Introduction

The viscosity of silicate glasses belongs to the most important properties both from the technological and theoretical point of view [1–7]. The structure relaxation as described by the Tool–Narayanaswamy–Mazurin’s (TNMa) model [8–14] is tightly bonded with the viscosity temperature dependence of both the metastable equilibrium melt and the glass with constant Tool’s fictive temperature [15, 16]. Although a large number of papers exists dealing with the temperature–composition dependence of viscosities of glass and of metastable melt, the systematic studies devoted to the compositional dependence of structural relaxation are still relatively scarce [8, 17–19]. The main effort is commonly concentrated on the methodological aspects of creating the relaxation models and the experimental work is carried out either on simple, one or two component glasses or on commercially produced glasses [17].

The present paper deals with the compositional series of sodium–magnesium–calcium silicate glasses with the constant NBO/T value (i.e. the number of non-bridging oxygens vs. tetrahedral network central atoms):

\[ \text{NBO/T} = \frac{2x(\text{SiO}_2) + x(\text{Na}_2\text{O}) + x(\text{MgO}) + x(\text{CaO})}{2} - 4 = \]

The magnesium free end-member is close to the common soda lime silica glass (e.g. window glass). The equimolar MgO/CaO substitution (i.e. the increasing x value) smoothly shifts the high temperature viscosity to higher values.

In the low temperature region the mixed alkali effect is demonstrated, and the highest viscosities are observed for the glasses M0 and M10. In the low temperature range the activation energy of viscous flow linearly decreases with the increasing x value \((E_{\text{act}}/\text{kJ mol}^{-1} = 479–9.0x)\). No significant dependence of activation energy on x was found in the high temperature range \((E_{\text{act}}/\text{kJ mol}^{-1} = 238.1\pm 4.2)\). The structural relaxation was measured by thermomechanical experiment and theoretically interpreted in the frame of Tool–Narayanaswamy–Mazurin’s model. The broadening of the relaxation time spectrum was observed for the calcium-magnesium glasses in comparison with the pure calcium or magnesium glasses.

Keywords: glass, glass transition, relaxation phenomena, thermomechanical analysis

**VISCOSITY AND STRUCTURAL RELAXATION OF 15Na_2O·xMgO·(10−x)CaO·75SiO_2 GLASSES**

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Temperature dependence of viscosity of title glasses \((x=0, 2, 4, 6, 8, 10, \text{abbreviated as M0, M2, M4, M6, M8, and M10, respectively})\) was measured by rotational viscometry (high temperature region: \(10^2–10^6.5\ d\text{Pas}\)) and thermomechanical analysis (low temperature region: \(10^8.5–10^{11.5}\ d\text{Pas}\)) and described by the Vogel–Fulcher–Tammann equation. The MgO/CaO equimolar substitution (i.e. the increasing x value) smoothly shifts the high temperature viscosity to higher values.

The magnesium free end-member is close to the common soda lime silica glass (e.g. window glass). The equimolar MgO/CaO substitution was chosen to appreciate the possible demonstration of the so-called mixed alkali effect (MAE) that manifests itself by the nonlinear compositional dependence of various properties possessing local maxima or minima [2, 20].

**Theoretical**

The temperature dependence of the viscosity of glass-forming melts is described with sufficient accuracy by the empirical Vogel–Fulcher–Tammann (VFT) equation [2, 20]:

\[ \log(\eta/\text{dPas}) = A + \frac{B}{T - T_0} \]  

where \(T\) is thermodynamic temperature and \(A, B\) and \(T_0\) are adjustable constants.

The viscous flow activation energy \(E_{\text{act}}\) is defined at constant pressure \(P\) by

\[ E_{\text{act}} = R \left( \frac{\partial \ln \eta}{\partial 1/T} \right)_P \]  

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where $\eta$ is the dynamic viscosity, $T$ is the thermodynamic temperature, and $R$ is the molar gas constant. Thus, the temperature dependent $E_{\text{act}}$ value follows from the VFT viscosity equation:

$$E_{\text{act}} = \ln(10)RB - \frac{T^2}{(T-T_0)^2}$$

However, in the narrow temperature range the temperature dependence of viscosity can be described with sufficient accuracy by the Arrhenius-like equation (also known as the Andrade’s (AND) equation [21]):

$$\log(\eta/d\text{Pas}) = A' + B' \frac{T}{T_0}$$

where $A'$ and $B'$ are adjustable constants.

In this case we obviously obtain the temperature independent value of activation energy of viscous flow characteristic for particular temperature-viscosity range:

$$E_{\text{act}} = \ln(10)RB'$$

The structural (or volume) relaxation is typically studied by dilatometry. In the present paper we use the method of thermomechanical analysis where during the zigzag time-temperature regime the length of the prismatic sample exposed to constant axial stress undergoes simultaneously the changes caused by viscous flow and by structural relaxation [22]. The method itself, as well as the optimization of the experimental schedule is discussed in our previous paper [23].

Let us consider the sample length, $l$, as a function of thermodynamic temperature, $T$, and Tool’s fictive temperature $T_f$:

$$d\ell = \left(\frac{\partial l}{\partial T}\right)_f dT + \left(\frac{\partial l}{\partial T_f}\right)_T dT_f = l(\alpha_g dT + \Delta \alpha dT_f)$$

where

$$\Delta \alpha = \alpha_m - \alpha_g$$

where $\alpha_g$ and $\alpha_m$ is the thermal expansion coefficient of glass and of metastable equilibrium melt, respectively. The values of both thermal expansion coefficients are considered as temperature independent in the present work.

In the case when viscous flow takes place, an additional source of changes of the sample length has to be included:

$$\frac{1}{l} \left(\frac{\partial \ell}{\partial t}\right)_{T,\tau} = \frac{\sigma}{3\eta}$$

where $\sigma$ is the axial stress, $t$ is the time, and $\eta$ stands for the viscosity. Let us suppose a change of the sample state from an initial state 1 to final state 2. The relative length change of the sample during the above transition, i.e. the sample strain, can be expressed as:

$$\varepsilon = \frac{l_2 - l_1}{l_1} = \int_a^b \alpha_g dT + \int_{T_1}^{T_2} \Delta \alpha dT_f -$$

$$\left(1 + \int_{T_1}^{T_2} \alpha_g dT + \int_{T_1}^{T_2} \Delta \alpha dT_f \right) \frac{\sigma}{3\eta} dT_f$$

The time course of fictive temperature $T_f$ is obtained within the frame of the Tool–Narayanaswamy–Mazurin’s model with the Kohlrausch–Williams–Watts’s relaxation function [24]:

$$M(\xi) = \exp(-\xi^b) \quad 0 < b \leq 1$$

where $b$ is a constant determining the width of the spectrum of relaxation times ($b=1$ corresponds to the single relaxation time) and $\xi$ is the dimensionless relaxation time:

$$\xi(t) = \int_0^t \frac{dt'}{\xi(\tau')} \int_0^\tau \frac{K}{\eta(t')} dt'$$

where $\tau$ is the relaxation time. The viscosity dependence on temperature and Tool’s fictive temperature can be expressed by the Mazurin’s approximation:

$$\log(\eta(T,T_f)) = \left(\frac{A+B(T-T_0) T_f}{T}ight) + \log \eta_0 \left(1 - \frac{T_f}{T}\right)$$

The modulus $K$ relating the viscosity and relaxation time in the Eq. (11) is considered as characteristic material constant dependent on the glass composition [25]. The VFT viscosity equation is used for the viscosity temperature dependence of metastable equilibrium melt in the Eq. (12). When the Andrade’s equation is used instead of the VFT equation then $T_0$ is set to zero and $A$ and $B$ are replaced by $A'$ and $B'$, respectively.

In principle, an arbitrary subset of the above model parameters, i.e. a subset chosen from $\{K, B, A \text{ or } A', B \text{ or } B', T_0, \eta_0, \alpha_g \text{ and } \alpha_m\}$, can be estimated by means of the non-linear regression analysis. Obviously, the lower is the number of estimated parameters the more statistically robust are the results of the regression analysis. Therefore those parameters that can be estimated with sufficient accuracy by an independent experiment are not optimized in the regression analysis.

**Experimental**

**Materials**

Glass batches were prepared from chemically pure $\text{Na}_2\text{CO}_3$, $\text{MgCO}_3$, $\text{CaCO}_3$ and $\text{SiO}_2$. These were...