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MATHEMATICAL DESCRIPTION OF AGEING KINETICS IN TOPOLOGICALLY DISORDERED SOLIDS

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Mathematical models of degradation kinetics in topologically disordered solids were developed on the example of spinel-type ceramics and chalcogenide glasses. It was shown stretched-exponential relaxation function was a unique analytical expression describing kinetics of the observed degradation processes in spinel-type ceramics, while bimolecular relaxation function was a most suitable one to describe decay in radiation-optical properties of chalcogenide glasses.

Key words: topologically-disordered solids, degradation, relaxation function.

Topologically disordered solids are specific materials due to their structural disordering revealed at different levels of nanoscale atomic subsystem (atoms and their groups, molecules, clusters, etc.). One of their typical representatives, the chalcogenide vitreous semiconductors (ChVS), is inorganic polymers with completely saturated covalent chemical bonding and uniform distribution of glass-forming structural units. The nanodisordered state of ChVS reveals in the deviation of lengths and angles of covalent bonds [1]. Other representative of topologically disordered substances, the microdisordered ceramics, is formed by interweaving of crystalline grains, grain boundaries and intrinsic intergranular pores [2].

The main feature of the above topologically disordered materials whichever their nature is degradation. This phenomenon can be observed as monotonic increase or decrease in the chosen exploitation parameter in the result of slow tending towards more thermodynamically equilibrium state.

The aim of this work is to compare the peculiarities of degradation kinetics in different kinds of topologically-disordered solids. The ChVS (the nanodisordered materials) and spinel-type ceramics (the microdisordered materials) were chosen as a model objects for our study.

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 a more thermodynamically equilibrium state can be described, in the most general form, by power-like differential equation:

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

where t is process duration, α and β are material-related constants. As it was first pointed out in [3, 4], there are 5 typical solutions (relaxation functions – RF) of the above differential equation (1) in dependence on α and β numerical values.

If $\alpha=1$ and $\beta=0$ (the case of monomolecular degradation), the solution of (1) is:

$$\eta = \eta_0 e^{-\frac{t}{\tau}}, \quad (2)$$

where $\eta_0 = e^c$, $\tau = \frac{1}{\lambda}$, c – constant of integration.

The monomolecular kinetics of degradation is a characteristic of activating processes, which describe transition towards thermodynamic equilibrium through one certain parameter. As a rule, these processes are determined by one unique or, at least, one prevailing value of activation energy, not disturbed by dispersive additional factors (structural, in the first hand).

If $\alpha=2$ and $\beta=0$ (the case of bimolecular degradation), the solution of (1) is:

$$\eta = \frac{\eta_0}{1 + \frac{t}{\tau}}, \quad (3)$$

where $\eta_0 = e^c$, $\tau = \frac{1}{\lambda}$, c – constant of integration.

This degradation is caused, as a rule, by recombination of specific defect pairs (electrons and holes, interstitials and vacancies, etc.) [5].

If $\beta \neq 0$ and arbitrary α (the partially-generalization degradation), the resolution of degradation equation (1) can be presented in the following form:

$$\eta = \frac{\eta_0}{\left(1 + \frac{t}{\tau}\right)^k}, \quad (4)$$

where $\eta_0 = c^{\frac{1}{\alpha-1}}$, $\tau = \frac{c}{\lambda(\alpha-1)}$, $k = \frac{1}{\alpha-1}$, $\alpha \neq 1$, $\lambda \neq 0$, c – constant of integration. This

RF is often used to describe post-irradiation thermal effects in oxide glasses [5].

If $\alpha=1$ and arbitrary β value the resolution of degradation equation (1) can be presented in the form of fully-generalized RF:

$$\eta = \frac{\eta_0}{\left(\left(1 + \frac{t}{\tau}\right)^k\right)^r}, \quad (5)$$

where $\eta_0 = c^{\frac{1}{1-\alpha}}$, $r = \frac{1}{\alpha-1}$, $k = 1 + \beta$, $\tau = \left(\frac{c}{\lambda} \cdot \frac{1 + \beta}{\alpha - 1}\right)^{\frac{1}{1+\beta}}$, c – constant of integration.

In the case of $\alpha=1$ and $\beta \neq 0$, the degradation kinetics is defined by so-called stretched-exponential RF, the most adequate mathematical function for structural, mechanical and electrical relaxation in a large number of topologically-disordered solids [6]:

$$\eta = \exp \left[- \left(\frac{t}{\tau} \right)^k \right], \quad (6)$$

where $\eta_0 = e^c$, $\tau = \left(\frac{1+\beta}{\lambda} \right)^{\frac{1}{1+\beta}}$, $k = 1 + \beta$, c – constant of integration, $\beta \neq -1$, $\lambda \neq 0$.

It should be noted, 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; the model of hierarchically limited relaxation dynamics is in the ground of the second group of mechanisms [7].

The different compositions of ChVC samples from the stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ and non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ systems were selected as nanodisordered materials. The technological peculiarities of glass preparation, condition of γ -quanta irradiation and optical measurements were described previously [8, 9]. The degradation kinetics of radiation-induced effects (RIE) was described by relative changes of optical absorption coefficient $\eta = \left(\frac{\Delta\alpha}{\alpha_o} \right)$.

The ceramic thermistors based on mixed transition-metal manganites $(Cu,Ni,Co,Mn)_3O_4$ of different chemical compositions obtained at a wide variation of the main technological parameters of their preparation were choose as microdisordered materials. The detailed information on technological features of thermistor preparation was presented in [10, 11]. The results of degradation kinetics were controlled by relative resistance drift $\eta = \left(\frac{\Delta R}{R_o} \right)$.

With a purpose of adequate mathematical description of the observed degradation kinetics in the above materials, the numerical values of different fitting parameters contained in the RFs 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.

It is know that Co^{60} γ -irradiation of ChVS causes shift to longer wavelength of their fundamental optical absorption edges – radiation-induced effect (RIE) [12, 13]. This RIE is unstable and decays monotonically with time to some residual value during 2–3 months after irradiation, forming a so-called dynamic component (the dynamic RIE) contrary to the static one, which remains unchangeable after irradiation. The typical time-dependent curves for η parameter in γ -irradiated $(As_2S_3)_{0,1}(Ge_2S_3)_{0,9}$ and $(As_2S_3)_{0,8}(Ge_2S_3)_{0,2}$ samples are shown in Fig. 1.

For adequate mathematical modelling of degradation kinetics in these ChVS, the η_o , r , κ and τ were calculated in such way to minimize the average square deviation *err* of experimentally measured points from above mentioned 5 relaxation function.

It was established that degradation kinetics of η parameter in γ -irradiated ChVS can be satisfactorily developed on the basis of stretched-exponential function, but with a

greatest accuracy can be described on the base of bimolecular RF too. It can be noted that bimolecular RF corresponds rigorously to annihilation kinetics of coordination defects with smaller energetic barrier, defined by differences in dissociation energies for switching chemical bonds [1].

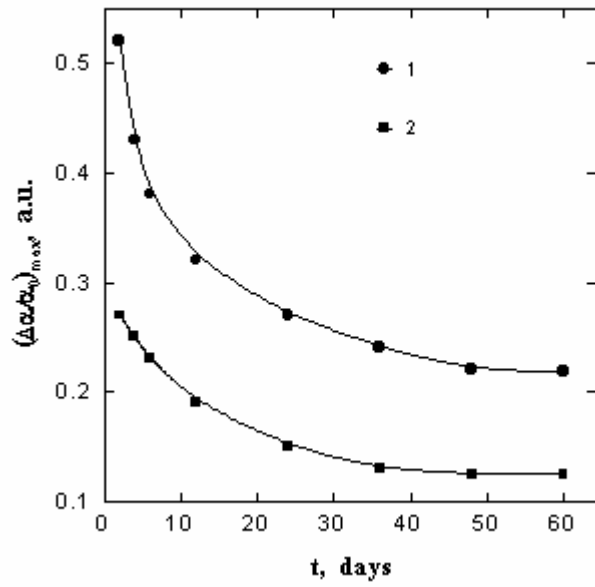


Fig. 1. The decay of $\chi = (\Delta\alpha/\alpha_0)_{\max}$ parameter in γ -irradiated $(\text{As}_2\text{S}_3)_{0,1}(\text{Ge}_2\text{S}_3)_{0,9}$ (curve 1) and $(\text{As}_2\text{S}_3)_{0,8}(\text{Ge}_2\text{S}_3)_{0,2}$ (curve 2) ChVS

The relative resistance drift $(\Delta R/R_0)$ in spinel-type $\text{Cu}_{0,1}\text{Ni}_{0,1}\text{Co}_{1,6}\text{Mn}_{1,2}\text{O}_4$ bulk ceramics caused by long-term ageing test at 170°C , was used as controlled parameter of the degradation kinetics of microdisorder state (see Fig. 2). As it exemplified from Fig. 2, 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). It was established that degradation kinetics in the investigated $\text{Cu}_{0,1}\text{Ni}_{0,1}\text{Co}_{1,6}\text{Mn}_{1,2}\text{O}_4$ ceramics can be well described by stretched-exponential RF. The similar results were obtained for some other ceramic samples within mixed transition-metal manganite system $\text{Cu}_x\text{Ni}_{1-x-y}\text{Co}_{2y}\text{Mn}_{2-y}\text{O}_4$ [3, 10]. It should be noted that this result is valid, while the microstructural mechanism associated with degradation has a more complicated character, including not only cation redistribution, but also interphase mass-exchanging processes.

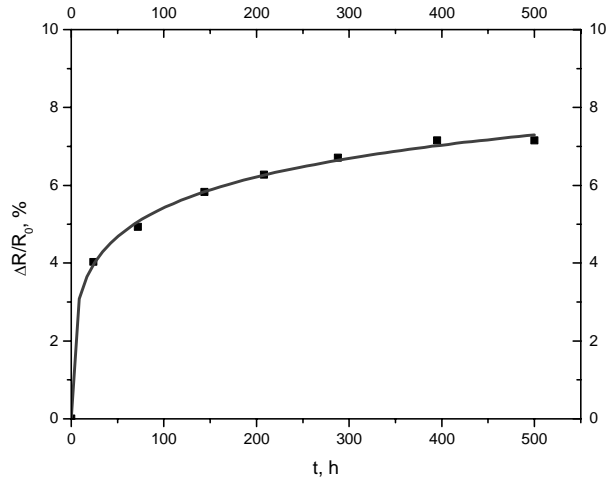


Fig. 2. Thermally-induced (170°C) relative resistance drift ($\Delta R/R_0$) in bulk $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics

The stretched-exponential relaxation kinetics dominates in topologically-disordered solid, in spite of their disordered state. However, the qualitative features of the observed dynamic RIEs in ChVS are due to annihilation of coordination defects with the smallest energies, can be well-described by bimolecular relaxation function, while despite of chemical composition and technological features of the investigated ceramics, the stretched-exponential RF is the unique analytical expression describing kinetics of the observed degradation processes.

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МАТЕМАТИЧНИЙ ОПИС КІНЕТИКИ СТАРІННЯ В ТОПОЛОГІЧНО НЕВПОРЯДКОВАНИХ ТВЕРДИХ ТІЛАХ

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На прикладі кераміки шпінельного типу і халькогенідних стекел розвинуто математичну модель кінетики деградації в топологічно-розпорядкованих тілах. З'ясовано, що кінетику деградації в шпінельній кераміці найдоцільніше описувати розширено-експоненціальною релаксаційною функцією, тоді як затухання радіаційно-оптичних властивостей халькогенідних стекел – бімолекулярною.

Ключові слова: топологічно-розпорядковані тіла, деградація, релаксаційна функція.

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