

STUDY OF ROCK GLASS VISCOSITY IN THE COURSE OF CRYSTALLIZATION BY A PENETRATION VISCOMETER

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Abstract

Time-temperature dependencies of viscosity of phase separated rock glass in the system $\text{Na}_2\text{O-K}_2\text{O-MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ have been measured by a penetration viscometer. The measurements were carried out isothermally at selected temperatures while the viscosity values varied in the range from $10^{8.4}$ to $10^{12.5}$ dPa.s.

On the detected time dependencies of viscosity, four subsequent characteristic regions were apparent where proceeding processes were observed in more details by x-ray diffraction and electron microscopy. These processes were preceded by phase separation which was very fast in the course of melted glass annealing and compensation of temperature in penetration viscometer, already.

It was detected that the processes are based on two crystallization stages for which the values of activation energy have been calculated.

Key words: crystallization, glass ceramic material, viscosity, penetration viscometer, activation energy

I. INTRODUCTION

Viscosity of glass is considerably varying with temperature and it is very sensitive to any changes of its structure, i.e. phase separation and crystallization. From a point of view of viscosity changes, both chemical composition of phases, and an arising texture, and ratio of phases volume is important, as well. At a relative concentrating of components decreasing the viscosity in matrix, the viscosity may even decrease, however, in most cases viscosity increases in the course of the process. A significant influence on a viscosity change has the arising texture, especially if spinodal decomposition or connection of secondary particles into the structure of two interconnected phases occurs. In these cases the viscosity may increase even by several orders. The viscosity change appears even in a two-phase system with solid spherical inclusions in glassy matrix, but it is much smaller than in the case of two interconnected phases.

Investigation of viscosity changes in the time dependence has been used already for a study of a number of phase separating and/or crystallizing glasses, for example opal glasses with fluorine and phosphorus content [1], borosilicate glasses [2], glass ceramic materials [3], or fused basalts [4].

During the study of properties of rock glasses based on granite and phonolite,

nucleated by CaF₂, an intensive phase separation and subsequent crystallization was observed (the investigated rock glass corresponds to the P-1383 glass in [5]). For completing the knowledge on these processes the penetration viscometer was used.

II. EXPERIMENTAL PROCEDURES

The rock glass has been prepared from glass melted in a pilot plant. This glass was re-melted in a PtRh crucible in electric furnace at 1490 °C during 70 minutes with stirring by PtRh stirrer, quenched by casting on an iron block to a shape of thin plate, thickness 4-10 mm and reannealed in electric furnace at 550 °C during 1 hour. The chemical composition of glass is given in Table 1.

Table 1 Chemical composition of rock glass (calculated from batch after correction to the real fluorine content)

Component	Content [wt. %]	Component	Content [wt. %]
SiO ₂	55.66	Fe ₂ O ₃	0.25
Al ₂ O ₃	15.17	FeO	0.82
CaO	11.35	MnO	0.01
MgO	7.35	TiO ₂	0.13
Na ₂ O	2.45	P ₂ O ₅	0.23
K ₂ O	3.89	F	4.65 ^x

^x - according to the chemical analysis (correction of sum to the fluorine content substituting oxygen

-1.96 wt.%)

Time dependencies of viscosity have been measured by a penetration viscometer. This viscometer is based on a principle of recording the time dependence of impression depth of loaded hemispherical penetration indenter to viscous body. The measurement gives absolute viscosity values in the range from 10⁸ to 10¹³ dPa.s and it is not necessary to introduce neither corrections nor experimental factors. The principle, description and verification of this apparatus function were published in 1980 [6].

A sample of glass in a form of polished disk was inserted into a preheated furnace of penetration viscometer and after 20 minutes the measurement started. This time, according to experimental verification, is necessary for the stabilization of sample and furnace temperature. For the following calculations this time of 20 minutes was subtracted. Further measurements were carried out after turning the sample in the apparatus always in 40th minute, and further on, every whole hour till the 6th hour from inserting the sample into the apparatus. In the case of fast viscosity changes, the intervals of measurement were shortened. The time dependence of viscosity at a constant temperature on the same sample was obtained by this procedure. Maximum temperature changes during measurement (from 20th minute) were ±1.5 °C. This procedure was repeated at 10 different temperatures.

The principle of proceeding processes was observed on selected heat treated samples by x-ray diffraction and transmission and electron scanning microscopy.

III. RESULTS

Time dependencies of rock glass viscosity obtained at different temperatures are given in Fig. 1a) to 1c). The curves of temperature dependence of viscosity for individual times of measurement are shown in Fig. 2. Three-dimensional diagram completely depicting the time-temperature dependence of viscosity is given in Fig. 3.

From the initial viscosity values (in the 20th minute from inserting the sample into the penetration viscometer) a viscosity curve of the phase separated glass has been calculated using the Vogel-Fulcher-Tammann (VFT) equation:

$$\log \eta = -0.792 + \frac{4538.8}{\tau - 333.1} \quad s = 0.025; \text{ validity from } 701 \text{ } ^\circ\text{C to } 826 \text{ } ^\circ\text{C} \quad (1)$$

where: η - viscosity [dPa.s]

τ - temperature [$^\circ\text{C}$]

With the use of viscosity values corresponding to the third region (i.e. nucleation region between the 1st and 2nd crystallization stage) a viscosity curve of partly crystallized glass has been analogically calculated in a form of VFT equation:

$$\log \eta = 9.298 + \frac{186.20}{\tau - 697.2} \quad s = 0.061; \text{ validity from } 771 \text{ } ^\circ\text{C to } 840 \text{ } ^\circ\text{C} \quad (2)$$

The results of crystalline phases identification of selected heat treated samples by x-ray diffraction are summarized in Table 2. The texture of samples in dependence on their heat treatment has been observed by transmission and electron scanning microscopy.

Table 2 Results of crystalline phases identification by x-ray diffraction in differently heat treated samples of rock glass

Heat treatment	Crystalline phases
723 °C/ 20 minutes	amorphous
723 °C/ 6 hours	F (few), P (few)
756 °C/ 6 hours	F, P
771 °C/ 6 hours	F, P
809 °C/ 6 hours	F, P, D (few), X (few)
840 °C/ 6 hours	F, P, D, X
900 °C/ 30 minutes	F, P, D, X

F - fluorite CaF_2 , P - fluorphlogopite $\text{KMg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$, D - pyroxene with structure similar to diopside $\text{CaMgSi}_2\text{O}_6$, X - unknown phase (characteristic diffraction lines from diffractometer, type Siemens U 13-008, radiation $\text{Cu K}\alpha$: 4.45/32; 3.82/44; 3.73/100; 2.862/52; 2.505/24; 1.869/18)

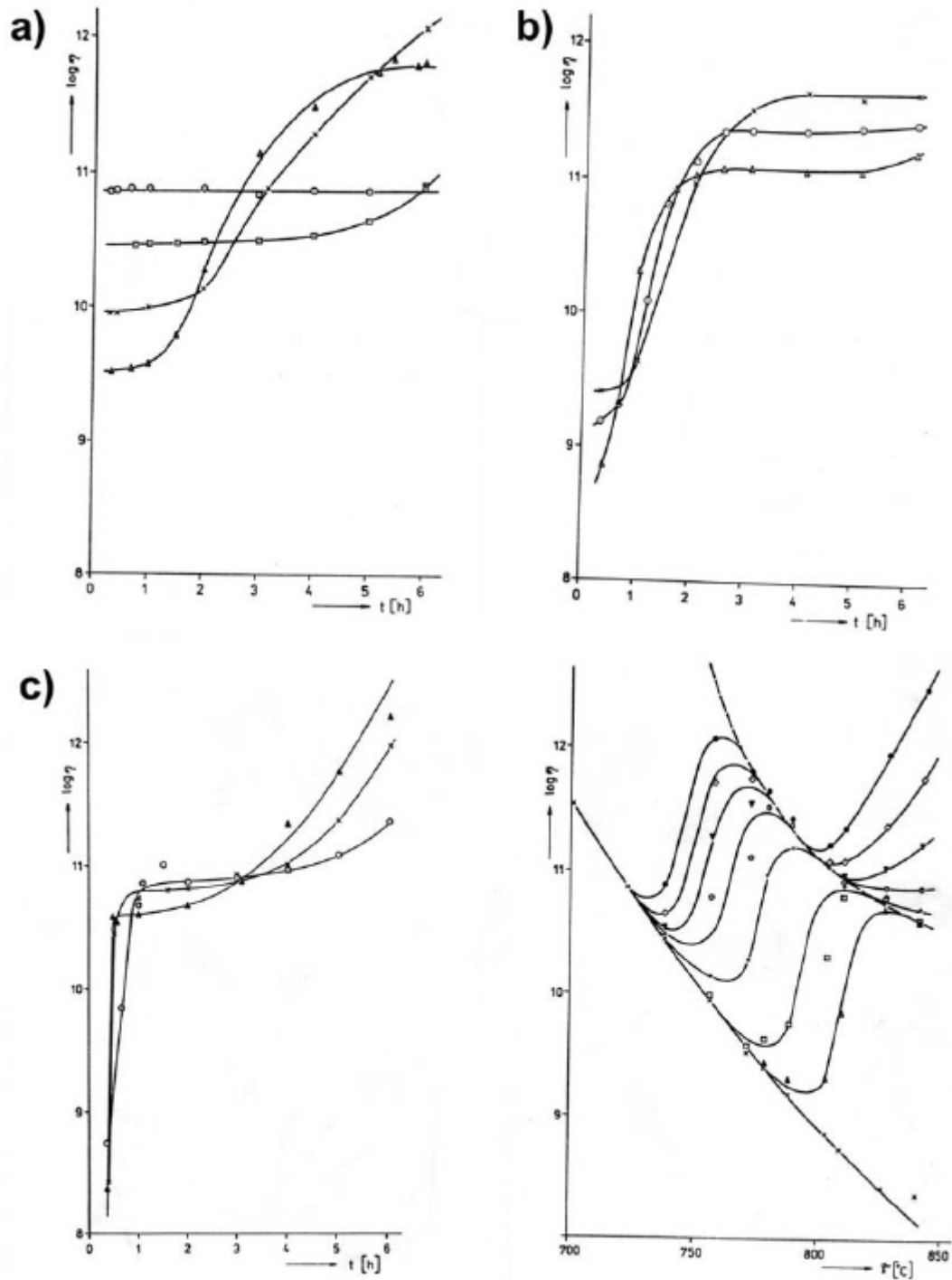


Fig. 1 Time dependence of rock glass viscosity
 a) ○ – 723 °C; □ – 738 °C; × – 756 °C; Δ – 771 °C
 b) × – 778 °C; ○ – 788 °C; Δ – 803 °C
 c) ○ – 809 °C; × – 826 °C; Δ – 840 °C

Fig. 2 Temperature dependence of rock glass viscosity with time isolines
 × – 20 min; Δ – 40 min; □ – 1 h; + – 2 h; ○ – 3 h; ▽ – 4 h; ◇ – 5 h; — – 6 h

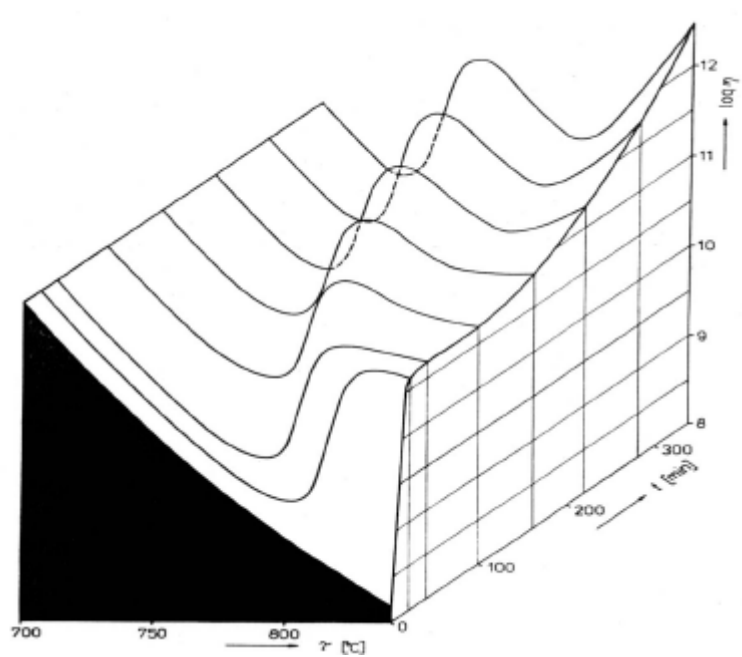


Fig. 3 Time-temperature dependence of rock glass viscosity (time without initial 20 minutes)

IV. DISCUSSION

Detected isothermal time dependencies of viscosity consisted of four consequential characteristic regions which were considerably differed at lower temperatures of measurement. With increasing measuring temperature the time of duration of individual regions shortened quickly and regions confluent.

With respect to a very fast phase separation of rock glass, the first observed region in which the viscosity did not noticeably change can be explained by eventual finishing of phase separation process, growth of the size of phase separated particles, and nucleation of crystallization of fluorite and fluorphlogopite. According to the results of x-ray diffraction and micrographs from transmission electron microscope the glass was phase separated and x-ray amorphous in the first region. Both initial reannealed sample, and sample tightly before beginning of measurement at the lowest temperature were in an advanced stage of phase separation in a form of small drops, size about $0.5 \mu\text{m}$. During the heat treatment at $723 \text{ }^\circ\text{C}$, the average size of phase separated regions was growing, only after 6 hours it reached size about $20 \mu\text{m}$.

The second region with a viscosity increase by two orders, was connected, according to the x-ray diffraction results, with contemporaneous crystallization of fluorite and fluorphlogopite. As it is seen in micrographs from transmission electron microscope, the crystallization was limited to phase separated particles, diameter about $20 \mu\text{m}$, which were crystallized inside to fine grains. In the interphase boundary were greater isometric crystals, size up to $2 \mu\text{m}$. Matrix surrounding the particles stayed homogenous without traces of crystallization. The viscosity increase in this region can be explained mainly by the fluorine and potassium bond from matrix into crystalline phases. These components as parts of glass considerably decrease the viscosity.

The third region where viscosity does not significantly change, corresponded to

the nucleation of the 2nd crystallization stage. According to the results of x-ray diffraction only fluorite and fluorphlogopite were present and they crystallized during the 1st crystallization stage. The rock glass in this region corresponded to the glass ceramic material with crystallized spherical particles, size about 20 μm and amorphous matrix around them, according to the micrographs from transmission electron microscope.

In the fourth region a crystallization of matrix occurred by contemporary precipitation of pyroxene crystals with structure similar to diopside and an unknown phase which did not correspond with its x-ray diffraction spectrum to any up to now described crystal phase occurring in this type of glass ceramic materials. Viscosity increased gradually even above the working range of the apparatus.

From the dependence of time necessary for reaching a half value of viscosity increase in the second region on the reciprocal value of absolute temperature (Fig. 4), an activation energy value of the 1st crystallization stage has been calculated. The theoretical interpretation of this energy is not explicit, since several processes can proceed at the same time in the system (phase separation, diffusion, nucleation and crystallization of two phases). The calculated value of this energy (469 kJ mol^{-1}) is near to the published activation energy value of nucleation of aluminium free fluorphlogopite crystallization preceded by phase separation (481 kJ mol^{-1}) [3]. For aluminium free fluorphlogopite crystal growth, however, the same author has detected considerably higher activation energy value (632 kJ mol^{-1}). The calculated activation energy value of the 1st crystallization stage is near to the activation energy value of viscous flow, as well, according to values of initial viscosity in a corresponding temperature range (445 kJ mol^{-1}). By a calculation of activation energy values from the start and the end of viscosity changes during the second region, similar values 422 kJ mol^{-1} and 430 kJ mol^{-1} , resp., were obtained. That shows the same mechanism in the course of the whole second region.

From the time dependence of the viscosity increase start in the fourth region on the reciprocal value of absolute temperature (Fig. 4), the activation energy value of the 2nd crystallization stage (233 kJ mol^{-1} using the time from the beginning of the measurement or 203 kJ mol^{-1} using the time from the end of the second region), has been calculated. These values considerably deviate from activation energy values of the 1st crystallization stage and even from activation energy of viscous flow according to the viscosity values corresponding to the third region (389 kJ mol^{-1}) and they are approximating to the activation energy value found at monomineral crystallization of pyroxene in fused basalt from Oharice (245 kJ mol^{-1}) [7].

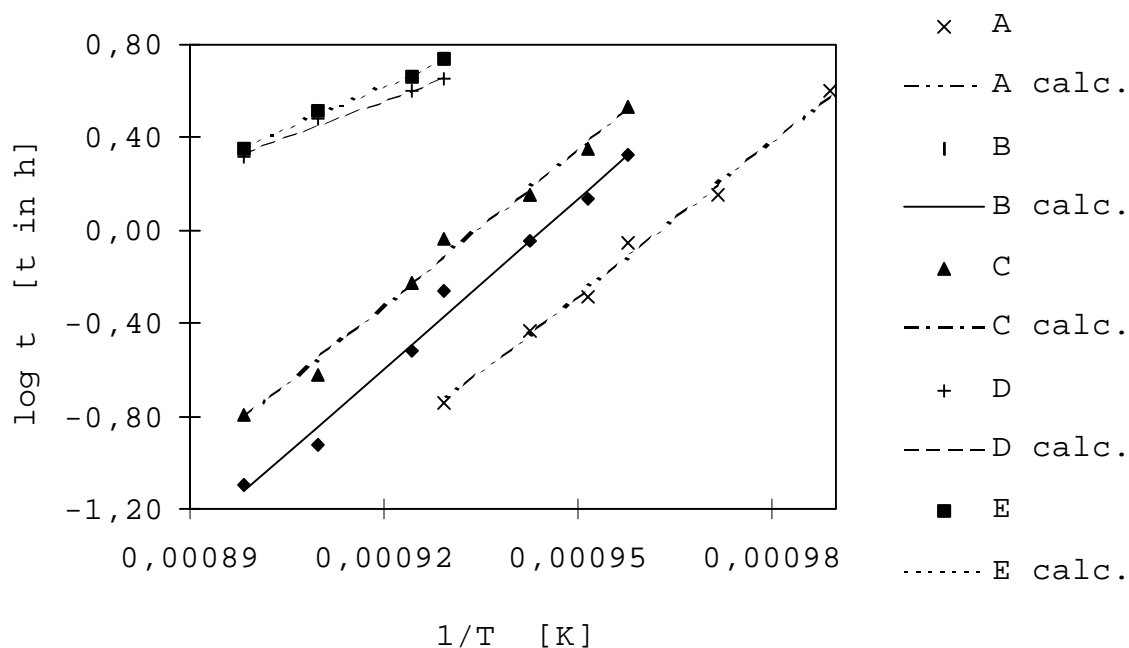


Fig. 4 Time dependencies on temperature for calculations of activation energy values
 Time necessary for change on isothermal viscosity curve:
 1st crystallization stage: A - start, B - mean, C - end
 2nd crystallization stage: D- start (time from the end of the 1st crystallization stage),
 E - start (time from the beginning of measurement)

V. CONCLUSIONS

The rock glass was very quickly phase separated in a form of spherical particles. Even before the beginning of the measurement the glass was phase separated and the particle size was about 0.5 μm . In the first region during which the viscosity did not change considerably, a growth of size of phase separated particles up to the size about 20 μm occurred, and contemporary a nucleation of crystallization of fluorite and fluorphlogopite appeared. In the second region the viscosity increased by two orders and crystallization of both mentioned phases in phase separated particles proceeded. Matrix did not crystallize and stayed glassy. The viscosity increase can be mainly explained by a decrease of fluorine and potassium content in matrix by a bond into crystalline phases with a content of these elements. A considered influence of the content of crystallized (originally phase separated) particles on viscosity in consequence of mechanical action as a suspension would be considerably lower. The measured material behaved, further on, like a glass melt after the 1st crystallization stage, only with shifted viscosity curve.

In the third region, without any significant viscosity changes, only nucleation of crystallization of phases in matrix occurred. The fourth region with a considerable viscosity increase was characteristic just by the crystallization of pyroxene with structure similar to diopside and by the unknown phase in matrix.

Activation energy of processes connected with both crystallization stages differed very significantly. For the 1st crystallization stage there was calculated the activation energy value 469 kJ mol^{-1} near both published activation energy value of

nucleation of crystallization of aluminium free fluorphlogopite preceded by phase separation (481 kJ mol^{-1}) [3], and activation energy of viscous flow in the corresponding temperature range (445 kJ mol^{-1}). Activation energy for the 2nd crystallization stage (233 or 203 kJ mol^{-1} according to the method of calculation) is near to the published activation energy of monomineral crystallization of pyroxene in fused basalt (245 kJ mol^{-1}) [7].

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