LOCALIZED VISCOUS FLOW IN THE OXIDE AND OXYNITRIDE GLASSES BY INDENTATION CREEP

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1. Introduction

Vickers, Brinell or Rockwell hardness tests are common methods for the investigation of the hardness, elastic, elasto-plastic and plastic behavior, yield strength, etc., of wide range of materials from soft and ductile metals up to brittle and very hards ceramics and glasses[1]. These tests are simple and the information is obtained from very small volume of the material. Instrumented indentation developed over last two decades based on the model of Oliver and Pharr[2] resulted in the measurement of a range of properties and parameters, which are not available from conventional hardness. Besides reduced elastic modulus, elastic and plastic work and several others, indentation creep data became available. However, the indentation creep used in the instrumented indentation is related to the deformation under the sharp indenter over relatively short period of time of tens of secondes up to several minutes at room temperature. Highly localized and concentrated stresses in brittle materials result in the formation of indentation damage, which contributes to the plasticity data. The tests without damage contribution are desirable to obtain concise data on plasticity of the studied materials. Creep resistance, viscous flow as well as time dependence of hardness can be successfuly determined at high temperatures using a modified indentation creep, which is a combination of the compressive creep testing and instrumented indentation with blunt indenter[3–8]. The first tests of this type with hemishperical indenter were performed by Heynes and Rawson in the 60-s to measure the viscosity of glasses[3]. The theoretical interpretation of this measurement was worked out by Douglas[4]. The flat ended cylindrical punch was used Yu and Li in the 70-s for investigation of creep properties of single crystals and they have proved that its results are equivalent to those of the tensile creep test[5,6]. During this measurement, a cylinder with the diameter d is pressed with the force F into the flat surface of the sample (Fig. 1) at the test temperature, T, and the depth of the indentation, h(t) is recorded as the function of elapsed time, t. The result is a conventional creep curve with an initial transient stage followed by a stage with the constant impression velocity, v = *dh/dt*. It was shown on various metals, glasses and ceramics that the indentation tests provide the same information on viscosity as tensile tests[5–8]. Viscosity of the glasses, h, was found to follow the relationship:

$$\eta = d\, k_1\, p/3\, k_2\, v$$

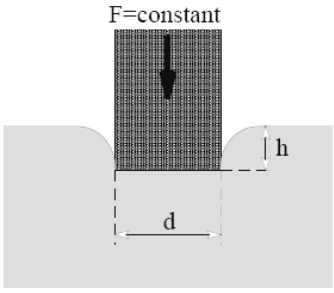

Fig. 1. **Schematic representation of the flat cylindrical punch indentation creep geometry**

where k_1 and k_2 are the geometrical coefficients and p is the pressure on the indentor. The values of k_1 and k_2 were determined experimentally and by FEM and they are in the range 0.3–0.4 and 0.76–1.0, respectively[9]. Thus, viscosity measured by the indentor with the diameter d and pressure

$p = 4F/\pi d^2$, is

$$\eta = c.\ p/\ v \qquad (1)$$

where $c = k_1 d/3\ k_2$. For the FEM values $k_1 = 0.3$ and $k_2 = 0.76$[9], the value $c = 0.13$ d is a constant of the indentor. The activation energy, Q, is given by the formula

$$\eta = \eta_0 \exp(Q/kT), \text{ resp. } \ln v = \ln p - \ln(c\eta_0) - Q/kT \qquad (2)$$

where h_0 is a constant and kT has its usual meaning.

Oxynitride glasses present in the advanced structural ceramics at the grain boundaries, originate from sintering additives. Despite being as only 1 nm thin films, they control high temperature behavior of these ceramics and the increase of their viscosity is crucial for the improvement of creep resistance of the whole material. The measurement of the viscosity of such thin films is currently experimentally not possible but it can be measured on the model bulk oxynitride glasses[10–12]. Viscosities of such glasses were already measured by compressive tests and it was shown that both, rare-earth additives and nitrogen content have significant influence on viscosity and transition temperature of these glasses[10–12].

The aim of the current work is to investigate viscosities of the selected oxynitride glasses by indentation method, to compare the obtained results with those from other methods and to prove suitability of indentation method for viscosity measurement of the oxynitride glasses.

2. Experimental part

Glass preparation

Four oxide and four 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 rare-earth oxides RE_2O_3 (RE = La, Sm, Yb, Lu). The ratio Mg: RE of 1:1 was constant and 20 e/o (equivalent %) for each element. The amount of silicon nitride powder was calculated in such a way that the resulting nitrogen contents were 0 e/o in the oxide and 20 e/o in the oxynitride glasses. The powders were homogenized, dried, uniaxially pressed, cold isostatic pressed and finally sintered in gas pressure sintering furnace at 1700 °C under 2 MPa of nitrogen pressure for 0.5 h (ref.[11,12]). The obtained pellets were cut on 3 mm thick slices ground and polished to obtain two parallel surfaces for the indentation tests.

Indentation creep

The tests were performed in the HTTF2 creep furnace in the temperature range 760–925 °C in air using SiC indenter with the diameter d = 2.1 mm under the stress p = 20 MPa. Experimental set-up is shown in Fig. 2. Penetration depth was measured as a difference between the data from two linear

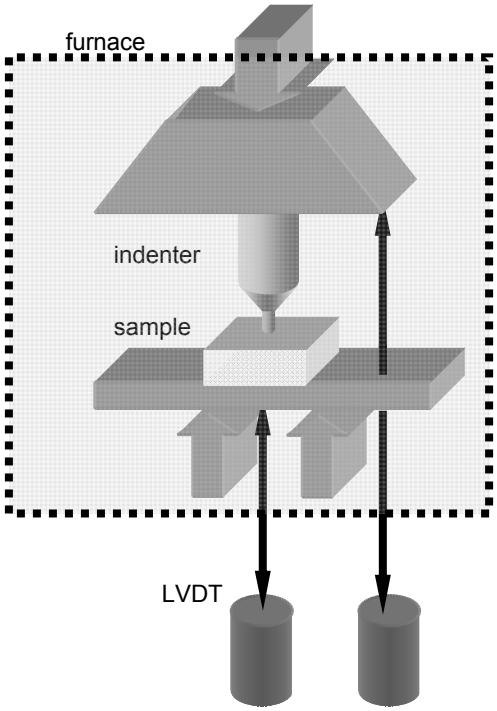

Fig. 2. **Schematic representation of the indentation creep test set-up**

variable differential transducers (LVDT). They were out of the furnace attached to the loading punches via thin alumina rods to compensate errors due to thermal expansion. The tests run from < 1 min at the highest temperatures up to around 20 hours at the lowest temperatures.

3. Results

Creep curves corresponding to the time dependence of the penetration depth of the indenter in the La-Si-Mg-O glass are compared in Fig. 3. Penetration rates in the studied temperature range 790–840 °C vary over three orders of magnitude. Similar differences were measured in the case of the corresponding oxynitride glasses, however, with a shift toward higher temperatures. As shown in Fig. 4, penetration rates of around $1 \cdot 10^{-5}$ mm s^{-1} obtained in La-oxide glass at ~ 805 °C occur at around 890 °C in Lu-Si-Mg-O-20 % N glasses.

Penetration rates were transferred into viscosity using Eq. (*1*) with c = 0.273 mm. Fig. 5 shows temperature dependence of viscosity of the La-Si-Mg-O glass. Glass transition temperature, T_g, was determined as a temperature in the middle of the range when viscosity changes from 10^{12} Pa s to $10^{12.6}$ Pa s. The viscosities of all glasses are summarized in Fig. 6. The viscosities of the oxide glasses are significantly lower than those of the corresponding oxynitride glasses. The

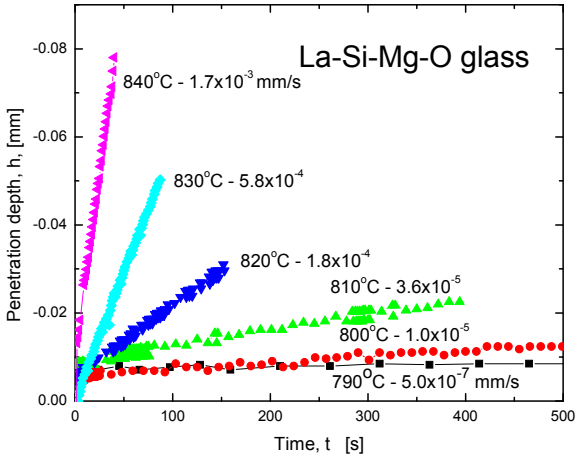

Fig. 3. **Time dependence of the penetration depth in La-Si-Mg-O glasses under stress of 20 MPa**

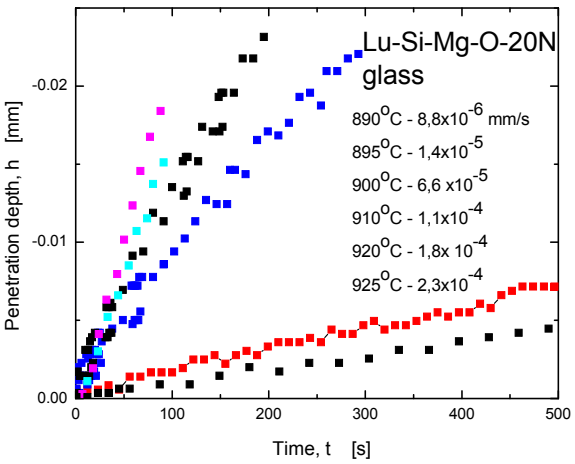

Fig. 4. **Indentation creep curves in Lu-Si-Mg-O-N glass under stress of 20 MPa**

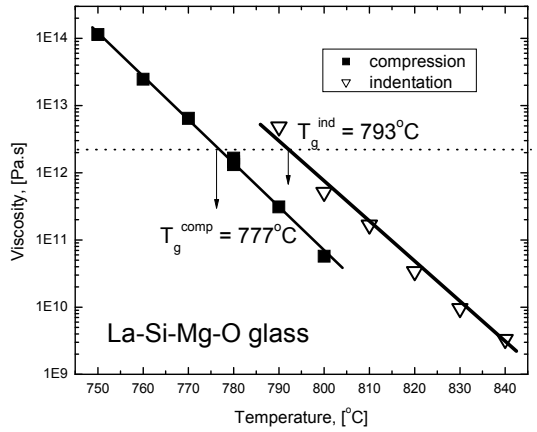

Fig. 5. **Temperature dependencies of viscosities obtained by indentation and compressive creep[11] methods**

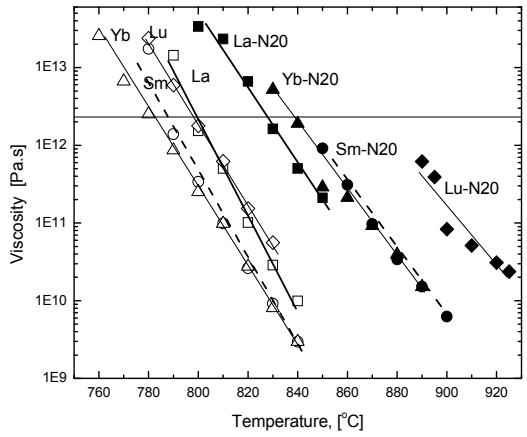

Fig. 6. **Summary of the temperature dependencies of viscosities of the studied oxide and oxynitride glasses obtained by indentation creep**

differences are up to 70 °C. However, the variations in T_g up to 45 °C can also be seen within each group. The lowest T_g belongs to La- and Yb-containing glasses whereas Lu-containing glasses always exhibit the highest T_g. The values T_g of as well as of the activation energies, which were determined from the Eq.(*2*), are summarized in Table I and compared with the values obtained earlier from the compressive creep tests on the same materials[11].

4. Discussion

The results indicate that the indentation creep method is capable of the determination of the viscosity of oxide and oxynitride glasses over five orders of magnitude and its results are comparable with those obtained by compressive creep method from considerably larger volumes of glass. However, some systematic differences were observed (see Fig. 5). T_g and viscosity from indentation creep are usually higher in the case of oxide and lower in the case of oxynitride

Table I
Summary of the indentation and earlier compressive creep tests in terms of T_g and activation energies

Material	$T_g^{indentation}$ [°C]	$T_g^{compression}$ [°C]	Q^{ind} [kJ mol^{-1}]	Q^{comp} [kJ mol^{-1}]
La-N0	793 ± 5	777 ± 5	1406±130	1373±129
La-N20	829 ± 6	853 ± 6	1095±91	1151±94
Sm-N0	790 ± 5	773 ± 5	1347±124	1313±122
Sm-N20	841 ± 7	859 ± 6	1096±90	1140±93
Yb-N0	782 ± 6	778 ± 6	1077±95	1097±97
Yb-N20	837 ± 7	857 ± 7	1007±81	1120±91
Lu-N0	800 ± 6	803 ± 6	1167±102	1151±100
Lu-N20	873 ± 7	889 ± 7	1055±82	1110±87

glasses while the activation energies are essentially the same. The differences in T_g are from 3 °C up to 24 °C and can be attributed to the differences in the coefficients k_1 and k_2 and to local inhomogeneities in the glasses. The activation energies obtained by indentation are in the range from 1050 kJ mol^{-1} up to 1400 kJ mol^{-1} with the highest values in the case of La- and lowest in Yb- and Lu-containing glasses. Note that these values are considerably higher than 400–550 kJ mol^{-1} reported for common Mg- or Pb-silicate glasses[7]. Such high activation energies reflect significantly stronger bonds in these glasses when RE and N are incorporated. The data in Table I indicate small but systematic decrease of activation energy of viscous flow in oxide glasses from 1400 kJ mol^{-1} to 1170 kJ mol^{-1} when the largest cation La is replaced by the smallest Lu cation, with the exclusion of Yb. Change of the RE type has exactly opposite effect on T_g (Yb is an exclusion[12]). Similar tendencies were observed in the oxynitride glasses and also in compressive creep tests[10–12]. Thus, viscous flow is influenced by at least three effects:

1. type of the cation modifier
2. RE cation size, and
3. N content.

Chemistry, resp. electronic structure of the RE modifiers seems to weaken the bonding with the ionic size decrease. On the other side, ionic size reduction results in density increase and tightening of the glass network, which partially compensate for the above weakening. Finally, nitrogen significantly increases cross-linking of the network which results in much larger increase of viscosity and transition temperatures than the modification of RE[12]. However, the reason why the activation energies of viscous flow in the oxynitride glasses are lower than in the corresponding oxide glasses is not clear.

5. Conclusions

It was shown that the indentation creep method with flat indenter is suitable for the determination of viscosity, T_g and activation energy of oxide and oxynitride glasses. The effects of RE-type and nitrogen content on the viscosity and glass transition temperature, which were measured earlier by the compressive creep method, were also confirmed. The differ-

ences in the measured viscosities result in the differences in T_g values up to 25 °C whereas the values of the activation energy remain identical. The variations in viscosity can be attributed to the differences in the coefficients k_1 and k_2 and to local inhomogeneities in the glasses. The effects of nitrogen and RE-type were attributed to the increase of network cross-linking and tightening of the glass structure when nitrogen and RE with smaller ionic radii are incorporated in the glass network, respectively.

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F. Lofaj *(Institute of Materials Research of SAS, Watsonova 47, 040 01 Košice, Slovakia):* **Localized Viscous Flow in the Oxide and Oxynitride Glasses by Indentation Creep**

Localized viscous flows in the oxide and oxynitride glasses were investigated by the indentation creep and the results were compared with the data obtained in compression. Despite general agreement between both methods, the observed differences can be attributed to geometrical factors and local inhomogeneities in the glass. RE type and nitrogen content exhibit strong influence on the glass viscosity. Their effects were related to the increase of network cross-linking and tightening of the glass structure when nitrogen and RE with smaller ionic radii are incorporated in the glass network, respectively.