Influence of pentoxide niobium on viscosity of glass melt.

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The viscosity of the system SiO_2-B_2O_3-Al_2O_3-CaO-Nb_2O_5 were investigated in the temperature range 1300-1800 K for Nb_2O_5 contents 3 - 25 wt. %. The activation energies of viscous flow and temperatures of crystallization were found. The parameters of viscosity, estimated from positions polymeric models of oxide melts structure, were well conformed with experimental data.

1. Introduction.

With development of new engineering areas the niobium glasses are object both scientific and practical interest. However physico-chemical properties of such substations in molten state, in particular viscosity, are investigated unsufficiently. From the not numerous literary data it is known, that the niobium behaviour in oxide melts depends on a nature of interpartial interactions and structure of these melts. For example, it is possible to note, that the increase of the contents Nb_2O_5 up to 20 % promotes destruction of aluminum–fluoride complexes and, accordingly, decrease of viscosity and activation energy of viscous flow in the system CaF_2 - Al_2O_3 - Nb_2O_5 [1]. On the contrary, the viscosity of melt Nb_2O_5 - SiO_2 - P_2O_5 - TiO_2 - FeO - MnO with growth of concentration Nb_2O_5 from 20 up to 28 % and comparable amounts (SiO_2 + TiO_2) is increased [2]. The submitted examples show, that niobium depending on a coordination environment, probably, can display itself as the cation-modifier, and complex-forming component.

In the present work we studied influence of pentoxide niobium on viscosity of glass melt containing (wt. %) 47.6 SiO_2, 13.3 B_2O_3, 12.5 Al_2O_3, 25.1 CaO, 1.5 FeO_x. With the constant relation of other components the contents Nb_2O_5 in this oxide system changed from 3 up to 25 % (0.7-7.4 mol %). The basic purpose of work was search of interrelation between the structural and transport characteristics in homogeneous liquid melt.

2. Experimental

The investigated melts were synthesized by melting of natural datolite concentrate and chemically pure SiO_2, Al_2O_3 and Nb_2O_5 in alundum crucible at temperature about 1773 K. The prepared glasses were then subjected to chemical analysis. The experiments on measurement of viscosity have carried out by a vibrating method [3] under lightly-oxidizing atmosphere within temperature range 1300-1800 K.

3. Results and Discussion

The polyterms of viscosity η - T show (Fig. 1) that all investigated melts are characterized by a large interval of hardening and sharp increase of η in crystallizing field. Using the approached equation

$$\eta = \eta_0 \exp\{E_\eta / RT\}, \qquad (1)$$

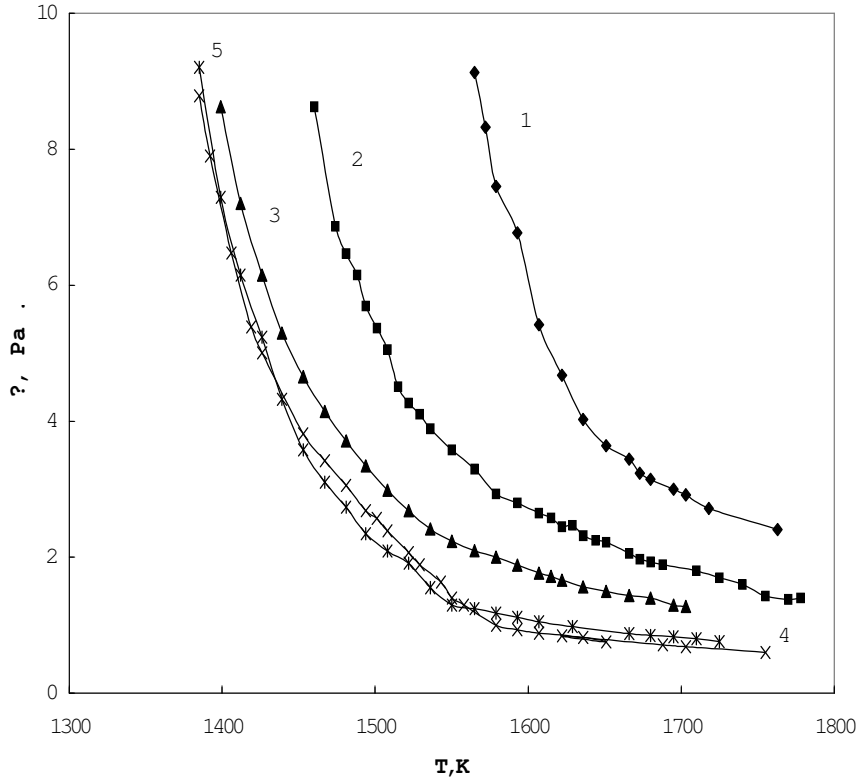

Fig. 1. Effect of temperature on viscosity of glass melt containing Nb_2O_5 in wt.%: 1 – 0, 2 – 3, 3 – 10, 4 – 20, 5 – 25.

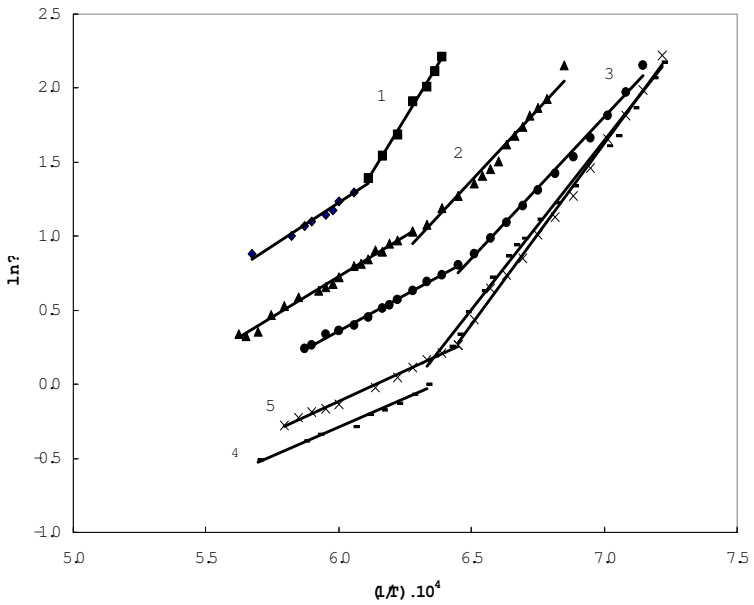

Fig. 2. Polyterms of viscosity for glass melt containing Nb_2O_5 in wt.%: 1 – 0, 2 – 3, 3 – 10, 4 – 20, 5 – 25.

Table 1. Effect of Nb_2O_5 on E_η и T_c in the system $CaO-SiO_2-B_2O_3-Al_2O_3-Nb_2O_5$

Nb_2O_5 ,wt. %	N_{SBA}	E_η , kJ/mole	T_c , K
0	0.703	113.0	1636
3	0.700	106.4	1593
10	0.685	64.8	1550
20	0.663	54.8	1558
25	0.651	55.1	1500

Table 2. The calculated (η^c) and experimental (η^{exp}) values of viscosity for the system $CaO-SiO_2-B_2O_3-Al_2O_3$

T, K	Composition, wt. %			
	32 CaO-46 SiO_2-9 Al_2O_3-13 B_2O_3		37.8 CaO-46.2 SiO_2-9.2 Al_2O_3-6.8 B_2O_3	
	η^{exp}, (Pa · c) · 10	η^c, (Pa · c) · 10	η^{exp}, (Pa · c) · 10	η^c, (Pa · c) · 10
1613	19.0	20.0	20.0	19.9
1623	18.5	18.8	18.5	18.1
1633	17.0	17.5	17.5	17.0
1643	16.0	16.3	16.5	15.7
1653	15.0	15.2	15.5	14.7
1663	13.5	14.2	14.0	14.1
1673	12.5	13.3	12.0	12.5

the activation energies of viscous flow E_η was determined from linear polyterms $\ln\eta$ - 1/T (Fig.2) and temperature of a beginning crystallization T_c was found on points of a break of the appropriate curves.

At temperatures less T_c the sizes of E_η were more than 200 kJ/mole. The increase of temperature resulted in essential decrease of activation energy of viscous flow up to values less than 115 kJ/mole.

At temperatures more T_c, corresponding to a homogeneous state of the melt, the values η and E_η decreased (Table 1) with increase of the contents Nb_2O_5. And, the rather sharp change of these

Table 3. Effect of Nb_2O_5 on viscosity in the system $CaO-SiO_2-B_2O_3-Al_2O_3-Nb_2O_5$

T, K	η^c, Pa · c					η^{exp}, Pa · c				
	Nb_2O_5, wt. %					Nb_2O_5, wt. %				
	0	3	10	20	25	0	3	10	20	25
1673	3.6	2.5	2.0	1.4	1.3	3.2	2.1	1.5	0.8	0.8
1693	3.4	2.2	1.8	1.3	1.2	2.9	1.8	1.4	0.7	0.8
1713	3.2	2.0	1.7	1.2	1.1	2.6	1.6	1.4	0.6	0.7
1733	2.7	1.7	-	1.1	1.0	2.4	1.5	-	0.6	0.6
1753	2.5	1.6	-	1.0	1.0	2.3	1.4	-	0.6	0.6
1773	2.3	1.4	-	0.9	0.9	2.2	1.3	-	0.5	0.6

parameters characterizing reduction of the sizes of structural units and (or) decrease of interaction energy between these units, was observed with increase of concentration Nb_2O_5 up to 10 wt.%. For concentration Nb_2O_5 10-25 wt. % the values η and E_η changed insignificantly that testified to close sizes of structural units in these melts.

The revealed alterations of viscosity and activation energy of viscous flow, apparently, can be caused by the changed sizes of basic units of viscous flow - silicon–boron-aluminum-oxygenous complexes and (or) formation of new niobium complexes with the smaller sizes and comparable amounts. To confirm the put forward assumptions the attempt of η calculation on one of variants of oxide melts polymeric model [4,5] was undertaken. The basic principle of this theory consists that oxide melts, in particular silicate, consist from linear and ramified anionic chains of various length which are taking place in dynamic balance:

$$Si_nO_{3n+1}^{2(n+1)-} + SiO_4^{4-} = Si_{n+1}O_{3n+3}^{2(n+2)-} + O^{2-} \quad (2)$$

or in the more simple form

$$2O^- = O^0 + O^{2-} \quad (3)$$

To calculate viscosity the little modified equation (1) was used. In the case of binary melts it has a kind [6]:

$$\ln\eta = A_\eta + E_\eta/RT + K_\eta \ln i', \quad (4)$$

where i' is average size of complex (or average number of net-forming atoms, for example Si, in this complex).

For multicomponent melt the expression (4) will be transformed in

$$\ln\eta = A_\eta' + E_\eta'/RT + K_\eta'\ln i', \quad (5)$$

where the average values of parameters A_η', E_η', K_η' [5] are calculated from the known data for binary systems.

It was recognized that niobium was an element forming anionic complexes with the sizes considerably smaller than silicon-oxygenous. Thus, the influence Nb_2O_5 on η is indirect, i.e. the additives Nb_2O_5 only reduce concentration SiO_2, that results to destruction of silicon-oxygenous anionic complexes. The given principle allows not take into account parameters A_η, E_η, K_η for binary niobium systems which to the present time are absent in the literature. Thus, the parameters A_η', E_η', K_η' were picked up by comparison of calculated and experimental data [7] on viscosity of the system similar researched.

The calculated and experimental data on viscosity of melt SiO_2-B_2O_3-Al_2O_3-CaO are given in the table 2 at temperatures 1613-1673 K. It is visible that with values E_η = 103.3 kJ/mole and A_η = -12 they are be satisfactorily coordinated. The specified values E_η and A_η futher were used for calculations of viscosity of melts containing Nb_2O_5.

The Table 3 show that the calculated and experimental η of niobium-containing oxide systems are satisfactorily coordinated for the contents Nb_2O_5 less than 20 % within temperatures 1673-1773 K. For concentration Nb_2O_5 20-25 % the divergence between calculated and experimental data are 30-45 % that is probably conditioned by essential increase of the contribution of niobium complexes as structural units of viscous flow in energy parameters.

Estimation of i' have been carried out by presenting E_η as the sum of the contributions of distortion of four forms of bonds: M^{2+}-O^{2-} (E_1), M^{2+}-O^- (E_2), Si-O^- (E'_2) and Si-O (E_3) [4] . For binary silicate melt this sum can be expressed as

$$E_\eta = N_O E_1 + 2\,[b\,(1- N_2) - N_O]\,E_{22} + [b\,(3N_2 -1) + N_O]\,E_3, \qquad (6)$$

where $b = i'\,(1 - N_O)/N_2$, $E_{22} = E_2 + E'_2$, N_O and N_2 are mole fraction of ions O^{2-} and SiO_2, accordingly.
Admitting that for $1/3 < N_2 < 1$ ions O^{2-} are absent, i.e. $N_O = 0$, expressions (6) can be resulted to:

$$E_\eta = i'\,[(2E_{22} - E_3)/N_2 + (3E_3 - 2E_{22})] = i'\cdot f\,(N_2) \qquad (7)$$

For the system SiO_2-B_2O_3-Al_2O_3-CaO-FeO-Nb_2O_5 it is possible to accept that $N_2 = N_{SBA}$ is the sum of mole fraction of acid oxides (SiO_2, B_2O_3, Al_2O_3) and i' is a amount of net-forming atoms (Si + B + Al) in complex anion of the average sizes being basic unit of viscous flow. In such case, taking into account that experimental E_η is possible rather well approximated by linear dependence
(Table 1) $E_\eta = k\,N_{SBA}$ and considering (7), we obtain:

$$\ln i'_1 + \ln f(NSBA) = \ln k_1 + \ln N_{SBA} \qquad (8)$$

$$\ln i'_2 + \ln f(NSBA) = \ln k_2 + \ln N_{SBA}, \qquad (9)$$

where i'_1 and i'_2 are average sizes anion with change of concentration Nb_2O_5 from 0 up to 10 wt. %.
According to experimental data $i'_1/\,i'_2 = k_1/\,k_2 = 9$.
Accepting that for 10-25 % Nb_2O_5 i'_2 = const, we find that $i'_1 = 9\,i'_2$.
Taking into account, that SiO_2 and CaO were in prevailling amount from acid and basic oxides, accordingly, in initial melt it was possible to accept [4], that E_{22} (in) = 5.0 - 5.5 and E_3 (in) = 2.0 - 3.0. Then, in initial melt i'_1 = 12 - 15, and the introduction Nb_2O_5 up to 10 % results to i'_2 = 1.4-1.6. That is, the additives Nb_2O_5 promote essential destruction of large silicon–boron-aluminum-oxygenous complexes up to anions containing 1 - 2 of net-forming atoms. Thus, according to the obtained results of measurements and

calculations of viscosity and earlier performed research of surface tension and density for the given system [8] it can be concluded, that niobium at these melts also displays complex-forming properties and, probably, will form anions of the small sizes NbO_x^{z-} described by weak external and strong internal bonds. According to spectroscopic researches [9] of firm glasses Li_2O-Nb_2O_5, Li_2O-RO-Nb_2O_5 (R-Ba, Ca, Mg) it is possible to assume, that niobium anions-monomers at large concentration Nb_2O_5 can be associated in more bigger complexes with fragments of octahedral structure.

4. Summary

Thus, the results of research have allowed experimentally to determine the transport characteristics glass melt and have shown, that the polymeric theory of oxide melts allowed rather well to approximate the obtained data.

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[1] Lepinskih, B. M. & Manakov, A. I. Physical Chemistry of Oxide and Oxide-Fluoride Melts. *Science. Moscow, 1977, 190 p.*

[2] Denisov, V. M., Belousova, N. V., Istomin, S. A., Bakhvalov, S. G. & Pastukhov, E. A Structure and Properties of Molten Oxides. *UD of RAS, Ekaterinburg, 1999, 498 p.*

[3] Solov'ev A. N. & Kaplun A. B. Vibrating Measurement Method of Viscosity of Liquids, *Science, Novosibirsk*, 1970, 127 p.

[4] Esin, O. A. *Proceedings of the Institute of Metallurgy*, USC of USSR, Sverdlovsk, 1978, N 31, pp. 3-20

[5] Novicov, V. K. *Rasplavy (Russ*.), 1987, v. 1, N 6, pp. 21-33.

[6] Novicov, V. K. & Nevidimov, V. N. *Izvestia VUZov. Chernay Metallurgia (Russ.),* 1999, N 11. pp. 9-12.

[7] Lepinskih, B. M.., Belousov, A. A., Bakhvalov, S. G., Vostryakov, A. A., Pastukhov, E. A. & Popova, E. A. Transport Properties of Metal and Slag Melts / Reference Book. *Metallurgia, Moscow,* 1995. 649 p.

[8] Krasikov, S. A., Upolovnikova, A. G., Timofeev, M. V., Chumarev, V. M. & Savushkina, O. G. *Extended Abstracts of XIX International Congress on Glass*: Scotland, Edinburg, July 1-6, 2001, pp. 322-323.

[9] Tatsumisago M., Hamada A., Minami T., & Tanaka M. *J. Non-Cryst. Solids*, 1983, v. 56, pp. 423- 428.