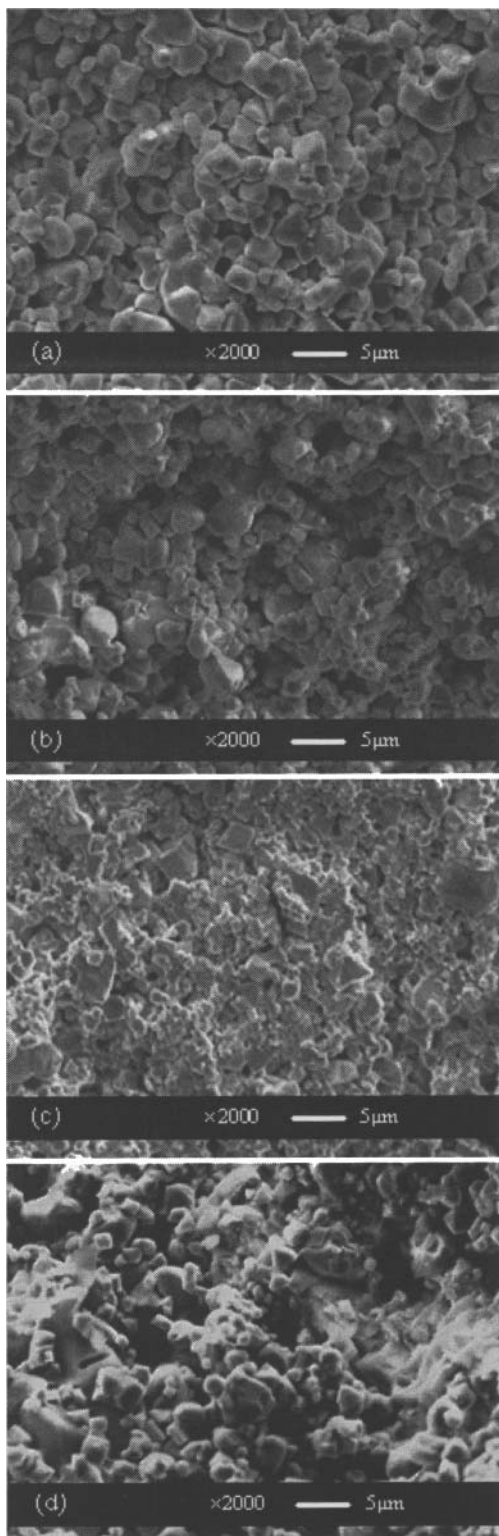


Figure 3. SEM micrographs of the samples with MnO₂ additions: (a) 0; (b) 0.5 wt%; (c) 1.0 wt%; (d) 2.5 wt%.

Non-isothermal Sintering Behavior

Linear shrinkage ($\Delta L/L_0$) of samples sintered at a constant heating rate of 10K min^{-1} is shown in Figure 4. MnO₂ shifts the onset of sintering towards lower temperatures from $1125\text{ }^\circ\text{C}$ for un-doped samples to $1068\text{ }^\circ\text{C}$ for 1 wt% MnO₂-doped samples.

Figure 4 shows the curves of shrinkage rate ($d(\Delta L/L_0)/dt$) as a function of temperature for different MnO₂ contents, and there is an obvious decrease in temperature of maximum shrinkage rate (T_{max}). For example, the temperature of maximum shrinkage rate decreases from $1290\text{ }^\circ\text{C}$ for un-doped samples to $1221\text{ }^\circ\text{C}$ for 1 wt% MnO₂-doped samples. The difference in values of T_{max} for both samples is close to $60\text{ }^\circ\text{C}$. When doping up to 2.5 wt%, T_{max} is lower than that for 1 wt% MnO₂-doped samples. Results obtained from non-isothermal sintering indicate MnO₂ can promote the densification process and reduce sintering temperature dramatically.

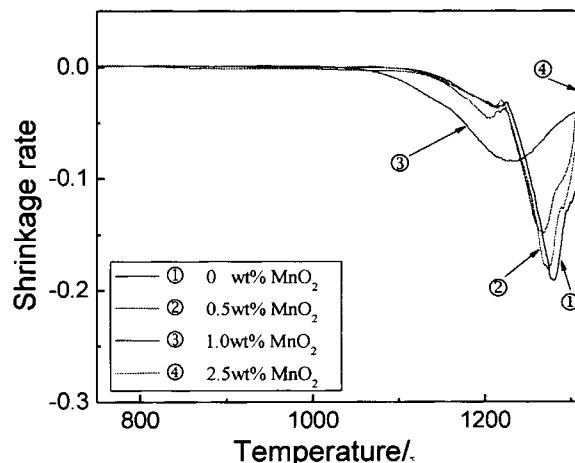


Figure 4. Shrinkage rate against sintering temperature for (1) un-doping, (2) 0.5, (3) and (4) 2.5 wt% MnO₂-doped ceramic samples sintered at a heating rate of 10 K min^{-1} .

Conclusion

The prepared samples are single phase cubic spinel structure. Decomposition of MnO₂ into Mn₂O₃ and MnO during sintering process is confirmed by differential scanning calorimetry (DSC). The value of lattice parameter for un-doped and 1 wt% MnO₂ doped samples is 8.31 \AA and 8.34 \AA , respectively.

Introduction of MnO₂ (i.e., 1.0 wt.%) into ceramic matrix is beneficial to promote sintering process. MnO₂ additive can reduce sintering temperature dramatically, and the temperature of maximum shrinkage rate decreases from $1290\text{ }^\circ\text{C}$ for the un-doped samples to $1221\text{ }^\circ\text{C}$ for 1 wt.% MnO₂-doped samples.

With 1 wt.% MnO₂ introduction, the values of both relative density and bending strength can reach a maximum, which are 93.6 % and 38.75 MPa. The temperature for 1 wt.% MnO₂-doped samples to reach the maximum shrinkage rate is $59\text{ }^\circ\text{C}$ lower than that of un-doped samples.

Acknowledgements

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