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The effect of a sintered microstructure on the electrical properties of a Mn-Co-Ni-O thermistor

Eun Sang Na*, Un Gyu Paik and Sung Churl Choi
Department of Ceramic Engineering, Hanyang University, Seongdong-Gu, Seoul 133-791, Korea

In this paper an attempt has been made to trace the relation between the sintered microstructure and electrical properties of a NTC thermistor (Negative Temperature Coefficient) in the Mn-Co-Ni system. The results indicate that the electrical resistivity and B constant increase as the sintering temperature increases, but porosity decreases. Various sintering parameters are also reported. Also considered was the possibility of a fuel level sensor application using the above mentioned material.

Key words: NTC (Negative Temperature Coefficient), fuel level sensor, thermistor, B constant.

Introduction

Semi-conducting ceramics usually exhibit a decrease in electric resistivity with increased temperature, but thermistors which in particular have high stability, productivity, resistivity rate, and thermal coefficient, have 10 times higher than a metal temperature coefficient of electric resistivity, and can be easily processed into variously shaped devices.

Demands of N.T.C. (Negative Temperature Coefficient, hereafter NTC) applied temperature sensors have been increasing, as the use of automotive, OA (operation automation), and other related equipment that need temperature control have increased in recent times. These applications especially require high stability, high precision, wide temperature range, high reliability, and linear behavior of thermal resistivity property [1].

Since the original work on NTC thermistors first took off in Philips laboratories for controlling resistivity in semiconducting oxide materials, a large number of technical articles have been written in the properties, preparation and applications [2].

In 1946, the Bell laboratory first developed the Mn-Ni complex sintered body. This was named a thermistor and put to practical use. Temperature sensors started receiving attention after the development of the Mn-Co-Ni triple component system in the early 1950s and later followed rapid progress on the manufacturing technology of Fe and Cu oxide included materials. The automobile industry especially saw an increasing number of these thermistors put to use in cars, as the industry trend shifted to lighter weight and more electronic device incorporated cars. Such examples include thermal sensors for warm pans, thermal sensors for air conditioners, fuel level sensors, temperature sensors for detecting the engine's cooling water, etc.

In this paper, measurements of the thermistor resistivity and B constant with changes in composition and sintering temperature for thermistors used in fuel level sensors are given, as are observations of the crystal structure and microstructure.

Experimental Procedure

In this study, oxides powders (Mn_3O_4, Co_3O_4, NiO and Fe_2O_3 with a purity above 99.9%) were used as starting materials. These materials were ball milled for 12 hrs for mixing. The mixtures were dried and calcined at 800°C for 2 hrs.

After completing these processes, 5 wt% PVA binder was mixed in to give green compacts. The green compacts (12 mm $\times$ 1 mm) of the calcined powders were obtained by die pressing at 120~130 MPa after addition of the binder. The binder was then burned off at 300°C for 2hrs. The green compacts were sintered at 1150, 1200, 1250, 1300°C for 2 hrs in air. The heating and cooling rate was 300°C/hr.

After firing at 1150~1300°C for 2 hrs, the grain size of the fired specimens was measured by the intercept method from photographs of the surface taken with a scanning microscope (SEM, Topcon, SN-300, Japan). The density of the thermistor was measured by the Archimedes method. Phase analysis was performed by an X-ray diffractometer (XRD, Rigagu, Cu K_α target, 40 kV, 30 mA).

To obtaine the electrical properties, the specimens were metalized with silver paste at 670°C for 12 minutes, and they were then aged in air for 24 hrs. A multimeter (Fluke 45, USA) was used to measure the resistance and B constant in an oil bath.

*Corresponding author:
Tel : +82-2-2292-3210
Fax: +82-2-2291-6767
E-mail: steave1@ihanyang.ac.kr

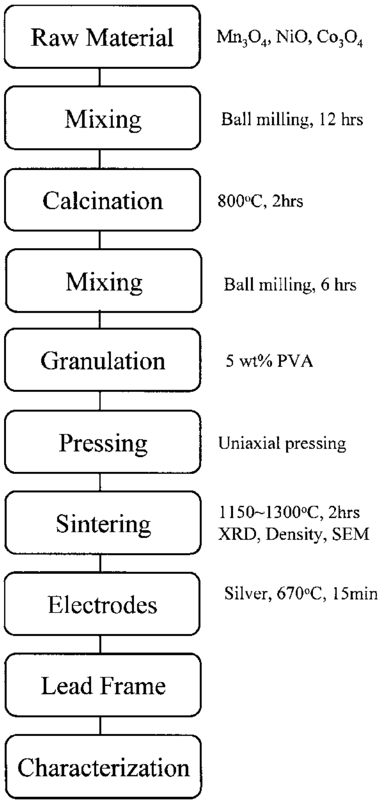

Fig. 1. Fabrication process flow of NTC (Negative Temperature Coefficient) thermistor.

The B constant is the material constant of a thermistor, and refers to the variety of resistance, determined from equation (1) [3]. (T_1, T_2 is 25°C, 75°C respectively)

$$B = \frac{\ln(R_{25}{}^{o}C/R_{75}{}^{o}C)}{1/298.155 - 1/348.155} \tag{1}$$

The thermal dissipation constant, δ, is an integer indicating the power needed to elevate the temperature of the thermistor device by 1°C when at thermal equilibrium using self heating, calculated using the following equation after generating the current and voltage and measuring the current (I), voltage (v), thermal equilibrium temperature of thermistor (T), and ambient temperature (T_a) until reaching equilibrium [3, 4].

$$W = I \cdot V = \delta \cdot (T - T_a) \tag{2}$$

Result and Discussion

Figure 2 shows the variation of bulk density of the Mn-Ni-Co thermistor with change of sintering temperature. The figure shows a rapid increase with temperature below 1250°C, but from 1300°C, a decrease in density is observed.

Such findings can be understood as the result of a decrease in porosity due to grain growth, as the sintering temperature increases. But with above 1300°C, the high sintering temperature brought about abnormal grain growth and big pores, pulling down the density. Also, the Fe_2O_3 dissolves into the spinel structure, increasing the vacant density of the oxygen ions and densifying the structure through volume diffusion, but when the sintering temperature is raised above 1300°C, a decrease in density is expected [5].

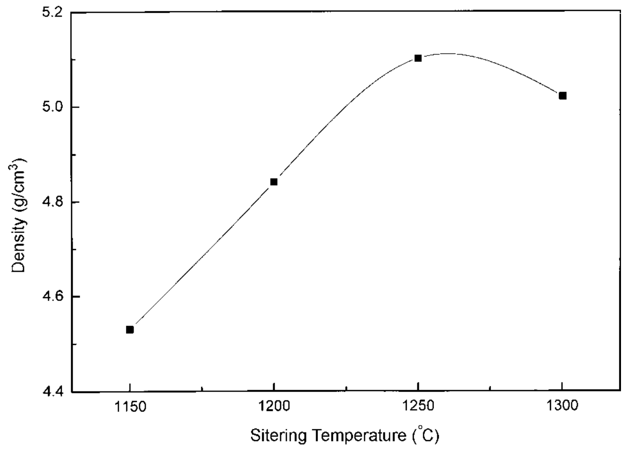

Fig. 2. Bulk density as a function of sintering condition.

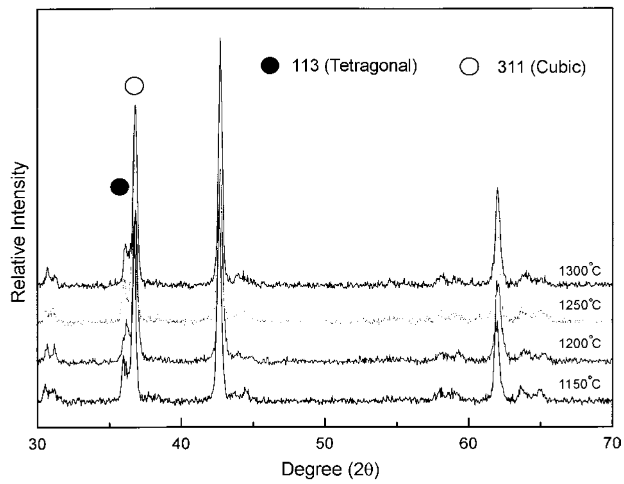

Fig. 3. XRD results as a function of sintering condition.

Figure 3 shows the X-ray diffraction output from each sintering temperature. The diffraction patterns are typical of those from a spinel structure, and a (311) cubic peak and (113) tetragonal peak between 2θ= 35~37° are both detected. This indicates a change from a tetragonal spinel structure to a cubic spinel structure, and no significant change with the sintering temperature is observed. Generally, the cation Fe^{3+} in the Fe_2O_3 is situated in the octahedral B site by substituting Mn^{3+}.

Figure 4 shows microstructural images of the sintered samples heat treated for 2 hrs at the selected temperatures. The images show an increase in grain size and a reduction of porosity with sintering

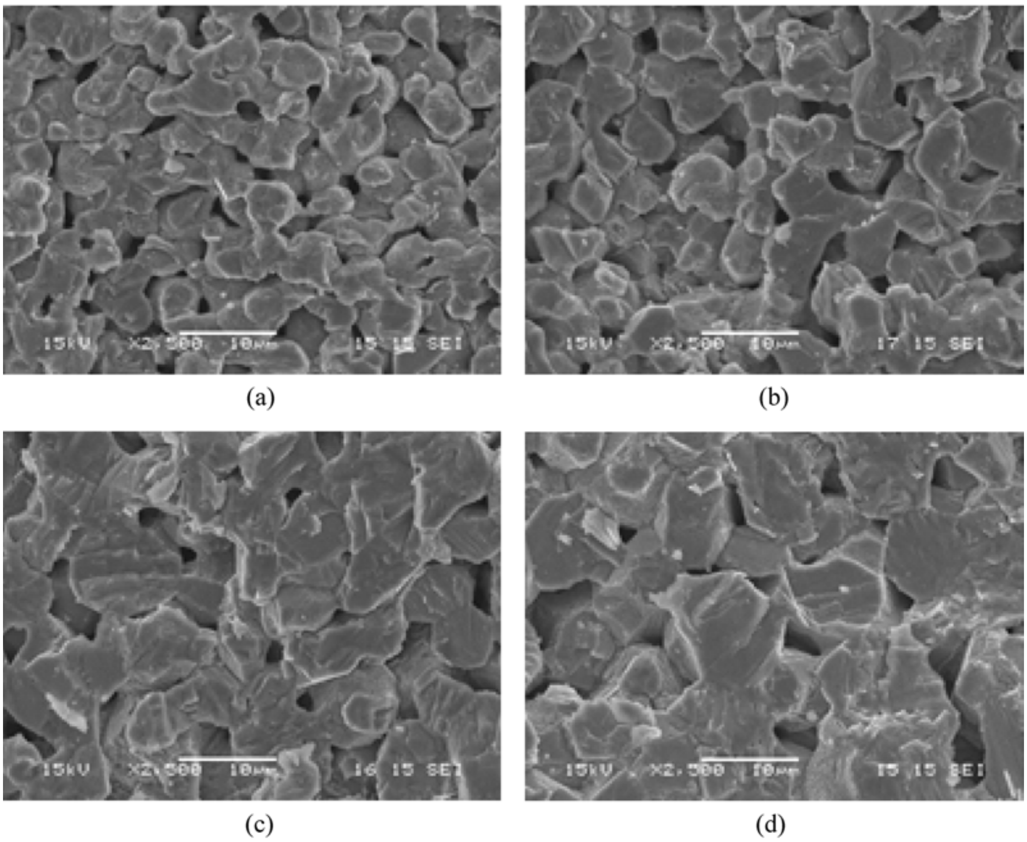

Fig. 4. Microstructure as a function of sintering condition; (a) 1150ºC, (b) 1200ºC, (c) 1250ºC and (d) 1300ºC

temperature. Especially noted is a homogeneous grain size at 1250ºC. Also, at 1300ºC, increased grain growth and formation of large pores from oversintering as noted in figure 2, lowers the density. From these results, it can be seen that in addition to the addivitives, the sintering temperature also acts as a vital factor in the sintered microstructre and density.

Figure 5(a) shows the change in resistivity with the measured change in temperature, exhibiting a typical NTC behavior. Three mechanisms, a non - stoichiometric crystal structure, crystals obtained through the dilution principle, and valency controlling semiconductor ion, but in reality, all three electrical conduction mechanisms are known to take part [3, 4]. In the case of this compound, Co_3O_4 and Mn_3O_4 are each intersoluted to Co^{2+} $[Co^{3+}$ $Co^{3+}]O_4$ and Mn^{2+} $[Mn^{3+}$ $Mn^{3+}]O_4$, divalent Co is situated in the tetrahedral site, and the trivalent Mn is situated in the octahedral site, forming a normal spinel. When NiO is added to Mn^{2+} $[Mn^{3+}Mn^{3+}]O_4$, Ni^{2+} substitutes Mn^{3+} in the octahedral site, and Mn^{3+}

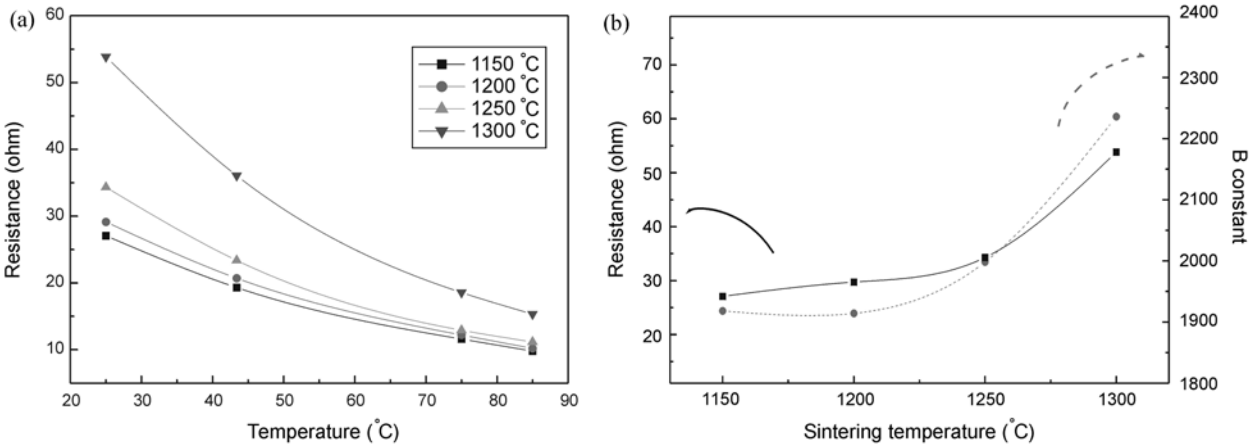

Fig. 5. Electrical Properties as a function of sintering temperature. (a) resistance vs. ambient temperature, (b) resistance and B constant vs. sintering temperature.

Table 1. The electrical properties of Mn-Ni-Co thermistor

	Density (gcm^{-3})	B contant (25/75)	R@25°C (Ω)	T.D.C.(OIL) (m WK^{-1})	T.D.C. (AIR) (m WK^{-1})
1150°C	4.53	1918	27.10	70.51	7.55
1200°C	4.84	1914	29.73	74.01	9.43
1250°C	5.10	1998	34.30	71.84	9.82
1300°C	5.02	2236	53.86	78.45	9.66

becomes Mn^{4+} to maintain electric neutrality, resulting in a decrease in resistivity, as the electron hopping probability of the Mn^{3+} ion, a valency controlling conduction mechanism between Mn^{4+} ions, increases [6, 7].

Figure 5(b), shows the change in resistivity and B constant with the sintering temperature, and an increase of the B constant and resistivity is generally observed with increasing sintering temperature. In the case of the B constant, a value of $2000 \pm 10\%$ is maintained throughout the whole temperature range. This tells us that it can cope with the surrounding temperature change in a fuel level sensor. Also, an increase in resistivity is noted in proportion to the sintering temperature and grain size.

Table 1 is a summary of the thermistor properties according to temperatures. In this study, the difference in the thermal dissipation coefficient in oil and in air was around 8 to 10 fold. This acts as information allowing the user to distinguish the position of the thermistor.

From the above results, the material constant B constant was found to proportionately increase with the sintered body's microstructure characterized by the porosity and grain size. In the case of fuel level sensors, the difference of the thermal dissipation coefficient of the material itself is generally used, as is a material with a small change in resistivity with the surrounding temperature. A compound such as the material investigated in this study with a B constant of $2000 \pm 10\%$, can be considered for such applications.

Conclusion

A change in microstructure in the Mn-Ni-Co oxide system was observed through changes in the sintering temperature, and the following results were obtained.

In this study, the sample sintered for 2 hrs at 1250°C was found to have a sintered density of 5.10 gcm^{-3}, B constant of 1998, and thermal dissipation coefficient of 71.84 mWK^{-1} in oil (9.52 mWK^{-1} in air). This is a compound that can use the device properties which in turn can use the thermal dissipation of the thermistor itself without having sensitivity to the surrounding temperature changes.

Also, the grain size increased with the sintering temperature, and the resistivity and B constant was also found to change proportionality.

References

1. J.G. Fagan and V.R.W. Amarkoon, Am. Ceram. Soc. Bull, 72 (1993) 70-78.
2. E.J.W. Verwey, P.W. Haayman and F.C. Romeyn, Philips Technical Review, 9 (1947) 239-248.
3. R.C. Buchana, “Ceramics Material for Electronics”, Marcel Dekker. Inc., New York (1986) 291-326.
4. H. Takuoki, K. Takayuki and M. Yoshihiro, National Technical Report. 28[6] (1982) 1123-1134.
5. D.W. Ready, J. Am. Ceram. Soc. 49[7] (1966) 366-369.
6. C. Carter and O. Mason, J. Am. Ceram. Soc. 71[4] (1988) 213-218.
7. S.K. Sarker, M.L. Sharma, H.L. Bhaskar and K.C. Nagpal, Journal of materials science, 19 (1984) 545-551.