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Journal of the European Ceramic Society 24 (2004) 1243–1246

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Ageing behavior of electrical resistance in manganite NTC ceramics

M.M. Vakiv[a], O.I. Shpotyuk[a,*], V.O. Balitska[a], B. Butkiewicz[b], L.I. Shpotyuk[a]

[a]*Lviv Scientific Research Institute of Materials, Scientific Research Company "Carat", 202, Stryjska Str., Lviv, 79031, Ukraine*
[b]*Institute of Electronic Systems, Warsaw University of Technology, 15/19, Nowowiejska str., Warsaw, 00-665, Poland*

Abstract

Experimental results on thermally induced degradation tests, carried out at relatively low ageing temperature (170 °C) in NTC thermistors based on $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ spinel-structured ceramics, are discussed. It is shown the kinetics of the observed degradation processes is described mainly by well known DeBast–Gillard or Williams–Watts relaxation function, the deviations from this conclusion being observed only in multiphase ceramic samples. The inhibition effect in ageing of the investigated ceramics is observed at small concentration of additional NiO-enriched rock-salt phase.

Keywords: Ageing; Degradation test; Electrical properties; Spinels; Thermistors

1. Introduction

The negative temperature coefficient (NTC) thermistors (TR) based on mixed transition-metal manganite electroceramics are widely used in various industrial and domestic applications.[1–3] The high demands to functional reliability put forward an actual problem on exact description for degradation kinetics of their main exploitation parameters, such as electrical resistance R and thermal constant B.

This problem was first described in details by J. Becker et al. yet in 1946.[2] It was shown particularly that electrical resistance R always rose with time t, the most essential relative resistance drift taking place in the first 50–200 h of isothermal exposure. These changes proceeded to saturation after more prolonged time period of degradation (500–1000 h) with an absolute value $R_{\max}$ determined by chemical composition of ceramic material, technological parameters of its preparation, physical properties of contact wires, etc. The similar behavior, differed only by some negligible qualitative peculiarities, were maintained in subsequent more than five decades of TRs study in scientific laboratories from all over the world.[1]

The first visual inspection of the above ageing kinetics in manganite-based TR testified in a favor of its possible exponential description. Moreover, this kind of monotonically-growth function was used recently by A. Felts et al. as the most suitable one for low-temperature isothermal degradation of B constant in $NiMn_2O_4$ TR.[3] However, any attempts to use another mathematical functions for ageing kinetics in these ceramic TR have not been considered.

Thus, in spite of a great number of experimental research fulfilled under different kinds of ceramic materials with well pronounced TR effect, the precise functional expression corresponding to their ageing kinetics has not been established up to now. This disadvantage is accepted especially sharp in comparison with a number of analytical functions available for time-dependent ageing phenomena in other topologically disordered solids.[4–8]

So, the aim of this work is to search the adequate functional expressions, which will be quite suitable for description of ageing kinetics in ceramic manganite-based TR in dependent on technological features of their preparation.

2. Experimental

The degradation kinetics was studied on the example of three batches (each of them involves three samples) of Ni-enriched TR of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ composition, which can be easy presented as mixture of three stoichiometric $NiMn_2O_4$, $CuMn_2O_4$ and $MnCo_2O_4$ spinel compounds taken in 0.8:0.1:0.1 ratio.[9] The real phase compositions of the investigated ceramics were

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[*] Corresponding author. Tel.: +380-322-631065; fax: +380-322-632228.
E-mail address: shpotyuk@novas.lviv.ua (O.I. Shpotyuk).

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doi:10.1016/S0955-2219(03)00377-7

determined by used programs of their high-temperature sintering.[9] The samples of batch 1 and 2 were shortly exposured at the sintering temperature of $T_s = 1200$ °C (about 1 h), the samples of batch 1 being quickly cooled then. The samples of batch 2 were kept additionally at the temperature of single spinel phase formation (920 °C) during 24 h.[1] The samples of batch 3 were exposured at $T_s = 1200$ °C during 3 h and then quickly cooled like as the samples of batch 1.

As a result, the samples of batch 2 were single phase, while the samples of batch 3 contained a high amount of additional NiO-enriched rock-salt phase. This additional phase existed only in a small amount in the samples of batch 1 (according to X-ray diffraction data).

The prepared samples were affected to thermal stresses at the temperature of 170 °C, the total duration of degradation test being 500 h. The results were controlled by relative resistance drift values $\eta = \Delta R/R_0$. All measurements were carried out in the normal conditions at 25 °C after certain hours of degradation (24, 72, 144, 208, 288, 395 and 500 h).

3. Results and discussion

It is known, the monotonically decaying kinetics of degradation, expressed in decreasing of controlled relaxation parameter η (t) with time t, is described by the next differential equation:

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\lambda\eta^{\alpha}t^{\beta}, \tag{1}$$

where λ is coefficient of proportionally, α and β are some material-related constants.[4,6]

Apparently, when the monotonically rising degradation kinetics takes place, the relaxation parameter $\eta(t)$ satisfies the next equation:

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = \lambda(1-\eta)^{\alpha}t^{\beta}. \tag{2}$$

The degradation kinetics is determined by a so-called relaxation function (RF), which can be presented for Eq. (1) in the form of

$$M_{\mathrm{p}}(t) = \frac{\eta_{\mathrm{t}} - \eta_{\infty}}{\eta_0 - \eta_{\infty}}, \tag{3}$$

where η_0 and η_∞ correspond to initial ($t=0$) and final ($t \to \infty$) values of $\eta(t)$, measured before and after degradation test.

In the case of growing kinetics, this RF is defined as

$$N_\eta(t) = 1 - M_\eta(t) = 1 - \frac{\eta_{\mathrm{t}} - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{\eta_{\mathrm{t}} - \eta_0}{\eta_\infty - \eta_0}. \tag{4}$$

It was pointed out previously that only five kinds of $M_\eta(t)$ or $N_\eta(t)$ RF corresponded for different types of degradation kinetics in dependence on α and β parameters (Table 1).[6]

In the case of $\alpha = 1$ and $\beta = 0$, we have the well-known monomolecular relaxation process, expressed by simple exponential dependence on time t (RF 1 in Table 1). If the degradation is caused by recombination of specific defect pairs such as electron-hole, vacancy-interstitial, etc. the underlying kinetics is determined by bimolecular RF (RF 2 in Table 1 obtained at $\alpha = 2$ and $\beta = 0$). The exact solution of the differential degradation equation at $\beta = 0$ gives the RF 3, exhibited "stretched" behavior owing to standard αth order kinetics of degradation. This RF 3 is often used for description of

Table 1
Relaxation functions $N_\eta(t)$, describing ageing kinetics in the investigated ceramic TR

Monomolecular RF 1 ($\alpha = 1$, $\beta = 0$)	$N_\eta(t) = 1 - \mathrm{e}^{-\frac{t}{\tau}}$ $\tau = \frac{1}{\lambda}, \ \ \lambda \neq 0$
Bimolecular RF 2 ($\alpha = 2$, $\beta = 0$)	$N_\eta(t) = 1 - \frac{1}{1 + \frac{\tau}{t}}$ $\tau = \frac{1}{\lambda}, \ \ \lambda \neq 0$
RF 3 ($\alpha \neq 0$, $\beta = 0$)	$N_\eta(t) = 1 - \frac{1}{(1 + t/\tau)^{\kappa}}$ $\tau = \frac{1}{\lambda(\alpha - 1)}, \ \ \kappa = \frac{1}{\alpha - 1}, \ \ \alpha \neq 1, \ \ \lambda \neq 0$
RF 4 DeBast–Gillard or Williams–Watts RF ($\alpha = 1$, $\beta \neq 0$)	$N_\eta(t) = 1 - \exp[-(t/\tau)^{\kappa}],$ $\tau = \frac{1+\beta}{\lambda}, \ \ \kappa = 1 + \beta, \ \ \beta \neq -1, \ \ \lambda \neq 0$
RF 5 ($\alpha \neq 0$, $\beta \neq 0$)	$N_\eta(t) = 1 - \frac{1}{(1 + (t/\tau)^{\kappa})^{r}}$ $\kappa = 1 + \beta, \ \ r = \frac{1}{\alpha - 1}, \ \ \tau = \left(\frac{1+\beta}{\lambda(\alpha\text{-}1)}\right)^{\frac{1}{1+\beta}}, \ \ \alpha \neq 1, \ \ \beta \neq -1, \ \ \lambda \neq 0$

post-irradiation thermal effects in some oxide glasses.[5] In the case of $\beta \neq 0$ and $\alpha = 1$, the relaxation process is described by stretched exponential RF 4, which is the most suitable for quantitative description of structural, mechanical and electrical degradation processes in glasses or other solids with so-called disperse nature of relaxation.[4] This RF 4 was introduced first by DeBast and Gillard,[7] as well as Williams and Watts.[8] The exact general solution of the degradation equation with arbitrary α and β values differed from 0 or 1 is be presented by RF 5 (Table 1).

The obtained experimental results of degradation tests for the investigated three TR batches are illustrates by Fig. 1. It is obvious that the monotonically rising kinetics corresponds them. So, the RF in the form of $N_\eta(t)$ defined by Eq. (4) must be used for functional description of these ageing tests. The shape of degradation curves corresponds to the greatest η increase in early hours of ageing, followed by saturation effect stretched from a few hundreds up to 500 h in dependence on technological regimes of TR preparation.

With a purpose of adequate mathematical description of the observed degradation kinetics, the numerical values of fitting τ, κ, and r parameters in the $N_\eta(t)$ were calculated in such a way to minimize the mean-square deviation *err* of the experimentally measured points from the checked RF shown in Table 1. The least-square deviation *err* for different RF, describing the observed ageing phenomena, are presented in Table 2.

It is established that ageing kinetics in the investigated TR samples of batch 2 (single-phase ceramics) can be described quite well by RF 4 (DeBast–Gillard or Williams–Watts RF). Indeed, in this case, *err* are the smallest and only two fitting parameters (τ, κ) are present in RF. This result is not surprising for us, because the stretched-exponential RF is proper to the typical topologically disordered solids, characterized by a dispersion of degradation parameters.[4]

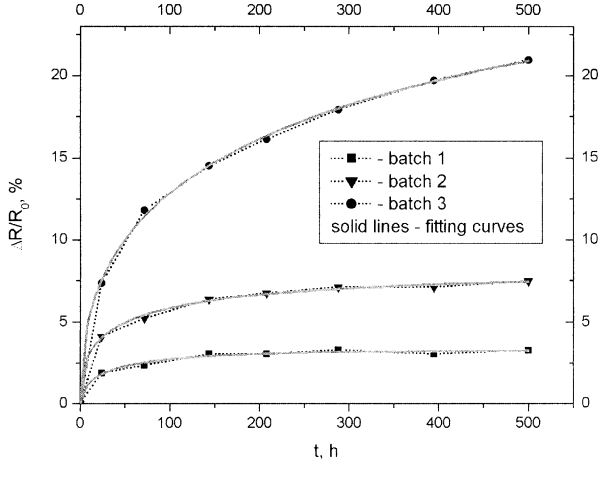

Fig. 1. The relatively resistance drift in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ TR in dependence on technological regimes of their preparation.

Table 2
Least-square deviations (*err*) for different relaxation functions, describing ageing tests in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$-based TR

No. of batch (No. of sample)	*Err*-values for different relaxation functions (RFs)				
	RF4	RF1	RF2	RF3	RF5
1 (1)	0.026	0.051	0.022	0.033	0.049
1 (2)	0.031	0.075	0.047	0.096	0.040
1 (3)	0.031	0.065	0.037	0.037	0.041
2 (1)	0.023	0.282	0.066	0.058	0.032
2 (2)	0.064	0.465	0.207	0.179	0.080
2 (3)	0.043	0.532	0.212	0.247	0.054
3 (1)	0.006	0.507	0.120	0.007	0.008
3 (2)	0.061	2.491	0.844	0.055	0.066
3 (3)	0.101	2.333	0.754	0.089	0.102

In more structurally complicated ceramics, contained additional phases such as NiO-enriched one (batch 1 and 3), the degradation kinetics is changed. The stretched-exponential DeBast–Gillard or Williams–Watts RF 4 can be further used to describe the observed time dependence of the relative resistance drift in the investigated TR, but a clear deviation towards three-parameter (τ, κ and r) fitting owing to generalized RF 3 or RF 5 is revealed too. Presumably, the overall degradation effect in multiphase manganite-based ceramics is composed of individual curves for each phase itself, the corresponding microstructural mechanism being determined by phase composition.

It should be noted that the "ideal" single-phase ceramics does not possess the better stability over the initially "bad" multiphase one (compare curve 2 and 3 in Fig. 1). However, the small amounts of additional phase, introduced in the samples of batch 1, inhibit sufficiently the development of thermal ageing (curve 1 in Fig. 1). We assume that origin of this inhibition effect is associated with stabilization of cationic distribution in the investigated spine–matrix ceramics owing to slight separation of additional phase.

4. Conclusion

The degradation kinetics of NTC $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics is determined mainly by its phase composition. The typical stretched-exponential behavior is proper to single-phase material, while the deviation towards general solution of degradation equation are observed in multiphase ceramic compositions. The inhibition effect in the degradation of the investigated ceramics is revealed, provided only a small concentration of additional phase is present in its structure. This conclusion should be necessarily taken into consideration to provide a high level of functional reliability for the developed mixed transition-metal manganite ceramics.

Acknowledgements

This work was supported by Science and Technology Centre in Ukraine (Project No 2080).

References

1. Sheftel, I. T., *Thermoresistors*. Nauka, Moscow, 1973.
2. Bekker, J. A., Green, C. B. and Pearson, G. L., Properties and uses of thermistors—thermally sensitive resistors. *Trans. Amer. Inst. Elect. Eng.*, 1946, **65**, 711–725.
3. Feltz, A., Topfer, J. and Schirrmeister, F., Conductivity data and preparation routes for $NiMn_2O_4$ thermistor ceramics. *J. Eur. Ceram. Soc.*, 1992, **9**, 187–191.
4. Mazurin, Î. V., Relaxation phenomena in glass. *J. Non-Cryst. Solids*, 1977, **25**, 130–169.
5. Griscom, D. L., Gingerich, M. E. and Friebele, E. J., Radiation-induced defects in glasses: origin of power-law dependences of concentration on dose. *Phys. Rev.Lett.*, 1993, **71**, 1019–1022.
6. Balitska, V. O., Shpotyuk, O. I. and Vakiv, M. M., Degradation of electron-induced dichroism in glassy As_2S_3-Sb_2S_3. *Ukr. J. Phys. Optics*, 2000, **1**, 107–110.
7. De Bast, J. and Gilard, P., Variation of the viscosity of glass and relaxation of stresses during stabilization. *Phys. Chem. Glasses*, 1963, **4**, 117–128.
8. Williams, G. and Watts, D. C., Non-symmetrical dielectric relaxation behavior arising from a simple empirical decay function. *Trans. Faraday Soc.*, 1970, **66**, 80–85.
9. Shpotyuk, O., Kovalskiy, A., Mrooz, O., Shpotyuk, L., Pechnyo, V. L. and Volkov, S., Technological modification of spinel-based $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ceramics. *J. Eur.Ceram. Soc.*, 2001, **21**, 2067–2070.