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Effect of annealing in O_2 or N_2 on the aging of $Fe_{0.5}Mn_{1.84}Ni_{0.66}O4$ NTC-ceramics

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Abstract

$Fe_{0.5}Mn_{1.84}Ni_{0.66}O_4$ NTC ceramic thermistors were annealed in nitrogen or oxygen atmosphere at 600 °C. The change of the electrical properties of the thermistors with time was reduced sharply by annealing in N_2, whereas it was enhanced upon annealing in O_2. N_2-annealed samples exhibited a less degree of redistribution of cations in the lattice as compared with O_2-annealed samples. The aging of the electrical properties is believed to result from the cation redistribution which in turn is favoured by the presence of cation vacancies. And 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.

Keywords: NTC; Aging; Cation redistribution; Vacancy

1. Introduction

Negative temperature coefficient (NTC) ceramic thermistors are increasingly used in various industrial and domestic applications, such as elements for suppression of in-rush currents, for temperature measurement and control, and for the compensation of other circuit elements [1]. The specific resistivity of these ceramics follows the well known Arrhenius relation: $\rho=\rho_0 \exp(E_a/kT)$, in which ρ is the specific resistivity, E_a the activation energy for electrical conduction, k Boltzmann's constant and T the absolute temperature. In practice, the NTC thermistors are routinely characterized by two parameters, B, the thermal constant (unit in Kelvin) which is related to $B=E_a/k$, and ρ 25 °C , the specific resistivity at 25 °C. Aging, i.e., the change of the electrical properties with time is the main problem limiting the application of the spinel-structured ceramic NTC thermistors. It is generally accepted that exchange of cations between the sublattice tetrahedral (A-sites) to the octahedral (B-sites) gives rise to the aging of the thermistors [2]. It is also suggested that the aging involves migration of cation vacancies from the grain boundaries to the grain interior [3]. In our previous work [4], it was found that $Fe_{0.5}Mn_{1.84}Ni_{0.66}O_4$ exhibits the severest aging in the $Fe_xMn_{2.34-x}Ni_{0.66}O_4$ ($0<x<1$)

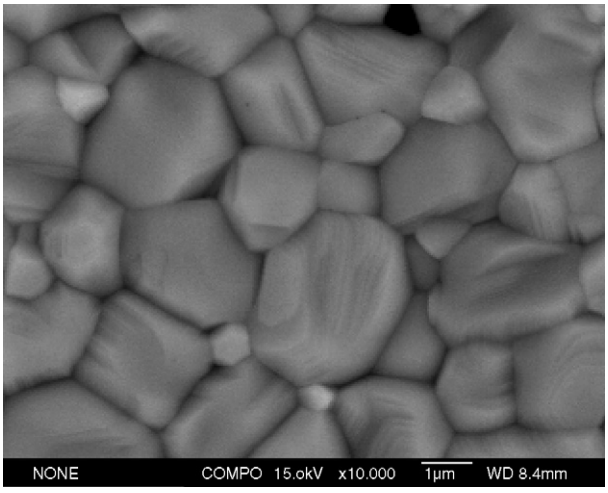

Fig. 1. SEM micrograph of the as-sintered sample.

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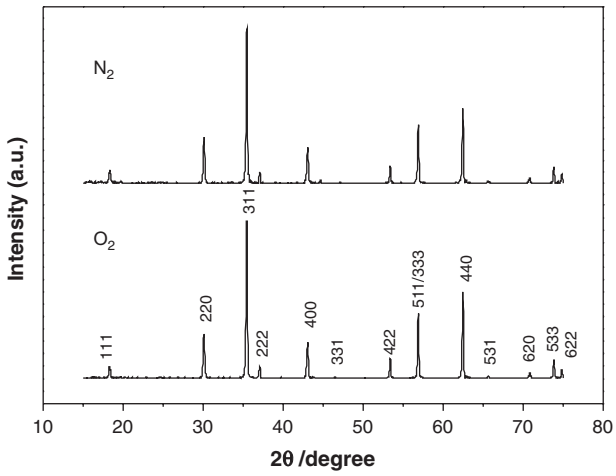

Fig. 2. X-ray diffraction patterns for the $Fe_{0.5}Mn_{0.94}Ni_{0.66}O_4$ annealed in O_2 and N_2.

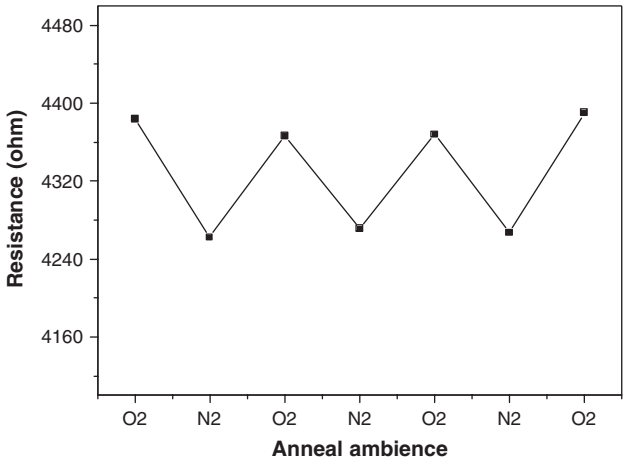

Fig. 3. Variation of resistance with alternation of annealing atmosphere.

series. And this paper is to investigate the effect of annealing atmosphere on the aging behaviour of that composition.

2. Experimental

$Fe_{0.5}Mn_{1.84}Ni_{0.66}O_4$ powders were prepared by the Pechini method [5]. Appropriate amounts of $Fe(NO_3)_3 \cdot 9H2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2$ were dissolved in deionized water, and citric acid (CA) and ethylene glycol (EG) were added to the solution with a molar ratio [Fe+Mn+Ni]:CA:EG=1:2:2. The pH of the solution was adjusted to about 3 with ammonia. The solution was first heated at 90 °C under stirring to yield a viscous solution, and then heated to 140 °C to transform to a resin. Upon further heating at elevated temperatures on a hot plate, spontaneous ignition of the resin occurred, yielding a fluffy ash. The ash was milled in ethanol for 24 h to break down the weak agglomerates in it, and dried at 75 °C followed by calcinations at 700 °C in air for 4 h. The calcined powders were milled in ethanol, dried, blended with an organic binder (PVA, n=1750, supplied by Shanghai Chemical Reagent Co. Ltd., China), and sieved. The powder was uniaxially pressed at 60 MPa into disks of diameter 6 mm and thickness 2 mm, and then isostatically pressed at 300 MPa. The disks were heated in air to 400 °C at a rate of 100 °C/h, kept at that temperature for 2 h to remove the organic binder, and subsequently heated to 1200 °C at a rate of 250 °C, maintained at that temperature for 10 h and furnace-cooled to room temperature. The two opposite sides of the as-sintered samples were polished and coated with platinum paste, heated at 850 °C for 15 min for metallization and quenched to room temperature. After metallization, samples were annealed in O_2 or N_2 (purity>99.999%) for 24 h at 600 °C with a heating rate of 5 °C/min, and then cooled to room temperature at the same rate.

The electrical properties of as-sintered as well as annealed samples were characterized. The resistances at 25 °C (R_{25}) and 50 °C (R_{50}) were measured by the two-probe technique with an Agilent 34401A digital multimeter. The thermal constant B was calculated according to the formula: $B=\frac{328.15\times298.15}{323.15-298.15}\cdot\ln\left(\frac{R_{25}}{R_{50}}\right)=3853.59*\ln(R_{25}/R_{50})$. The specimens were aged in air at 150 °C for 1000 h, and the aging is characterized by $\Delta R/R_0=(R-R_0)/R_0$, in which R_0 and R are the electrical resistance at 25 °C before and after the aging. The specific resistivity, thermal constant and aging coefficients are averaged over three samples. The samples were analyzed by powder X-ray diffraction (XRD) analysis using a PHILIPS X'Pert diffractometer ($CuK_\alpha\lambda$=1.5418 Å) with a step size of 2θ=0.0167°. The density ρ of the sintered sample was measured using Archimedes method, and the relative densities (ρ_{rel}) was determined according to the formula $\rho_{rel}=\rho/\rho_{th}$, in which ρ_{th} is the theoretical density calculated from lattice parameters derived from XRD analysis. The microstructure of the sintered sample was examined with Scanning Electron Microscopy (SEM, JSM-6700F, JEOL). For the SEM analysis sintered samples were polished, and thermally etched at temperature of 1150 °C. The grain size of the sintered sample was estimated using the method described by Mendelson [6].

3. Results and discussion

The relative density of the sintered ceramic was measured to be about 95%. SEM examination shows that the sintered ceramic is well densified, and consists of grains of 5~8 μm (Fig. 1). XRD

Table 1
Resistivity, B value and aging coefficient of annealed and as-sintered samples

	Resistivity (Ω cm)	B (K)	Aging coefficient (%)
Annealed in O_2	4727	3706	10.7
Annealed in N_2	4640	3725	0.6
As-sintered	4680	3710	4.0

Table 2
Intensity of (220) and (440) reflections of fresh and aged powdered samples, annealed in O_2 and N_2

	I_{220}	I_{440}	I_{220}/I_{440}
Annealed in N_2 (fresh)	6161.8±60	7990.5±80	0.77±0.02
Annealed in N_2 (aged)	6158.1±60	7820.3±80	0.79±0.02
Annealed in O_2 (fresh)	1718.7±20	2401.4±20	0.72±0.02
Annealed in O_2 (aged)	1980.9±20	2424.4±20	0.82±0.02

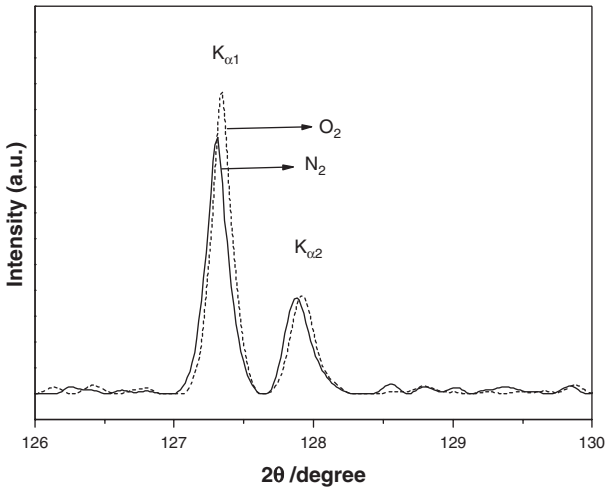

Fig. 4. (844) Reflections in XRD of the $Fe_{0.5}Mn_{0.94}Ni_{0.66}O_4$ after annealing in O_2 and N_2.

analysis reveals that the ceramic retains the single-phase spinel structure after annealing in O_2 or N_2 (Fig. 2). Table 1 summarizes the electrical properties of the as-sintered and annealed ceramic thermistors. It can be seen that in comparison with the as-sintered ceramic, the drift in electrical resistivity with time is reduced significantly for the N_2-annealed ceramic, whereas it is enhanced remarkably for O_2 annealed ceramic. Fig. 3 shows the variation of the electrical resistance with the alternation of annealing O_2 and N_2 atmospheres at 600 °C for 24 h. Clearly, the variation of the electrical resistance is reversible with respect to the change in the annealing atmosphere, and the resistance of the samples annealed in O_2 is considerably larger than in N_2.

It is generally accepted that electrical conduction in AB_2O_4 spinel-structured NTC oxides is via hopping of electrons between the Mn^{3+} and Mn^{4+} ions on the B-sites along the <110> directions [7]. And it has already been shown that the change of the electrical properties of the ceramic with time is related to the exchange of cations among the A- and B-sites in the spinel lattice [2]. Therefore, the effect of the annealing atmosphere on the aging of electrical properties of the ceramic may be related to the cation exchange. It has been revealed that the intensity ratio of the (220) and (440) reflections (I_{220}/I_{440}) are very sensitive to the cation distribution in the spinel [8]. The XRD intensity, in principle, can be calculated using the formula as suggested by Buerger [9]: $I_{hkl}=|F_{hkl}|^2 \cdot P \cdot L_P T \cdot A$, where I_{hkl} is the integrated intensity, F_{hkl} the structure factor, P the multiplicity factor for the plane (hkl) and L_P the Lorentz polarization factor, $L_P=(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$. In calculating the ratio of the intensities of XRD signals, the absorption factor (A) and temperature (T) need not to be taken into account. By using the Powdercell software [10] one can examine how the intensity ratio of the peaks is affected by the cation distribution in the AB_2O_4 spinel. Simulation with this program shows that the I_{220}/I_{440} intensity ratio increases with increasing occupancy of the heavier cations on the A-sites, whereas the ratio decreases with increasing occupancy of the heavier cations on the B-sites. In the present study, in order to assess the effect of the annealing atmosphere on the cation distribution, sintered ceramics were crushed into powers, and then annealed in O_2 or N_2 at 600 °C for 24 h. The annealed powders were aged at 150 °C for 1000 h. Intensities of the (220) and (440) reflections of powers were measured with scanning rate of 0.5°/min before and after aging, and the results are summarized in Table 2. Note that the area of reflection peaks was integrated with a relative error of less than 1%. The aging caused an increase of the I_{220}/I_{440} ratio by 14% from 0.72 to 0.82 for the O_2-annealed sample, and for N_2-annealed sample, the intensity ratio increased by only 3% from 0.77 to 0.79. This indicates that the O_2-annealed sample underwent a larger degree of cation redistribution among the A- and B-sites than the N_2-annealed sample.

The effect of annealing atmosphere on the cations redistribution in the spinel can be explained in term of defect chemistry. The interaction of the NTC spinel oxides with the ambient oxygen has been described by Groen et al. using the Kroger–Vink notation in accordance with the reaction stoichiometry [3]:

$$1/2\ O_2 \rightleftharpoons O_O^x + 1/4V_A'' + 1/2V_B''' + 2h.$$

The concentrations of cation vacancies V_A and V_B are altered also by the migration of cations from the B-sites to the A-sites:

$$M_B + V_A \rightarrow V_B + M_A$$

Obviously, annealing at a higher oxygen partial pressure (in pure O_2) favours the formation of cation vacancies, especially at the B-site [11]. In contrast, annealing at a lower oxygen partial pressure (in N_2) favours the annihilation of the cation vacancies. The creation and annihilation of cation vacancy should result in a change in the lattice parameter of the oxides. It is found that the lattice parameter for the sample annealed in O_2 is somewhat smaller than that annealed in N_2 as shown in Fig. 4. (The XRD measurements were repeated three times, and results were almost the same.) This gives evidence that a higher concentration of cation vacancies is present in the sample annealed in O_2 than in N_2. The presence of cation vacancies in the spinel thus favours the redistribution of cations under a thermal stress, giving rise to the change in electrical properties with time.

4. Conclusions

$Fe_{0.5}Mn_{1.84}Ni_{0.66}O_4$ NTC ceramic thermistors annealed in nitrogen exhibit much improved aging behaviour, and undergo a less degree of cation redistribution among the A- and B-sites in the spinel, as compared with thermistors annealed in O_2. Annealing of the spinel-structured ceramic at a proper oxygen partial pressure leads to the reduction of cation vacancies, inhibiting the cation redistribution and thereby suppressing the aging of the electrical properties.

References

[1] Rousset, R. Legros, A. Lagrange, J. Eur. Ceram. Soc. 13 (1994) 185.
[2] T. Battault, R. Legros, A. Rousset, J. Mater. Res. 13 (1998) 1238.
[3] W.A. Groen, C. Metzmacher, P. Huppertz, S. Schuurman, J. Electroceramics 7 (2001) 77.

[4] Z.B. Wang, C.H. Zhao, P.H. Yang et al., J. Eur. Ceram. Soc. (in press).
[5] L.W. Tai, P.A. Lessig, J. Mater. Res. 7 (1992) 502.
[6] M.I. Mendelson, J. Am. Ceram. Soc. 52 (1969) 443.
[7] E.D. Macklen, J. Phys. Chem. Solids 47 (1986) 1073.
[8] D.S. Birajdar, U.N. Devatwal, K.M. Jadhav, J. Mater. Sci. 37 (2002) 1443.
[9] M.J. Buerger, Crystal Structure Analysis, Wiley, New York, 1960.
[10] W. Kraus and G. Nolze, Powdercell2.4 [software], Federal Institute for Materials Research and Testing, Germany.
[11] B. Gillot, M. El Guendouzi, J. Solid State Chem. 106 (1993) 443.