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Preparation of $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ Nano-Ceramics by Sol-gel auto combustion and N_2 Annealing for High Reliable NTC Thermistor

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Abstract: $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ nano-ceramics have been successfully prepared by sol-gel auto combustion. The microstructure and phase of these samples was observed by using Scanning Electron Microscopy and X-Ray Diffraction. The diameters of $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ ceramic particles pre-fired at 800℃ range from 52 to 83nm. The powder sintered at above 1050℃ has the compact and uniform spinel structure. We have investigated the electrical characteristics of these thermistors at different sintering temperatures and concluded that the sample sintered at 1200℃ is sufficient to form the appropriate spinel phase. Moreover, the thermistor annealed for 72h at 450~550℃ in N_2 atmosphere has the drift value of <0.7%.

Keywords: Sol-gel auto combustion; Fe-Mn-Ni-O system; NTC thermistor; Aging, N_2 annealing

I INTRODUCTION

NTC (Negative Temperature Coefficient) thermistors are widely used in industrial applications such as temperature measurement, control and compensation.

One important problem in using of NTC thermistor is to overcome the aging phenomenon [1, 2]. Their electrical properties change with time particularly when the temperature increases and it is the main reason why they are unable to use at temperatures above 150℃. Aging of electrical properties attributes to non-equilibrium states that exist inherently in semiconducting NTC ceramics [3].

In order to solve this problem, the previous authors doped the oxides of transition metals such as Zn, Co, Cr and Zr to nickel manganite materials and improved their aging characteristics and stability [4-12]. In addition, some authors employed various new powder preparation methods thereby changing parameters of both electrode coating and heat treatment after sintering [13-15].

Z. B. Wang and his colleagues reported that the improved aging behaviour of the N_2-annealed thermistor is explained by the reduction of the concentration of the cation vacancy upon annealing under lower oxygen partial pressure and the suppression of cation redistribution. [16]. However, they did not determine the reasonable temperature and time in N_2 annealing for high reliable NTC thermistor.

Wenwen Kong explained about the influence of oxygen atmosphere annealing on the thermal stability of $Mn_{1.2}Co_{1.5}Ni_{0.3}O_{4\pm\delta}$ ceramic films fabricated by RF magnetron sputtering [17].

The sol-gel auto combustion method is an advanced process that is widely used in the nanopowder synthesis of Mn-Co-Ni-O NTC thermistor and several ferrite materials [18-27]. But, I could not find a report about the preparation of $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ nano-ceramics by sol-gel auto combustion.

So, the aim of this paper is to research the electrical properties of $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ nanoceramic material prepared by a more convenient sol-gel auto combustion method and determine the reasonable temperature and time in N_2 annealing.

II. EXPERIMENTAL PROCEDURE

The analytical grade $Fe(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2$ $6H_2O$, $Mn(NO_3)_2 \cdot$were mixed in molar ratio of $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ and dissolved in deionized water. This solution, citric acid and ethylene glycol were mixed in molar ratio of 1:2:4.4. A small amount of ammonium hydroxide was carefully added into the solution to change the pH value to 7. The solution was heated at 80℃ and stirred by using a magnetic stirrer continuously.

Because of evaporation, the viscous solution was turned into a dried gel. When the gel was ignited in the air, it burnt in a self-propagating combustion way and it turned to lose powder.

The prepared mixture powder was pre-sintered at 800℃ for 2h and ball-milled for 36h in ethyl alcohol slurry and dried at 80℃. Pellets of diameter 4mm, thickness 2mm were shaped from the powder under 30MPa pressure with 5wt% PVA binder. These pellets were classified into 4 batches and each of them was sintered at 1 050, 1 150, 1 200 and 1 250℃ for 2h in the air, respectively. For metallization, these sintered pellets were coated with Ag paste on their both faces.

In order to determine the annealing temperature and time in the N_2 atmosphere, the N_2 gas was flowed with the rate of 4L/min into the quartz tube furnace (diameter 50mm, length 400mm). The specimens of 16 batches were in this furnace and maintained respectably at 350, 450, 550 and 650℃ for 24, 72, 96 and 144 h.

The precursor powder was analyzed using X-ray

diffraction (D8-Advance diffractometer) for phase identification. The particle morphology in the pre-sintered powder and sintered pellets were observed with a Scanning Electron Microscope (Quantum 200). The electrical resistance was measured with a digital multimeter (DT9208A) at 25℃ and 50℃, respectively.

The B value was calculated by the following equation:

$$B=3\,853.89\times Ln\,(R_{25}/R_{50}) \qquad (1)$$

where R_{25} and R_{50} are the resistance measured at 25℃ and 50℃.

Then the specimens were cooled to 25℃. Their electrical parameters were measured and compared with the parameters before annealing.

III RESULTS AND DISCUSSIONS

3.1 Phase formation and microstructure

From X-ray diffraction analysis, we find that the spinel phase was formed in the powders pre-fired at 800℃.

Fig. 3 is SEM photograph of specimen pre-sintered at 800℃. As seen in this figure, the diameter of power particles ranges from 52 to 83nm. The relative densities of all the specimens were calculated at different sintering temperatures. (Fig. 1)

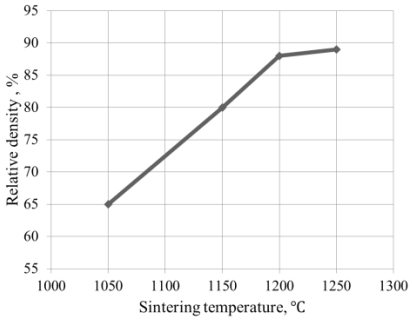

Fig. 1. The relationship between relative density and sintering temperature

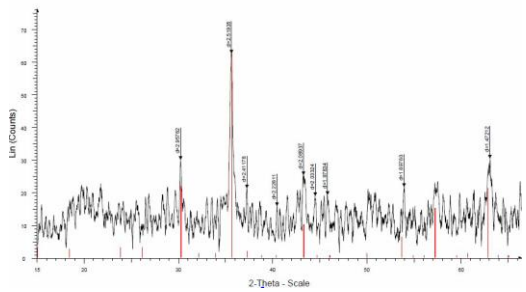

Fig.2. X-ray diffractogram of powder after firing at 800℃

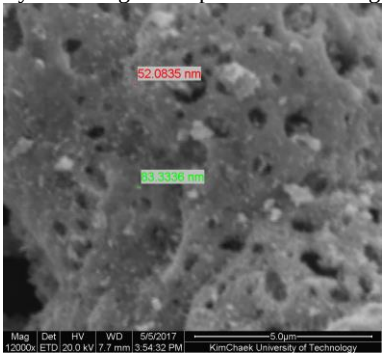

Fig.3. SEM photograph of specimen pre-sintered at 800℃

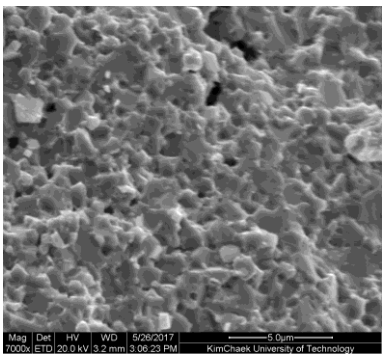

Fig.4.SEM photograph of the specimen sintered at 1 050℃

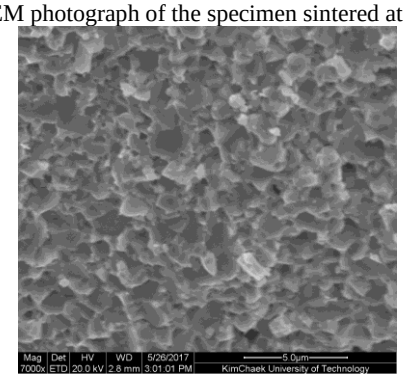

Fig.5.SEM photograph of the specimen sintered at 1 200℃

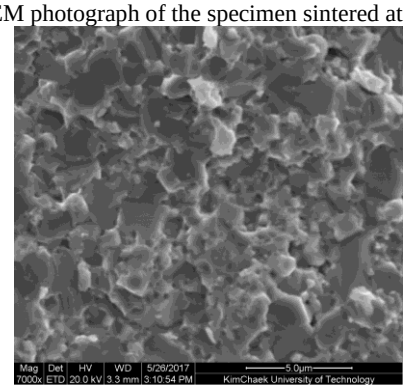

Fig.6.SEM photograph of the specimen sintered at 1 250℃

From Fig.1, we find that the relative density gets saturated when sintered at 1 200℃ and a high sintering temperature is necessary for densification of ceramics.

The SEM photograph of the specimen sintered at 1050℃ shows that the specimen is comparatively compact and its particles are dispersed uniformly and are fine without any big particle. (Fig. 4)

The specimens sintered at 1 200℃ and 1 250℃ were denser than at 1 050℃. (Fig. 5 and Fig. 6) and there are no too big particles. However, it is difficult to get the homogeneous system of ceramic material because the particle growth is active above 1 200℃ (Fig.6).

3.2 Electrical properties

Fig.7 represents the resistivity at 25℃ and the B values of all the specimens.

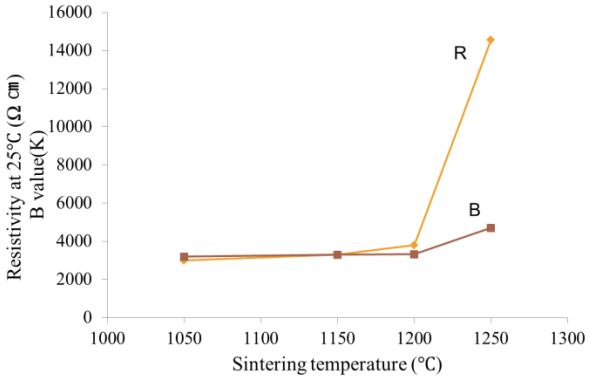

Fig.7. The resistivity and B value of sintered sample vs. the sintering temperature.

For the Fe-Mn-Ni-O_4 ceramics, higher sintering temperatures than 1250℃ lead to NiO separation according to

$$FeMnNiO_4 \rightarrow a\mathrm{NiO} + \frac{a}{6}O_2 + \frac{3-a}{3}Fe_{\frac{3}{3-a}}Mn_{\frac{3}{3-a}}Ni_{\frac{3(1-a)}{3-a}}O_4 \quad (2)$$

where a is the number of moles of the separated NiO phase.

The resistivity of the sintered sample at 1250℃ is suddenly increased because the amount of the insulated NiO phase increases at this temperature.

3.3 Observation of the aging phenomenon

The analytical result of the resistivity and B values above shows that the specimen sintered at 1200℃ is suitable for the manufacture of temperature sensors.

Therefore, we observe in detail the aging phenomenon of the specimen sintered at 1200℃.

The main problems are to analyze the effects of N_2 annealing temperature and time on the thermistor prepared by sol-gel auto combustion and to determine the reasonable annealing temperature and time.

The drift value η is calculated according to

$$\eta = (R_1 - R_0)/R_0 \times 100\ (\%) \qquad (3)$$

where R_0 is the resistance at 25℃ before annealing and R_1 is the resistance at 25℃ after annealing. Fig.8 represents the drift value of the samples.

From Fig.8, we find that the sample annealed at 450℃ for 72h has the drift value of 0.7%. When the annealing temperature is at above 550℃, the drift value rather decreases, but the specimens show a partial change in mechanical characteristics of the ceramics due to the sudden temperature stress. From this results, it is found that the annealing in N_2 atmosphere is reasonable at 450~500℃ for 72h.

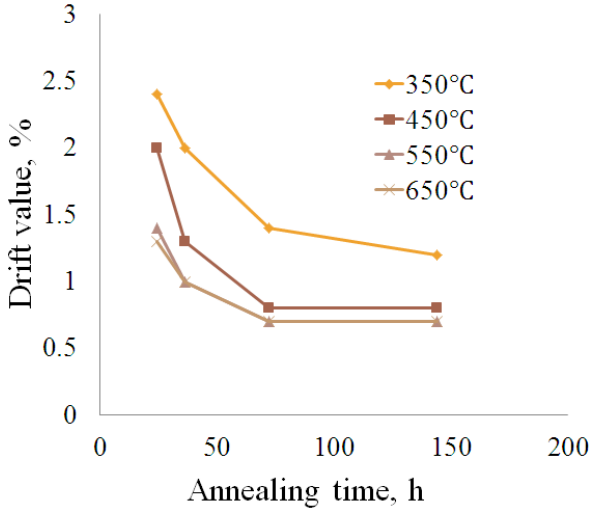

Fig.8. The drift value vs. the annealing temperature and time.

IV CONCLUSIONS

$Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ nano-ceramic material was prepared by sol-gel auto combustion process and its microstructure and phase were observed with SEM and XRD. The results show that $Fe_{0.8}Mn_{1.54}Ni_{0.66}O_4$ ceramic material pre-sintered at 800℃ and then sintered at above 1150℃, has the compact and uniform spinel structure. We have investigated the electrical characteristics of these thermistors at different temperatures and concluded that the sample sintered at 1 200℃ is sufficient to form the appropriate spinel phases. Moreover, it is observed that the thermistor heat-treated for 72h at 450~550℃ in N_2, has the drift value of <0.7%.

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