Silikáty 26, s. 251—259 (1982)

MEASURING VISCOSITY WITH THE PENETRATION VISCOMETER I

A Study of the Viscosity of Industrially Fused Basalts in the Course of Separation and Starting Crystallization

PETR EXNAR, JAN VOLDÁN

State Glass Research Institute, Škroupova 957, 501 92 Hradec Králové

Received 7. 4. 1981

Viscosity was measured of basalt glasses of industrially fused olivinic basalts (Slapany and Nová Baňa) on the penetration viscometer in the temperature range 660—780 °C using time dwells of 20, 40, 60, 120, 180, 240, 300 and 360 min. The viscosity values were found to vary from 10^8 up to over 10^{12} dPa.s. The course of viscosity curves contributed to better understanding of the complex course of nucleation in basalt glasses.

INTRODUCTION

The method of viscosity measurement on a penetration viscometer, which has been described in the present periodical [1] was applied to the range of nucleation and initial crystallization of basalt glasses, obtained by fusion of olivinic basalts from Slapany and Nová Baňa, on which temperature-time viscosity measurements were carried out in the 660—780 °C temperature range.

EXPERIMENTAL

The specimens employed

The two initial basalt glasses were prepared by melting the natural rocks in PtRh crucibles at 1500 °C. The total time of melting amounted to 3 hours, wherein for the last about 100 minutes the melts were efficiently agitated with a PtRh mixer to achieve perfect homogenization. After casting onto a steel grate the specimens of the glasses obtained were cooled for 1 hour at 600 °C (for the Slapany raw material) and for 1 hour at 550 °C (for the Nová Baňa material).

The measuring procedure

The specimen in the form of a polished disk of basalt glass was placed in a tempered furnace of the penetration viscometer and measurement was started after 20 minutes. This period of time, as verified experimentally, is necessary for equalizing the specimen and furnace temperature. The subsequent measurements were always carried out after turning the specimen in the apparatus, at first after 40 minutes and subsequently after each hour up to 6 hours after placing the specimen in the apparatus. The method ensured determination of the time dependence of viscosity at constant temperature on one and the same specimen. The procedure was repeated at 12 various temperatures in the case of the Slapany basalt glass, and at 14 various temperatures in that of the Nová Baňa basalt glass.

Temperature dependence of viscosity

The first viscosity values measured (i.e. those obtained within 20 minutes after placing into the apparatus) were used for calculating the viscosity curve. The constants of the approximation Vogel—Fulcher—Tammann equation (further on the VFT equation), holding for the Slapany basalt glass, are listed in Table I. Viscosity of the Nová Baňa basalt glass specimen was additionally measured with a ball viscometer at 1200 °C. The respective results and the data obtained with the penetration viscometer were used for computing the constants of the VFT equation describing the viscosity of the Nová Baňa basalt glass (without the effect of separation and crystallization) in the wide temperature range of 660 to 1200 °C. The values of constants are likewise listed in Table I.

Table I

The constants of the Vogel-Fulcher-Tammann equation for measuring the viscosity of basalt melts (holds for glassy state and homogeneous melts)

Basalt	A	B [°C]	t_0 [°C]	Validity range [°C]
Slapany	—0.67	3195.6	415	660—780
Nová Baňa	—3.00	4565.9	358	660—1200

Notice:

The Vogel-Fulcher-Tammann equation:

$$\log \eta = A + \frac{B}{t - t_0}$$

where t is temperature [°C]

A, B, t_0 are constants

Measuring results

The essential shape of the time dependence of viscosity at constant temperature is identical for both basalt glasses. Its course is schematically shown in Fig. 1. Following an initial delay, represented by region A, where viscosity undergoes no distinct

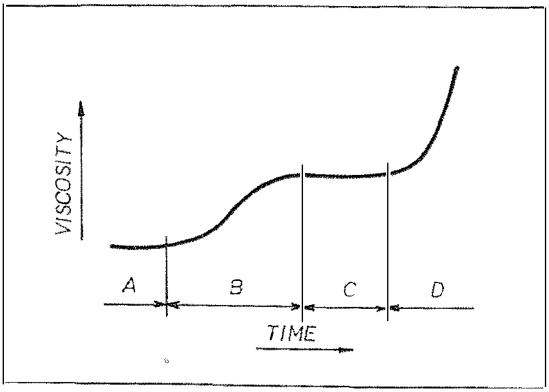

Fig. 1. Schematic plot of the isothermic time dependence of the viscosity of basalt melts.

changes, there follows region B in which viscosity increases by 0.3 to 0.7 order of magnitude. Then follows the C region, where viscosity is virtually constant or shows a mild increase. In the subsequent D region, the viscosity increases very rapidly to a value over 10^{13} dPa . s, that is beyond the working range of the viscometer. The low-temperature isothermic measurements yielded a constant viscosity of the basalt glass throughout the entire 6 hours, which corresponded to the A region. The rate of the processes increased with increasing temperature of the isothermal measurements, and the 6-hour measurements gradually included the further characteristic regions according to Fig. 1, until at the highest isothermic measuring temperatures the increase in viscosity in terms of time was so fast that phase D was reached within as little as 90 minutes from placing the specimen in the apparatus.

The mutual comparison of the effects of time and temperature of the isothermic tests on the changes in viscosity for the Slapany basalt glass is best illustrated by Figs. 2 and 3. The analogous diagrams for the Nová Baňa basalt glass (Figs. 4 and 5) are very similar.

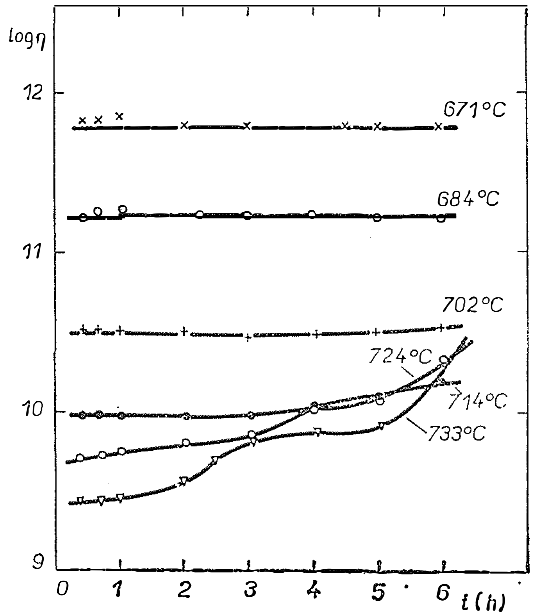

Fig. 2. Isothermic time dependences of the viscosity of the Slapany basalt melt at lower temperatures.

The temperature dependence of viscosity for both basalt glasses in the 660—780 °C temperature range is plotted in Figs. 6 and 7 together with the time isolines for 40 minutes, 1, 2, 3, 4, 5 and 6 hours. Their course indicates that the initial viscosity values (measured 20 minutes after placing the specimen in the apparatus) would somewhat deviate from the expected course only at the highest measuring temperatures (781 or 767 °C). Finally, Fig. 8 shows a three-dimensional diagram of the viscosity of the Slapany basalt glass in terms of temperature and time.

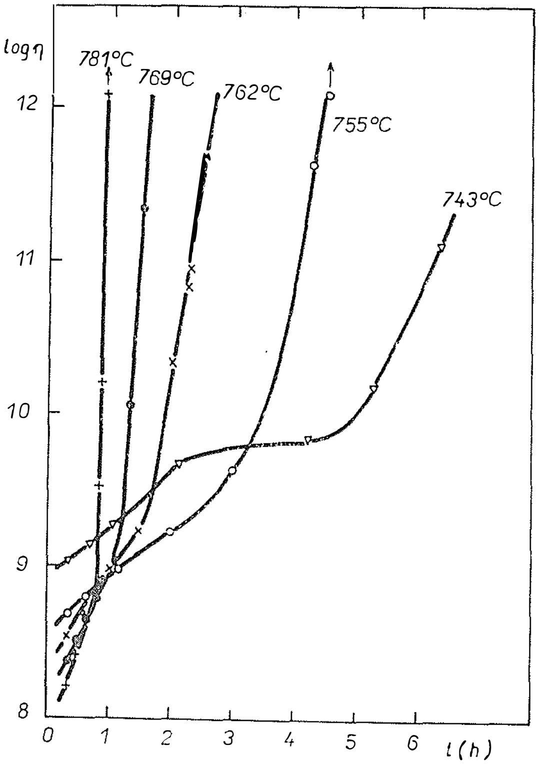

Fig. 3. Isothermic time dependences of the viscosity of the Slapany basalt melts at higher temperatures.

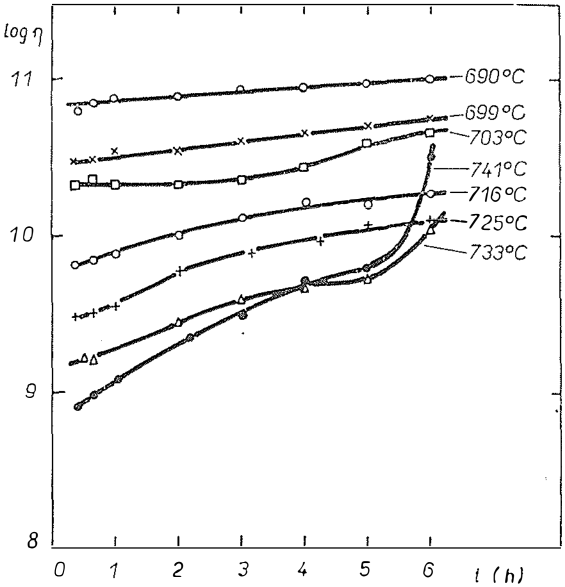

Fig. 4. Isothermic time dependences of the viscosity of the Nová Baňa basalt melt at lower temperatures.

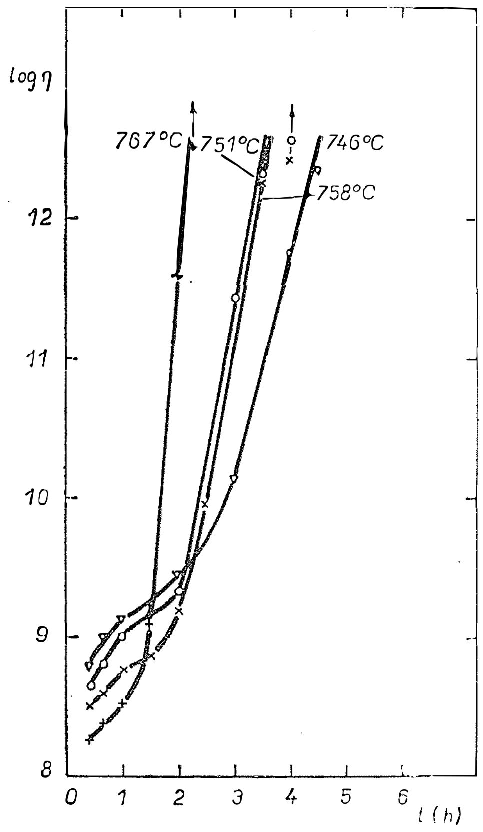

Fig. 5. Isothermic time dependences of the viscosity of the Nová Baňa basalt melt at higher temperatures.

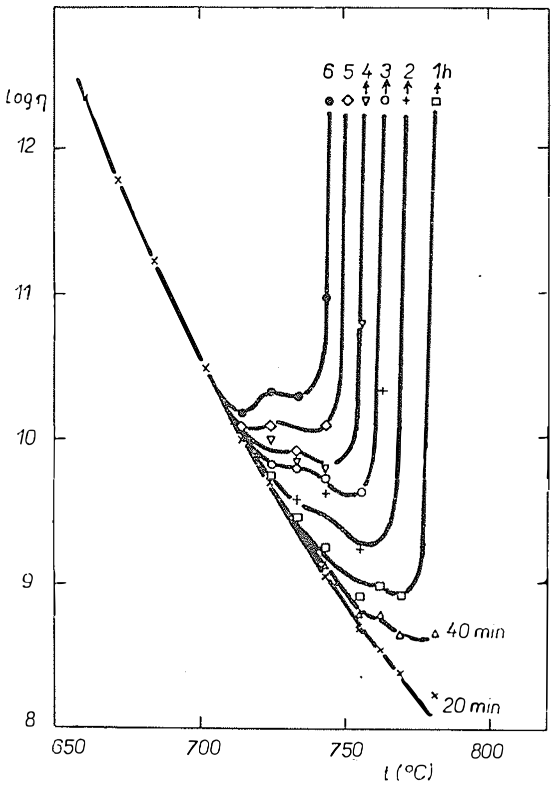

Fig. 6. Temperature dependence of the viscosity of the Slapany basalt melt with time isolines.

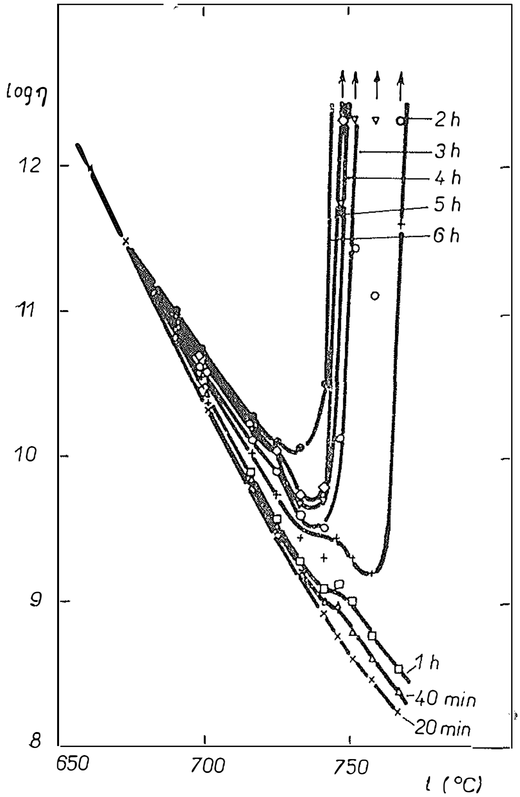

Fig. 7. Temperature dependence of the viscosity of the Nová Baňa basalt melt with time isolines.

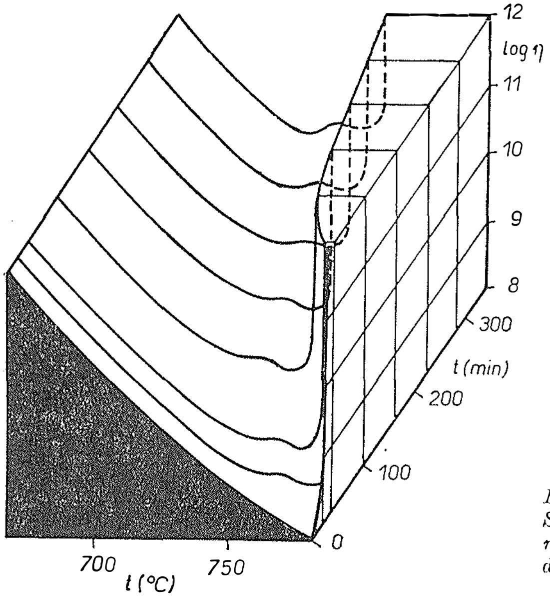

Fig. 8. Dependence of the viscosity of the Slapany basalt melt on temperature and time. The time is plotted without the introductory 20 minutes necessary for tempering the specimen.

INTERPRETATION OF RESULTS

The initial dwell (region A), where no crystalline phase has been detected by X-ray analysis and no inhomogeneity has been determined by means of the electron microscope, represents the so-called "incubation period" of nucleation due to separation, i.e. the time required for rearrangement of the viscous melt structure necessary for creating the conditions for the expected reaction, in this instance separation of phases at the given temperature. According to Mazurin [2], viscosity is a highly sensitive property for the study of such structural changes. In both basalts studied the temperature region in question is that above the softening point of basalt glass (i.e. above 670—675 °C), where $\log \eta \approx 11$. The course of viscosity curves shows that the lower the heat treatment temperature (i.e. the higher the viscosity) the longer the incubation period τ. For instance, with the Slapany basalt at $t = 714$ °C, $\tau = 3$ hours, at 743 °C, $\tau =$ about 1 hour and at 743 °C, τ is shorter than 20 minutes.

Region B involves the separation proper, i.e. separation of the initial homogeneous glass melt into two phases, as has been confirmed in the previous study [3] and by the electron micrographs (Figs. 9 and 10). The basalts in question exhibit separation in the viscosity range of 10^9 — 10^{10} dPa. s. The viscosity of separated glasses is decisively determined by the viscosity of the continuous matrix, being only sligtly affected by the separated droplets. As the viscosity of separating basalt glasses increases it seems obvious that viscosity-reducing oxides become mostly concentrated in the droplets. This is probably the case of FeO, Fe_2O_3, CaO, MgO and Al_2O_3. Compared to to other separating glasses (e.g. borosilicate glasses), the viscosity increase during the isothermic dwell in the separation range is relatively small (by 0.3 to 0.7 order of magnitude), obviously increasing with increasing separation temperature. The measuring indicates that the lower the melt viscosity, the higher the separation into the two phases: at viscosity $\log \eta = 10$ (i.e. at 714 °C) the separation will take more than 3 hours, whereas at $\log \eta = 9$ (i.e. at 743 °C) a state of equilibrium is attained within less than 2 hours.

The measurements performed have shown that the actual nucleation brought about by separation of phases in the basalts in question proceeds best in the temperature range of 700 to 750 °C (the optimum temperature being between 720 and 740 °C) which is a temperature higher by about 50 °C than the temperature specified for foreign basalts in literature [4], [5]. The nucleation dwell takes 2—3 hours. Determination of these values represents a practical contribution to the available knowledge, in particular with respect to the development of petrositals.

In the C region, the viscosity undergoes no practical changes during the isothermic heat teatment, which indicates that the separation has essentially been concluded and a state of equilibrium has been established. According to X-ray diffraction studies, magnetite nuclei are developed in the separated droplets enriched with Fe oxides.

The D region is characteristic of the crystallization proper. The study of slag-sitals has shown that when the melt viscosity drops below 10^9 dPa.s, a very rapid crystallization takes place [6]. In the case of basalts, when the heat treatment temperature exceeds 750 °C, crystallization occurs immediately, namely abrupt growth of pyroxen on the magnetite crystals being formed (Fig. 10). In view of the isomorphous substitution, which is characteristic for pyroxene, the crystallization is taken part in by almost all the oxidic melt components, so that both crystallization and the increase in viscosity are very rapid, the latter being raised by more than 4 orders of magnitudes within less than 1/2 hour. The total time of nucleation (incubation period τ, separtion proper and the subsequent formation of magnetite nuclei) is thus shortened to a period of 1/2 to 3/4 hour.

CONCLUSION

The results obtained can be summarized as follows:

1. Using time-temperature measurement of viscosity of basalt glasses it has been found that nucleation proper and the starting crystallization consists of four subsequent separate processes which tend to fuse into one at higher temperatures:
a) incubation separation period,
b) separation of phases, proper,
c) formation of magnetite nuclei,
d) growth proper of pyroxene crystals on magnetite nuclei.

2. Regions of suitable temperatures and the length of time dwells have been established for all these processes, which allows to suggest a rational procedure for heat treatment aimed at nucleation and controlled crystallization for the purpose of obtaining fine-grained petrositals.

3. Both basalt melts in question are similar in the course and character of the phenomena eventually providing the final fine-grained crystallization.

4. The results have proved the possibility of using the penetration viscometer for studying the progress of separation, nucleation and initial crystallization of basalt melts, as their viscosity reacts sensitively already to the initial stages of these phenomena.

References

[1] Exnar P., Hrubá M., Uhlíř J., Voldán J.: Silikáty *24*, 169 (1980).
[2] Mazurin O.: *Liquation Phenomena in Glasses. P.* 30—35 (in Russian), AN USSR, Izdat. Nauka, Leningrad 1969.
[3] Voldán J.: Sklář a keramik *30*, 180 (1980).
[4] Beall G. H., Rittler H. L.: Corning Glass Works, US P 3,557,575, appl. 26. 1. 1971.
[5] Tarlakov Ju. P., Venzel L. I., Chlodnova E. F.: *Proceedings of the Symposium on Catalyzed Crystallization of Glasses* (in Russian), Moscow, 21.—23. 11. 1978, p. 50—51.
[6] Bondarev K. T.: Slag-Sital — the Material of the Future. *Proceedings IX. ICG*, Versailles, 27. 9.—2. 10. 1971, p. 1237—1250.

MĚŘENÍ VISKOZITY PENETRAČNÍM VISKOZIMETREM

I. Studium viskozity provozně tavených čedičů v průběhu odmísení a počínající krystalizace

Petr Exnar, Jan Voldán

Státní výzkumný ústav sklářský, Hradec Králové

Byly proměřeny časově teplotní závislosti viskozity čedičových skel provozně tavených čedičů Slapany a Nová Baňa na penetračním viskozimetru. Měření byla provedena izotermicky při zvolených teplotách v rozmezí 660 až 780 °C po předchozím temperování 20 min až 6 h. Hodnoty viskozity při tom kolísaly v rozsahu 10^8 až nad 10^{12} dPa.s.

Z průběhu viskozitních křivek byl blíže pochopen složitý průběh nukleace studovaných čedičových skel skládající se ze čtyř po sobě následujících samostatných dějů, které za zvýšených teplot splývají:
a) inkubační perioda odmísení, kdy se viskozita nemění (oblast *A*);
b) vlastní odmísení fází, charakterizované zvyšující se viskozitou (oblast *B*);
c) vznik nukleačních zárodků magnetitu (oblast *C*);
d) vlastní růst krystalů pyroxenu na zárodcích magnetitu, kdy se viskozita prudce zvyšuje o několik řádů (oblast *D*).

Obr. 1. Schematický nákres izotermické časové závislosti viskozity čedičových tavenin.
Obr. 2. Izotermické časové závislosti viskozity čedičové taveniny Slapany při nižších teplotách.
Obr. 3. Izotermické časové závislosti viskozity čedičové taveniny Slapany při vyšších teplotách.
Obr. 4. Izotermické časové závislosti viskozity čedičové taveniny Nová Baňa při nižších teplotách.
Obr. 5. Izotermické časové závislosti viskozity čedičové taveniny Nová Baňa při vyšších teplotách.
Obr. 6. Teplotní závislost viskozity čedičové taveniny Slapany s časovými izoliniemi.
Obr. 7. Teplotní závislost viskozity čedičové taveniny Nová Baňa s časovými izoliniemi.
Obr. 8. Závislost viskozity čedičové taveniny Slapany na teplotě a čase. Čas je vynesen bez úvodních 20 minut, nutných k vytemperování vzorku.
Obr. 9. Snímek z elektronového mikroskopu z lomové plochy čedičového skla Nová Baňa, temperovaného 6 h při 725 °C (TEM, neleptáno).
Obr. 10. Snímek z elektronového mikroskopu z lomové plochy čedičového skla Nová Baňa, temperovaného 6 h při 741 °C (TEM, neleptáno).

ИЗМЕРЕНИЕ ВЯЗКОСТИ С ПОМОЩЬЮ ВИСКОЗИМЕТРА ВДАВЛИВАНИЯ

1. Исследование вязкости плавленых промышленным путем базальтов во время расслоения и начинающей кристаллизации

Петр Экснар, Ян Волдан

Государственный научно-исследовательский институт стекла, Градец Кралове

Измеряли временно температурные зависимости вязкости базальтовых стекол плавленных промышленным путем базальтов Слапаны и Нова Баня с помощью вискозиметра вдавливания. Измерения проводили изотермически при подобранных температурах в пределах 660—780 °C после предварительного темперирования от 20 минут до 6 часов. Величины вязкости колебались в пределах от 10^8 до 10^{12} дПа. с. и выше.

Ход кривых вязкости помагает более подробно понять сложный ход нуклеации исследуемых базальтовых стекол, состоящих из четырех последующих друг за другом самостоятельных процессов, которые при повышенных температурах совпадают:
а) инкубационный период расслоения, когда вязкость не изменяется (область *A*);
б) собственное расслоение фаз, характеризующееся повышающейся вязкостью (область *B*);
в) возникновение зародышей нуклеации магнетита (область *C*),
г) собственный рост кристаллов пироксёна на зародышах магнетита, когда вязкость резко повышается на несколько порядков (область D).

Рис. 1. Схема изотермической временной зависимости вязкости базальтовых расплавов.
Рис. 2. Изотермические временные зависимости вязкости базальтового расплава Слапаны при более низких температурах.
Рис. 3. Изотермические временные зависимости вязкости базальтового расплава Слапаны при более высоких температурах.
Рис. 4. Изотермические временные зависимости вязкости базальтового расплава Нова Баня при более низких температурах.
Рис. 5. Изотермические временные зависимости вязкости базальтового расплава Нова Баня при более высоких температурах.
Рис. 6. Температурная зависимость вязкости базальтового расплава Слапаны с временными изолиниями.
Рис. 7. Температурная зависимость вязкости базальтового расплава Нова Баня с временными изолиниями.
Рис. 8. Зависимость вязкости базальтового расплава Слапаны от температуры и времени. Время изображено без первоначальных 20 минут, необходимых для темперирования пробы.
Рис. 9. Съемка из электронного микроскопа из поверхности преломления базальтового стекла Нова Баня, темперированного 6 часов при 725 °C (TEM, нетравлено).
Рис. 10. Съемка из электронного микроскопа из поверхности преломления базальтового стекла Нова Баня, темперированного 6 часов при 741 °C (TEM, нетравлено).

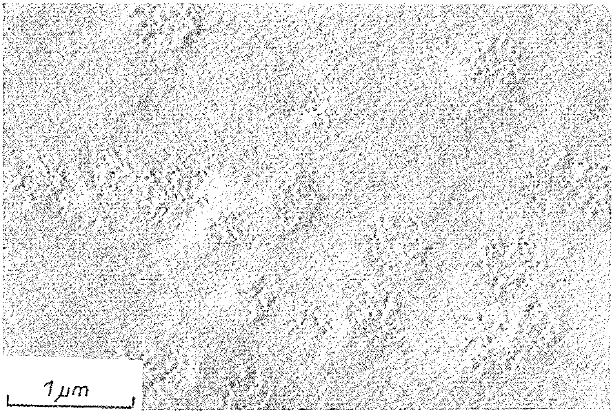

Fig. 9. Electron micrograph of a fracture surface of the Nová Baňa basalt glass tempered for 6 hours at 725 °C (TEM, not etched).

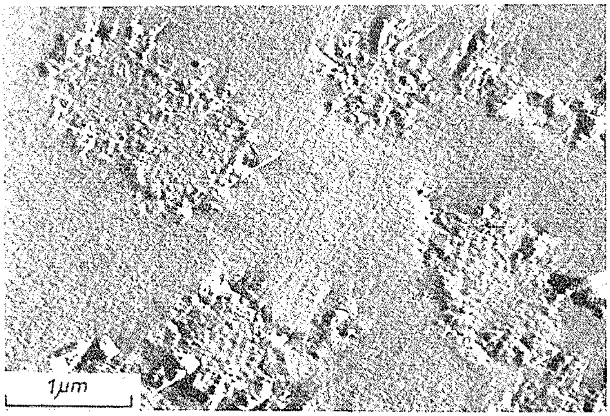

Fig. 10. Electron micrograph of a fracture surface of the Nová Baňa basalt glass, tempered for 6 hours at 741 °C (TEM, not etched).