

Step-wise Fractal Kinetics in Physical Ageing: Compositional Complexity in Network Glass-Formers

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Abstract. Sigmoid behavior of natural physical ageing in network glass-formers revealing multi-step-wise growing kinetics of enthalpy losses $\Delta H(t)$ is studied at the example of glassy Se-rich arsenoselenides As-Se ($\text{As}_{10}\text{Se}_{90}$, $\text{As}_{20}\text{Se}_{80}$ and $\text{As}_{30}\text{Se}_{70}$). It is shown that phenomenological description of this ageing kinetics can be adequately developed in terms of first-order relaxation processes, tending atomic structure of a glass from initial towards more thermodynamically equilibrium state. The microstructure mechanism of natural physical ageing is explained by specificity of structural-topological complexes in the studied glasses (ratio between structural fragments having heteropolar As-Se and homopolar As-As and Se-Se covalent chemical bonds). This kinetics is shown to obey characteristic stretched exponential behavior originated from a number of growing steps, attributed to interconnected processes of chalcogen chains alignment and cooperative shrinkage of a whole glassy-like network. Developed model of natural physical ageing explains well the observed stretch-exponential behavior of low-temperature relaxation kinetics in terms of hierarchically-constrained mixed serial-parallel relaxation events having different atomic precursors, such as Se-based chains - Se-Se-Se-, =As-Se-Se- and =As-Se-As=) This phenomenological ageing kinetics can be decomposed into a few elementary components, each of them approaching to single exponential dependence.

Keywords: Chalcogenide Glasses, Physical Ageing, Differential Scanning Calorimetry, Glassy Network, Structural Fragments.



1. Introduction

The natural physical ageing (PhA) is known to be an important phenomenon for amorphous solids, because it results in uncontrolled time drift of such their important exploitation properties as atomic density, elastic modulus, brittleness, permeability, strength, fracture energy, deformation, etc. [1]. Nevertheless, the microstructural characteristics of PhA have not been studied enough, known only some reports related to PhA in silicate glasses [2-4]. However, the silicate glasses (characterized by over-constrained structural networks) possess very slow relaxation kinetics at ambient conditions [3] typically resulting in simple exponential dependence, which can be accepted only as a partial case for overall natural PhA kinetics.

From this point, the chalcogenide glasses (ChG) are more suitable objects for detailed examination of PhA kinetics, because they allow studying of almost complete picture of PhA at quite acceptable timescales ranging from a few days or even hours (in the case of very chalcogen-rich compositions) up to years or even decades (in case of chalcogen-depleted compositions) [5-7].

In general, the compositional variations in the ability to PhA are determined by a number of Lagrangian constraints per atom n_c of ChG-forming networks built of fully-saturated covalent chemical bonds assuming their equivalence with movement stretching and bending limitations (mechanical constraints). Under this definition, the covalent bonding Z can be described by mean number of covalent bonds per one atom of glass-forming network. The under-constrained networks possessing $Z < 2.4$ and smaller n_c , which are less than dimensionality of space $n_c < 3$, are subject to pronounced drift in their properties caused by thermodynamically-driven forces tending the system towards more favorable energetic state. In contrast, the over-constrained ($Z > 2.4$, $n_c > 3$) and optimally-constrained ($Z = 2.4$, $n_c = 3$) ChG do not age at normal conditions at all, demonstrating strong non-ageing ability.

In this paper, the kinetics peculiarities of natural PhA will be studied in under-constrained of $As_{10}Se_{90}$ ($Z = 2.1$, $n_c = 2.25$), $As_{20}Se_{80}$ ($Z = 2.2$, $n_c = 2.5$) and $As_{30}Se_{70}$ ($Z = 2.3$, $n_c = 2.75$) ChG and comparative analysis will be developed for this compositional row of glass formers taking into account their main structural features in respect to previously analyzed [6].

2. Experimental

The ChG of binary As_xSe_{100-x} ($x = 10, 20, 30$) system were prepared by conventional melt-quenching route in the evacuated quartz ampoules from a mixture of high-purity elemental precursors, as described elsewhere [7].

Amorphous state and composition of the as-prepared ChG were controlled visually by a characteristic conch-like fracture, data of X-ray diffraction and X-ray photoelectron spectroscopy. Bulk samples in the form of thick (~3 mm) plates, prepared for differential scanning calorimetry (DSC) measurements, were used for the investigations.

DSC measurements were performed using NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC traces being recorded in ambient atmosphere with $q = 5$ K/min heating rate. More detailed description of the measurements protocol can be found in [7].

3. Results

The curve of time-dependent enthalpy losses $\Delta H(t)$ in $As_{10}Se_{90}$ ChG associated with long-term PhA is presented on Fig. 1.

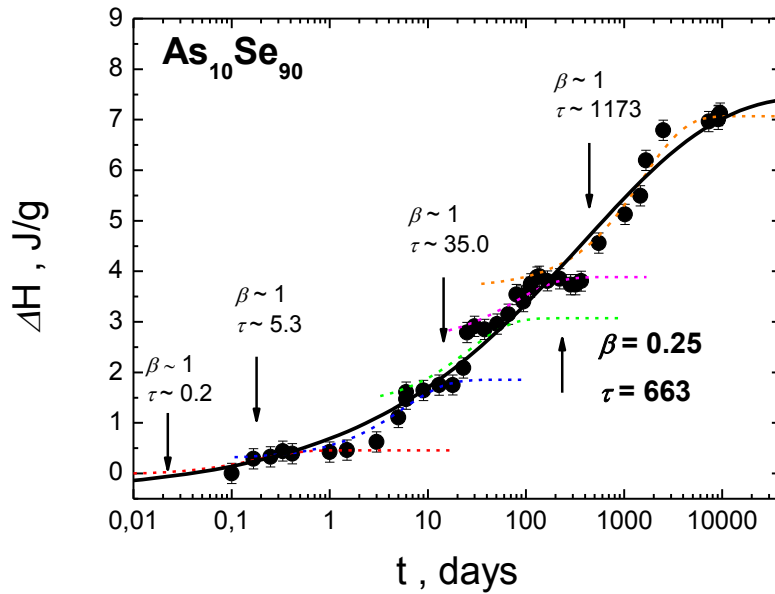


Fig. 1. Kinetics of $\Delta H(t)$ losses in $As_{10}Se_{90}$ ChG decomposed in four-steps serial single-exponential processes

As it follows from Fig.1, the kinetic of PhA in $As_{10}Se_{90}$ ChG exhibits well-expressed four-steps character. The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in this $As_{10}Se_{90}$ glass during natural PhA with the stretched-exponential relaxation function gives numerical values of time constant $\tau \cong 663$ days and power index (index of non-exponentiality or dispersivity) $\beta = 0.25$.

Taking into account that this kinetics is characterized by hierarchically-constrained mixed serial-parallel relaxation behavior, it can be conveniently modeled by the following expression:

$$\Delta H_i(t) = \sum_{i=1}^n \theta(t - \Delta t_i) \left[a_i + b_i \left(1 - \exp\left(-\frac{t - \Delta t_i}{\tau_i} \right) \right) \right], \quad (1)$$

where a_i and b_i are materials-related parameters connected with amplitude of the relaxation process, τ_i is effective time constant (the relaxation time), Δt_i is a so-called retardation time (the parameter giving time delaying of the next step of PhA in respect to the previous one), $\Theta(t-\Delta t_i)$ is the Heaviside step function, whose value is accepted to be 0 for negative arguments ($t < \Delta t_i$) and 1 for positive arguments ($t \geq \Delta t_i$), and n is number of steps in the relaxation kinetics. The results of the modelling with eq. (1) and corresponding fitting parameters for four-steps serial presentation of PhA in $\text{As}_{10}\text{Se}_{90}$ ChG are given in Table 1.

Table 1. Fitting parameters in eq. (1), describing PhA kinetics in $\text{As}_{10}\text{Se}_{90}$ ChG.

Step # (duration, days)	Fitting goodness r^2	a_i , J/g	b_i , J/g	a_i+b_i , J/g	τ_i , days	Δt_i , days
$i=1$ (0÷1.5)	0.008	0	0.46	0.46	0.2	0
$i=2$ (1.5÷20)	0.022	0.46	1.52	1.98	5.3	1.7
$i=3$ (20÷365)	0.038	1.98	1.82	3.80	35.0	16.5
$i=4$ (365÷10000)	0.034	3.80	3.27	7.07	1173	340

The curve of time-dependent enthalpy losses $\Delta H(t)$ in $\text{As}_{20}\text{Se}_{80}$ ChG associated with long-term PhA is presented below on Fig. 2.

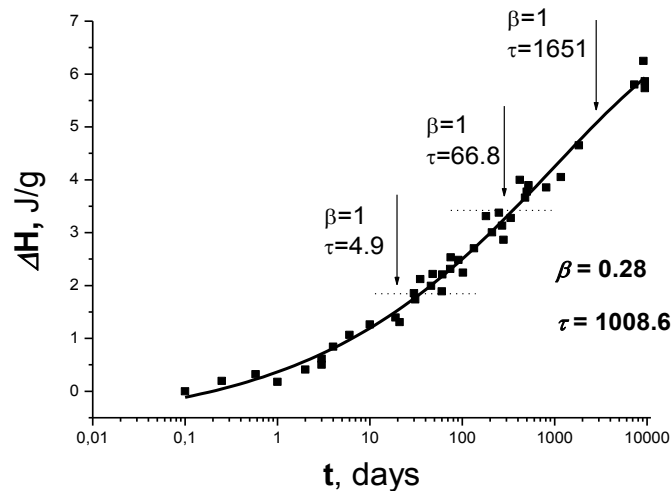


Fig. 2. Kinetics of $\Delta H(t)$ losses in $\text{As}_{20}\text{Se}_{80}$ ChG decomposed in three-steps serial single-exponential processes

The kinetic of PhA in $As_{20}Se_{80}$ ChG exhibits two-steps behaviour, the values of PhA is expected smallest as compared with the same in $As_{10}Se_{90}$ ones (number of constrains per atom $n_c = 2.5$). The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $As_{30}Se_{70}$ ChG during PhA with stretched-exponential relaxation function gives $\tau=1008.6$ days and $\beta = 0.28$. The results of the modelling with eq. (1) and fitting parameters for this three-step serial presentation of PhA kinetics in $As_{20}Se_{80}$ ChG are gathered in Table 2.

Table 2. Fitting parameters in eq. (1) describing PhA kinetics in $As_{20}Se_{80}$ ChG.

Step # (duration, days)	Fitting goodness r^2	a_i , J/g	b_i , J/g	a_i+b_i , J/g	τ , days	Δt_i , days
$i=1$ (1÷20)	0.0933	0	1.4	1.4	4.9	0
$i=2$ (20÷335)	0.03705	1.4	2.0	3.4	66.8	17.5
$i=3$ (335÷10000)	0.04821	3.4	2.7	6.1	1651.4	305

The curve of time-dependent enthalpy losses $\Delta H(t)$ in $As_{30}Se_{70}$ ChG associated with long-term PhA is presented on Fig. 3.

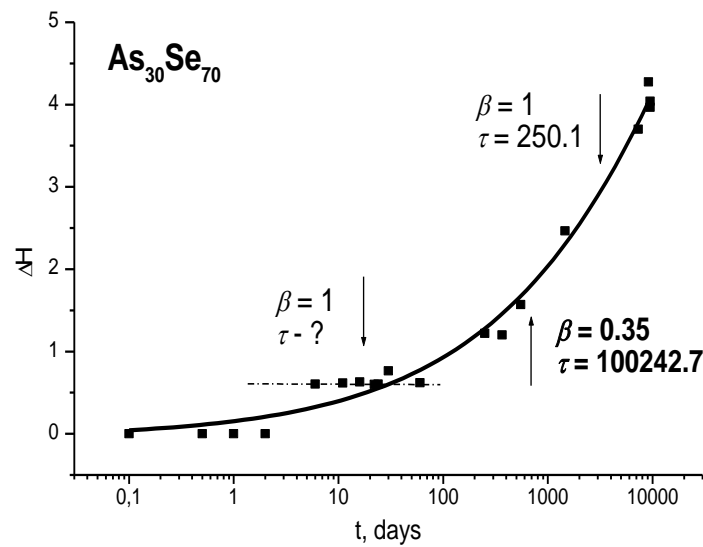


Fig. 3. Kinetics of PhA in $As_{30}Se_{70}$ ChG deconvoluted in two-steps serial single-exponential processes

The kinetic of PhA in $\text{As}_{30}\text{Se}_{70}$ ChG exhibits two-steps behaviour, the values of PhA is expected smallest as compared with the same in $\text{As}_{10}\text{Se}_{90}$ and $\text{As}_{20}\text{Se}_{80}$ ones (the number of constrains per one atom $n_c = 2.75$). The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $\text{As}_{30}\text{Se}_{70}$ ChG during PhA with the stretched-exponential relaxation function gives $\tau \cong 100242.7$ days and $\beta = 0.35$. The results of modelling with eq. (1) and fitting parameters for two-steps serial presentation of PhA kinetics in $\text{As}_{30}\text{Se}_{70}$ ChG are gathered below in Table 3.

Table 3. Fitting parameters in eq. (1) describing PhA kinetics in $\text{As}_{30}\text{Se}_{70}$ ChG.

Step # (duration, days)	Fitting goodness r^2	a_i , J/g	b_i , J/g	a_i+b_i , J/g	τ , days	Δt_i , days
$i=1$ (1÷300)	0.022	0	0.7	0.7	-	0
$i=2$ (300÷10000)	0.0265	0.7	3.3	4	1398	250

4. Discussion

The mechanism of PhA in ChG is known to be based on elementary relaxation acts (twisting) of inner Se atoms within double-well potentials associated with high flexibility of chalcogen chemical bonds [7-9].

As it follows from above experimental results, the PhA in the studied ChG exhibits well-expressed step-wise character, showing some kinds of plateaus and steep regions. The increasing of As content leads to decreasing of PhA in full accordance to increased n_c values (from 2.25 for $\text{As}_{10}\text{Se}_{90}$ to 2.5 for $\text{As}_{20}\text{Se}_{80}$ and 2.75 for $\text{As}_{30}\text{Se}_{70}$ ChG). Moreover, with increase in As content, the values of non-exponentiality index β in the stretched-exponential relaxation function describing observed kinetics increases (from 0.25 for $\text{As}_{10}\text{Se}_{90}$ to 0.28 for $\text{As}_{20}\text{Se}_{80}$ and 0.36 for $\text{As}_{30}\text{Se}_{70}$ ChG). This means, obviously, the decrease in the dispersivity of the system, so the number of steps in the PhA kinetics decreases too (from 4 for $\text{As}_{10}\text{Se}_{90}$ to 3 for $\text{As}_{20}\text{Se}_{80}$ and 2 in $\text{As}_{30}\text{Se}_{70}$ ChG).

These features can be well explained by accepting main microstructure signatures of the studied ChG.

Thus, in $\text{As}_{10}\text{Se}_{90}$ ChG, the Se atoms created -Se-Se-Se- chains ($n_c = 2.0$) and =As-Se-Se- ($n_c = 2.45$) fragments taken in 67:33 ratio, while in As_{20}Se this ratio become only 25:75. In contrast, in $\text{As}_{30}\text{Se}_{70}$ ChG, the intermediate surroundings of Se atoms significantly changes: -Se-Se-Se- chains disappear, and principally new =As-Se-As= ($n_c = 3.00$) structural environment is formed instead (the ratio between =As-Se-Se- and =As-Se-As= fragments reaches as high as 29:71).

Under such conditions, three types of double-well potentials can be assumed for central Se atoms in the studied ChG owing to their immediate surroundings,

namely -Se-Se-Se-, =As-Se-Se- and =As-Se-As= fragments with differ heights of energetic barriers.

It is well known that -Se-Se-Se- fragments possess the smallest height of energetic barrier, while =As-Se-As= fragments are characterized by the highest barrier. Therefore, -Se-Se-Se- fragments relax on the initial stages of PhA with characteristic time constant $\tau \sim 4.9$ days, and =As-Se-As= fragments relax at the final stage of natural PhA with characteristic time constant $\tau \sim 1200\div 1600$ days (see Tables 1-3), although (according to serial-parallel specificity of long-term natural PhA) the relaxation of all structural fragments present in the glass occurs on each stage.

Since the content of -Se-Se-Se- structural fragments in $\text{As}_{20}\text{Se}_{80}$ ChG (25 %) is less than in $\text{As}_{10}\text{Se}_{90}$ (67 %) [7], the initial two steps in $\text{As}_{20}\text{Se}_{80}$ glasses arise very quickly. Therefore, its separate distinction is not possible under such condition (see Fig. 2), and, consequently, both first and second steps cooperate giving the smallest value of time constant τ .

In case of $\text{As}_{30}\text{Se}_{70}$ ChG, the homoatomic -Se-Se-Se- structural fragments are absent at all, and initial stage of relaxation are caused mainly by shrinkage of =As-Se-Se- structural fragments, producing only two steps in the final relaxation kinetics.

It should be noted that the retardation times Δt_i in eq. (1) remain on the same order for all types of relaxing atomic environments whichever the glass composition (Table 1-3).

Conclusions

It is shown that kinetics of enthalpy losses $\Delta H(t)$ caused by natural physical ageing in Se-rich As-Se ChG during more than two decades exhibited well-expressed step-wise behavior. The microstructure mechanism of this relaxation in the studied ChG is shown to be governed by structural-topological nature of corresponding glassy network.

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