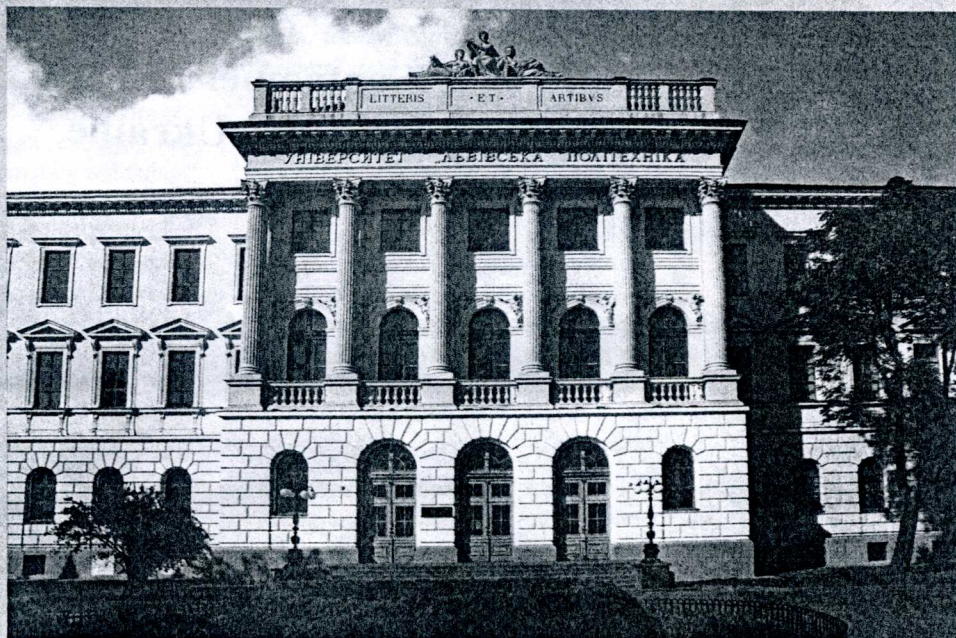# OMEE

Proceedings

of the International Conference on
Oxide Materials
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(OMEE-2012)

September 3–7, 2012

Lviv, Ukraine

Proceedings

International Conference on

Oxide Materials
for Electronic Engineering –
fabrication, properties and applications

OMEE-2012

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On the Kinetics Description of Below-T$_g$ Structural Relaxation in Network Glass Formers

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Abstract. *Phenomenological description of below-T$_g$ structural relaxation known as long-term natural physical ageing in network glass formers exemplified by binary arsenic selenides was adequately developed within first-order kinetics. This kinetics was shown to obey a character stretched exponential behavior being treated as sequence of aligning-shrinkage stages throughtout glassy matrix.*

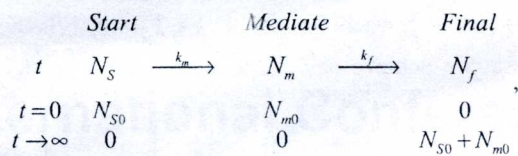**Key words:** kinetics, relaxation, physical ageing, network glass, double-well potential.

I. INTRODUCTION

Numerous research suggests that long-term physical ageing in network glass formers like glasses (both oxide and chalcogenide) occurs well below T_g through known Johari-Goldstein (JG) β-relaxation mechanism [1,2] which can be considered as initiating stage for α-relaxation [1]. Structural data for Se-rich As-Se glasses suggest that mechanism of physical ageing is based on the elementary twisting of inner Se atoms within double-well potentials (DWP) associated with high flexibility of chalcogen bonds [3-5]. In the first approximation, these twisted Se atoms (*cis-trans* reconfigurations) can be accepted as elementary JG β-relaxation precursors. They should result in the appearance of aligned Se-based regions in a glass network and, consequently, local free volume released by twisted atoms. We can assume that appearance of local free volumes around collapsed Se-based regions is accompanied by elastic strains in their immediate surroundings. This initial stage of physical ageing is responsible for the lowering of glass transition temperature during first period of natural storage. If the accumulated elastic energy is high enough, the cooperative rearrangements can occur, eliminating redundant free volume from considered local regions, which leads to lowering the internal energy of the system at this particular local scale. Happening at a larger scale, these processes should lead to a general shrinkage of glass network. Therefore, in the second stage of physical ageing, a general shrinkage of glass network takes place, which can be assigned to JG β-relaxation-facilitated α-relaxation. This process is a reason for increase in glass transition temperature and enthalpy losses in DSC experiments [3,5].

II. EXPERIMENTAL – KINETICS MODELING ALGORITHM

Let's consider the process of twisting of Se atoms within DWP in more details. Three possible DWP can be assumed for central Se atoms owing to their immediate surrounding – -Se-**Se**-Se-, =As-**Se**-Se- and =As-**Se**-As=. Obviously, they differ by energetic parameters, which are determined by type of surrounding atoms (As or Se). Owing to a magnitude of physical ageing in As-Se ChG [6], the lowest barrier for Se twisting should be expected for homoatomic Se-Se-Se, while the highest one for heteroatomic As-Se-As surrounding. Let's denote an average relative probability of Se atom twisting within the above DWPs as k_m and probability of further atomic shrinkage as k_f. If these rates are time-independent, then ageing can be presented by scheme:

$$
\begin{array}{ccccc}
 & Start & & Mediate & & Final \\
t & N_S & \xrightarrow{k_m} & N_m & \xrightarrow{k_f} & N_f \\
t=0 & N_{S0} & & N_{m0} & & 0 \\
t\to\infty & 0 & & 0 & & N_{S0}+N_{m0}
\end{array},
$$

where N_S denotes concentration of atomic sites described by DWP as precursors for Se twisting (N_{S0} is their initial concentration); N_m is the concentration of precursors for shrinkage (the aligned chains), which originate from preliminary stage of DWP twisting (N_{m0} is the initial concentration of twisted Se atoms), N_f is the concentration of aligned chains in a glass network affected by shrinkage.

It is obvious that at each time moment the overall amount of inter-balanced sites is kept:

$$N_S + N_m + N_f = N_{S0} + N_{m0}$$

Then, for the considered network the classical first order differential rate equations, which govern changes in the concentration of twisted (mediate alignment stage) and densified (final shrinkage stage) sites, can be composed as:

$$
\begin{cases}
\dfrac{dN_m}{dt} = k_m N_S - k_f N_m \\
\dfrac{dN_f}{dt} = k_f N_m
\end{cases}
$$

Solutions of these rate equations can be considered in terms of microstructural mechanism of physical ageing.

In case the measured property is sensitive to both stages of ageing (mediate alignment and final shrinkage), the next *master equation* should be used to describe kinetics:

$$F(t) = N_m(t) + N_f(t) = N_{m0} + N_{s0}\left(1 - e^{-kt}\right)$$

If the measured physical quantity is more sensitive to one of these stages, then each component of the above master equation should be considered separately:

$$N_m(t) = \frac{N_{S0}k_m}{k_f - k_m}e^{-k_m t} - \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0}\right)e^{-k_f t}$$

$$N_f(t) = \left(N_{S0} + N_{m0}\right) - \frac{N_{s0}k_f}{k_f - k_m}N_{s0}e^{-k_m t} + \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0}\right)e^{-k_f t}.$$

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Two principally different possibilities in view of these solutions are to be analyzed:

(1) the mechanism happens once during overall ageing with k_m and k_f rates dependent on time reflecting statistical distribution of atomic sites involved into alignment-shrinkage process;

(2) the overall processes are routinely repeated in such a way that final stage becomes the initial stage for subsequent alignment-shrinkage process of newly formed network (the serial processes), or, alternatively, the independent relaxation processes with different k_m and k_f rates occur simultaneously (the parallel processes).

In the first case, it is necessary to consider the dependence of rates k_m and k_f on a time t. Therefore, let's assume the existence of a single fractional exponent β to describe statistical distributions of atomic sites involved into alignment-shrinkage processes of physical ageing. Then, in accordance with general principle of relaxation, the Kohlrausch relaxation function can be derived from simple exponential kinetics by introducing change of dimensionless variable $kt \rightarrow (kt)^\beta = \xi$, where $0 \le \beta \le 1$, $k = k_m + k_f$ [7].

In this case, we achieve new dispersivity-related master equation:

$$F(t) = N_m(t) + N_f(t) = N_{m0} + N_{S0}\left(1 - e^{-\left(\frac{t}{\tau_m}\right)^\beta}\right),$$

with individual components defined as

$$N_f(t) = \left(N_{S0} + N_{m0}\right) - \frac{N_{S0}k_f}{k_f - k_m}e^{-\left(\frac{t}{\tau_m}\right)^\beta} + \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0}\right)e^{-\left(\frac{t}{\tau_f}\right)^\beta}$$

$$N_m(t) = \frac{N_{S0}k_m}{k_f - k_m}e^{-\left(\frac{t}{\tau_m}\right)^\beta} - \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0}\right)e^{-\left(\frac{t}{\tau_f}\right)^\beta}$$

where $\tau_f = \frac{k^{\frac{1}{\beta} - \beta}}{k_f^{\frac{1}{\beta}}}$, $\tau_m = \frac{k^{\frac{1}{\beta} - \beta}}{k_m^{\frac{1}{\beta}}}$ and $k_f \ne k_m$.

III. RESULTS AND DISCUSSION

The straightforward fitting of the experimental data taken from [3] with last dispersivity-related master equation gives τ_m and β values as summarized in Table 1.

It can be seen, the further we are from the completeness of physical ageing, the higher is β, tending overall below-T_g relaxation process to single-exponential one.

Table 1. Fitting parameters describing ageing kinetics in glassy As-Se

Glass composition	τ_m (days)	Non-exponentionality index β
Se	$2 \cdot 10^{-1}$	0.16
$As_{10}Se_{90}$	$7 \cdot 10^2$	0.25
$As_{20}Se_{80}$	10^3	0.28
$As_{30}Se_{70}$	10^5	0.35

The effective time constant τ_m reveals strong dependence on glass composition, demonstrating colossal increase on more than five orders with As content reaching $As_{30}Se_{70}$. These τ_m values can be conditionally distinguished on three groups centred near 10^{-1}, 10^3 and 10^5 days, testifying in a favour of principal difference in the corresponding DWP initiating initial stage of physical ageing (the aligning of Se chains). Thus, in case of pure g-Se, this process is governed mainly by homoatomic -Se-Se-Se- environment, while mixed homo-hetero-atomic =As-Se-Se- environment occurs more effective for physical ageing in g-$As_{10}Se_{90}$ and g-$As_{20}Se_{80}$. With tending towards chemically stoichiometric arsenic sulphide, the heteroatomic =As-Se-As= environment becomes favorable resulting in strong two-orders increase in τ_m value. This consideration agrees well with compositional features of this binary As-Se system examined with high-resolution XPS [6].

So, from the present findings, it can be speculated that stretched exponential α-relaxation in network glass formers like As-Se glasses originates from sequent JG β-relaxation processes, each of them being described simply by single exponential kinetics. Within this assumption, the α-relaxation-controlled event can be considered as a termination process for JG β-relaxation, which triggers the system into "initial" state. Then all the processes start as before, but with growing energetic barriers and time constants involved.

This picture is supported by recent investigations of atomic dynamics at the nanoscale in network glasses [8]. The proposed phenomenological model can also explain the exponential behavior of natural physical ageing in silicate glasses [9]. In the latter case, the beginning stage of physical ageing is captured and, therefore, it should be well fitted by simple single-exponential rather than stretched exponential relaxation function. This conclusion is well confirmed by present studies, where fractional β parameter used to describe the overall ΔH (t) kinetics increases with departure from the completeness of natural physical ageing, the tendency which corresponds to transition from Se-rich to $As_{30}Se_{70}$ glass (Table 1).

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