

# Thermal Relaxation of Liquid Borosilicate's Structure that Reflects the Slowness of the Silicon-Oxygen Complexes' Depolymerization

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## Abstract

Modeling of relaxation processes in the liquid borosilicate was performed. The kinetic scheme of temperature relaxation of the melts' structure is proposed. The scheme **reflects** the slowness of the depolymerization of silicon-oxygen complexes. The influence of various physicochemical factors on the relaxation processes' rate and the time of reaching equilibrium was analyzed.

**Keywords:** liquid borosilicate, relaxation of structure, depolymerization, silicon-oxygen complexes

Until recently it was thought that at temperatures higher than the glass transition temperature  $T_g$  oxide melts have a structure close to equilibrium. Because of this the influence of structural relaxation on the experimental dependences of various properties, such as viscosity or conductivity of oxide melts, during characterization was neglected.

However there is evidence in literature that structural transformations in oxide melts at high temperatures also occur. Thus, according to [1] in acidic oxide melts (silicates, borates, aluminates), even at elevated temperatures, when the viscosity exceeds  $1 \text{ Pa} \cdot \text{s}$ , a concentration of complex polyanions is high. In these systems processes of polymerization, depolymerization and disproportionation are taking place when the temperature changes. Large size and complexity of the polymer structures may slow relaxation of melt's structure.

In this paper, we propose a model that takes into account the influence of the slowness of the silicon oxide melt complexes' depolymerization reaction on the kinetics of structural relaxation.

The model is based on the connection of the platinum electrode's potential with the effective concentration of free oxygen ions in melt:

$$\varphi = \text{const}(T) + \frac{RT}{2F} \ln \frac{p_{O_2}^{1/2}}{a_{O^{2-}}} = \text{const}. \quad (1)$$

The electrode potential which is registered in the experiment, changes with time during melt's structure relaxation.

In a first approximation, the oxygen ions' activity  $a_{O^{2-}}$  can be characterized by the concentration of free oxygen ions ( $c$ ) [2]. Based on the experimental data, if the melt's structure is equilibrium, the electrode potential is rapidly becoming constant and close to equilibrium. It can be assumed that, expression (1) is true for a melt with a nonequilibrium structure, but in this case  $\varphi$  characterizes a non-equilibrium concentration of free oxygen ions. It means that the electrode potential must change when melt structure changes (relaxes). The equation that represents the relation of the measured electrode's potential with the concentration ( $c$ ) of free oxygen ions  $O^{2-}$  has the form:

$$\frac{c}{c_p} = e^{\frac{2F}{RT} \Delta\varphi}, \quad (2)$$

where  $\Delta\varphi$  - the difference between the equilibrium and the current value of the potential of the investigated electrode ( $\Delta\varphi = \varphi_p - \varphi$ );  $c_p$  - the equilibrium concentration of free ions  $O^{2-}$ . The value of  $c$  drops with decreasing temperature. The reduction of the  $\Delta\varphi$  over time to zero can be expected with structure's slow relaxation.

Relaxation model is based on considering the slowness of the depolymerization reaction of silicon-oxygen complexes. Relaxation model in general is of the form of:



in this case free oxygen ( $O^{2-}$ ) interacts with a bridge ( $O^0$ ) with the formation of end-ion ( $O^-$ ).

The rate of the depolymerization reaction is characterized by the transconductance of the  $\Delta\varphi$  on time (t) dependence:

$$V = - \frac{dc}{dt} = - c \frac{2F}{RT} \frac{d\Delta\varphi}{dt}. \quad (3)$$

We can neglect the reverse reaction (a) when it is far from equilibrium. In this case the process' kinetic equation has the form:

$$V = k c^n, \quad (4)$$

where  $n$  - the order of reaction (a).

Excluding  $V$  from the equations (3) and (4), we find

$$-\frac{d\Delta\varphi}{dt} = \frac{RT}{2F} k c^{n-1} \quad (5)$$

The transconductance of the experimental curve  $\Delta\varphi = f(t)$  first (far from equilibrium) increases with time, although the concentration (c) decreases. According to equation (5) this suggests that the reaction order (a) far from equilibrium is less than one.

Based on the above, we can propose the following mechanism of the process. Free ions  $O^{2-}$  cannot interact with any bridging atoms  $O^0$ , as they can't reach them. To interact, it is necessary for structures' defect to arise around  $O^0$  particles, which facilitate the reagents' contact. Such defects' formation reaction is zero order by ions  $O^{2-}$  and might be slowed:



where  $O_*^0$  - "active" bridging oxygen, in contact with defects.

In this case the dependence  $\Delta\varphi$  on time  $t$  has the following form:

$$\left(1 + \frac{1}{k_p c_p^2}\right) \ln \frac{e^{\frac{2F}{RT} \Delta\varphi_0} - 1}{e^{\frac{2F}{RT} \Delta\varphi} - 1} - \frac{1}{k_p c_p^2} \frac{2F}{RT} (\Delta\varphi_0 - \Delta\varphi) + e^{\frac{2F}{RT} \Delta\varphi_0} - e^{\frac{2F}{RT} \Delta\varphi} = \frac{k_{(\delta)}}{c_p} t \quad (6)$$

The figures 1-3 show the theoretical curves " $\Delta\varphi - t$ " calculated according to the equation (6).

The time to reach the inflection point on the dependence " $\Delta\varphi - t$ " increases slightly and is about 70 minutes with a decrease the rate' constants ( $k_{(\delta)}$ ) of the reaction of "active" particles bridging oxygen  $O_*^0$  formation, which figure 1 shows.

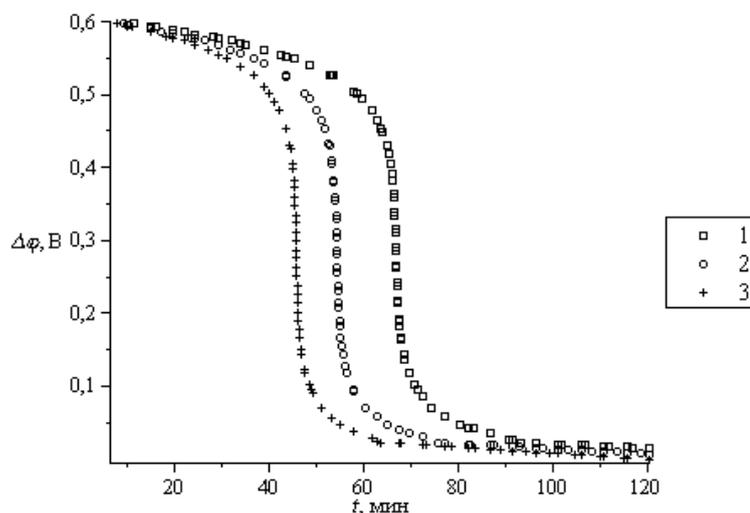


Figure 1. The calculated dependence of the potentials difference  $\Delta\varphi$  vs the time  $t$  for liquid borosilicate at different ratios  $k_{(\sigma)}/c_p$

$$k_{(\sigma)}/c_p = 43 \text{ (1)}, 53 \text{ (2)}, 63 \text{ (3)}$$

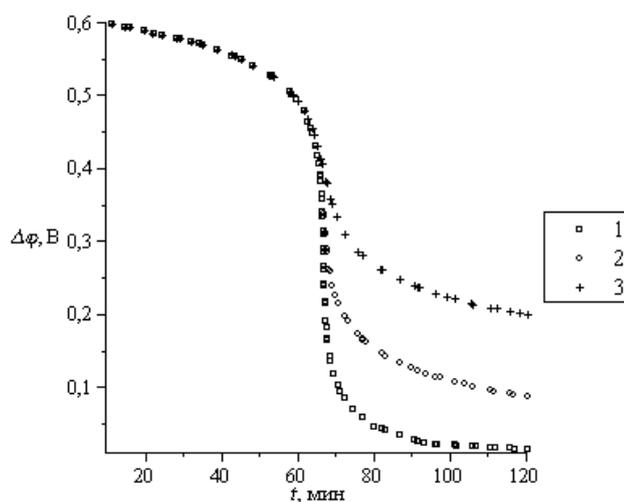


Figure 2. The calculated dependence of the potentials difference  $\Delta\varphi$  vs the time  $t$  for liquid borosilicate at different ratios  $1/k_p c_p^2$

$$1/k_p c_p^2 = 7,2 \cdot 10^4 \text{ (1)}; 7,2 \cdot 10^5 \text{ (2)}; 7,2 \cdot 10^6 \text{ (3)}$$

With increasing constant  $1/k_p c_p^2$  ( $k_p$  - the equilibrium constant of the depolymerization reaction involving “active” bridging oxygen  $O_*^0$  particles) the initial branch of the curve (fig. 2) does not change, but the time of equilibrium state approach is increased to 2 hours and more. Increasing the temperature of the melt, in contrast, significantly reduces the relaxation time and the transition to the equilibrium state, as melt’s depolymerization processes is accelerated (fig. 3).

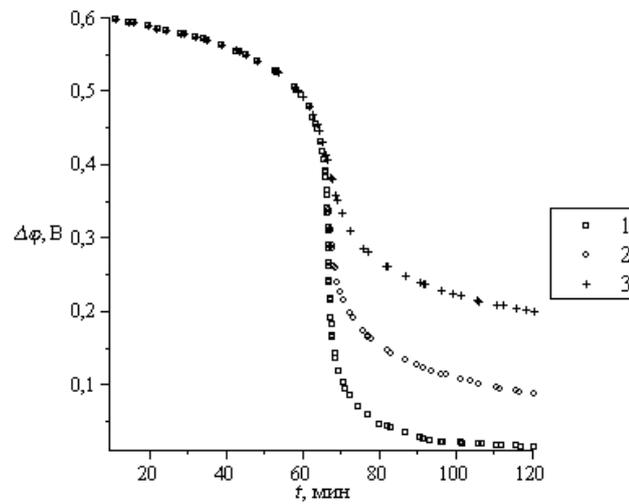


Figure 3. The calculated dependence of the potentials difference  $\Delta\varphi$  vs the time  $t$  for liquid borosilicate at different temperatures

$$T = 1173 \text{ K (1); } 1213 \text{ K (2); } 1293 \text{ K (3)}$$

## References

- [1] V. K. Novikov. Development of silicate melts' polymer model, *Melts*, **6** (1987), 21-33.
- [2] I. V. Tymoshenko, A. F. Borisov, Application of EMF method to study the structure of glass industrial composition, *Glassy State*, (1970), 242-246.

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