

Kinetics models describing degradation-relaxation effects in nanoinhomogeneous substances

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Abstract. The mathematical models of degradation-relaxation kinetics are considered for jammed systems composed of screen-printed spinel $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ and conductive Ag or Ag-Pd alloys. Structurally-intrinsic nanoinhomogeneities due to Ag and Ag-Pd diffusants embedded in spinel phase environment are shown to define governing kinetics of thermally-induced degradation obeying an obvious non-exponential behaviour in the resistance drift. The stretched-to-compressed exponential crossover is detected for degradation-relaxation kinetics in these systems with conductive contacts made of Ag-Pd and Ag alloys. Under essential migration of conductive phase, the resulting kinetics is thought to be considerable two-step diffusing process originated from Ag penetration deep into spinel ceramics.

1. Introduction

The jammed systems prepared from high-temperature state by so-called fluid-to-solid transition compose an important class of substances for practical using [1]. Being quenched in far-from-equilibrium configuration, these materials demonstrate response on different degradation-relaxation inputs, tending towards equilibrium in the controlled parameter $N(t)$ through compressed-exponential relaxation (CER) kinetics (super-exponential, i.e. faster than simple exponential decay):

$$N_{\eta}(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \quad (1)$$

with scaling (viz. compressing) exponent $\beta > 1$ and characteristic decay time τ .

Despite recent progress in the functional characterization of such substances [1-6], their phenomenological behaviour has been remained mysterious in many aspects, especially from a point of mathematical modelling and prediction.

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This work deals with specificity of thermally-induced electric degradation-relaxation phenomena revealed in heterogeneous jammed solid-state system composed of the same ceramics matrix with different types of diffusion agents (diffusants), exemplified by thick-film structures of spinel $(\text{Cu,Ni,Co,Mn})_3\text{O}_4$ manganites with screen-printed conductive layers composed of “pure” Ag and Ag-based (made of Ag-Pd conductive paste C1216) alloys [7-11].

2. Experimental

2.1. Nanoinhomogeneous ceramics preparation

The starting ceramics were synthesized by sintering route (1040 °C, 4 h duration) using reagent grade Cu carbonate hydroxide, and Ni, Co, Mn carbonate hydroxide hydrates [12-14]. The paste was prepared by mixing powder of basic $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics with МБ-60 glass, Bi_2O_3 (used as inorganic binder) and some organic vehicle. Then, the paste was printed on alumina substrates (Rubalit 708S) with conductive Ag-Pd layer screen printed from C1216 paste using a manual screen-printing device equipped with a steel screen. Finally, the thick-film structures were fired at 850 °C.

The prepared thick-film spinel-conductor systems were subjected to degradation under storage at 170 °C within (24-360 h) [7-10]. The results of aging tests were controlled by relative resistance drift (RRD), e.g. changes in electrical resistance $\Delta R/R_0$ detected under normal conditions, the confidence interval in the RRD measuring error-bar being no worse than $\pm 0.2\%$. Additional deviations in some points were allowed due to faults in an exact reproduction of degradation cycles (cooling regime from aging temperature, influence of environment and humidity, etc.). Statistical analysis testified these factors introduced additional error of about $\pm 0.2\%$ in $\Delta R/R_0$ values. So, the overall uncertainties in electrical measurements within this aging protocol did not exceed $\pm(0.4-0.5)\%$.

2.2. Mathematical simulation procedure

With a purpose of adequate mathematical description of degradation-relaxation kinetics in $\Delta R/R_0$ values, the numerical values of fitting parameters in typical relaxation functions (RF) were calculated in such a way to minimize the mean-square deviation *err* of experimentally measured points from chosen RF, taken as adequate solution of general degradation equation in a power-like form [15-17]:

$$\frac{d\eta}{dt} = -\lambda\eta^\alpha t^\gamma, \quad (2)$$

where power indexes α and γ as well as λ coefficient are some material-related constants.

All RFs can be determined from this eq. (2) in dependence on controlled relaxation parameter $\eta(t)$. As was pointed out in [15-17], there are five typical kinds of RFs, which can be considered as partial solutions of the equation (2) in dependence on numerical α and γ variables.

In case of $\alpha=1$ and $\gamma=0$, we have a well known monomolecular relaxation kinetics with RF 1, expressed by simple exponential dependence on time t with $\tau=1/\lambda$ ($\lambda \neq 0$):

$$\eta = a(e^{-t/\tau} - 1). \quad (3)$$

If the degradation is caused by recombination of specific types of defect pairs, the governing kinetics is defined by bimolecular RF 2 at $\alpha=2$ and $\gamma=0$ ($\tau=1/\lambda$, $\lambda \neq 0$):

$$\eta = a\left(\left(1 + \frac{t}{\tau}\right)^{-1} - 1\right). \quad (4)$$

The exact solution of equation (1) at $\gamma=0$ gives RF 3, which exhibits character “stretched” behaviour owing to standard α^{th} -order kinetics of degradation ($\tau=1/\lambda(\alpha-1)$, $\beta=1/(\alpha-1)$, $\alpha \neq 1$, $\lambda \neq 0$):

$$\eta = a \left(\left(1 + \frac{t}{\tau} \right)^{-\beta} - 1 \right). \quad (5)$$

In case of $\alpha=1$ and $\gamma \neq 0$, the relaxation process is described by stretched exponential RF 4 with $\tau=(1+\gamma)/\lambda$, $\beta=1+\gamma$, $\beta \neq 1$ and $\lambda \neq 0$:

$$\eta = a \left(e^{\left(-\frac{t}{\tau} \right)^{\beta}} - 1 \right). \quad (6)$$

Noteworthy, in dependences of β values, this RF 4 can be presented in stretched-exponential ($\beta < 1$) or compressed-exponential ($\beta > 1$) form, thus corresponding to above eq. (1). The exact solution of eq. (2) with arbitrary values of α and γ (both different from 0 or 1) can be presented by RF 5 with $\tau=(1+\gamma)/\lambda(\alpha-1)$, $\beta=1+\gamma$, $r=1/(\alpha-1)$, $\alpha \neq 1$, $\beta \neq 1$ and $\lambda \neq 0$:

$$\eta = a \left(\left[\left(1 + \frac{t}{\tau} \right)^{\beta} \right]^{-r} - 1 \right). \quad (7)$$

This formalism of eqs. (4)-(8) is applied to select the best RF describing degradation-relaxation kinetics in terms of minimal mean-square deviations between experimental points and modeling curve.

3. Results and discussion

The both types of the studied nanoinhomogeneous substances demonstrate monotonically growing tendency in the RRD (in electrical resistance $\Delta R/R_0$), this behavior having more threshold-like character in case of screen-printed $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ spinel ceramics with conductive Ag contacts as it shown previously in [7-11]. These dependences for $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ thick films to determine the best one describing this kinetics (the results for $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ thick films prepared with screen-printed Ag-Pd and Ag contacts are given in Tables 1 and 2, respectively).

Table 1. Parameters of the RFs, describing $\Delta R/R_0$ kinetics in thick-film $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ with Ag-Pd contacts.

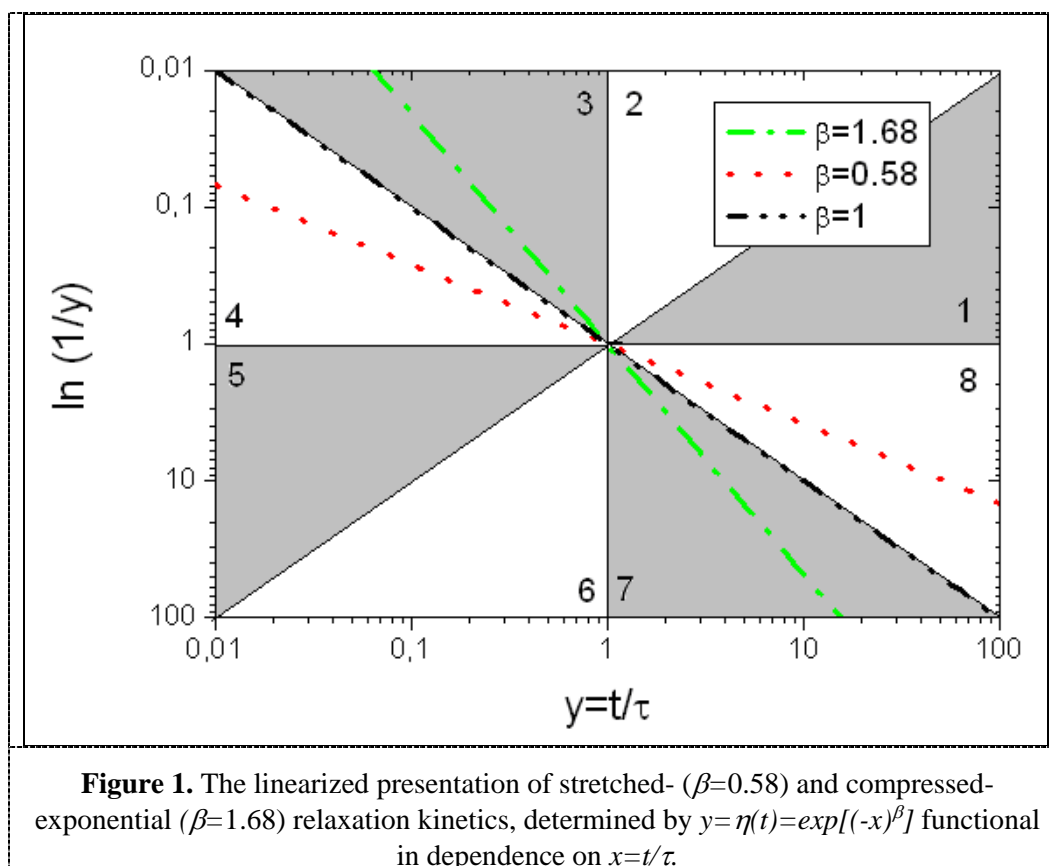
	<i>err</i>	<i>a</i>	τ	β	<i>r</i>
RF 1	0.22	6.9	22.5	-	-
RF 2	0.06	7.8	17.4	-	-
RF 3	0.04	10.6	5.2	0.32	-
RF 4	0.05	7.8	32.3	0.58	-
RF 5	0.05	9.3	12.5	0.81	0.66

Table 2. Parameters of the RFs, describing $\Delta R/R_0$ kinetics in thick-film $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics prepared with conductive screen-printed Ag contacts.

	<i>err</i>	<i>a</i>	τ	β	<i>r</i>
RF 1	0.06	6.9	279	-	-
RF 2	0.07	11.3	444	-	-
RF 3	0.08	8.3	1014	3.07	-
RF 4	0.001	4.8	154	1.68	-
RF 5	0.002	5.1	251	1.82	2.73

The best results of modelling for thick-films $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics with Ag-Pd contacts (see table 2) can be presented by a well-known stretched-exponential RF 4 given by equation (7) with a character non-exponentiality index β approaching ~ 0.58 and effective time constant τ tending towards ~ 32 h. In contrast, with changing in the conductive material of electrical contacts (under transition to the same thick-films $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics with Ag contacts), the governing degradation-relaxation kinetics is drastically changed attaining an obvious CER character with over-unity compressibility index $\beta = 1.68$ and time constant τ reaching ~ 154 h.

The crossover of the detected degradation-relaxation kinetics from stretched-exponential ($\beta = 0.58$) to CER ($\beta = 1.68$) in the studied jammed system (caused by change in the diffusant type in a contact with $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ spinel ceramics) is well depicted in the linearized form as it shown on figure 1. Within this presentation in y - x variables, the stretched-exponential behaviour (with $\beta = 0.58$) is defined by experimental points grouped along red-coloured dotted straight line in the 4-8 octants, while the CER behaviour (with $\beta = 1.68$) is defined by experimental points grouped along green-coloured dash-double-dotted line penetrating the 3-7-th octants.



The EDX study of Ag distribution profiles taken on fresh cut-sections of thick-film ceramics-Ag structures before and after degradation testing shows essential metallic penetration into ceramics [11].

The metallic Ag appears in the regions of spinel ceramics adjusted to conductor contact, as well as in deep intrinsic region in ceramics bulk. In case of conductive Ag-Pd contact, the metallic Ag penetrates only in short pre-contact region. It is known that conductive material penetrating spinel ceramics reduces electrical resistivity, thus resulting in negative RRD for such thick-film systems [10,11]. This diffusive-related process is strongly thermally-activated, in contrast to own structural changes occurring in ceramics body, which produces rather positive feedback in the RRD due to increased defectiveness of spinel matrix [14].

The negative RRD quickly saturates with conductive material penetrating into ceramics as it character for thick films of $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ spinel supplied by conductive Ag-Pd alloy contacts. Under these conditions, the whole Ag-Pd alloy behaves as one “cumulative” diffusing agent with a significantly suppressed possibility for Ag atoms migration. The resulting kinetics of such diffusive degradation-relaxation process attains strong tendency to yield stretched-exponential scenarios.

However, if Ag penetration is not sufficiently inhibited in a spinel ceramics by Pd addition, as for $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ thick films with contacts made of pure screen-printed Ag, the kinetics of the resulting diffusive process is principally changed. The overall diffusion-limited relaxation in the studied thick-film system occurs as two-step penetration of conductive agent (Ag) into spinel body.

4. Conclusions

Nanoinhomogeneous due to metallic diffusants (Ag and Ag-Pd alloys) in $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ spinel ceramics are shown to be decisive factors governing kinetics of thermally-induced degradation tests under 170 °C obeying an obvious non-exponential behaviour in relative resistance drift. Two different degradation-relaxation kinetics are detected for the same thick-film $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ spinel ceramics in dependence on supplied metallic contacts. If Ag migration is inhibited in ceramics by Pd addition due to conductive Ag-Pd alloy, the governing kinetics attains a stretched exponential form with stretching exponent $\beta = \sim 0.58$ typical for one-stage diffusion in structurally dispersive media. Under Ag penetration into ceramics, as for thick-films supplied by Ag contacts, the degradation-relaxation kinetics drastically changes, attaining a compressed-exponential form with compressibility index $\beta = 1.68$. The resulting kinetics in this case is though to be attributed to two-step diffusing process originated from Ag penetration deep into spinel $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics body.

5. References

- [1] Cipelletti L, Ramos L, Manley S, Pitard E, Weitz D A, Pashkovski E E, Jahnsson M 2003 *Faraday Discuss* **123** 237
- [2] Narayanan R A, Thiyagarajan P, Lewis S, Bansal A, Schadler L S, Lurio L B 2005 *Phys. Rev. Lett.* **97** 075505
- [3] Srivastava S, Kandar A K, Basu J K, Mukhopathyay M K, Lurio L B, Narayanan S, Sinha S K 2009 *Phys. Rev. E* **79** 021408
- [4] Hashimoto C, Ushiki H 2000 *Polym J* **32** 807
- [5] Hamm P, Helbing J, Bredenbeck J 2006 *Chem Phys* **323** 54
- [6] Nakamura H K, Sasai M, Takano M 2004 *Chem Phys* **307** 259
- [7] Klym H, Balitska V, Shpotyuk O, Vakiv M 2005 *Chemia Ochrona Srodowiska (Pol.)* **10** 33
- [8] Hadzaman I, Klym H, Shpotyuk O 2014 *Int J. Nanotechnol* **11** 843
- [9] Klym H, Hadzaman I, Shpotyuk O 2014 *Can J. Phys* **92** 822
- [10] Klym H, Balitska V, Shpotyuk O, Hadzaman I 2014 *Microelectronics Reliability* **54** 2843
- [11] Shpotyuk O, Brunner M, Hadzaman I, Balitska V, Klym H 2016 *Nanoscale Res Lett* **11** 499
- [12] Shpotyuk O, Balitska V, Brunner M, Hadzaman I, Klym H 2015 *Phys. B* **459** 116
- [13] Altenburg H, Plewa J, Plesch G, Shpotyuk O 2002 *Pure Appl Chem* **74** 2021
- [14] Vakiv M, Shpotyuk O, Balitska V, Butkiewicz B, Shpotyuk L 2004 *J Europ Cer Soc* **24** 1243
- [15] Balitska V, Shpotyuk O 2006 *Archives of Mater* **4** 189.
- [16] Balitska V, Butkiewicz B, Shpotyuk O, Vakiv M 2002 *Microelectronics Reliability* **42** 2003
- [17] Vakiv M, Shpotyuk O, Mrooz O, Hadzaman I 2001 *J Europ Ceram Soc* **21** 1783