

VOLUME AND SURFACE CRYSTALLIZATION DURING FORMATION OF GLASS-CERAMIC MATERIALS

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The effect of heat treatment on the course of crystallization in bulk and in the surface layers during the formation of β -quartz s.s. and β -spodumene s.s. glass ceramics was studied. The results suggest that the different kinetics of phase transformation in volume and in the surface layers is responsible for the formation of stress at the sample surface during the formation of glass ceramics.

INTRODUCTION

The controlled crystallization of glasses enables preparation of useful polycrystalline materials (glass-ceramics) which are non-porous with a uniform crystalline structure; the crystal size and distribution of crystals can be controlled by a suitable heat treatment. The choice of the initial composition then permits these materials to be prepared in an exceptionally wide range of chemical and phase composition of the crystalline and residual glass phases, structure, properties and fields of application [1, 2, 3].

Knowledge of the controlled conversion of glasses into glass-ceramic materials including processes such as metastable separation in the liquid phase, various types of nucleation processes, crystal growth and secondary growth can be utilized to yield reproducible results in the industrial production of various types of glass-ceramic materials with required volume properties.

However, the useful properties of glass-ceramic materials are often greatly affected by the surface and subsurface material layers. It is a rule rather than an exception that the crystallization of glasses in the surface and subsurface layers during the formation of glass-ceramic materials takes place in quite a different manner than in the bulk of the glass [4, 5, 6, 7].

The formation of surface and subsurface layers with different properties is desirable if full control is possible but undesirable if it cannot be controlled for objective or other reasons. The basic question therefore arises of how to control the surface crystallization by a selected heat treatment or by choice of the volume composition to obtain the required properties in the bulk and also in the surface layers at the same time. From this point of view, the relationships between the factors which govern the crystallization kinetics at the surface and in the bulk are of great importance.

It is well known that heterogeneous nucleation (SURF) can reduce the thermodynamic barrier to homogeneous nucleation (VOL).

$$\Delta G^*_{(\text{SURF})} \approx G^*_{(\text{VOL})} \cdot f(\Theta)$$

so that the phase transformation is accelerated during surface crystallization or takes place at smaller undercooling (ΔT) [8, 9, 3].

The typical course of the phase transformation, i.e. the degree of transformation in dependence on time and temperature, is then expressed by the TTT diagram in Fig. 1a.

Surface crystallization (considered as a thin surface layer) for every chosen thermal treatment precedes volume crystallization. The difference in the degree of crystallization in the effective surface layer and in the bulk in dependence on time leads to the formation of a maximum.

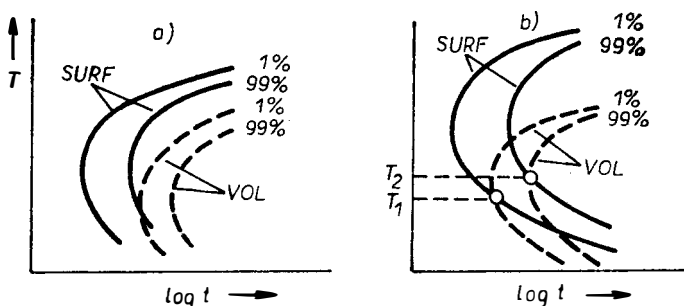


Fig. 1. Schematic transformation curves (t vs. T at constant $X = 1$ and 99%) for crystallization in the bulk and in the effective surface layer (see the text).

Another factor to be considered in multicomponent liquids is the difference in the chemical compositions in the surface and subsurface layers with respect to the composition in bulk of the sample. The components will tend to form a distribution in the surface layer such that the resulting surface energy is minimal (the Gibbs adsorption isotherm). The relevant excess of the component in the surface layer is defined in terms of the surface concentration:

$$\Gamma_{i(\text{SURF})} \approx - \frac{1}{RT} \cdot \frac{d\gamma}{d \ln C_{i(\text{VOL})}}$$

where Γ_i is the surface concentration of component i (mol/cm²)

C_i is the molar concentration of component i in the bulk

γ is the surface tension.

The equation describes the relationship between the concentration of the component at the surface and in the bulk of the sample and generally expresses that only the given component will accumulate in the boundary layer, where $d\gamma/dC_i < 0$, i.e. the component whose increasing concentration reduces the surface tension. On the contrary, the boundary layer will be depleted in this component when $d\gamma/dC_i > 0$. Different concentrations of the components in the surface layer will affect the phase transformation kinetics. The different crystallization kinetics in the surface layer and in the bulk of the sample can be analyzed on the basis of the TTT diagram. It can be seen from the Fig. 1b that, when the sample is heat treated at temperatures higher than T_2 , the crystallization in the surface layer will precede the crystallization in the bulk and, at temperature lower than T_1 , the opposite will occur. In the temperature range between T_1 and T_2 bulk crystallization is initially delayed but after some time it precedes crystallization in the surface layer.

Other factors can also affect the surface composition profile and the course of the crystallization in surface layers such as the effect of the atmosphere, melt history, or depletion of readily volatile components in the surface layers. These factors are given by the preparation conditions and, except for the last one, they can be considered as constant in this study.

In addition, the findings on the influence of heat treatment on the course of crystallization in the bulk and in the surface layers of the sample during the formation of glass-ceramic material based on β -quartz s.s. and β -spodumene s.s. are described.

EXPERIMENTAL

Plates with dimensions of 50×10 mm, and thickness of 4 mm were used to investigate the base glass of the $\text{LiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ($\text{MgO} \cdot \text{ZnO} \cdot \text{TiO}_2 \cdot \text{ZrO}_2 \cdot \text{Na}_2\text{O} \cdot \text{K}_2\text{O}$) system. The course of the crystallization for a selected heat treatment was followed up by X-ray-diffraction analysis and by dilatometric measurement. The surface stress as well as its profile in the cross section was evaluated using a polarizing microscope with a compensation wedge and a Senarmont compensator. The DTA of glass powders with different particle size was carried out to estimate differences in the volume and surface crystallization.

The effect of time on the crystallization

During the heat treatment of the mother glass, β -quartz s.s. crystallizes as a metastable phase; β -spodumene s.s. crystallizes after a longer time or at higher temperatures.

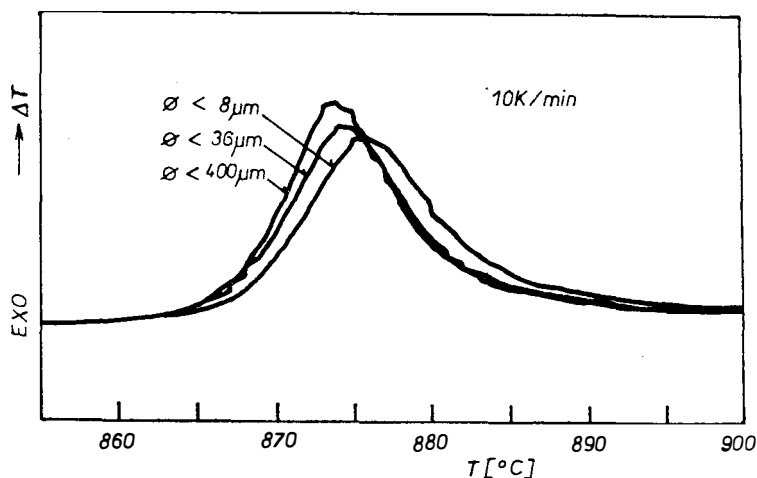


Fig. 2. DTA curves of powdered samples.

(i) Crystallization of β -quartz s.s.

During the formation of β -quartz s.s. glass-ceramic, mechanical stress on sample surface was observed. X-ray diffraction analysis indicated that crystallization in the bulk of the sample during constant temperature heat treatment precedes crystallization in the surface layer. If the glass exhibits both volume and surface crystallization, their ratios can be estimated from the shift in the DTA peak for coarse and fine particles [3]. DTA curves for powdered samples (200 mg) of the base glass with particle sizes of $< 8 \mu\text{m}$, $< 36 \mu\text{m}$ and $< 400 \mu\text{m}$ are shown in Fig. 2. The shift of the DTA peaks to higher temperatures with a decrease in the particle radius (increase in the surface area) clearly indicates the suppression of the crystallization in the surface layer and also indicates that the crystallization is not initiated on the glass surface by surface nucleation (compare Fig. 1a).

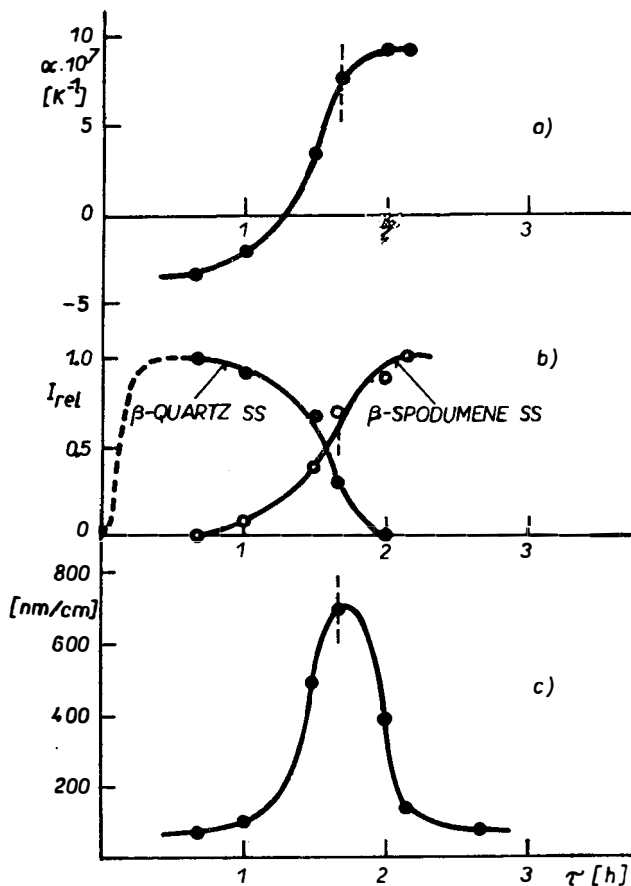


Fig. 3. Time dependence of expansion, relative X-ray diffraction intensity and compressive stresses created during heat treatment at 940°C of nucleated base glass.

(ii) Crystallization of β -spodumene s.s.

The initial glass was first heated to the nucleation temperature, 740 °C. Then the samples were placed in a furnace with a crystallization temperature of 940 °C and removed at time intervals of 3 hours. The measured values of the thermal expansion coefficient, intensity of characteristic X-ray diffraction lines for β -quartz and β -spodumene s.s. and the values of the surface stress formed on the samples (see Fig. 3) show that the phase transformation is accompanied by the creation of compressive stresses on the sample surfaces which reach a maximum just before completion of phase transformation in the bulk of sample.

The effect of temperature on the crystallization

The effect of temperature on the crystallization has been followed on samples pretreated at 740 °C for two hours and at 840 °C for two hours so that total transformation to β -quartz s.s. has been achieved. These samples were then heat treated at temperatures of 925 °C, 940 °C and 970 °C for a preset time. The kinetics of phase transformation of β -quartz s.s. to β -spodumene s.s. has been followed by X-ray diffraction analysis and mechanical stresses on the sample surfaces were simultaneously measured.

The dependence of the transformation degree on time can be expressed in terms of the Avrami relationship

$$X_t = 1 - \exp(-Kt^n)$$

where X_t is the degree of transformation, t is time and n is the Avrami constant (Fig. 4a). The corresponding time dependence of the measured compressive stresses on the sample surfaces is given in Fig. 4b. From Fig. 4 it can be seen that surface

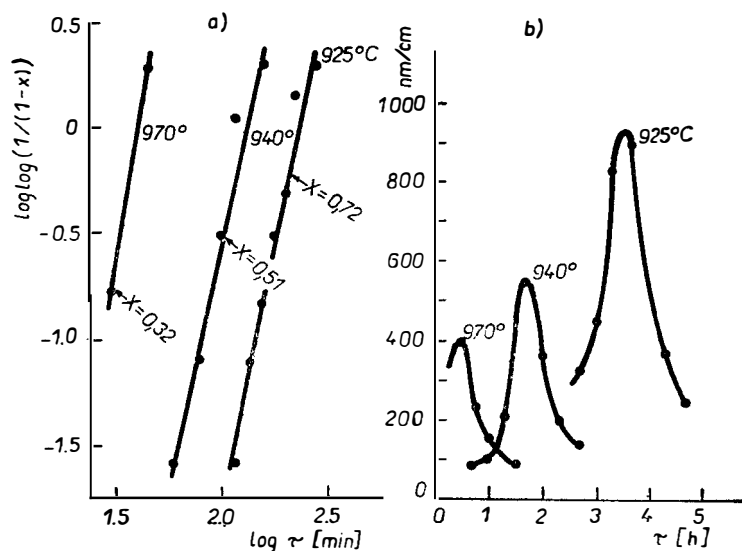


Fig. 4. Avrami plot of spodumene s.s. crystallization (a) with corresponding time dependence of stress formation in the sample surface (b) at the given temperature ($n = 0.32$ — 0.51 — 0.72 at which the maximum stresses occur).

stresses not only depend on the crystallization time, but also depend strongly on the crystallization temperature. It is obvious from Fig. 4 that the same degree of transformation (X) can be attained under various heat treatment conditions (temperature and time) but only one heat treatment gives maximum values of compressive stresses for the required transformation degree (X). Surface stresses are created as a result of delayed phase transformation on the sample surface. This has been demonstrated by X-ray diffraction analysis performed on the sample surface and on the sample after grinding off the surface layer. These X-ray diffractograms of the sample heat treated at 925 °C for 3.5 hours are shown in Fig. 5. While the phase transformation in the bulk of the sample was greater than 50 %, the phase transformation in the surface layer did not begin.

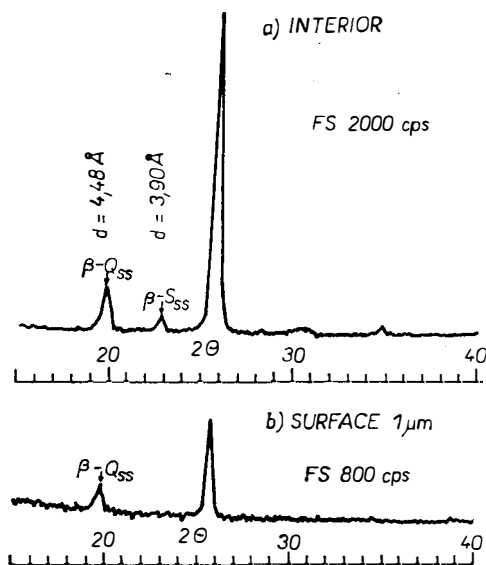


Fig. 5. Thin-film X-ray diffraction patterns (a) from the interior and (b) from the surface of a sample indicating the delayed phase transformation of B-quartz s.s. in the surface layers.

As pointed out above, these experimental results can be interpreted by model TTT-curves for the phase transformation (volume/surface) which also explains the temporary formation of stresses on the sample surfaces as a consequence of different phase transformation kinetics at the surface and in the bulk of the material, even when the stress release through relaxation processes must be also considered. From this point of view it would seem possible to effectively influence the optimal course of the phase transformation not only in the bulk but also in the surface layers by the choice of suitable heat treatment.

It seems likely that the origin of different courses of the crystallization kinetics in the bulk and at the surface of the glass could lie in differences in the chemical composition of the surface layers. Further systematic research in this field is necessary for it to be possible to control this factor by varying the bulk composition.

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OBJEMOVÁ A POVRCHOVÁ KRYSTALIZACE PŘI TVORBĚ SKELNĚ KRYSTALICKÝCH MATERIÁLŮ

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Poznatky o řízení přeměny skla na skelně krystalický materiál umožňují dosažení reprodukovatelných výsledků při výrobě různých typů skelně krystalických materiálů s požadovanými objemovými vlastnostmi. Užité vlastnosti skelně krystalických materiálů jsou však v mnohých případech významně ovlivněny povrchovými a podpovrchovými vrstvami materiálů.

Je spíše pravidlem než výjimkou, že krystalizace skel v povrchových vrstvách, při tvorbě skelně krystalických materiálů probíhá zcela odlišně, než je tomu uvnitř (v objemu) vzorku, což může mít pozitivní, ale i negativní vliv, zejména na mechanické vlastnosti. Odlišný průběh kinetiky fázové přeměny na povrchu a v objemu vzorku může být komplexně analyzován na základě diagramu TTT (obr. 1).

Při tvorbě skelně krystalických materiálů na bázi systému $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (TiO_2 , ZnO_2 , Na_2O , K_2O) bylo experimentálně zjištěno, že krystalizace pevných vzorků β -křemene se v povrchových vrstvách zpokojuje za krystalizací v objemu vzorku, o čemž svědčí jak měření rtg-difrakcí analýzy, tak i měření DTA na vzorcích s odlišnou zrnitostí (obr. 2).

Kinetika následné fázové přeměny pevných roztoků β -křemene na β -spodumen u tohoto typu sklokeramiky byla sledována rtg-difrakční analýzou a současně byla měřena mechanická pnutí na površích vzorků, která se vytvářela následkem zpokoování fázové přeměny v povrchových vrstvách (obr. 5). Závislost stupně přeměny na čase byla zpracována pomocí Avramiho vztahu (obr. 4a). Odpovídající časové závislosti změřených mechanických tlakových pnutí (obr. 4b) vykazují maxima. Výsledky shrnuté v obr. 4 ukazují, že stejný stupeň přeměny lze dosáhnout při různých podmínkách tepelného zpracování (tj. teplotě a čase), ale pouze při jediném tepelném zpracování pro daný stupeň přeměny lze dosáhnout současně maximálních hodnot tlakových pnutí na povrchu skelně krystalického materiálu. Zdá se pravděpodobné, že původ rozdílného průběhu kinetiky krystalizace na povrchu a v objemu vzorku je nutno hledat v odlišném chemickém složení povrchových vrstev.

Obr. 1. Schematické znázornění křivek fázové přeměny (t vs T při konstantním $X = 1$ a 99 %) v objemu a v efektivní povrchové vrstvě vzorku (viz text).

Obr. 2. DTA křivky práškových vzorků.

Obr. 3. Časová závislost teplotní roztažnosti (a) relativní intenzity charakteristických difrakčních čar ($d = 4,48 \text{ \AA} - Qss$ a $d = 3,90 \text{ \AA} - Sss$) (b) a tlakových napětí (c) během tepelného zpracování vzorků základního skla při 940 °C.

Obr. 4. Avramiho závislost krystalizace pevného roztoku β -spodumenu (a) s odpovídající časovou závislostí vytvářených tlakových napětí na povrchu vzorku (b) při dané teplotě. ($X = 0,32$ až $0,51-0,72$ jsou stupně přeměny, při kterých napětí dosahuje max. hodnot).

Obr. 5. Rtg-difrakční záznamy z povrchu (b) a z objemu (a) vzorku indikující zpoždění fázové přeměny pevných roztoků β -křemene v povrchové vrstvě.

УПРАВЛЯЕМОЕ ПРЕВРАЩЕНИЕ СТЕКЛА
В СТЕКЛОВИДНЫЙ КРИСТАЛЛИЧЕСКИЙ МАТЕРИАЛ

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Данные относительно управляемого превращения стекла в стекловидный кристаллический материал предоставляют возможность достижения воспроизводимых результатов при получении разных типов стекловидных кристаллических материалов с требуемыми объемными свойствами. Однако на полезные свойства стекловидных кристаллических материалов оказывают весьма часто существенное влияние поверхностные и подповерхностные слои материала.

Почти как правило, а не исключение, является то, что кристаллизации стекол в поверхностных слоях при образовании стекловидных кристаллических материалов протекает совсем по-другому, чем внутри (в объеме) материала, что может оказывать как отрицательное, так положительное влияние на механические свойства. Различный ход кинетики фазового превращения на поверхности и в объеме образца можно подвергнуть подробному анализу, используя ТТТ диаграмму (рис. 1).

При образовании стекловидных кристаллических материалов на основе системы $\text{LiO}_2\text{—Al}_2\text{O}_3\text{—SiO}_2$ (TiO_2 , ZnO_2 , Na_2O , K_2O) было экспериментальным путем установлено, что кристаллизация твердых образцов β -кварца в поверхностных слоях опаздывает за кристаллизацией в объеме образца, свидетельством чего является как измерение ртг-дифракционного анализа, так и измерения ДТА, проводимых на образцах с разной величиной зерна (рис. 2).

Кинетику последовательного фазового превращения твердых растворов β -кварца в β -сподумен у данного типа стеклокерамики исследовали с помощью ртг-дифракционного анализа и одновременно измеряли механические напряжения на поверхностных образцах, образовавшихся в результате опаздывания фазового превращения в поверхностных слоях (рис. 3). Зависимость степени превращения от времени исследовали с помощью отношения Аврами (рис. 4а). Соответствующие временные зависимости измеряемых механических напряжений давления (рис. 4б) дают максимумы. Результаты, обработанные на рис. 4, показывают, что одинаковую степень превращения можно получить при разных условиях термической обработки (т. е. температуре и времени), но только при единственной термической обработке для данной степени превращения можно получить одновременно максимальные величины напряжения давления на поверхности стекловидного кристаллического материала. Оказывается, что причину разного хода кинетики кристаллизации на поверхности и в объеме образца приходится искать в различном химическом составе поверхностных слоев.

Рис. 1. Схематическое изображение кривых фазового превращения (t в с, T при постоянном $X = 1$ и 99 %) в объеме и эффективном поверхностном слое образца (см. текст).

Рис. 2. ДТА кривой порошкообразных образцов.

Рис. 3. Временная зависимость термического расширения (а) типичных дифракционных время ($d = 4,48\text{Å} - Q_{ss}$ и $d = 3,90\text{Å} - \Delta_{ss}$) (б) и напряжений давления (с) во время термической обработки образцов основного стекла при 940°C .

Рис. 4. Зависимость кристаллизации Аврами твердого раствора β -сподумена (а) с отвечающей временной зависимостью образовавшихся напряжений давления на поверхности образца (б) при данной температуре. ($X = 0,32 - 0,51 - 0,72$ представляет степень превращения, при которой напряжение достигает максимальных величин).

Рис. 5. Ртг-дифракционные записи из поверхности (а) и из объема (б) образца, являющиеся свидетельством опаздывающегося фазового превращения твердых растворов β -кварца в поверхностном слое.