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Effect of Grain Size and Microstructures on Resistivity of Mn–Co–Ni Thermistor

M. Hosseini & B. Yasaei

Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran

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Abstract: In this paper an attempt has been made to trace the relation between microstructure, grain size and electrical properties of NTC thermistors with the composition $(NiMnCo)_3O_4$. The results indicate that the electrical resistivity decreases as the grain size increases, but for a broad range of grain size it is relatively constant. When the grain size is very small and also when very large the change in resistivity is significant. Various microstructure parameters are also reported. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Since the original work carried out on NTC thermistor in the Philips laboratories[1] for controlling resistivity in semiconducting oxide materials, a large number of technical articles have been written on the properties, preparation and applications.

The reliability and reproducibility of NTC thermistor have been studied[2,3] and dependence of resistivity with composition also has been reported,[4–6] but the dependence of grain size and microstructure has not been studied in detail.

Attainment of high density controlled grain size microstructures and appropriate dimensional designs are important factors in good sensor design. Usually the grains of slowly cooled ceramics are free from lattice defects such as dislocation or planar defects.[7] The aim of this paper is to study the effect of resistivity of Mn–Co–Ni thermistor on grain size and microstructures when they are slowly cooled ceramics. Otherwise quenched ceramics are always multiphase with a high density of dislocation and planar defects. Although mono-phase spinel structure has been obtained by water quenching the rock–salt type oxide[8] but the procedure is not straightforward.

2 EXPERIMENTAL PROCEDURE

High purity manganese oxide, cobalt and nickel carbonate were wieghted in a molar ratio 1:1:1 and well mixed. The mixture was calcinated at 1200°C for 4 h. The sintering temperature with maximum temperature in the soak section was 1300°C that is held for 5 sets of specimen for a period of 1, 3, 7, 9, 11 h. Careful temperature control is maintained through the sintering cycle with a microprocess control furnace model Labotherm HT 04/17. The electrical resistance was measured at constant dc voltage (5V). The grains size were observed from SEM photographs, and microstructure parameters were determined by the Heyn intercept method.[9]

3 RESULTS AND DISCUSSION

Figure 1 shows the resistance–temperature response of specimens between 20 and 100°C. The specific resistivities at room temperature vary from $1.17\times10^4\,\Omega$-Cm for sample 1 (smallest grain size) and $0.89\times10^4\,\Omega$-Cm for sample 5 (largest grain size). It decreases to $0.13\times10^4\,\Omega$-Cm for sample 1 and to $0.09\times10^4\,\Omega$-Cm for sample 5 at 91°C.

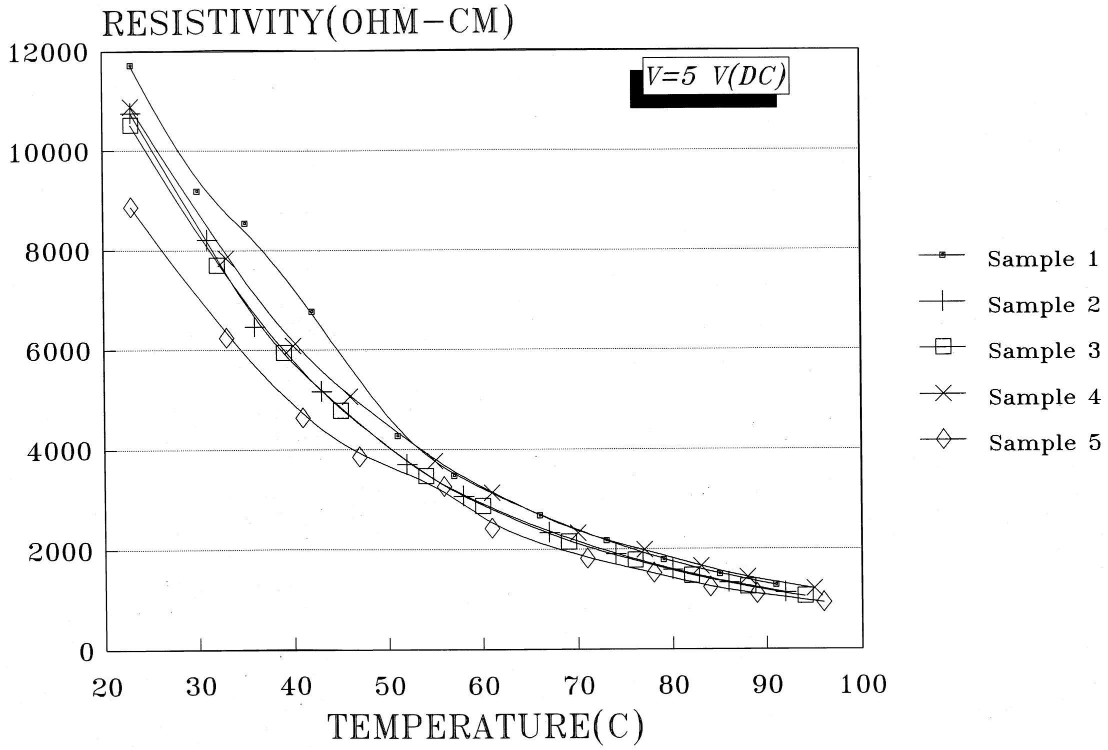

Fig. 1. Specific resistivity (in Ω-Cm) as function of temperature for 5 sets of NTC thermistor.

The experimental measurements of microstructure's parameters in single phase ceramics determined from area and lineal analysis. It entails measuring and then summing the areas of intersection of a constituent with the plane of polish. If a single random traverse is made on randomly selected plane of polish, then the traverse can be regarded as having been placed at random in the 3-dimensional structure, and the lineal fraction gives a direct estimate of volume fraction. However, a series of traverse will be made on one plane of polish, and in this case the areal fraction is estimated.[9] The results are shown in Table 1.

In this table S_V is surface area per unit test volume and defines as

$$S_V = 2N_{(av)L}$$

where $N_{(av)L}$ is the average number of interceptions of features per unit length of test line, σ is the variance and define as

$$\sigma = \frac{1}{N}\sum_{i=1}^{N}\sqrt{(x_i - x_{av})^2} \text{ and } x_{av} = \frac{1}{N}\sum_{i=1}^{N} N_{x_i}$$

l_{av} is the average grain size, λ is the mean free distance between grains, ρ is the specific resistivity, B is the material constant and α is temperature coefficient.

The relationship between grain size and the period of maximum temperature in the soak section is shown in Fig. 2. The results show as the sintering time increased the grain size increased. As the temperature is raised, the final grain size is larger, since the growth rate increases more rapidly than the rate of nucleation.

The relationship between specific resistivity and grain size is shown in Fig. 3. The results indicate that the electrical resistivities decrease as the grain size increase, but for a broad range of grain size from 9 μm until about 15 μm is relatively constant. When the grains size is very small less than 9 μm

Table 1. Electrical and microstructures parameters

Samples	Sintering times	S_V				$\sigma(l_{av})/l_{av}$ and	(ρ)		B		α
	(h)	μm^{-1}	$\sigma(S_V)/S_V$	$l_{av}(\mu m)$	$\lambda(\mu m)$	$\sigma(\lambda)/\lambda$	$\times 10^4(\Omega\text{-Cm})$	$d(\rho)/\rho$	$\times 10^{-3}$	$\sigma(B)/B$	$\%k^{-1}$
1	1	0.226	0.22	8.56	0.29	0.12	1.17	0.02	3.53	0.09	−4.03
2	3	0.198	0.16	9.25	0.85	0.10	1.07	0.02	3.68	0.10	−4.20
3	7	0.174	0.05	11.2	0.47	0.04	1.05	0.02	3.65	0.06	−4.16
4	9	0.122	0.12	15.78	0.61	0.08	1.09	0.02	3.46	0.07	−3.95
5	11	0.104	0.14	18.65	0.58	0.10	0.89	0.02	3.44	0.07	−3.93

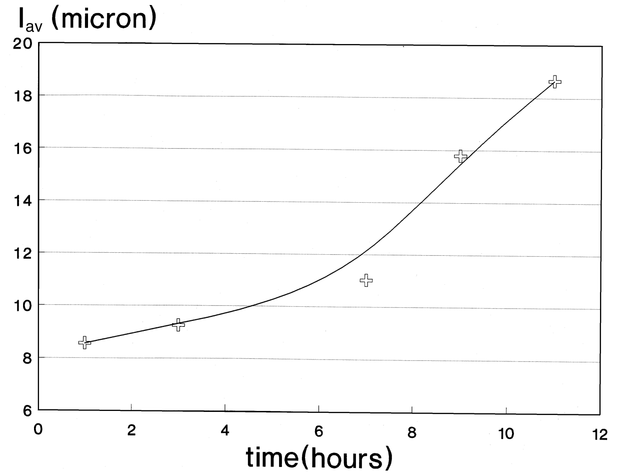

Fig. 2. Grain size dependencies of sintering time.

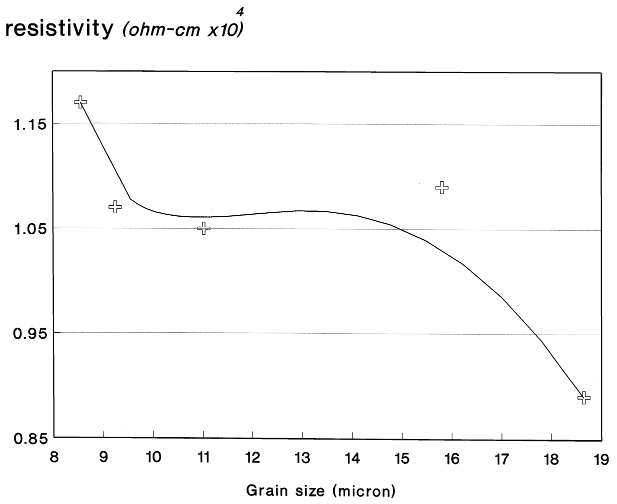

Fig. 3. Grain size dependencies of specific resistivity for NTC thermistor.

and also at very large grain size higher than 15 μm the change in electrical resistivity is significant. However as it can be seen that significant shifts in electrical properties and stability of such devices occur with minor shifts in processing conditions and sintering cycles.

We have measured the temperature coefficient, α, and material constant, B, data is given in Table 1, but no significant correlation was found.

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