

# Diffusion Processes in the Liquid Borosilicate with Nonequilibrium Structure

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## Abstract

The influence of temperature relaxation of the liquid borosilicate structure for diffusion coefficients of nickel cations ( $D_{\text{Ni}^{2+}}$ ) was investigated. On the termotime curves of the diffusion coefficients, obtained in the slow heating (equilibrium conditions) and rapid cooling hysteresis is observed. This demonstrates the slowness of the borosilicate complexes reconstruction. During isothermal exposure values  $D_{\text{Ni}^{2+}}$  approached equilibrium for several dozens of minutes.

**Keywords:** liquid borosilicate, structural relaxation, diffusion coefficients

Establishing a relationship between the structure and transport properties of borosilicate melts is one of the fundamental problems of physical chemistry. The structure of oxide melts in many respects defines their physicochemical properties, the rate of interaction with metal alloys, service characteristics of enamel and glass.

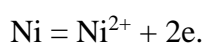
Investigation of the temperature and time dependences of the nickel ions' diffusion coefficients was carried out in the melt  $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$  with the addition of 0.5 wt. % NiO in equilibrium and non-equilibrium conditions by Faraday impedance. In the experiment, the frequency dependences of the electrode impedance's constituents at a particular selected temperature were obtained under equilibrium conditions. They were satisfactorily described by the model curves, obtained for the equivalent electrical circuit that contained the Warburg impedance, indicating that the inhibition of diffusion processes with the

participation of nickel ions. To increase the measurement speed in non-equilibrium conditions the determining of active and capacitive component of the electrochemical cell was carried out only at two frequencies ( $f_1$ ,  $f_2$ ), in the frequency range where the condition:

$$X_{f1} - X_{f2} = R_{f1} - R_{f2}.$$

is fulfilled.

It shows the diffusion mode of the electrode process taking place on the investigated nickel electrode:



The calculation of the diffusion coefficients were performed on experimentally found Warburg's constant ( $A$ ):

$$D_{\text{Ni}^{2+}} = \left[ \frac{RT}{\sqrt{2} n^2 S F^2 C_0 A} \right]^2$$

Figure 1 shows the dependence of the diffusion coefficients of nickel ions in the temperature range 970-1170 K during heating and cooling of the melt. Heating was slow, and held at each temperature for at least 30 minutes, reaching equilibrium values  $D_{\text{Ni}^{2+}}$  at each temperature. Cooling was quick at a rate of 4 K / min, i.e. in nonequilibrium conditions.

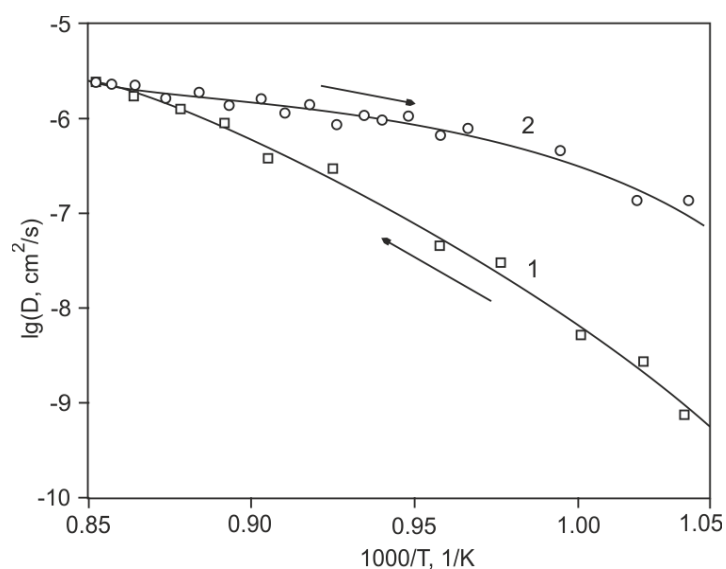


Figure 1: The temperature dependences of  $D_{\text{Ni}^{2+}}$ .  
1 - slow heating; 2 - rapid cooling.

It can be seen that the heating curve is below the cooling curve. At a temperature of 970 K, the diffusion coefficients differ from their equilibrium values ( $\sim 6,8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ ) by 2 orders of magnitude. During further isothermal holding of the melt values  $D_{\text{Ni}^{2+}}$  are approaching to equilibrium.

For the studied borosilicate melts it is possible to follow mechanism of relaxation processes. With increasing temperature, depolymerization of single silica-boron-oxygen grid happens due to the transition of boron coordination from 4 to 3 [1, 2] and releasing of free oxygen ions for further destruction of the silicon-oxygen complexes. While NiO dissolves in the channels between the grid areas, spatially separating it into silica and boron-oxygen components. Upon cooling with the speed 4 K / min the melt's structure does not have time to go back to its original state. This is apparently due to transition of free oxygen ions from the silicon-oxygen areas for boron-oxygen inhibited by virtue of the stiffness of covalent bonds which give rise to a rather high potential barrier [3]. As a result of the boron's transition from 3 to 4 coordination can be delayed, and boron does not have time to integrate into the silica-boron-oxygen network. Thus, the relaxation of the borosilicate melt's structure is constrained not the diffusion of cations-modifiers, but the permutations of the oxygen ions.

Dependences of the diffusion coefficients of nickel ions from time, obtained by isothermal melts' exposure with a nonequilibrium structure after rapid cooling to 940 K are shown in Fig. 2.

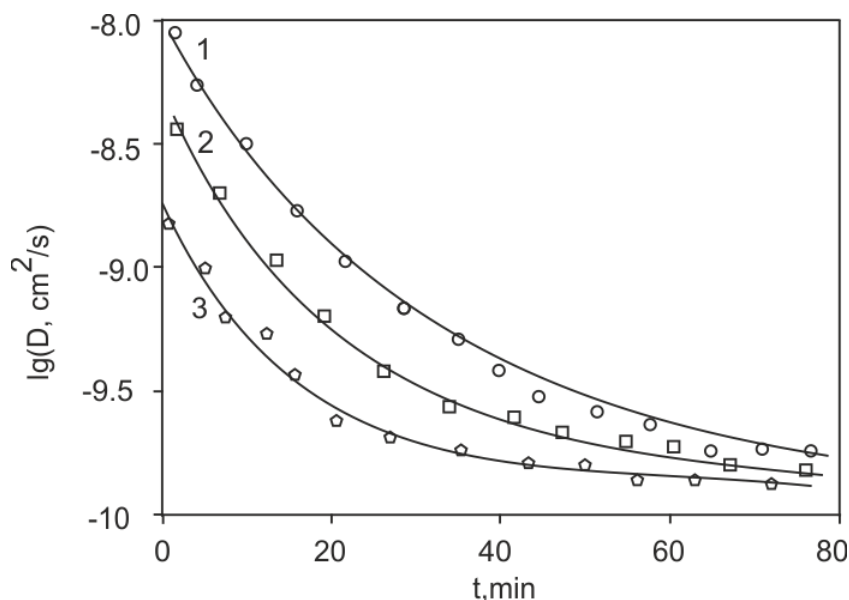


Figure 2: The time dependences of  $D_{\text{Ni}^{2+}}$  at 940 K, obtained after cooling from the melt at different temperatures.

T, K: 1 – 1150, 2 – 1100, 3 – 1050.

As can be seen, the time to reach the equilibrium state by melt at this temperature is approximately 40-80 minutes and depends on the temperature from which cooling of the melt began. The higher the temperature, the more the test's structure differs from the equilibrium melt at a temperature of 940 K, the greater the contrast of  $D_{\text{Ni}^{2+}}$  from the equilibrium value. Therefore, restructuring borosilicate complexes at the same cooling rate is slowed down, which affects the diffusion coefficient of nickel cations.

Our data on the presence of hysteresis in the dependences of the nickel cations diffusion coefficients on the temperature agrees with the results of measurements [2] of the temperature dependence of the borate melts viscosity ( $\eta$ ) fairly well. The cooling curve " $\ln \eta - 1/T$ " located below the heating curve and the equilibrium curve, which, according to the authors of [2], indicates inhibition processes of coordination reconstruction of boron.

Overall, the results confirm the slowness of the anionic polymerization and coordination processes reconstruction in borosilicate melts above the liquidus line.

## References

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