

The effect of cation composition on the electrical properties and aging of Mn-Co-Ni thermistors

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Abstract

The aim of this paper is to investigate the effects of nickel-containing compositions on the electrical properties and aging of NTC thermistors with the composition $(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_4$ (where $x + y + z = 3$) at room temperature. The results indicate that the electrical resistivities decrease as the nickel content increases, but reach a minimum value and then increase. The results five months after manufacture time show also that as the content of nickel increases the samples are more stable. The effects of nickel on the material constants (B, A) and various other electrical parameters are also reported. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

The resistivity of NTC thermistor is tied to the generation of a mixed valency in the cation sublattice. By varying the metal content and control of the micro-structure the desired resistivity can be achieved. The choice of additive can even alter the electronic conduction mechanism from p to n type [1]. A large number of technical articles have been written on the effect of varying cation composition [2–6], the effect of impurities [6,7] and grain size dependencies [8] upon the structural and electrical properties of Mn-Ni, Mn-Co and Mn-Co-Ni oxide systems.

The introduction of copper oxide into NTC thermistor compositions to produce devices of lower resistivity have the consequence of reducing the stability of the final thermistor [5]. The admixtures of bismuth also decrease the resistivity, but it leads to a more defective crystalline structure [9]. The introduction of a very small amount of Fe has a very large effect on the electrical properties of the thermistor [7].

The ability to produce a reliable device is a complicated task. The mechanical, chemical, and electrical aspects that influence the performance and stability of NTC thermistor have been reviewed [7]. However, the

devices made from manganese, nickel, and cobalt oxide normally possess stability better than 1% resistance change per year [10]. It seems that this system for most devices still gives a much better response.

On the stability of these thermistors very little has been reported in the literature [10–12]. We have measured the dependence of resistivity, material constants (B, A) and other electrical parameters upon Ni content of $(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_4$ (where $x + y + z = 3$) at the time of production and after 5 months.

2. Experimental procedure

High purity manganese, cobalt and nickel oxide were weighed and mixed according to prescription $(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_4$ where $y = z = 1$ and x vary from 0 to 1 as shown in Table 1. The mixture was calcinated at 900°C for 5 h. The samples are sintered at a temperature of 1250°C with heating rate of 6°C/min and a cooling rate 8°C/min and soaking time 6 h. Careful temperature control is maintained through the heating cycle with a micro-processor controlled furnace model Labotherm HT 04/17. The electrical resistance was measured at constant d.c. voltage with a high resolution digital voltmeter. The specimens were held with a holder in a bath of silicon oil and temperature measured with a high resolution (0.1°C) microprocessor-based, digital thermometer

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Table 1

The composition formula for prescription $(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_4$

Composition $y = z = 1 \quad x = 0 \text{ to } 1$				Area/thickness S/d (cm)	Resistivity $\times 10^3$ (Ω cm)	
Samples	Ni_x	Mn_y	Co_z		ρ (25°C)	$\pm \Delta\rho$
A1	$x = 0.0$	$y = 1$	$z = 1$	13.63	27.55	0.55
A2	$x = 0.2$	$y = 1$	$z = 1$	13.59	11.35	0.22
A3	$x = 0.4$	$y = 1$	$z = 1$	13.64	16.77	0.33
A4	$x = 0.6$	$y = 1$	$z = 1$	13.63	23.04	0.46
A5	$x = 0.8$	$y = 1$	$z = 1$	13.39	26.92	0.53
A6	$x = 1.0$	$y = 1$	$z = 1$	13.65	71.55	1.43

model Fluke-51. An external k-type thermocouple with a tolerance $\pm 1.1^\circ\text{C}$ over the range of 0 – 250°C is used as temperature sensor.

3. Results and discussion

3.1. Electrical Characteristics

Fig. 1 shows the resistance-temperature response of samples between 25 and 100°C . The specific resistivity at room temperature vary from $71.5 \times 10^3 \Omega\text{-cm}$ for sample A6 (with 1 mol of nickel) and to $11.3 \times 10^3 \Omega\text{-cm}$ for sample A2 (with 0.2 mol of nickel). It decreases to $6.06 \times 10^3 \Omega\text{-cm}$ for sample A6 and to $1.08 \times 10^3 \Omega\text{-cm}$ for sample A2 at 100°C .

Fig. 2 shows the room temperature values of the d.c. specific resistance of samples as function of nickel content. The specific resistance (ρ) was determined from $R = \rho d/S$ by measuring the sample resistance (R) and thickness/area (d/S). The sample error $\Delta\rho/\rho$ including the effect of small variations of geometry was found to be $\Delta\rho/\rho \leq \pm 0.02$. The resistivity at $x=0$ is high and decreases with increasing nickel content, but at $x=1$ it increases again.

The material constant (B) and the temperature coefficients (α) are as follows:

$$B = \ln \frac{(\rho_1/\rho_2)}{(1/T_1 - 1/T_2)} \quad (1a)$$

$$\alpha = (-B)/T_2 \quad (1b)$$

The total error of B and α deduced from partial differentiation of these equations are:

$$\begin{aligned} dB/B = & [1/\ln(\rho/\rho_2)](d\rho_1/\rho_1 \\ & + d\rho_2/\rho_2) + [1/(T_2 - T_1)](dT_2 + dT_1) \\ & + dT_1/T_1 + dT_2/T_2 \end{aligned} \quad (2a)$$

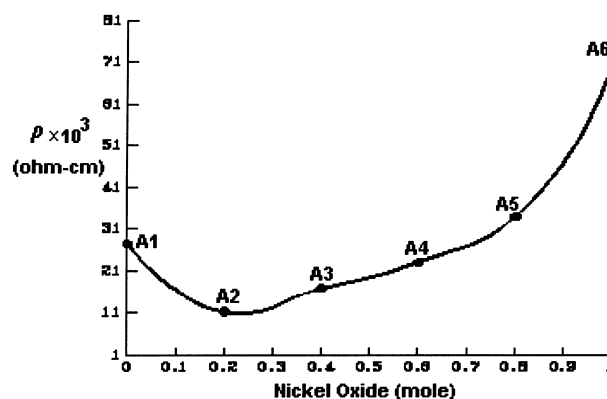


Fig. 2. Specific resistivity (in $\Omega\text{-cm}$) as function nickel content.

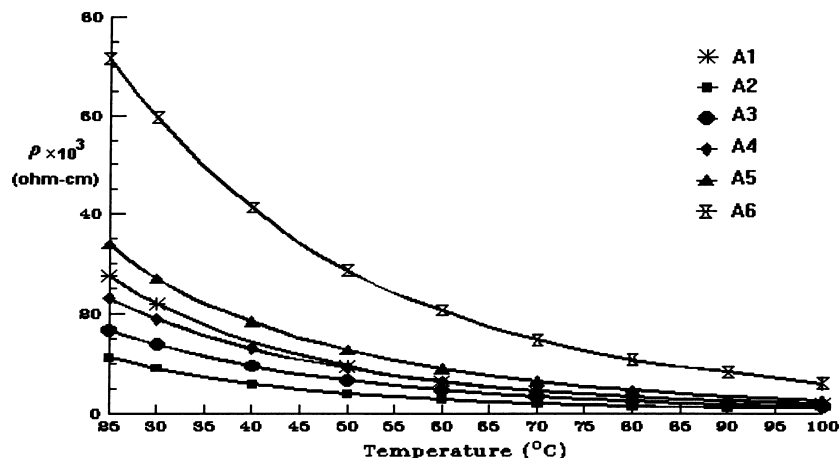


Fig. 1. Specific resistivity (in $\Omega\text{-cm}$) as function of temperature for 6 sets of NTC thermistors.

$$d\alpha/\alpha = dB/B + 2(dT/T) \quad (2b)$$

The error $\Delta B/B$ and α for each sample are shown in Table 2. The constant B has a tolerance of about $\pm 180^\circ\text{C}$, but due to the spread in B -value, the deviation from this value at temperature other than 25°C is greater than the specified tolerance at 25°C . The temperature tolerances (ΔT) corresponding with the spread in ρ_{ref} and B -value can be calculated from Eq. (1) as follows:

$$\pm \Delta T = [1/(B/T^2)] \cdot (\Delta \rho_{\text{ref}}/\rho_{\text{ref}}) \text{ for } T = T_{\text{ref}} \quad (3a)$$

$$\pm \Delta T = [1/(B/T^2)] \cdot [\Delta \rho_{\text{ref}}/\rho_{\text{ref}} + \Delta B(1/T - 1/T_{\text{ref}})] \text{ for } T < T_{\text{ref}} \quad (3b)$$

$$\pm \Delta T = [1/(B/T^2)] \cdot [\Delta \rho_{\text{ref}}/\rho_{\text{ref}} + \Delta B(1/T_{\text{ref}} - 1/T)] \text{ for } T > T_{\text{ref}} \quad (3c)$$

where T_{ref} is the reference temperature, usually 25°C . Fig. 3 shows the temperature tolerance as a function of the temperature.

The constant A and various other electrical parameters were measured and the results are shown in Table 2. In this table q is an activation energy that obeys the resistivity-temperature relationship of the form:

$$\rho = \rho_o \exp(q/kT) \text{ or } R = A \exp(B/T) \quad (4)$$

V_{max} is the turnover voltage or voltage maximum and defined [5] as:

$$V_{\text{max}} = [R_{\text{amb}} K (T_{\text{max}} - T_{\text{amb}}) \exp(B/T_{\text{max}} - B/T_{\text{amb}})]^{1/2} \quad (5)$$

where K is the dissipation constant in $\text{mW}/^\circ\text{C}$, R_{amb} and T_{amb} are ambient resistance and ambient temperature respectively.

Finally τ is the thermal time constant and defined as the ratio of the heat capacity (H) of thermistor to its dissipation factor (δ). If the thermistor has a uniform temperature during cooling, the following equation is valid for the cooling of an NTC in the time interval Δt :

$$-H\Delta T = \delta(T - T_o)\Delta t \quad (6)$$

Table 2
Electrical and other parameters

Samples	B (K)	$\frac{\Delta B}{B}$	A ($\text{m}\Omega\cdot\text{cm}$)	α [25°C] (K^{-1})	$\Delta\alpha$ (K^{-1})	q (eV)	V_{max} (V)	τ (s)
A1	4020.77	0.047	050.84	-4.42	0.053	0.33	40	315
A2	3471.81	0.049	101.25	-3.89	0.055	0.29	36	425
A3	3664.67	0.048	067.91	-4.17	0.054	0.31	39	415
A4	3620.17	0.048	119.35	-4.09	0.064	0.31	45	420
A5	3442.13	0.049	112.29	-4.17	0.055	0.31	50	340
A6	3649.85	0.048	320.20	-4.15	0.054	0.31	70	425

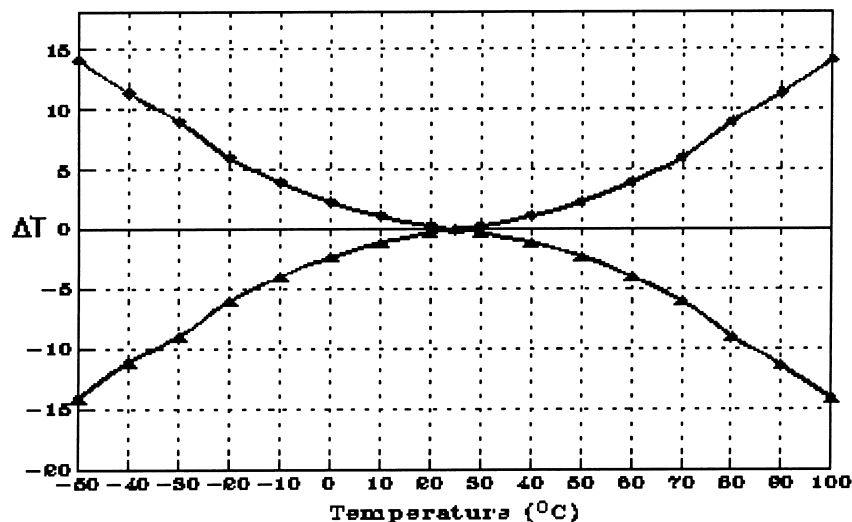


Fig. 3. The temperature tolerance as a function of the temperature.

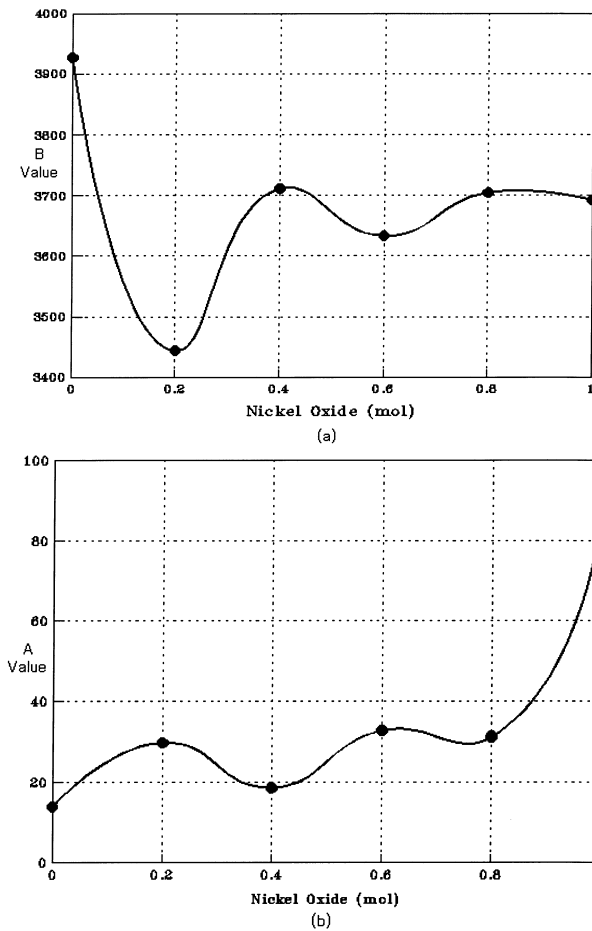


Fig. 4. (a) Material constant B and (b) constant A according to Ni content.

The solution to this equation for any value of t in seconds is:

$$(T - T_{\text{amb}}) = (T_o - T_{\text{amb}}) \exp(-t/\tau) \quad (7)$$

in which T_o is the temperature when the time $t = 0$ and τ is the cooling time constant in seconds.

The effects of nickel content on constants B and A , are shown in Fig. 4. The results show that the maximum variation in B occurred when the content of nickel is small and for constant A the maximum variation occurred when the content of nickel is high.

3.2. Aging

The measurement results of the variation in the constants B and A after 5 months of manufacture time are indicated in Fig. 5. It seems when the content of nickel increases the samples are more stable. At low nickel content, the slow diffusion of nickel occurs from one lattice site to another that changes the cation distribution. This change in cation distribution will change the effective

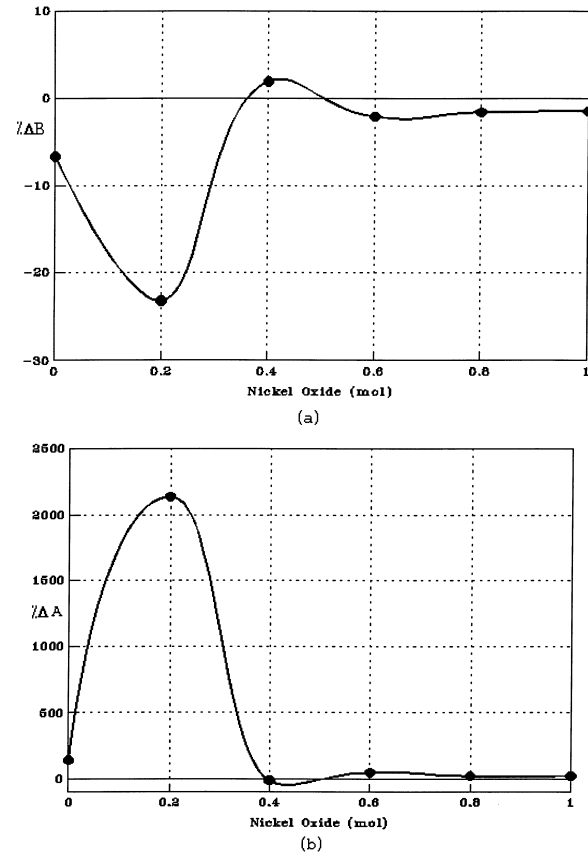


Fig. 5. (a) Variation in constant B and (b) in constant A after 5 months with Ni content.

carrier concentration and hence the material resistivity. When the amounts of nickel content increase, since most lattice sites are saturated, very little diffusion takes place, and the samples are more stable. Since most of the aging occurred within the first week or two, suggesting that if they were pre-aged the subsequent resistance change would be of the order 1 or 2% in the following year.

4. Conclusions

The ability to produce a reliable NTC thermistor is a complicated task, and it is difficult to draw any very definite conclusions from various aspects that influence the stability of these devices. The following conclusions can, however, be drawn:

- The electrical resistivity decreases as the nickel content increases, but reach a minimum value when the amount of nickel is about 0.2 mol and then increases.
- Although the long-term stability depends on too many factors that affecting the performance, but one of them is the nickel content. At low nickel content, the slow diffusion of nickel occurs from

one lattice side to another and this changes the cation distribution and hence the material constant. At high nickel content, most lattice sites are saturated and very small diffusion takes place, and the samples are more stable.

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