THE EFFECT OF LANTHANIDES ON VISCOSITY OF RE-Si-Mg-O-N GLASSES

Compressive creep behavior of RE-Si-Mg-O-N glasses (RE = La, Yb, Sm and Lu) was investigated to determine temperature dependency of their viscosity in temperature range from 770 °C up to 895 °C. Viscosity and heat transfer through the glass (T_g) were increased by > 10 times and by 26 °C, when La is replaced with Lu in the corresponding glasses. Assuming valence Z = +3 and coordination number CN = 6 of the RE ions, T_g depends approximately linearly on cationic field strength except Yb. T_g of Yb-containing glass also falls on linear dependence provided CN = 8 in the case of Yb. Lanthanides seem to modify the structure of the corresponding glasses and bond strength rather than the mechanisms of deformation.

Key words: lanthanides, oxynitride glass, viscosity, heat transfer through the glass, cationic field strength

Utjecaj lantanida na viskoznost stakla RE-Si-Mg-O-N. Ispitivano je puzanje stakla RE-Si-Mg-O-N (RE=La, Yb, Sm i Lu) pod tlakom radi određivanja ovisnosti viskoznosti o temperaturi u temperaturnom području od 770 °C - 895 °C. Viskoznost i prijenos topline kroz staklo (T_g) povećane Si za > 10 puta i za 26 °C kad je La zamijenjen s Lu u odgovarajućim staklima. Ako pretpostavimo da je valentnost Z = +3, a koordinacijski broj CN = 6 RE iona, T_g ovisi približno linearno o čvrstoći kationskog polja, osim za Yb. T_g stakla koja sadrže Yb također se svode na linearnu ovisnost pod uvjetom daje CN = 8 a u slučaju Yb. Čini se da lantanidi modificiraju strukturu odgovarajućih stakala i čvrstinu veze a ne mehanizmi deformacije.

Ključne riječi: lantanidi, oksinitridno staklo, viskoznost, prijenos topline stakla, čvrstoća polja kationa

INTRODUCTION

The interest of researchers and industry for the rare-earth (RE) containing oxynitride glasses originates from their efforts to develop ceramics with better high temperature behavior. High resolution electron microscopy studies revealed that the grain boundaries in silicon nitride and other structural ceramics consist of glasses, which are relatively similar to RE-oxynitride glasses [1]. They are the residues of liquid phase sintering and remain as an intergranular glass at the grain boundaries. Despite its small thickness, the residual glass films control room and high temperature properties. The concept of grain boundary engineering [2] combined with high purity powders and better densification technology, resulted in remarkable improvements of silicon nitride ceramics [3-6]. The latest generations of materials can sustain temperatures by 180 °C greater than the earlier grades. Apparently, the increase is due to the presence of Lu in the residual glass [5, 6]. Thus,

detail study of the effect of Lu on the properties of glasses is necessary.

Over the years, oxynitride glasses themselves have become interesting object of studies because of a wide range of mechanical, electrical and optical properties and possibilities for their control [7-19]. The oxides of lanthanides with high atom number as network modifiers are very effective in modifying variety of properties because of so called "lanthanide contraction" - elements with higher atom number have smaller ionic radii [20]. Smaller atoms can be more easily incorporated in the glass network and produce more tight structure with better rheological properties. Number of experimental studies confirmed linear correlations between ionic radius of the corresponding lanthanide and thermal expansion coefficients, viscosity, molar volume and softening temperatures in RE-Si-Al-O-N glasses [8-11, 18, 19]. Another important factor controlling rheological properties of glass is the presence of nitrogen, which acts as a network former [7, 13-19].

The earlier studies on oxynitride glasses were focused mostly on the effect of several lanthanides on the pre-determined properties at one or two levels of nitrogen con-

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tent [7-11, 15]. Lutetium was not included and the concentration of nitrogen was usually below 20%. The effects of Lu on various properties were described only in very recent work of Becher on RE-Si-Al-O-N glasses [18]. They observed significant increase in density, glass transition temperature, microhardness and Young's modulus when larger lanthanides were replaced by smaller ones and with the increase of nitrogen content. These changes were attributed to the abi1ity of RE ions to generate strong cross-linking bonds and nitrogen, which modifies network strength and non-bridging anion content. However, this work is limited to Al-containing glasses. Aluminium forms solid solutions when added into silicon nitride ceramics. Therefore, the aim of the current work is to investigate temperature dependence of the viscosity in the Mg-containing oxynitride glasses with different lanthanides, including Lu, to have a reference for better understanding of the creep behavior of silicon nitride ceramics.

EXPERIMENTAL PROCEDURE

Glass Preparation

Four glass formulations have been prepared at the University of Karlsruhe from the mixtures of powders of SiO_2

Table 1. **The composition of the powder mixtures used for the preparation of the glasses. The designation of the samples indicates type of rare-earth element added into the oxynitride glass**
Tablica 1. **Sastav smjese praha koja se koristi za pripremu stakla. Oznake uzorka označavaju tip elementa rijetke zemlje koja se dodaje oksinitridnom staklu**

Glass system	Eq. [%]				
	Si	RE	Mg	O	N
Sm-glass	60.0	20.0	20.0	80.0	20.0
La-glass	60.0	20.0	20.0	80.0	20.0
Yb-glass	60.0	20.0	20.0	80.0	20.0
Lu-glass	60.0	20.0	20.0	80.0	20.0
Glass system	Mol. [%]			
	RE_2O_3	SiO_2	MgO	Si_3N_4
Sm-glass	13.4	39.7	40.1	6.8
La-glass	13.4	39.7	40.1	6.8
Yb-glass	13.4	39.7	40.1	6.8
Lu-glass	13.4	39.7	40.1	6.8
Glass system	Wt. [%]			
	RE_2O_3	SiO_2	MgO	Si_3N_4
Sm-glass	37.8	30.2	20.2	11.7
La-glass	46.7	25.9	17.3	10.1
Yb-glass	51.5	23.6	15.8	9.2
Lu-glass	51.7	23.4	15.5	9.1

+ RE_2O_3 + α - Si_3N_4 + MgO, where RE = La, Sm, Yb, and Lu. The content of the rare-earth elements and the amount of silicon nitride powder added were calculated in such away that the resulting RE, nitrogen and Mg content were 20 eq. % each. The composition of the individual powder mixtures in molar % and weight % are summarized in Table 1.

The corresponding powders were homogenized, sieved, cold isostatically pressed and melted in a graphite-heated gas-pressure sintering furnace under 1 MPa of nitrogen at 1 710 °C for 0.5 h. The furnace was cooled down with the rate > 100 °C/min above 1200 °C. The resulting glass samples were rounded pellets with a diameter of 3 cm, fiat from the bottom and with slightly rounded top.

The pellets were cut by a 1ow speed diamond saw into bars with the size of approximately 2 x 2 x 5 mm for creep tests and ground.

Viscosity measurement

The viscosities of the corresponding glasses were determined from the compressive creep experiments performed in the modified bending creep furnace (Model HTTF 2, SFL Ltd./Instron, Inc., UK) in air with temperature range from 773 °C up to 893 °C under stresses of 10 MPa, 20 MPa and 30 MPa. The specimens were placed in the furnace between two alumina supports used to transfer the load from the lever arm of the dead weight system. Elongation was measured as a difference between two LVDT's, which were attached to the lower and upper alumina supports via thin alumina rods.

The samples were heated with the rate of 5 °C/min up to 893 °C under a small preload < 1 MPa). Only a short (5 - 10 min) dwelling time was allowed for temperature stabilization to prevent 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 having reached 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 °C - 20 °C and creep-relaxation cycle repeated. Such procedures were repeated at 6 - 9 different temperatures for each sample. The stress of 10 MPa was generally used for the measurements. Additional tests under loads corresponding to 15 MPa, 20 MPa and 30 MPa were performed to obtain stress dependence of compressive creep rates.

Viscosity of the corresponding glass, η, was calculated from the measured strain rate according to the formula:

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

where

σ   is the applied stress,
ε̇   was taken from the minimum strain rate measured during creep tests,
υ   is the Poisson's ratio.

The value of υ = 0.3, which was reported for similar glasses in the literature, [16] was used in Eq. (1). The glass transition temperature, T_g, was determined as the average temperature corresponding to the range of viscosities 1.10^{12} Pa·s and $1.10^{12.6}$ Pa·s from the temperature dependence of the corresponding viscosities. The activation energies were calculated from the linear fits of the Arrhenius dependence of the glass viscosity on inverse temperature.

RESULTS

Figure 1. is a comparison of four creep curves obtained at identical conditions, 877 °C and 10MPa in different glasses. Evidently, their creep behavior depends on the composition. La-containing glas s exhibits the lowest creep
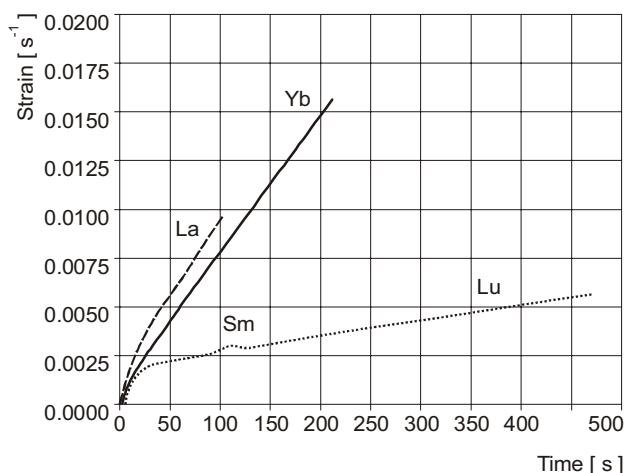

Figure 1.   **A comparison of compressive creep behavior of RE-Si-Mg-O-N glasses (RE = La, Sm, Yb and Lu)**
Slika 1.   **Uspoređivanje puzanja stakla pod tlakom RE-Si-Mg-O-N (RE-La, Sm, Yb, Lu)**

resistance whereas Lu is the most creep resistant at this temperature. Figure 2. shows the corresponding stress exponents in Yb-containing glass at three different temperatures - 856.4 °C, 826.6 °C and 805.4 °C, which are above T_g, approximately equal to T_g and below T_g, respectively. The rates in other RE-containing glasses are also included for comparison. The exponents vary around unity regardless of glass composition. Figure 3. illustrates temperature dependence of the viscosities of different glasses calculated from minimum creep rate s according to Eq. (1). The viscosities obtained at temperatures 770 °C - 900 °C are in the range from 10^{10} Pa·s up to 10^{16} Pa·s. Activation
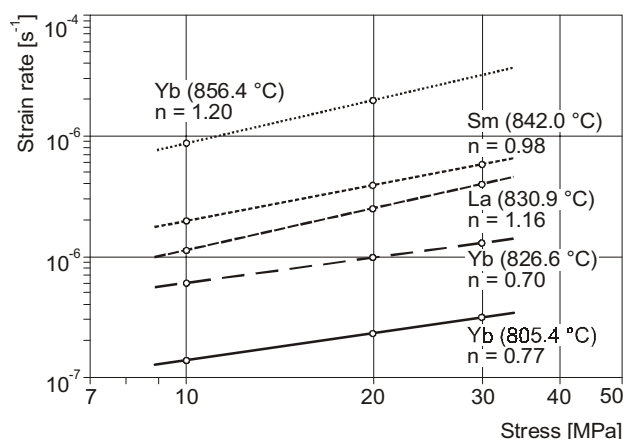

Figure 2.   **Stress dependence of the compressive creep rate s in RE-Si-Mg-O-N glasses under different conditions indicates that viscous flow is the main creep mechanism**
Slika 2.   **Ovisnost naprezanja o brzini puzanja stakla pod tlakom RE-Si-Mg-O-N pod raznim uvjetima ukazuje da je protok viskoznosti glavni mehanizam puzanja**

energies, which were calculated from Arrhenius dependence, are shown in Figure 4. They are in the range from 970 kJ/mol to 1130 kJ/mol.
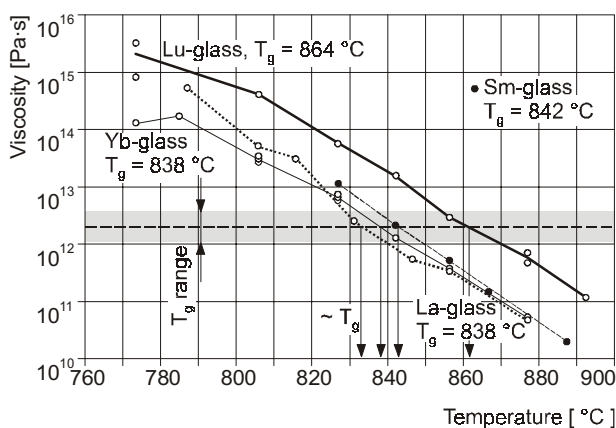

Figure 3.   **Temperature dependence of the viscosity of RE-Si-Mg-O-N glasses calculated from compressive creep tests**
Slika 3.   **Ovisnost viskoznosti stakala RE-Si-Mg-O-N o temperaturi izračunata na osnovu ispitivanja puzanja stakla pod tlakom**

DISCUSSION

Figure 1. clearly demonstrates the effect of rare-earth elements on creep resistance of the oxynitride glasses. Stress exponents of an unity indicate that deformation in current glasses occurs via viscous flow, that is via rearrangement of structural units of the corresponding material. Structure of the glass consists of a network of SiO_4 tetrahedrons. Variations in deformation rates among different glasses would result from the variations in the strength of the bonds in the network. This can be quanti-

fied as the cationic field strength. The cationic field strength (*CFS*) is determined as:

$$CFS = Z / r^2$$

where

Z is the valence,
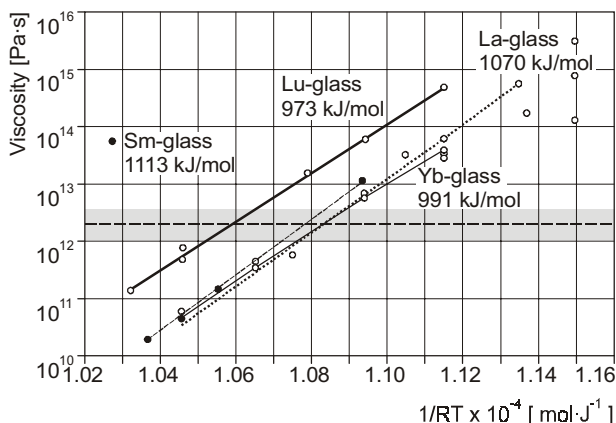*r* is the ionic radius of the corresponding element.

Figure 4. **Arrhenius plot of the viscosities of RE-Si-Mg-O-N glasses**
Slika 4. **Arrhenijev grafički prikaz viskoznosti stakla RE-Si-Mg-O-N**

Typical Z values for the oxides of the rare-earth elements included in the study, ionic radii and the corresponding *CFS* are summarized in Table 2. Numerous earlier stud-

Table 2. **Ionic radii and the corresponding *CFS* of the lanthanides with different valence and coordination numbers based on data from Shannon**
Tablica 2. **Radijusi iona i odgovarajući *CFS* lantanida s drugačijom valencijom i koordinacijskim brojevima zasnivanim na podacima Shanona**

RE-containing glass	Ionic radius, [A] and *CFS* [A^{-2}] for Z = + 3, CN = 6	Ionic radius, [A] and *CFS* [A^{-2}] for Z = + 3, CN = 7	Ionic radius, [A] and *CFS* [A^{-2}] for Z = + 3, CN = 8	Ionic radius, [A] and *CFS* [A^{-2}] for Z = + 2, CN = 6
La-glass	1.032 2.817	1.100 2.479	1.160 2.229	- -
Sm-glass	0.958 3.269	1.020 2.883	1.079 2.577	- -
Yb-glass	0.868 3.981	0.925 3.506	0.985 3.092	1.020 1.922
Lu-glass	0.861 4.047	- -	0.977 3.143	- -

ies showed that many physical properties, such as hardness, elastic moduli, thermal expansion coefficient, density, glass transition temperature and others, depend linearly or almost linearly on *CFS* [8-11, 18, 19]. High resolution electron microscopy studies in silicon nitrides revealed even linear dependence of the intergranular amor-

phous film thickness on the ionic radius of the corresponding lanthanide dissolved in the glass [22]. Linear dependence results from lanthanide contraction and increase of cross-linking of the network containing smaller lanthanide cations. Glass transition temperature usually depends\linearly on ionic radius, that is, glasses containing lanthanide with higher atom number and smaller ionic radius should have greater viscosity [8-11, 18]. Figure 5. is the dependence of T_g and activation energy on *CFS*. *CFS* is calculated based on data of Shannon for oxides [21] and assuming that $Z = +3$ and the coordination number is 6. The error bars in the case of T_g denote the range of temperatures corresponding to the viscosities in the range from 10^{12} Pa·s to $10^{12.6}$ Pa·s. The range of T_g in the case of RE-Si-Mg-O-N glasses is from 838 °C for RE = La and 864 °C for RE = Lu. These values are by 100 °C - 110 °C lower than T_g found in RE-Si-Al-O-N glasses with similar nitrogen content (~ 945 °C for RE = La and ~ 975 °C for RE = Lu) [18] due to the presence of Mg instead of Al. However, the effect of lanthanides is similar for both types of glasses. Replacement of La for Lu results in an increase of T_g by approximately 30 °C.
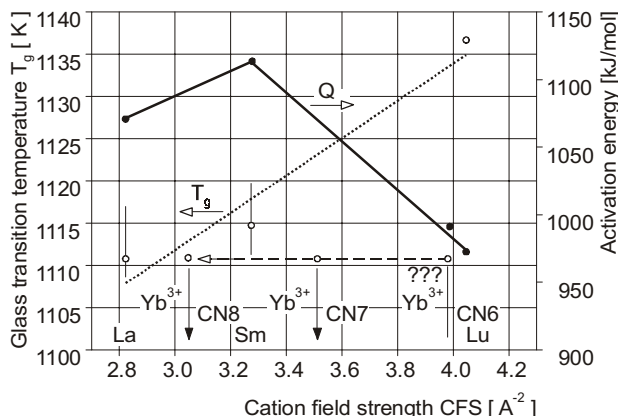

Figure 5. **The dependence of glass heat transition and activation energy based on calculated viscosities. *CFS* assumes $Y = +3$ and $CN = 6$. Error bars correspond to the range of viscosities from 10^{12} Pa.s to $10^{12.6}$ Pa.s**
Slika 5. **Ovisnost prijenosa topline i energije pokretanja zasnovane na izračunatoj viskoznost. *CFS* pretpostavlja $Y = +3$ i $CN = 6$. Šipke grešaka odgovaraju području viskoznosti od 10^{12} Pa. s do $10^{12.6}$ Pa. s**

Linear dependence of T_g is possible among La-, Sm- and Lu-containing glasses, however, T_g in the case of Yb-containing oxynitride glass is evidently out of the linear dependence. Similar deviations from linearity were often reported for various properties of the oxynitride glasses. For instance, Ramesh observed deviations from linearity in density and thermal expansion coefficient in Eu containing glass and in microhardness in Y-glass [10].

Menke reported similar deviations in T_g and thermal expansion coefficient for Dy-, Y -, Er- and Yb-containing glasses [11]. Linearity was obtained when the change of

the coordination number from $CN = 6$ to $CN = 7$ was considered for high atom number lanthanides [11]. Different coordination numbers mean different ionic radii and *CFS*. Similar approach can be used in the current case for Yb-containing oxynitride glass. According to Table 2., four states of Yb cations are possible depending on Z and CN in oxides. Glass transition temperature of Yb-containing oxynitride glass would fall on linear fit from other data in the case of CFS close to 3. O A^{-2}, that is in the case of $CN = 8$ instead of $CN = 6$. Change of Z or using $CN = 7$ cannot provide linearity of T_g data. Thus, the change of coordination number in Yb-containing oxynitride glass would explain the differences in creep resistance and viscosity seen in Figure 1. and Figure 3.

Changing coordination number was used to linearize the *CFS* dependence of the micro-, nano-hardness and elastic moduli of Y -Si-Mg-O-N glasses at room temperature in similar set of the oxynitride glasses [19]. However, hardness and elastic moduli of the corresponding Yb-glass fit the dependence without the change in *CN*. The difference can result from different conditions. At temperatures of above 800 °C, phase and accompanying structure changes are possible. Both assumptions agree with the idea of Menke [11] that the variations in the properties result not only from smaller lanthanide atoms but also from corresponding changes in the structure of these glasses.

The apparent activation energies in the studied RE-Si-Mg-O-N glasses are in the range from 970 kJ/mol up to 1113 kJ/mol, which agrees with the range of the activation energies found in silicon nitride ceramics. The variations and maximum difference of < 150 kJ/mol in the apparent activation energy between different glasses in the current case seem to be small. Since lanthanide replacement affects T_g rather than activation activation energy, it can be concluded that rare-earth elements affect bond strength in the glass whereas deformation mechanism remains the same.

The increase of viscosity when Yb is replaced by Lu in the oxynitride glass is more than 1 order of magnitude. Although it would increase creep resistance of silicon nitride ceramics substantially, it can explain only partially up to 5 orders of magnitude difference between the older and the newest Lu-containing silicon nitride ceramics. It is possible, that additional factors, e. g. the effect of nitrogen, are contributing to the effect of lanthanides.

CONCLUSIONS

The comparison of creep behavior and viscosities of RE-Si-Mg-O-N glasses with 20 eq. % of nitrogen and 20 eq. % of RE (RE = La, Sm, yb or Lu) confirms a possibility of tailoring properties via selection of the lanthanide added into the oxynitride glass. Viscosities and glass transition temperatures of the corresponding glasses can be increased by more than one order of magnitude or by approximately 26 °C when La is replaced with Lu. Assuming valence $Z = +3$ and coordination number $CN = 6$ of the RE ions, glass softening temperature s depend approximately linearly on cationic field strength, except Yb. However, T_g of Yb-containing glass also falls on linear dependence provided $CN = 8$ in the case of Yb. The apparent activation energies are within relatively narrow range from 970 kJ/mol to 1130 kJ/mol.

Lanthanides seem to modify the structure of the corresponding glasses and bond strength rather than the deformation mechanism.

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