Původní práce

NUCLEATION OF Li$_2$O . 2 SiO$_2$ FROM MELT AND FROM GLASS

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*Nucleation of the Li$_2$O . 2 SiO$_2$ phase from glass shows a distinct depend-
ence on melting temperature while there is just a minute dependence on melting
temperature for nucleation of the phase from melt. The largest amount of
nuclei is formed in glass if this is heated closely above the melting temperature
of the Li$_2$O . 2 SiO$_2$ phase. Monomers play a major part in the nucleation
process in melts whereas polymerized units behave in this way in glass.*

INTRODUCTION

The paper is concerned with the effect of melting temperature on nucleation of the
Li$_2$O . 2 SiO$_2$ phase on cooling down from melt as well as on heating up of glasses
of the same composition. The nucleation was followed indirectly by the DTA method
according to Marotta et al. [1, 2].

Nucleation in glass proceeds under conditions different from those of nucleation
in melt. There are differences particularly in temperature, viscosity and structure
of the parent phase. In melt, in a liquid medium, nucleation takes place close below
the melting temperature or the liquidus temperature. In the case of glass, the tem-
perature maximum of the steady state nucleation rate occurs in the region of its
transformation temperature.

According to Kirkpatrick [3], nucleation in silicate melts depends above all on the
molecular processes taking place at the boundary cluster (or nucleus)—parent phase.
The main factors involved are the type of units (SiO$_4^{-4}$, SiO$_3^{-2}$, SiO$_2$, SiO^{+2}) which
become attached to the cluster, and the number of interrupted Si—O bonds resulting
from this. The kinetic barrier of the unit-to-cluster attachment is the lower, the
lower the number of Si—O bond interruptions the process requires.

The study had the aim to assess nucleation of the Li$_2$O . 2 SiO$_2$ phase under various
conditions from the standpoint of Kirkpatrick's theory.

EXPERIMENTAL

Glass having the stoichiometric composition Li$_2$O . 2 SiO$_2$ and prepared in the
usual way [4] was used in the study. Crystallization of glasses and melts was followed
by means of the DTA 404 apparatus by Netzsch using Pt crucibles and samples
of constant weight (0.394 g). The DTA measurements were carried out in two ways:

a) crystallization from melt—the samples were held for 2 hours at 1 030—1 500 °C
directly in the DTA apparatus and then followed by to DTA at a cooling rate of
20 °C min^{-1}.

b) crystallization of glass—the samples were kept for 2 hours in an electric furnace

at 1 030—1 500 °C in Pt crucibles of the DTA apparatus. The crucible with the sample was then rapidly quenched in an ice-water mixture to produce glass. The DTA was then performed at a heating rate of 20 °C min⁻¹.

The DTA curves of the crystallization of glasses (Fig. 1) as well as of melts (Fig. 2) are very distinct, showing well defined peak temperatures (Tables I and II) and with melts also the onsets of exothermic deflections. The reproducibility of the experi-
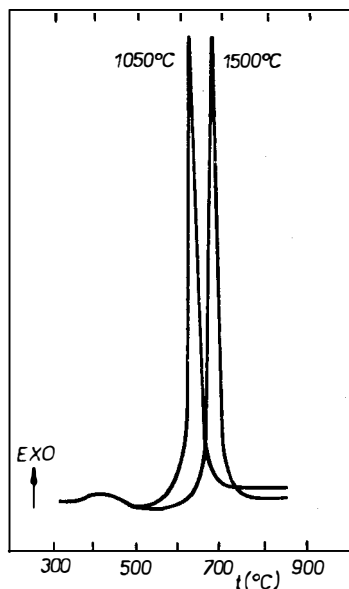

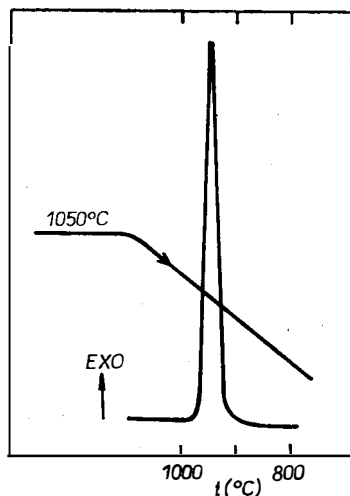*Fig. 1. DTA curves of the crystalliza-tion of glasses having the composition Li₂O . 2 SiO₂, melted for 2 hours at the given temperatures (1 050°C, 1 500 °C).*

Fig. 2. DTA curve of the crystalliza-tion of melt having the composition Li₂O . 2 SiO₂ which was kept for 2 hours at 1 050 °C.

Table I

Parameters of DTA curves of the crystallization of melts prepared at temperature t; t_m is the DTA crystallization peak temperature, t_z is the temperature of deflection onset, Δt is the undercooling ($t_t = 1\ 034$ °C)

t [°C]	t_z [°C]	t_m [°C]	Δt [°C]
1 500	985	955	49
1 400	985	955	49
1 200	980	950	54
1 100	980	950	54
1 050	980	950	54
1 030*)	—	—	—

*) crystalline phase

ments was ± 3 °C. The temperatures of the peaks are used in the calculation of the nucleation parameters.

The identical crystalline phase of $Li_2O . 2 SiO_2$ was identified in the crystallized melts and glasses by powdered X-ray phase analysis.

Table II

Dependence of the relative number of nuclei, N/N_0, and the DTA crystallization peak temperature t_m, on the glass melting temperature t

t [°C]	t_m [°C]	N/N_0
1 500	695	1.0
1 350	680	2.1
1 200	660	6.0
1 100	645	13.5
1 050	635	23.6
1 030*)	—	—

*) crystalline phase

ANALYSIS OF RESULTS

Under the standard conditions of DTA crystallization of the glass or melt, the temperature position of the DTA peak is a function of the number of nuclei in the sample [1, 2]. In the analysis at increasing temperature (crystallization of glass), a shift of the DTA peak towards lower temperatures corresponds to an increased number of nuclei in the sample. The opposite applies to crystallization of melts (on cooling); a higher number of nuclei is indicated by higher temperatures. Crystallization from melt will proceed at a lower undercooling, closer to the melting or liquidus temperature.

The relative number of nuclei, N/N_0, is a function of temperatures T_m [1, 2]:

$$\ln N/N_0 = \frac{E_c}{R} \left(\frac{1}{T_m} - \frac{1}{T_m^0} \right), \tag{1}$$

where E_c is the activation energy of crystal growth,

T_m, T_m^0 are the crystallization peak temperatures of the samples.

The temperature of 968.2 K was chosen for T_m^0 (Table II). It is the peak temperature of the DTA curve due to crystallization of glass which was melted at the highest temperature of 1 500 °C. The lowest number of nuclei was formed in this sample during the DTA, and the sample therefore crystallized at the highest temperature.

Equation (1) allows the relative number of nuclei, N/N_0, to be calculated for a known value of E_c. Use was made of the value 385 kJ mole^{-1} presented by Freiman and Hench [7].

The values of the relative numbers of nuclei N/N_0 depend on the temperatures of melting of the glasses (Table II). In glass melted close above the melting temperature of the $Li_2O . 2 SiO_2$ phase there arise, under identical conditions, about 24 times more nuclei than in glass melted at 1 500 °C.

DISCUSSION

In the crystallization of melts, the temperatures of the DTA peaks depend only little on the temperature at which the samples have been melted; the differences established are at the limit of the measuring error. This result may have been affected by the measuring method which did not allow the rate of cooling to be increased above 20 °C min^{-1}. As a consequence, the high-temperature structures had probably not survived the cooling down to the crystallization temperatures, i.e. $49-54$ °C (Table I) below the melting temperature of the $Li_2O . 2 SiO_2$ phase (1 034 °C — [5]).

More favourable conditions exist for the investigation of nucleation in glass. A small amount of melt in a Pt crucible was rapidly quenched in an ice-water mixture. The quenching took just several seconds. Under these conditions one may assume better preservation of melt structures corresponding to the respective melting temperatures. A distinct influence of melting temperature on nucleation of the $Li_2O . 2 SiO_2$ phase was found for the glass in question. The number of nuclei in the samples increased significantly with decreasing melting temperature. The highest number of nuclei occurs in samples of glass melted close to the melting temperature of the crystalline substance, $Li_2O . 2 SiO_2$.

According to Kirkpatrick [3], the nucleus begins to grow from monomer by an associative process. Certain basic units attach themselves gradually to the monomer. Each monomer is therefore a potential point of nucleation. More favourable conditions for nucleation thus arise at a higher number of monomers and at a generally lower polymeration degree. According to the given theory and on the condition that the structure of high-temperature melt has been preserved down to the crystallization temperature, the number of nuclei should grow with the temperature of melting. As a consequence of the inadequate rate of cooling the experimental conditions only imply that the conclusion is correct (Table I). In spite of this the agreement with the given theory is highly probable for the nucleation of the $Li_2O . 2 SiO_2$ phase from melt of the same composition.

In the case of nucleation of $Li_2O . 2 SiO_2$ from glass there appears a disagreement with the theory mentioned above. The relatively highest number of nuclei occurs in glass which has been melted closely above the melting point (Table II), where the highest polymeration degree of the equilibrium melt can be considered. Moreover, the vitrification brought about by quenching should further promote this polymeration.

The results indicate that with nucleation from glass, the decisive part is not played by monomers as in the case of nucleation from melt, but rather by polymerized units, from subcritical clusters to nuclei in size. The first stage of nucleation of crystalline phase in glass can be a process not involving mass transfer, i.e. conversion of a polymeric cluster to a crystalline cluster or to a nucleus. This point of view appears to be supported by the finding that the temperature of the maximum equalized rate of nucleation in the glasses is in the range of the transformation temperature [6].

CONCLUSION

Nucleation of the crystalline phase of $Li_2O . 2 SiO_2$ from melt is practically independent of the temperature of melting. In contrast to this, a marked dependence of the number of nuclei on the temperature of melting was observed in the case of glass, where the largest number of nuclei is formed when the glass has been melted

closely above the melting point of the Li$_2$O . 2 SiO$_2$ phase. The number of nuclei formed in glass melted at 1 050 °C is roughly 24-times higher than that arising in glass melted at 1 500 °C, under otherwise identical conditions. Monomers participate more in the formation of nuclei in melt whereas polymerized units play a more important part in nucleation from glass.

References

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NUKLEÁCIA Li$_2$O . 2 SiO$_2$ Z TAVENINY A ZO SKLA

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Sledoval sa vplyv teploty tavenia na nukleáciu kryštalickej fázy Li$_2$O . 2 SiO$_2$ z taveniny a zo skla rovnakého zloženia metódou DTA podľa Marotta a spol. [1, 2].

Vzorky (0,394 g) sa pripravovali priamo v Pt tégliku prístroja DTA fy Netzsch 404 a tavili sa 2 h pri teplotách 1 050—1 500 °C. Sklá sa pripravovali chladením Pt téglikov s taveninami v zmesi ľadu a vody. Pri DTA taveniny sa ochladzovali a sklá ohrievali rýchlosťou 20 °C . min⁻¹.

Nukleácia fázy Li$_2$O . 2 SiO$_2$ zo skla vykazuje výraznú a z taveniny len nepatrnú závislosť od teploty tavenia. V skle najväčší počet nukleí sa vytvára, ak sa sklo taví tesne nad teplotou topenia fázy Li$_2$O . 2 SiO$_2$. V tavenine je to naopak. V procese tvorby nuklea v tavenine sa viac uplatňujú monoméry a v skle polymerizované celky.

Obr. 1. DTA krivky kryštalizácie skiel zloženia Li$_2$O . 2 SiO$_2$ *tavených 2 h pri uvedených teplotách (1 050, 1 500 °C).*

Obr. 2. DTA krivka kryštalizácie trveniny zloženia Li$_2$O . 2 SiO$_2$, *ktorá sa temperovala 2 h pri teplote 1 050 °C.*

ОБРАЗОВАНИЕ ЗАРОДЫШЕЙ Li$_2$O . 2 SiO$_2$ ИЗ РАСПЛАВА И СТЕКЛА

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Исследовали влияние температуры плавления на образование зародышей кристаллической фазы Li$_2$O . 2 SiO$_2$ из расплава и стекла одинакового состава с помощью метода ДТА по Маротту и сотр. [1, 2].

Пробы (0,394 г) получали прямо в Pt тигле прибора ДТА фирмы Netzsch 404 и расплавляли их 2 часа при температурах 1050—1500 °С. Стекла получали охлаждением Pt тиглей с расплавами в смеси льда с водой. При ДТА расплавы охлаждались и стекла нагревались скоростью 20 °С . мин⁻¹.

Образование зародышей фазы Li$_2$O . 2 SiO$_2$ из стекла имеет резкую и из расплава только незначительную зависимость от температуры плавления. В стекле наибольшее

количество зародышей образуется тогда, когда стекло плавится при температуре, незначительно выше температуры плавления фазы $Li_2O \cdot 2 SiO_2$. В расплаве это наоборот. В процессе образования зародышей в расплаве находят большее применение мономеры, а в стекле полимеризованные целые.

Рис. 1. ДТА кристаллизации стекол составом $Li_2O \cdot 2 SiO_2$, *расплавляемых 2 часа при приводимых температурах (1050, 1500 °C).*

Рис. 2. ДТА кривая кристаллизации расплава составом $Li_2O \cdot 2 SiO_2$, *темперированного при температуре 1050 °C.*

YANG W. J.: FLOW VISUALIZATION III (Vizualizace proudění III). Springer-Verlag, Berlin—Heidelberg—New York—Tokyo, 1985, 889 str., 910 obr., cena 288 —, DM.

Je známo, že Leonardo da Vinci (1452—1519) byl první, kdo načrtl profily volných proudů a jejich tvarování. Mimo jiné také navrhl pozorování vnitřních proudů ve vodě umístěné ve skleněné nádobě pomocí rozptýlených částeček v tekutině. Proto byly způsoby a metody pozorování toku tekutin pozorovány a popisovány již od středověku.

V současné době do oblasti zkoumání vizualizace a popisu toku tekutin zasáhly zásadním způsobem počítače, zvláště pak počítače umožňující grafický výstup. Jde o barevnou grafiku a také o zobrazení toků tekutin pomocí digitálních obrazů. Toto vše přineslo revoluční přeměny v technice a vědě zobrazování toku tekutin.

Kniha, která je svým obsahem velmi rozsáhlá (893 stran velkého formátu), je sborníkem třetího mezinárodního symposia o zobrazování toků, které se konalo v r. 1983 v USA (University of Michigan, An Arbor, Michigan). Prvá dvě symposia se konala v r. 1977 v Japonsku (Tokyo) a v r. 1980 v NSR (Bochum). O rozsáhlosti symposia svědčí i to, že probíhalo ve 35 sekcích.

Podobně jako symposium tak i kniha je rozdělena na 2 základní části. Prvá se týká metod vizualizace toků a druhá jejich aplikací. Jednotlivé části obsahují tyto podkapitoly, které obsahují průměrně 10 příspěvků na dané téma.

Jsou to:
1. Metody
1.1 Značkovací metody
1.2 Metody povrchového toku
1.3 Metody indukované chemickou reakcí a laserem
1.4 Optické metody
1.5 Výpočetní grafické metody
1.6 Metody zobrazování procesů
2. Aplikace
2.1 Oddělené proudění
2.2 Víření a proudy hladiny
2.3 Supersonické proudění a tlakové vlny
2.4 Tryskové proudění
2.5 Vnitřní proudění
2.6 Proudění ve vrstvách a v mezní vrstvě
2.7 Reologie
2.8 Lodě a vlny
2.9 Aerodynamika, atmosféra a oceanografie
2.10 Kapalinové stroje
2.11 Přenos tepla
2.12 Spalování
2.13 Biomedicinální aplikace

Kniha má výbornou grafickou úpravu. Jednotlivé články jsou doplněny řadou schematických obrázků, obrázků zobrazujících proudění a bohatým přehledem literatury. Knihu je tak možno doporučit všem zájemcům zajímajícím se o proudění tekutin (plyny a kapaliny), tj. jak pracovníků v oblasti výzkumu, tak i studujícím.

Kasa