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The effect of nitrogen on viscosity of La-Si-Mg-O-N glasses by compressive creep and dilatometry*

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Viscosity as a function of temperature and nitrogen content and the glass transition temperature (T_g) were investigated in 20La-60Si-20Mg-O-N glasses with nitrogen contents varying from 0 to 28 eq.% (e/o) using compressive creep and dilatometric experiments. Although T_g obtained from dilatometry were 6–12°C lower than the lower limit of the transition temperature range from creep, both methods revealed identical and linear dependencies of T_g on N content. The average activation energy was 1184 ± 36 kJ/mol and viscous flow remains the deformation mechanism in all glasses regardless of nitrogen content. Addition of 28 e/o N in oxide glass resulted in an increase of T_g by 94–105°C and an increase in viscosity of around 5 orders of magnitude. These changes are greater than those reported in similar Al-containing glasses. Linear increase of T_g and compactness of the glass with nitrogen content result from enhanced cross-linking of the glass network.

1. Introduction

The first extensive studies of the oxynitride glasses appeared in 1980-s after discovery of this class of materials [1–6]. It was found out that nitrogen acts as a network former, which can partially substitute oxygen in the silica network [1–9]. Because of triple valence of nitrogen, glass network containing nitrogen is tighter and more cross-linked. This results in linear increase in hardness [2, 3, 10–13], Young's modulus [10, 13–16], thermal expansion coefficient [3, 5, 11, 14, 17], glass transition temperature (T_g) [3, 6, 11, 16, 17] etc., as a function of nitrogen content.

The studies of the properties of the oxynitride glasses focused mainly on the Y- and Al-containing systems because of their relationship to Sialon ceramics [3, 6, 8, 9–13, 15–17]. The studied properties usually included hardness, elastic moduli, thermal expansion and dilatometric T_g. Viscosity of such glasses was considerably less investigated. The earlier [11, 18] as well as some of more recent works [12, 19–23] showed that viscosity and T_g of the RE-Si-Al-O-N glasses (RE = rare-earth modifiers) increase linearly with the increase of nitrogen content. Rouxel *et al.* analyzed relationship between creep and viscosity and adopted bending creep method for viscosity measurement [20]. However, bending creep requires relatively large samples, which are not always available. Besson *et al.* [21] used compressive creep method with considerably smaller samples and compared T_g from such creep with dilatometry, differential thermal analysis (DTA) and ultrasonic measurements of Young's modulus at high temperatures in RE–SiAlON glasses (RE = Y, La, Eu, Er). This comparison revealed acceptable differences in T_g among different methods: T_g from dilatometry were 8 to 29°C lower than T_g determined from DTA. Data from creep tests were within the range of temperatures defined by DTA and dilatometry. The ultrasonic method gave T_g which were up to 60°C lower than those from DTA. Thus, compressive creep seems to be suitable and experimentally simple method for simultaneous measurement of viscosity and T_g. Becher *et al.* [23] also used this method to investigate the effects of lanthanides on viscosity and other properties of RE-Si-Al-O-N glasses. However, the effect of nitrogen was not investigated systematically in this study. It was addressed in a recent work of Pomeroy *et al.* on Y-Mg-Si-Al-O-N using dilatometry, where T_g increased linearly with N content increase [16]. The replacement of Mg by Y and nitrogen for oxygen were found to be independent and additive in agreement with the earlier conclusion of Drew *et al.* [6]. Saito *et al.* investigated the effect of nitrogen on viscosity of

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Y-Al-Si-O-N melts at 1450–1600°C in rotary viscosimeter [22]. Although the trends in viscosity change as a function of N content were similar, this technique is not applicable at temperatures below glass softening temperature and requires special equipment.

Our first viscosity studies involved compressive creep method and focused on the effect of RE additives in Mg-containing glasses in order to avoid SiAlON formation [24, 25]. RE included Sc, Y, La, Sm, Yb and Lu and the corresponding RE-Si-Mg-O-N glasses contained 20 and 24 eq.% (e/o) nitrogen. This is obviously insufficient to reveal the effect of nitrogen over wide range of nitrogen concentrations. Moreover, the differences in viscosities of RE-Si-Mg-O-N glasses when RE = La was replaced by Lu, were lower than those reported for RE-Si-Al-O-N glasses. It was not clear, if these discrepancies result from the presence of Mg instead of Al, different nitrogen contents, insufficient homogeneity of these glasses or from other reasons.

The first step in the control of the properties of the oxynitride glasses at elevated temperatures is the development of simple and reliable technique for their investigation. Then, the effect of nitrogen and RE modifiers can be studied independently. The aim of the current work is to compare the results of two different techniques, compressive creep and dilatometry, in order to investigate the effect of nitrogen on viscosity and glass transition temperature in La-Mg-Si-O-N glasses. Creep will provide viscosity as a function of temperature and T_g estimate whereas the dilatometric T_g data will be used as a reference to evaluate the accuracy of the compressive creep method.

2. Experimental procedure

2.1. Glass preparation

Six oxynitride glasses were prepared from the mixture of powders of SiO_2 (Aerosil OX 50, Degussa-Hüls AG, Germany), MgO (MgO 500 A, UBE Ind. Ltd., Japan),α-Si_3N_4 (SN-E10, UBE Ind. Ltd., Japan) and La_2O_3 (Lanthan (III)-Oxid, Merck, Germany). The ratio Mg:La of 1:1 was constant and 20 e/o for each element. The amount of silicon nitride powder was calculated in such a way that the resulting nitrogen contents were 0, 10, 20, 22, 24 and 28 e/o. The powders were homogenized, dried, uniaxially pressed, CIP-ed and finally sintered in gas pressure sintering furnace at 1700°C under 2 MPa of nitrogen pressure for 0.5 h [26]. Specimens with the size of approximately 3 mm × 4 mm × 10.5 mm were cut and ground for compressive and dilatometric experiments.

2.2. Dilatometry

Dilatometric experiments were carried out in a horizontal dual-rod dilatometer (DIL 802, Bähr Thermoanalyse GmbH, Germany) in flowing N_2, heating rate of 1 K/min and sapphire standard. Two series of dilatometric experiments were performed. The first set of experiments on as-produced samples was used to estimate T_g. Each glass was then annealed for one hour in air at a temperature approximately 10°C above such fictive T_g and then slowly cooled to reduce the prehistory effect. Second set of experiments on the pre-annealed samples yield final data. T_g was determined from the intersection of the tangents of thermal expansion curve of the solid glass and that of the glass "melt". The accuracy of T_g determination was ± 3°C. Glass softening temperature, T_L, also called Littleton temperature, was determined from the maximum of the dilatometric curve with the accuracy better than ± 2°C.

2.3. Viscosity measurement

The viscosities of the corresponding glasses were determined from the compressive creep experiments performed on the samples after dilatometric experiments in the modified bending creep furnace (Model HTTF 2, SFL Ltd./Instron, Inc., UK) in air in the temperature range from 750°C up to 910°C [24, 25]. The specimens were placed between two alumina supports, which transfer the load from the lever arm of the dead weight system. Elongation was measured as a difference between two linear variable differential transducers attached to the lower and upper alumina supports via thin alumina rods. The accuracy of the measurement was better than 0.2 μm.

The samples were heated with the rate of 5°C/min up to maximum 910°C under a small preload (<1 MPa). Only a short (<10 min) dwelling time was allowed for temperature stabilization to avoid excessive crystallization of the glass. Deformation accumulated during each step was intentionally limited only to approximately 0.5% strain to prevent systematic errors due to cross section changes and barreling during subsequent steps. After reaching steady-state rate or predetermined strain, sample was unloaded and strain relaxation recorded within the period comparable to the duration of the creep experiment. Then, temperature was reduced by 10–20°C and creep-relaxation cycle repeated. Such procedure was repeated at least at 7 different temperatures for each sample. Minimum strain rates were measured always under the stress of 10 MPa, however, additional loads corresponding to 15 and 20 MPa were used at one temperature for most of the glasses to obtain the stress exponents.

Viscosity of the corresponding glass, η, was calculated from the minimum strain rate, $\dot{\varepsilon}$ according to the formula

$$\eta = \frac{\sigma}{2(1+\upsilon)\dot{\varepsilon}}, \tag{1}$$

where σ is the applied stress and υ is the Poisson's ratio. The values of υ were in the range from 0.280 to 0.294 and taken from our earlier study [25]. The glass transition temperature, T_g, was determined as the average temperature corresponding to the range of viscosities from 1.10^{12} and $1.10^{12.6}$ Pa·s on the temperature dependence of the corresponding viscosities. Note that the technique and the method of calculation are very similar to the parallel plate method (ASTM C 1351M-96) and that used by Besson *et al.* [21] and

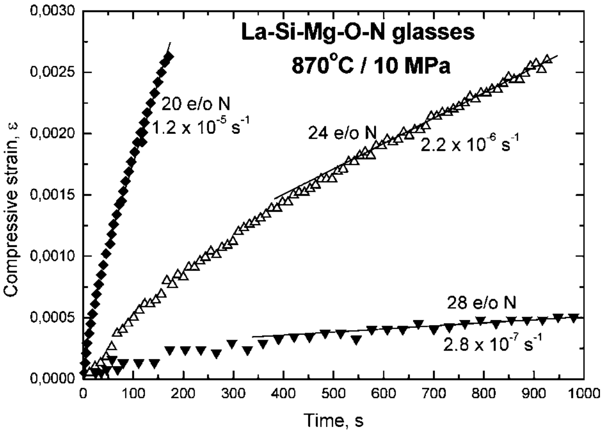

Figure 1 The comparison of the creep curves in La-Si-Mg-O-N glasses with different nitrogen content under identical conditions.

Becher *et al.* [23], which enables fair comparison of the viscosities of the Al- and current Mg-containing glasses with the same rare-earth additives.

3. Results

3.1. Nitrogen effect on viscosity

Fig. 1 is a comparison of three creep curves obtained at identical conditions, 870°C under stress of 10 MPa in the glasses with 20, 24 and 28 e/o N. The minimum creep rates between the glasses with 20 and 28 e/o N differ by almost two orders of magnitude and the corresponding viscosities change approximately 44 times.

The viscosities of the La-containing glasses summarized in Fig. 2 reveal nitrogen effect in the whole range of nitrogen contents studied. Addition of 28 e/o N into oxide glass resulted in 105°C increase of T_g. Simultaneous minimum creep rate decrease at same temperature cannot be measured directly because the corresponding temperature ranges do not overlap. Linear extrapolation of the viscosity fit for the glass with 28 e/o N to lower temperatures results in the difference of viscosity of around 6 orders of magnitude, which is obviously overestimated due to the neglecting of the deviations of viscosity from linearity at temperatures substantially below T_g [19–21]. The difference in viscosities of the oxide and oxynitride glasses with 22 or 24 e/o N, which fall in the temperature overlap, was around 2×10^4. Thus, the difference in the case of glass containing 28 e/o N would be maximum 10^5. Fig. 3 shows that T_g depends linearly on nitrogen content in these glasses. The apparent activation energies are summarized in Fig. 4 as a function of viscosity on inverse temperature. The activation energies calculated from the creep rates give identical values. They are in the range from 1126 kJ/mol up to 1232 kJ/mol without clear dependence on nitrogen content.

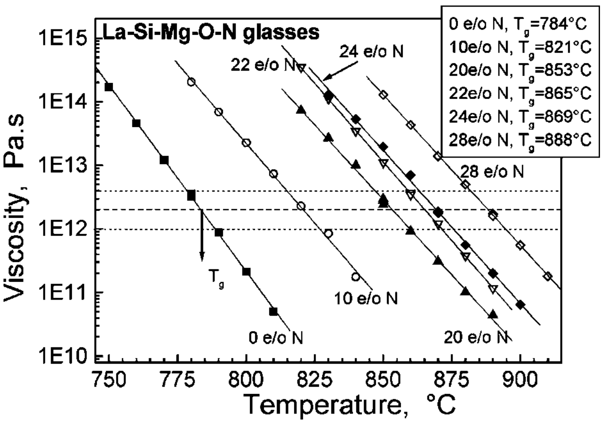

Figure 2 Viscosity of the studied La-Si-Mg-O-N glasses as a function of temperature and nitrogen content.

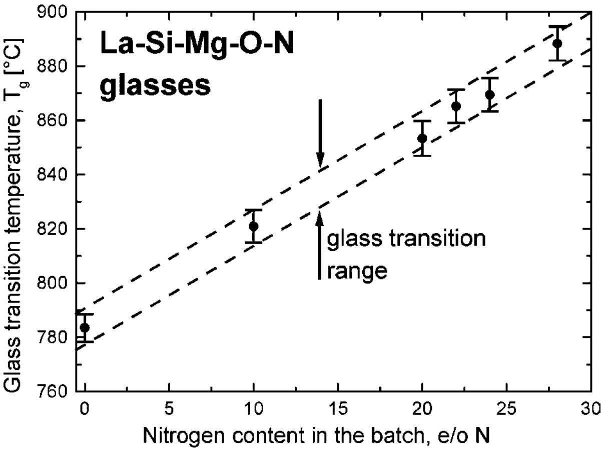

Figure 3 Glass transition temperature of La-Si-Mg-O-N glasses is a linear function of nitrogen content. Error bars indicate the glass transition range and the full symbols correspond to the average temperature in this range.

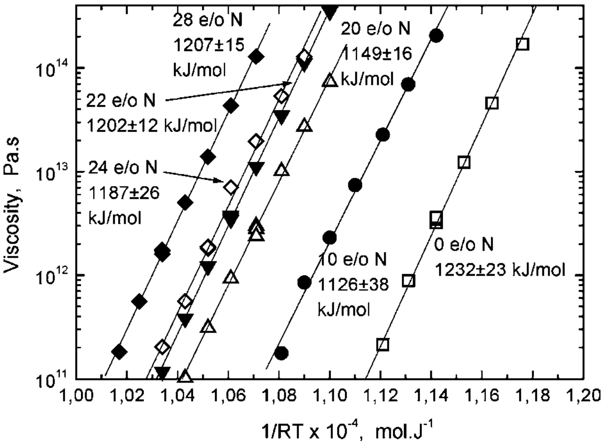

Figure 4 Arrhenius plot of the obtained viscosities and the corresponding activation energies in the glasses with different *N* content.

The stress exponents obtained over relatively narrow range of stresses from 10 to 30 MPa oscillated around unity with the average value of 1.06 ± 0.18 with the minimum and maximum values of 0.83 and 1.32, respectively. This suggests that compressive creep occurs via regular viscous mechanism regardless of N content.

3.2. Dilatometry

Dilatometry provided information about glass transition temperature and glass softening temperature called also Littleton temperature (T_L). They are illustrated in Fig. 6 as a function of fractional glass compactness and nitrogen content. Fractional glass compactness is

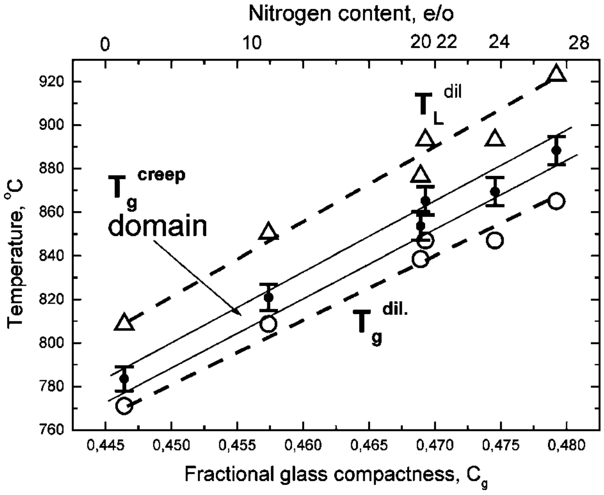

Figure 5 The comparison of the glass softening temperature (T_L) and T_g obtained from dilatometric experiments with T_g from creep. Error bars in creep data indicate temperatures corresponding to the range of viscosities from 10^{12} to $10^{12.6}$ Pa·s.

defined as

$$C_g = \frac{\sum_1^i x_i v_i N}{\sum_1^i x_i m_i} \rho, \tag{2}$$

where x_i is the fraction of the corresponding ionic species i, m_i is the ionic mass of the species, N is the Avogadro's constant and ρ is glass density. The volume of the ionic species, v_i, was calculated from their ionic radii of the corresponding species as given by Shannon [27]. Density of the corresponding glasses was reported previously [25].

The comparison of Figs 4 and 5 indicates that T_g depends on fractional glass compactness linearly in similar way as on nitrogen content. The values of T_L are approximately 54–63°C higher than the corresponding T_g measured by dilatometer, however, only 26–31°C higher than T_g from creep experiments. Thus, the average values of T_g from creep are overestimated by 12–23°C in comparison with the dilatometry values.

4. Discussion

4.1. Creep vs. dilatometry

The variations between creep- and dilatometry-based glass transition temperatures in Fig. 5 are from 12°C in the oxide glass up to 24°C in the glass containing 28 e/o N and with the highest C_g value. There are both principal and experimental reasons for such difference. It is known, that T_g obtained from dilatometry is usually related to the onset of the transition whereas T_g from DTA determines the end of transition [21]. Thus, dilatometric T_g should be compared with the temperature corresponding to the viscosity of 10^{12} Pa·s rather than with the average temperature in the viscosity range 10^{12}–$10^{12.6}$ Pa·s. Such approach reduces the difference between creep and dilatometric T_g to 6–17°C, which is relatively a good agreement. The other experimental reasons can be related to the true temperature of the sample. The distance between the sample and thermocouple in dilatometric experiments was only 1 mm whereas it was up to 5 mm in the case of creep experiments. This may result in an overestimation of the temperature of the sample. T_g is also sensitive to the pre-history of the sample. The properties of the glass samples after dilatometric experiments at slow heating rates can be slightly different from those during subsequent creep experiments at comparable temperatures. Although all these factors contribute to the overestimation of T_g from creep, the differences are acceptable and the tendency toward its increase as a function of N content is identical for both methods. It increases linearly with C_g, N content and the slopes of the fits for T_g and T_L are similar. Thus, creep method seems to be suitable for the fast measurement of temperature dependence of viscosity and T_g estimation.

4.2. Viscous flow mechanism

Although nitrogen significantly modifies viscosity and T_g, no effects were observed with regard to the viscous flow mechanism. Stress exponents were close to 1.0 regardless of nitrogen content. This confirms that deformation occurs via conventional viscous flow in both oxide and oxynitride glasses. The average activation energy determined from viscosity data was 1184 ± 36 kJ/mol and no dependence on nitrogen content was found. Rouxel *et al.* demonstrated that the activation energy from creep should correspond to the activation energy for viscosity as a consequence of the constant Poisson's ratio over the whole temperature range [20]. As expected, the activation energies calculated from creep rates gave identical values as the values from viscosity.

Besson *et al.* obtained the apparent activation energy of 934 kJ/mol for 21.4La-Si-21.4Al-O-13N glass, 992–1150 kJ/mol for various Y-containing oxynitride glasses and the decrease in the activation energy at temperatures below T_g [21]. It was attributed to the thermal component while the structural component of the activation energy diminished. However, such transition was not observed in the current glasses because of lack of data at this temperature range. The activation energies reported in YSiAlON glasses were around 900 kJ/mol and roughly coincided with the activation enthalpy measured at $T > T_g$ [20]. Slightly lower value of 780 kJ/mol was found in 30La-Si-25Al-O-30N glasses [23]. In our previous work on La-Si-Mg-O-N glasses with the chemical composition very similar to that in the current glasses, however, with insufficient homogeneity, the activation energy was around 1070 ± 150 kJ/mol [24, 25]. This is close enough to the values obtained in the current set of glasses, however, it is almost 300 kJ/mol greater than in the other materials. The reason for the differences in the activation energy from different authors in the glasses with La modifier is not clear. Nitrogen seems to play a small role in activation energy changes, therefore, the effects can result only from the presence of Al and RE-modifier contents.

4.3. Nitrogen effects

The introduction of 28 e/o N in the studied glass resulted in 94–105°C increase in T_g, 114°C increase in

T_L and up to 5 orders of magnitude increase in viscosity of the corresponding La-Si-Mg-O-N glass. This is by 100 times greater than about a 1000-fold increase in the viscosity value accompanied by a shift upwards of 100°C in T_g in the La-Si-Al-based glasses by substitution of 30 eq.% of O by N [23]. In contrast to that, 3 orders of magnitude and 80°C increase in viscosity and T_g, respectively, were reported in YSiAlON glasses containing 4.8 wt% N (∼21.5 e/o N) [20]. Thus, viscosity change differs only by a factor of 20 and T_g increase agrees well with the difference in T_g between current oxide and oxynitride glasses containing 22 e/o N (see Fig. 2). It should be noted that the absolute values of T_g in the case of current La-Si-Mg-O-N glasses are approximately 90°C lower than those of La-Si-Al-O-N glasses with similar N content [23]. These differences, similarly as those in activation energy, may result from the presence and different contents of Al instead of Mg. However, additional structural studies are required to understand the roles of Al and Mg in the property variations in the relevant oxynitride glasses.

Nitrogen effect on viscosity and glass transition temperature can be described in the well known terms of the increase of interconnectivity in the glass network due to the replacement of bivalent oxygen atoms by trivalent nitrogen. Such assumption is supported by the fact that C_g and density as well [25] increase with the N content increase (see Fig. 5) although N anions have smaller atomic weight and bigger ionic radius than the replaced O ions. The introduction of nitrogen into glass network occurs via formation of (SiO_3N), (SiO_2N_2) and other units in the oxynitride glasses at the expense of Q^2 (SiO_{2-}^{3}) units, which are dominant in the oxide glass [25]. The amount of bridging anions in the nitrogen-containing units increases two- and three-fold, respectively. Greater cross-linking of the glass network causes that compactness increases despite opposite tendency resulting from geometrical and atomic weight considerations. This enhances rigidity of the structure and increases refractoriness of the oxynitride glass as a function of N content (Fig. 5).

5. Conclusions

The comparison of the glass transition temperatures on 20La-60Si-20Mg-O-N glasses obtained from compressive creep data and dilatometry revealed only 6–12°C difference and both methods show identical and linear dependencies of T_g on nitrogen content. Thus, compressive creep method was confirmed to be simple and suitable method for viscosity studies of glasses. An average stress exponent of 1.06 ± 0.18 indicates that creep occurs via viscous flow mechanism. The average activation energy for all glasses was 1184 ± 36 kJ/mol and no dependence on nitrogen content was found. Obviously, viscous flow remains the same deformation mechanism regardless of nitrogen content. Substitution of 28 e/o of O by N in the glass resulted in an increase of T_g by 94–105°C and a change in viscosity of up to 5 orders of magnitude. These changes are greater than those reported in the comparable glasses containing Al instead of Mg. Linear increase of T_g and compactness of the glass with nitrogen content result from enhanced cross-linking of the glass network.

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