Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1277–1280
www.elsevier.com/locate/jeurceramsoc

On the role of mass-transfer processes in ageing of manganite electroceramics

M. Vakiv[a], I. Hadzaman[a], O. Shpotyuk[a,*], O. Mrooz[a], J. Plewa[b], H. Altenburg[b], H. Uphoff[b], O. Bodak[c], P. Demchenko[c]

[a]Scientific Research Company "Carat", Lviv Scientific Research Institute of Materials, 202, Stryjska Str., UA-79031, Lviv, Ukraine
[b]Fachhochschule Münster/University of Applied Sciences, SIMa and Supraleiter-Keramik-Kristalle, 39, Stegerwaldstrasse, D-48565 Steinfurt, Germany
[c]Ivan Franko National University of Lviv, Department of Inorganic Chemistry, 6, Kyryla i Mefodiya Str., UA-79005, Lviv, Ukraine

Abstract

Ageing phenomena in NTC thermistors based on copper–nickel–cobalt manganite electroceramics under thermal exposure at 125 and 170 °C during 1000 h are studied. The observed relative resistance drift is compared with the results of XRD, ceramics microstructure characterization (optical microscopy, SEM), electron probe microanalysis, as well as thermogravimetry measurements. It is shown, at the example of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ electroceramics, that the microstructure origin of ageing phenomena can be adequately explained by thermally stimulated mass-transfer processes in the ceramic body.

Keywords: Ageing; Spinels; Thermistors; Transition metal oxides; X-ray methods

1. Introduction

Mixed transition-metal manganite electroceramics for negative temperature coefficient (NTC) thermistors must ensure a high stability of electrical properties under long-term exposure at elevated temperatures, i.e. at 125÷170 °C. That is why ageing phenomena (changes in the electrical resistance with time, particularly under thermal stress) is an important problem under broad consideration.[1-5]

This paper deals with ageing behavior of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ electroceramics. It is spinel-structured composition inside quaternary Cu–Ni–Co–Mn oxide system, restricted by spinel-structured $CuMn_2O_4$, $NiMn_2O_4$ and $MnCo_2O_4$ compounds taken in 0.1:0.8:0.1 ratio.

It is known, that $NiMn_2O_4$ spinel is thermodynamically stable in narrow temperature region, which lies between 730 and 950-960 °C.[5,6] However, the upper temperature limit is 907 °C, according to other data.[3] $NiMn_2O_4$ compound decomposes above this temperature evolving oxygen with formation of NiO and Mn-enriched spinel phases:[5]

$$NiMn_2O_4 \rightarrow \alpha NiO + \frac{a}{6}O_2 + \frac{3-a}{3}Ni\frac{(3-3a)}{3-a}Mn\frac{6}{3\text{-}a}O_4. \quad (1)$$

Our previous studies show that the similar decomposition reaction is initiated at higher sintering temperatures in the spinel-structured cubic (space group $Fd\overline{3}m$) single phase $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics sintered in air at $T_s = 920$ °C.[7] Thus, the investigated ceramics sintered at $T_s = 1170$ °C contains two crystalline phases: the residual tetragonally distorted spinel phase (space group $I4_1/amd$) with modified chemical composition and secondary phase - solid solution based on NiO (the NaCl-type structure, space group $fm\overline{3}m$).

This paper presents the results of X-ray diffraction (XRD) measurements for the aged (held for 1000 h at 170 °C) ceramics of the above composition. To explain ageing phenomena in NTC thermistors based on $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics ($T_s = 1170$ °C), the obtained results will be compared with our previous data on electrical measurements, optical microscopy

* Corresponding author. Tel.: +380-322-638303; fax: +380-322-632228.
E-mail address: shpotyuk@novas.lviv.ua (O. Shpotyuk).

0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00378-9

and SEM, electron probe microanalysis, as well as thermogravimetric study.[8,9]

2. Experimental

The $CuCO_3 \cdot Cu(OH)_2$, $NiCO_3 \cdot m Ni(OH)_2 \cdot n H_2O$, $CoCO_3 \cdot m Co(OH)_2 \cdot n H_2O$ and $MnCO_3 \cdot m Mn(OH)_2 \cdot n H_2O$ reagents were used to prepare the experimental ceramic samples. The starting components were weighted, wet-milled, dried and calcinated in air at 700 °C for 4 h. The obtained powders were again wet-milled, dried, blended with organic binder, sieved and pressed into disks under ≈100 MPa pressure. The blanks were sintered in air for 1 h at $T_s = 1170$ °C.

To measure electrical resistance, the flat surfaces of ceramic disks were coated by silver paste. The Pt-leads were placed into the silver paste. The mechanical properties of fitted wires were achieved owing to metallization process at 850 °C.

Ageing tests were carried out during 1000 h at 125 and 170 °C, the HPS-222 (Tabaj, Japan) chambers being used. Each experimental batch included three non-encapsulated NTC thermistors. The stability of studied ceramic samples was estimated by the relative resistance drift (RRD) values ($\Delta R/R_0$) after several hours of storage at the above temperatures. The electrical resistances were measured at 25±0.1 °C with a precise digital multimeter.

The microstructure observations ("Nikon" optical microscope) and electron probe microanalysis (Camebax device) were carried out on polished and etched sections of as-sintered ceramic disks before (non-aged) and after 1000 h storage at 170 °C (aged). The content of transition metals was determined using $K\alpha$ lines. Preliminary optical and electron probe studies for as-sintered and additionally treated at 850 °C ceramic samples (the temperature conditions of metallization) showed their microstructure similarity.

The scanning electron microscopy (SEM) investigations (LEO 982 field emission scanning electron microscope) were done on freshly prepared chips of non-aged and aged ceramic samples. The thermogravimetric analysis (TGA) was performed with Netzsch STA 409 thermal analyzer.

X-ray diffraction (XRD) powder patterns for aged (sintered at 1170 °C (1 h), treated at 850 °C and held for 1000 h at 170 °C) ceramics were recorded at room temperature using a powder HZG-4a diffractometer with Cu $K\alpha$ radiation. The measurements were carried out in a step regime ($\Delta 2\theta = 0.02°$; $15.00 \leqslant 2\theta \leqslant 121.38$). The profile analysis was performed using the method of approximation of X-ray reflections by pseudo Voigt function. The lattice parameters and crystal structure of the phases were refined using Rietveld method with the FULLPROF.2k program[10] from the WinPLOTR software.[11]

3. Results and discussion

The investigated $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ NTC samples show a typical RRD kinetics during ageing tests.[8,9] The greatest $\Delta R/R_0$ values are observed in the early hours of ageing followed by complete saturation achieved at ∼500 h. The higher the temperature, the greater the saturation RRD value. Thus, ageing at 170 °C leads to ∼7.5% in $\Delta R/R_0$ value, while ageing at 125 °C—only to ∼6%.

The microstructure observations for non-aged and aged ceramics by means of optical microscopy[9] show heterogeneous two-phase materials—the main spinel-based phase and additional phase. Visually, the amount and grain sizes of additional phase are higher in aged ceramics, compared with non-aged. The SEM image for non-aged $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics presented in,[9] the SEM image for aged ceramics is shown in Fig. 1.

According to the results of electron probe microanalysis (Table 1), the spinel phase for both ceramics has modified composition (it is depleted in Ni and enriched in Mn) in comparison with basic composition of ceramics. Moreover, after ageing the higher degree of modification of the spinel phase is observed (compositions of the spinel phase for aged and

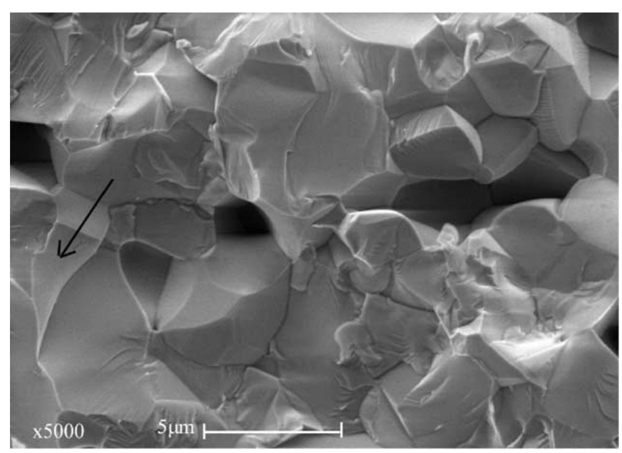

Fig. 1. SEM image for aged $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics (the grain of the additional phase among the grains of the spinel phase is marked).

Table 1
Content of components in the spinel phase for basic (calculated due to chemical formula), non-aged and aged $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics

Content, at.%	Basic	Non-aged	Aged
Cu	1.43	1.3	1.3
Ni	11.43	9.2	8.2
Co	2.86	2.6	2.8
Mn	27.14	28.2	29.4
O[a]	57.14	58.7	58.3

[a] The content of oxygen was determined as difference: 100, total content of metals.

non-aged ceramics are $Cu_{0.09}Ni_{0.59}Co_{0.20}Mn_{2.12}O_4$ and $Cu_{0.09}Ni_{0.67}Co_{0.19}Mn_{2.05}O_4$, respectively). This additional phase for aged and non-aged ceramics contains, besides a high amount of Ni, some amounts of Cu, Co and Mn, the total content of metals and oxygen being ~1:1. so it can be concluded that this additional phase is a solid solution of Cu, Co and Mn in NiO.

The refinement of crystal structure of the investigated ceramics after ageing was performed assuming the existence of two phases. The data of electron probe microanalysis for the spinel phase were used in starting models for refinement. The final results of X-ray structure analysis are given in Tables 2 and 3. The proposed distribution of transition metals is empirical in view of the small difference of their scattering amplitudes. But, really, the best results of refinement were obtained exactly for these distributions. Comparison of the observed and calculated XRD profiles is shown in Fig. 2. For the investigated aged ceramics, as in the case of non-aged ones,[7] the typical image of a two-phase sample is observed. Reflections of NiO-based solid solution besides reflections of spinel phase are observed. The fraction of the additional phase is 26.14% (as

Table 2
Experimental and final refined crystallographic data for aged $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics

The spinel phase	
Space group	$I4_1/amd$ (setting 2)
Lattice parameters (Å)	
a	5.9478(7)
c	8.394(2)
	$c/a = 1.4113$
Cell volume (Å^3)	296.96(8)
Radiation and wavelengths (Å)	Cu $K\alpha$
	1.54056 1.54439
Angular range $2\theta_{min}$–$2\theta_{max}$ (degrees)	15.00–121.38
2θ-step of scanning (degrees)	0.02
Number of measured reflections	77
Number of fitted parameters	27
Reliability factors	
R_{Bragg}	0.0464
R_F	0.0461
χ^2	1.34
R_{wP} (not corrected for background)	0.0153
R_{wP}	0.178
The NiO-based solid solution	
Space group	$Fm\bar{3}m$
Lattice parameter *a* (Å)	4.1876(4)
R_{Bragg}, R_F	0.0412 0.0302
Fraction (%)	26.14(1)

Table 3
Atomic parameters, displacements (B_{iso}, Å^2) and occupations (*G*) for the spinel phase in aged $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics

Atom	Site	*x*	*y*	*z*	B_{iso}	*G*
Mn	4*b*	0	1/4	3/8	0.4(1)	0.41(9)
Co	4*b*	0	1/4	3/8	0.4(1)	0.2
Ni	4*b*	0	1/4	3/8	0.4(1)	0.39(9)
Mn	8*c*	0	0	0	0.2(1)	0.84(9)
Cu	8*c*	0	0	0	0.2(1)	0.05
Ni	8*c*	0	0	0	0.2(1)	0.11(9)
O	16*h*	0	0.533(2)	0.248(2)	0.3(2)	1

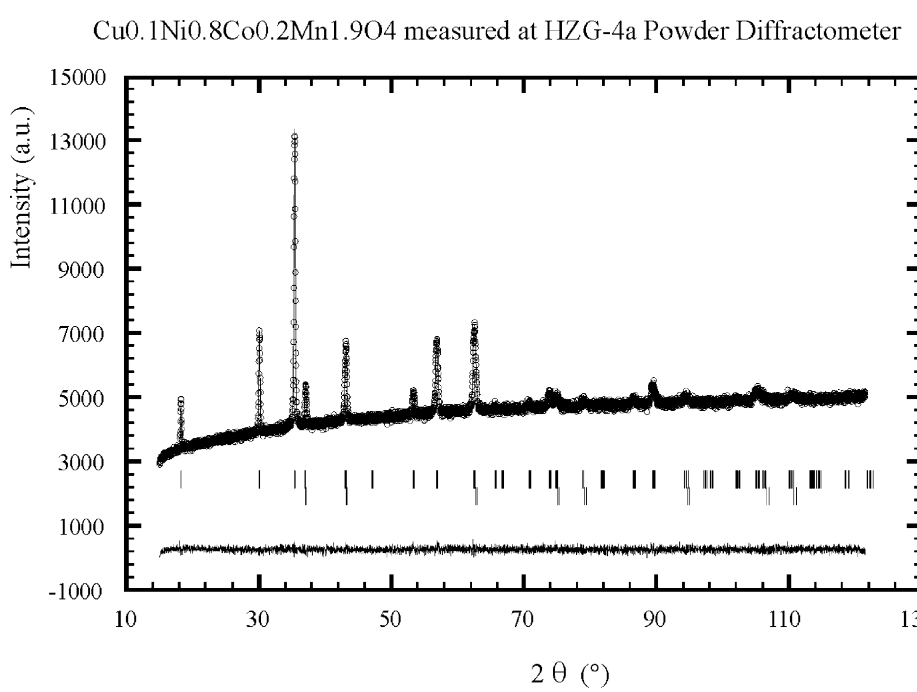

Fig. 2. Observed (circles), calculated (solid line) and differential (bottom) XRD profiles (Cu $K\alpha$-radiation) for $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ aged ceramics. Upper bar: reflections of the spinel phase, lower bar: reflections of the solid solution based on NiO with the NaCl-type structure.

determined by rietveld method), which is higher than in non-aged ceramics (10.61%).[7]

The higher degree of modification of the spinel phase and the higher fraction of additional phase, determined for aged ceramics (in comparison with those for initial ceramics), can be treated as a result of further proceeding of the spinel decomposition reactions with oxygen release under prolonged thermal exposure during ageing tests. The TGA measurements in air prove the higher mass gain for aged ceramics as compared with non-aged.[9] Aged samples show the additional mass gain (as against to non-aged samples), which begins from $\sim$450 °C and proceeds up to $\sim$900 °C, ended by a slight 0.4–0.5 mass.% saturation effect. This is additional evidence that de-oxidation reactions in the studied ceramics take place during ageing.

Thus, at the basis of the obtained experimental results, we can conclude that the de-oxidation reaction like to (1), accompanied by the appearance of MO-type solid solution with the NaCl-type structure and residual M_3O_4 spinel phase with modified chemical composition, is activated at the high temperature sintering of ceramics. The de-oxidation reaction proceeds further during prolonged ageing tests, resulting in the observed RRD rise. The amount of MO-based solid solution with lower conductivity (compared with the spinel phase)[12] increases finally in the overall phase balance, some MO-enriched grains growing sufficiently in sizes and being separated evidently in the ceramic microstructure.

4. Conclusions

The RRD observed in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ electroceramics during prolonged ageing tests at 125 and 170 C is explained by thermally stimulated mass-transfer processes, which proceed in the ceramic body. Owing to decomposition (de-oxidation) reaction activated at the high sintering temperature ($T_s = 1170$ C), the initial (non-aged) NTC electroceramics contain two crystalline phases: the tetragonal distorted spinel phase with modified composition and the additional NiO-based phase with the NaCl-type structure. After exposure at elevated temperatures, the higher fraction of the additional phase in ceramics is determined by XRD. It confirms that the de-oxidation reaction proceed further during ageing tests, giving the observed RRD values.

References

1. Castelan, P., Ai, B., Loubiere, A., Rousset, A. and Legros, R., Ageing study of NTC thermistors by thermopower measurements. *Sensors and Actuators A*, 1992, **33**, 119–122.
2. Fritsch, S., Sarrias, J., Brieu, M., Couderc, J. J., Baudour, G. L., Snoeck, E. and Rousset, A., Correlation between the structure, the microstructure and the electrical properties of nickel manganite negative temperature coefficient (NTC) thermistors. *Solid State Ionics*, 1998, **109**, 229–237.
3. Csete de Györgyfalva, G. D. C. and Reaney, I. M., Decomposition of $NiMn_2O_4$ spinel: an NTC thermistor material. *J. Eur. Ceram. Soc.*, 2001, **21**, 2145–2148.
4. Groen, W. A., Metzmacher, C., Zaspalis, V., Huppertz, P. and Schuurman, S., Aging of NTC ceramics in the system Mn–Ni–Fe–O. *J. Eur. Ceram. Soc.*, 2001, **21**, 1793–1796.
5. Feltz, A. and Pölzl, W., Spinel forming ceramics of the system $Fe_xNi_yMn_{3-x-y}O_4$ for high temperature NTC thermistor applications. *J. Eur. Ceram. Soc.*, 2000, **20**, 2353–2366.
6. Jung, J., Töpfer, J., Mürbe, J. and Feltz, A., Microstructure and phase development in $NiMn_2O_4$ spinel ceramics during isothermal sintering. *J. Eur. Ceram. Soc.*, 1990, **6**, 351–359.
7. Bodak, O., Akselrud, L., Demchenko, P., Kotur, B., Mrooz, O., Hadzaman, I., Shpotyuk, O., Aldinger, F., Seifert, H., Volkov, S. and Pekhnyo, V., Microstructure, crystal structure and electrical properties of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics obtained at different sintering conditions. *J. Alloys Compd.*, 2003 (in press) (reference JALCOM 8066).
8. Shpotyuk, O., Vakiv, M., Mrooz, O., Hadzaman, I., Altenburg, H., Plewa, J. and Uphoff, H., Aging phenomenon in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ NTC ceramics. In *Proceedings of the 7th Conference & Exhibition of the European Ceramic Society, Brugge, Belgium, 2001*. Trans Tech Publications, Switzerland, pp. 1317–1320.
9. Mrooz, O., Hadzaman, I., Vakiv, M., Shpotyuk, O., Plewa, J., Altenburg, H. and Uphoff, H., Aging of copper–nickel–cobalt–manganite NTC thermistors". in *Proceedings of the 23rd International Conference on Microelectronics, Nis, Yugoslavia, 2002*. IEEE Catalog No. 02TH8595 ISBN 0-7803-7235-2, pp. 375–378.
10. Rodriguez-Carvajal, J., FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis, in Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, p. 127.
11. Roisnel, T. and Rodriguez-Carvajal, J., WinPLOTR: a Windows tool for powder diffraction patterns analysis. In *Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)*, ed. R. Delhez and E. J. Mittenmeijer, 2000, pp. 118–123
12. Sheftel, I. T., *Thermistors*. Nauka, Moscow, 1973.