ON THE NON-EXPONENTIAL DEGRADATION KINETICS IN TOPOLOGICALLY-DISORDERED SUBSTANCES

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ABSTRACT

The peculiarities of non-exponential degradation kinetics in topological-disordered solids are analyzed. It was shown that degradation transformations, described by ideal exponential function, are determined by one value of activation energy independently to the structural dispersivity of the system, while the non-exponential degradation kinetics corresponds to stretched or suppressed exponential-power-like relaxation function. The stretched degradation kinetics is proper to own degradation transformations in one-type systems. The degradation transformations, including two or more different elementary processes, are described by suppressed kinetics.

INTRODUCTION

It is well-known, that degradation processes or, in other words, the time-dependent drift of chosen control parameter η in topologically-disordered substances, caused by their tending to more thermodynamically equilibrium state, can be described, in the most general form, by power-like differential equation:

$$\frac{d\eta}{dt} = -\lambda \eta^\alpha t^\beta \qquad (1)$$

where t is process duration, α and β are material-related constants.

As it was first pointed out in [1-6], there are 5 typical solutions of the above differential equation (1) in dependence on α and β numerical values, each of them containing a basic t-dependent functional called the relaxation function (RF). These solutions are gathered in Table 1. The RF is numerically equal to relative change of the control parameter η in the moment t. For simplicity, the RF is typically presented in the normalized form, i.e. within 0-1 limiting domain.

If $\alpha=1$ and $\beta=0$, the simple exponential monomolecular RF is valid (RF (1) in Table 1). If degradation is caused by recombination of specific defect pairs (electrons and holes, interstitials and vacancies, etc.), then their degradation is determined by bimolecular RF (RF (2) in Table 1), which corresponds to $\alpha=2$ and $\beta=0$. The strict resolution of degradation equation at $\alpha\neq0$ and $\beta=0$ can be presented in the form of partly-generalized RF (3), this function being often used for description of thermally-induced effects in some oxide glasses. In the case of $\alpha=1$ and $\beta\neq0$, the degradation kinetics is defined by stretched-exponential RF (4),

the most adequate mathematical function for structural, mechanical and electrical relaxation in a large number of topologically-disordered solids. The exact solution of the general degradation equation is given by fully-generalized RF (5).

Table 1. Relaxation function for analytical description of degradation kinetics

RF (1) monomolecular RF (α=1, β=0)	$\eta(t)\sim$ $exp\left[-\left(\dfrac{t}{\tau}\right)^{\kappa}\right]$	$\tau = \dfrac{1}{\lambda}$	$\lambda \neq 0$
RF 2 bimolecular RF (α=2, β=0)	$\eta(t)\sim\left(1+\dfrac{t}{\tau}\right)^{-1}$	$\tau = \dfrac{1}{\lambda}$	$\lambda \neq 0$
RF (3) partly-generalized RF ($\alpha\neq0$, β=0)	$\eta(t)\sim\left(1+\dfrac{t}{\tau}\right)^{-\kappa}$	$\tau = \dfrac{1}{\lambda\cdot(\alpha-1)}$	$k=\dfrac{1}{\alpha-1}, \alpha\neq1$, $\lambda\neq0$
RF (4) DeBast-Gillard or Williams-Watts RF (α=1, $\beta\neq$0)	$\eta(t)\sim\left(1+\dfrac{t}{\tau}\right)^{-\kappa}$	$\tau = \dfrac{1+\beta}{\lambda}$	$k=1+\beta, \beta\neq-1$, $\lambda\neq0$
RF (5) FULLY-GENERALIZED RF ($\alpha\neq0$, $\beta\neq$0)	$\eta(t)\sim$ $exp\left[-\left(\dfrac{t}{\tau}\right)^{\kappa}\right]$	$\tau = \left(\dfrac{1+\beta}{\lambda\cdot(\alpha-1)}\right)^{\frac{1}{1+\beta}}$	$\alpha\neq1, \beta\neq-1$, $\lambda\neq0$

Therefore, at α =1 and arbitrary β value, all RFs are exponential-power-like ones, since their t-dependences attain a character exponential form with power-like index:

$$\eta(t)\sim exp\left[-\left(\frac{t}{\tau}\right)^{\kappa}\right] \qquad (2)$$

Within this approach, the τ value in the functional (2) is numerically equal to the time domain, which corresponds to e-times decrease of the control parameter η:

$$\tau = \frac{1+\beta}{\lambda} = \frac{\kappa}{\lambda} \qquad (3)$$

If β parameter equals *0* (or, equivalently, if κ = *1*), the exponential-power-like RF (2) transforms into ideal exponential RF called sometimes the monomolecular or Debye RF [7]:

$$\eta(t)\sim exp\left[-\left(\frac{t}{\tau}\right)\right] \qquad (4)$$

By the definition, the relaxation constant τ is introduced only for the above ideal exponential-like degradation process. So, despite numerical coincidence, the τ parameter in the functional (4) is not relaxation constant in a strong meaning of this term [8].

Exponential or monomolecular kinetics of degradation is a characteristic of activating processes, which describe transition towards thermodynamics equilibration state through one certain parameter. As a rule, these processes are determined by one unique or, at least, one prevailing value of activating energy, not disturbed by dispersive additional factors (structural, in the first hand). It is quite understandable, that these processes are generally observed in crystallographically ordered solids (single- and polycrystalline).

Thus, the exponential RF (4) is not applied for relaxation processes in dispersive substances such as topologically-disordered solids. Nevertheless, it unexpectedly gave a quite good result for simulation of degradation kinetics of electro-induced dichroism in vitreous arsenic trisulfide [9]. This result itself testifies that, in spite of dispersive character in atomic structure of chalcogenide glasses caused by short- and medium-range ordering structural fluctuations (lengths and angles of covalent chemical bonds, distances between directly non-bonding atoms and more extended atomic blocks, etc.) [10], defect centres responsible for this effect annihilate with one primary value of activation energy. This energy seems to be close to the dissociation energy of covalent chemical bonds forming the glassy-like network. By using the technique of differential IR Fourier-spectroscopy of induced optical reflectivity, it was shown that in the case under consideration the above defects are undercoordinated atoms, remained after radiation-induced destruction of As-S covalent bonds, which initially form the pyramidal $AsS_{3/2}$ complexes [11].

Sometimes, the degradation kinetics appears as a consequence of simultaneous contribution of several individual relaxation processes, each of them being a simple exponential-like. In this case, the total degradation process, naturally, is an exponential-like one, being adequately described by linear combination of individual functional (4) with a set of independent relaxation times τ. The overall number of constituent RFs can be a large enough in dependence on the type of the investigated system. So, in particular, Kovacs A.J., Hutchinson J.M. and Aklonis J.J. shown that, for a some glasses, the relaxation kinetics described by RF (2) with power-like index $\kappa = 0,455$ can be transferred into more optimal function, containing as high as 33 simple exponential components like to RF (4) [12].

In turn, the power-like index κ in the functional (2) determines the deviation from ideal exponential-like kinetics, obtained at $\kappa = 1$, but not the approaching to this kinetics. That is why, sometimes, they call it the non-exponentionelity index. In other words, all exponential-power-like RFs corresponding to κ values more or less than 1,0 in accordance to (2), are non-exponential ones. They are shown graphically on Fig. 1 as plot of control parameter $y = \eta(t)$ dependingly on

$x = t/\tau$ for a wide domain of κ values, including 0; 0.3; 0,5; 0,7; 1,0; 1,5; 2,0; 3,0

and 1000. It is necessary to note that ($x = \dfrac{t}{\tau} = 1$; $y = e$) point is general (i.e. focal) one for all family of exponential-power-like RFs, obtained at different values of power-like index κ, as well as for ideal exponential RF (4).
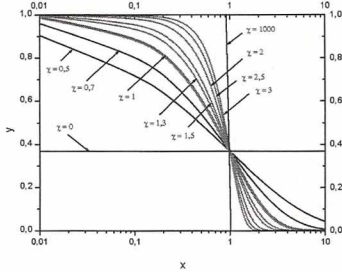

Figure 1. Stretched ($0 < \kappa < 1$) and suppressed ($\kappa > 1$) character of exponential-power-like RF $y = \eta(t) = exp[(-x)^{\kappa}]$ in dependence on $x = \dfrac{t}{\tau}$ in semi-logarithmic scale

STRETCHED EXPONENTIAL KINETICS

If $0 < \kappa < 1$, the RF (2) attains a so-called extended or stretched-exponential character, which describes the chosen degradation process, assuming a continuous spectrum of relaxation times. Many authors call this RF "stretched-exponential" [13], however, this term seems be not quite ideal. Other alternative terms can be met in the specialized literature, using, in part, the names of authors firstly applied this RF. Thus, this function is used as Williams-Watts function after the names of authors, which applied it to describe the dielectric relaxation kinetics in polyetylenacrylate [14]. Another alternative term is the De Bast-Gilard RF after the names of authors, used this function to describe the mechanical stress relaxation in glasses [15]. As for us, the best term for this RF is the Kohlrausch function, who was the first applied it for relaxation processes in complex electronic and molecular systems [16]. The combined term of this RF are also met in the form of KWW or Kohlrausch-Williams-Watts function) [17].

The mechanisms of degradation processes in topologically-disordered systems, resulting in stretched-exponential relaxation kinetics, are quite different. Two main groups can be distinguished among them. The first group explores mechanisms in terms of dispersive transport in disordered structures [18, 19]. The character defects in these structures responsible for a deviation from thermodynamic equilibration state take part in multiple capture-elimination acts of excited carriers before being finally stabilized within degradation test. The quantitative parameters of elementary capture and elimination acts form a continuous spectrum in agreement with structural disordering of solid system. The model of hierarchically limited relaxation dynamics [19] is in the ground of

the second group of mechanisms. Within this model, each individual relaxation transformation in disordered solid is possible after previous relaxation events, formed the favourable conditions for its realization (as free-volume space, in part).

It should be noted that all parameters in the stretched-exponential RF carry their strongly-defined physical meanings. Thus, in particular, the κ index in functional (2) determines the time width of relaxation process (the relaxation process become time-infinite, provided κ tends to 0). As it testified from Fig.1, the stretched-exponential behaviour corresponds to a more smooth decaying of control parameter $y = \eta(t)$ in the region of short times ($x = \frac{t}{\tau}$ <1) and a more late decaying in the region of long times ($x = \frac{t}{\tau}$ >1) in comparison with simple exponential RF obtained at $\kappa = 1$. With other words, the ideal exponential curve (4) by transforming into stretched-exponential one extends in time, tending asymptotically to straight line y=e with $\kappa = 0$. The linearization form of this RF was shown in Fig. 2.

Taking into account, that stretched-exponential RF corresponds to relaxation kinetics in supposition on dispersive transport in disordered systems [18, 19], it should be expected it will be the most optimal one to describe the degradation kinetics in electrophysical properties of variable-composition materials, provided these phases are identical in their origin. It means that kinetic curves of thermoinduced degradation processes for one-type topology-disordered systems (for example, ceramic composites sintered at high temperatures, covalent-bonded network glasses quenched from a melt, etc.) will be attain a character extended behaviour proper to the stretched-exponential RF with $0 < \kappa < 1$, whichever their phase composition (and, consequently, the technological regimes, which determines this composition).
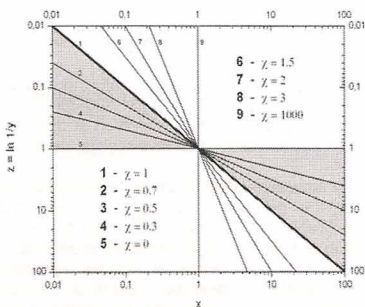

Figure 2. Linearization form of stretched ($0 < \kappa < 1$) and suppressed ($\kappa > 1$) exponential-power-like RF $y = \eta(t) = exp[(-x)^{\kappa}]$ in dependence from $x = \frac{t}{\tau}$ in logarithmic scale

As an example, the degradation kinetics of relative resistance drift $(\Delta R/R_0)$ in spinel-type $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ bulk ceramics caused by long-term ageing test at 170 °C can be considered (see Fig. 3). The investigated ceramics contained three phases – the base spinel-type phase of the above composition, the Co-enriched rock-salt phase and slight remainders of non-identified phase. This ceramic specimen is widely used in functional electronics, being one of the most perspective materials for negative temperature coefficient thermistors, temperature sensors, in-rush current limiters, etc. [20-23]. Despite three phases in the final chemical composition, they are fully identical in their origin because of high sintering temperature of ceramics (1200 °C). So, the investigated samples can be considered as typical representative of uniform one-type topology-disordered system.
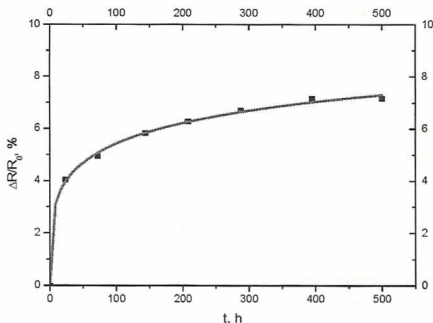

Figure 3. Thermally-induced (170 °C) relative resistance drift $(\Delta R/R_0)$ in bulk $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics

As it exemplified from Fig. 3, the observed thermally-induced degradation curve has a character sharp-growing shape in the first 100-200 hours of degradation test, followed with slow tending to relative saturation at more prolonged storage (400-500 hours). The maximal value of relative resistance drift is as high as 6-7 %.

With a purpose of adequate mathematical description of the observed degradation kinetics, the numerical values of different fitting parameters contained in the RFs (Table 1) were calculated in such a way to minimize the mean-square deviation *err* of the experimentally measured points from the chosen RF possible as adequate solution of general degradation equation (1). The most suitable RFs describing observed degradation kinetics can be chosen at the basis of comparison of the calculated *err* values. The developed PC-program package permits us to establish unambiguously, on the basis of the obtained experimental data, the type of RF describing observed degradation transformations and, consequently, to assume their microstructural mechanism.

As it testified from Table 2, the degradation kinetics in the investigated $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ bulk ceramics can be well described by stretched-exponential RF (4). Indeed, in this case, the low values of *err* = 0.017 are achieved at a relatively small number of fitting parameters (τ=360 hours and κ = 0.3). The similar results were obtained for some other ceramic samples within mixed transition-metal manganite system $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ [24, 25]. It should be noted that this result is valid, while the microstrustural mechanism associated with degradation carries a complicated character, including not only cation redistribution, but also interphase mass-exchanging processes [26].

Table 2. Mean-square deviations (*err*) for different RFs, describing ageing phenomena (at 170 °C) in $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ bulk ceramics and thick films

Sample	*err*				
	RF (1)	RF (2)	RF (3)	RF (4)	RF (5)
Bulk ceramics	0.402	0.129	0.047	0.017	0.023
Thick films	0.055	0.068	0.079	0.002	0.003

Thus, the stretched-exponential relaxation kinetics dominates in ceramic composites in spite of their chemical composition, provided all phases formed during their sintering have one-type origin.

SUPPRESSED EXPONENTIAL KINETICS

However, not only the stretched-exponential RF (2) at $0<\kappa<1$ can be obtained as direct solution of the general differential equation of degradation (1), but also a so-called suppressed-exponential RF as a subject to the condition $\kappa >1$. As it was shown from Fig. 1, this kind of kinetics corresponds to smaller changes in control parameter $y = \eta(t)$ at $x = {}^t\!/_\tau <1$ and considerably greater changes at $x = {}^t\!/_\tau >1$. As a result, the time domain of relaxation process shortens and removes in the region of $t \approx \tau$. The observed degradation kinetics attains a specific threshold-like shape, i.e. the changes of the controlled parameter $y = \eta(t)$ are negligible in the beginning and in the end of degradation test, the most substantial jump observing near $x = {}^t\!/_\tau =1$. The suppressed-exponential RF transforms into step-like function of y = 1 height with κ tending to infinity, it being strongly attached to the focal point ($x = {}^t\!/_\tau = 1$; $y = e$).

Such behaviour, probably, is proper to complex physical processes in topology-disordered solids, which include two and more elementary components of principally different origin. Diffusion, evaporation, adsorption, burning-out of inner phase inclusions, chemical interaction between main phase and impurities, etc. can serve as typical examples of the above processes in ceramics. As a rule, they need different energies to be realized. In addition, they are time-interdependent, since each next component occurs only after previous one. In

other words, the main relaxation process in the region of $x = {}^t\!/_\tau$ =1 begins only after a certain preparation stage with essentially less activation energy.

As an example, the degradation kinetics of relative resistance drift $(\Delta R/R_0)$ in spinel-type $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ thick films samples caused by long-term ageing test at 170 °C can be considered (see Fig. 4) [26].

The investigated thick films contained main spinel-type phase ($Fd\overline{3}m$ crystallographical group) and remainders of organic component SM-2 in glassy binder NT-521-4 with a small quantity of Bi_2O_3. In the process of manufacturing, these films are annealed at 850 °C (duration of annealing – 15 min) with following temperature decrease. The duration of technological sintering process was about 45 min. This time is not enough to stabilize the monophase film composition. With the purpose of carried out of the electrophysics measurement, the thick films were directly inflicted not on alumina ceramic substrate (Rubalit 708S), but on previously prepared silver contact plate. Thus, the samples represent themselves as a complicate solid system, included silver electrodes and thick film, content the crystal grains of spinel-basic $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$, grain boundaries, internal pores and also glass NT-521-4 with the organic impurities. The total duration of degradation test was 356 h., and electric resistance measurement R was measured at 25 °C after the following state during 64, 104, 144, 198, 251, 304 and 356 h.
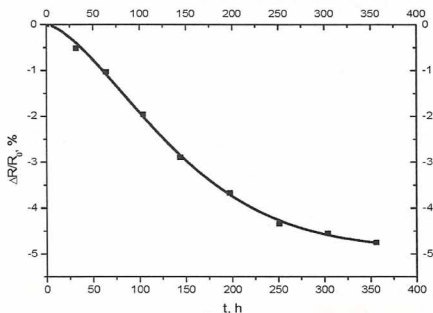

Figure 4. Thermally-induced (170 °C) relative resistance drift $(\Delta R/R_0)$ in $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ thick films

It was shown recently, that in $Cu_{0.8}Ni_{0.1}Co_{0.2}Mn_{1.9}O_4$ and $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ thick films, which are characterized by a homogeneous structure at practically complete absence of organic remainders, a so-called "thermal shock" effect was observed [27]. This effect reveals in sharp increase of electric resistance in the first cycle of degradation with its following stabilization in further process of degradation test. It was assumed that, unlike to ordinary bulk ceramics with a

large content of internal voids and character τ values at the level of several hundreds of hours [28], the investigated films with relatively uniform structures and small porosity (owing to glass additives) show a quick drift kinetics just after a few first hours of degradation test. In other words, the mechanism of thermally-induced degradation is the same in bulk ceramics and thick films, but all difference between them appears only in the duration of the observed resistance changes.

Another picture is observed for $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ thick films (see Fig. 4). The own structural changes in them are extremely small, they distinguishing at the general background of more essential processes, connected with organic remainders. As a result, instead of positive $\Delta R/R_0$ changes character for own thermally-induced degradation in practically all ceramic composites [28], the opposite "negative" effect of resistance decrease occurs in the investigated $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ thick films. Using the above mentioned searching procedure to obtain the optimum analytical solutions for general differential degradation equation (1) [1-3], it was established that kinetics of this effect can be simply described by suppressed-exponential RF with $\kappa \approx 1.5$.

By investigating the element composition of the aged thick films (in perpendicular direction to silver electrodes) before and after degradation test with LEO 982 scanning electron microscope, it was detected the penetration of metallic Ag into film body on almost 4-5 μm, the greatest Ag agglomerates being revealed near grain boundaries. This effect is accompanied by disappearing of character light raid proper to not burning-out remainders of organic binder. It means that, at least, two interconnected processes are activated during degradation test - the burning-out of remainders of organic binder between contacting spinel grains with simultaneous Ag penetration into appeared free-volume space. As a result, the resistance of thick film decrease not only due to improvement in intergranual contacts (i.e. film densification) but also due to Ag appearance in the intergranual space.

CONCLUSIONS

Thus, degradation transformations with ideal exponential-like kinetics are possible in topology-disordered substances independently on their structural dispersivity, provided they are determined by one prevailing value of activation energy. In all other cases, the non-exponential degradation kinetics (or, alternatively, the exponential-power-like kinetics) associated with stretched- or suppressed-exponential RF is expected. The stretched-exponential or exponential-power-like kinetics with an index of $0 < \kappa < 1$ are characteristic for own degradation transformations in the same types ones on the nature systems. Degradations transformations including two and more elementary, on principle different on the origin, can be described to the suppressed exponential-power-like RF.

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