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Decrystallization of Glass-ceramics under Ion Exchange Diffusion

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Abstract

Experimental results of studying ion exchange process in glass-ceramics are presented. For the first time, it is discovered that the process may result in the disappearance of the crystalline phase in the layers undergoing ion exchange diffusion. This new phenomenon has been called the effect of decrystallization. The effect has been observed in a ceramic material formed out of a photosensitive Ag-doped lithium-silica glass, which can be crystallized owing to the photo-induced formation of fine silver particles as the nuclei for the growth of $Li_2O{\cdot}SiO_2$ crystals. Samples of the glass-ceramics were subjected to ion exchange in $NaNO_3$ salt melt at the temperature at which viscosity of the initial glass is equal to 10^8 Ns/m^2. On processing, pure vitreous layers under all the faces of the sample processed have been obtained, the depth of those layers depending on the processing time. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

One of the ways to form bulk or film ceramics is to crystallize glass. Such ceramics are called glass-ceramics. Usually, glass crystallization takes place at temperatures above the glass transition temperature but below the solidus temperature of the glass-forming system. From the viewpoint of equilibrium thermodynamics, the only way to transfer such ceramic materials back to the vitreous state is to heat the system above the liquidus temperature and then to cool it quickly. However, the present work demonstrates another way for that transformation.

2 Glass-ceramics Preparation

The glass-ceramics was formed out of a photosensitive glass. The glass was an alkali-silica glass (20 mol% of $LiNO_3$ and 70 mol% of SiO_2) doped with small quantities of Ag, Ce, and Sb cations. The exact glass composition is given in Table 1. Introducing those cations allows the glass to be crystallized in a controllable manner. Exposing that glass to UV radiation with following thermal processing at a temperature a little above the glass transition temperature (T_g) gives rise to fine particles of amorphous silver. When heated, the glass crystallizes, those silver particles acting as nuclei for crystallization.[1] By altering the exposure time and varying the schedule of the glass annealing, it is possible to form glass-ceramics with pre-assigned sizes and concentration of the crystals formed. For the glass-ceramic samples to be produced the following processing was used: (1) 1 h UV exposure; (2) heating for 1 h up to 470°C; (3) annealing at 470°C for 4·5 h; (4) heating up to 610°C; (5) annealing at 610°C for 0·5 h additionally. (T_g of the glass is equal to 442°C.) Upon processing, a glassy material with a high concentration of white cubic crystals of size smaller than 3 micrometers was obtained. The size of the crystals was estimated with a microscope. In accordance with X-ray diffractive analysis, the crystals grown were $Li_2O{\cdot}SiO_2$.

The initial glassy preforms for preparing glass-ceramic samples were plates of about 2 mm thick. During exposure, a ring array mask was used, the mask covering only half of one of the big sample faces. The rings were of 0·3 mm in diameter. The ceramic material was obtained only in the regions exposed to UV radiation. As a result, one half of each sample was pure ceramic and the other had the structure of glassy channel array embedded into ceramic substance. The distances between the nearest channels were 0·4 mm each.

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Table 1. Composition (by batch) of the glass used

Oxide of	*Si*	*Li*	*K*	*Na*	*Al*	*Ag*	*Ce*	*Sb*	*Zn*
Mol%	71·2	20·8	3·0	1·1	3·0	0·05	0·03	0·05	0·8

3 Experimental Procedure and Results

The samples of the glass-ceramics involved underwent the ion exchange processing in $NaNO_3$ salt melt at the temperature 560°C at which viscosity of the initial glass was equal to 10^8 Ns/m^2. At that temperature one can consider that only alkali cations diffuse and all the others do not move. Besides, it should be noted that the diffusion of alkali cations within crystals is negligible compared with the diffusion within the vitreous material of the same composition. Thus, we had the case of Li-for-Na ion exchange diffusion within the vitreous constituent of the ceramic material.

The samples were under Li-for-Na ion exchange during 1·5, 3, and 5 h. Upon processing, the samples were washed in warm water. Then, both large faces of the sample were polished down to the sample thickness equal to 0·7 mm and the edges of the polished samples were studied with an optical microscope and Mach-Zehnder interferometer.

The ion exchange diffusion results in pure vitreous layers under the samples faces, i.e. all the crystals within those layers have disappeared. The depth of the layers depends on the processing time. It was the first time that this new phenomenon had been observed. I have called the phenomenon the effect of decrystallization. The pictures in Fig. 1(a) and (b) taken with a microscope illustrate that effect. In this figure, one can see the edge of the glass-ceramic sample before ion exchange processing (a) and after 5 h processing (b). Using the channel array as a reference scale enables us to make the express size estimation of the vitreous layer depth in looking over the samples with a microscope. The sample after 5 h processing has the vitreous layer of 0·27 mm thick. Besides the decrystallized layers, the processing has led to cracking the samples and to partial crystallization of the glassy channels. It is to be noted that the channels shown in Fig. 1(b) have not been affected by the ion exchange, for the polishing removed the vitreous layers under the large faces of the sample.

The samples after 1·5 and 3 h processing have the same external features. The only difference is the depth of the vitreous layers, which are of 0·12 mm thick after 1·5 hours and 0·19 mm after 3 h.

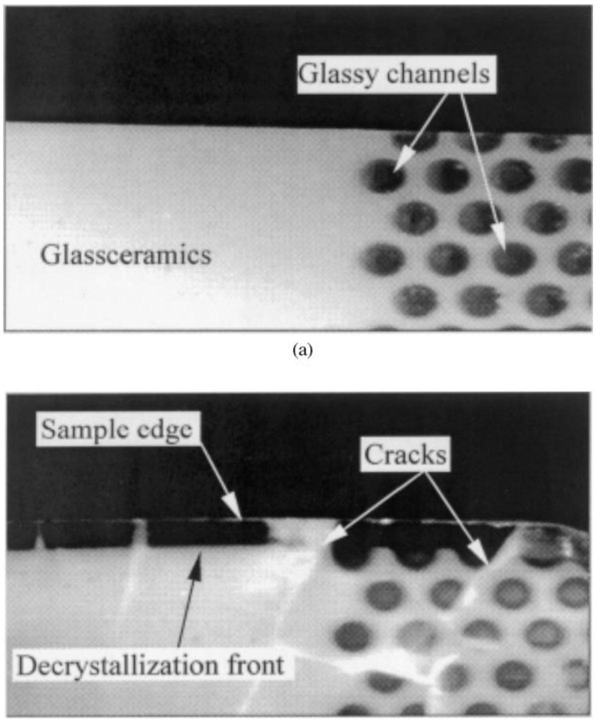

Fig. 1. The pictures of the glass-ceramics sample (a) before and (b) after 5 h ion exchange processing at the temperature 560°C, where viscosity of the initial glass is equal to 10^8 Ns/m^2. The sample after processing has a vitreous layer between the sample edge and the edge of the decrystallization front. The depth of the layer is equal to 0·27 mm. Besides, one can see the process lead to cracking the sample and crystallization of the glassy channels. It is to be noted that the initial glass, which is in the channels, crystallizes while the ion exchange leads to the decrystallization of the glass-ceramics.

4 Discussion

Primarily, I would like to review briefly the conventional viewpoints[2,3] on glass and glass crystallization. Glass is known to be an overcooled liquid that is obtained in fast cooling and stays in the metastable state due to the kinetic restrictions, which are the only factors keeping the system from crystallization. That metastable state is one of equilibrium all the way down to the glass transition temperature (T_g). Below T_g, the state becomes non-equilibrium owing to the strong temperature dependence of the structure relaxation rate. At those temperatures, the relaxation rate is too small for the glass structure to follow its equilibrium state in cooling.[2] Due to the Boltzmann factor, heating (above T_g) leads to increasing the statistic average number of such elementary submolecular formations that are thermal-excited enough to overcome the energy barrier and to form stable crystal nuclei. An intensive growth of the nuclei takes place at temperatures a little higher than the temperature of the nucleation. Both processes, that is, crystal growth and nucleation, can make the glass leave the metastable state for the ground state, with the glass forming a crystalline mixture or a certain glass-ceramic substance.[3] Thus, from the conventional viewpoint the glass crystallization is understood to be a movement of that glass-forming system to the ground state and, therefore, this process is irreversible if the system never comes above the liquidus temperature.

Glass crystallization under the high-temperature ion exchange (the temperature is between glass transition temperature and solidus temperature) is not an unexpected phenomenon. The phenomenon can be easily explained by the above-described thermodynamic approach, if that ion exchange results in some new glass composition, which can be unstable at the processing temperature. In this case, the ion exchange process results in the crystalline layer adjacent to all the faces of the glass sample processed. The authors observed the latter in Li-for-Na high-temperature ion exchange in alkali-niobium-silicate glass (unpublished results). The contrary phenomenon, that is, the disappearance of the crystals embedded in some glassy substance under ion exchange, could not be explained by this approach without extraordinary assumptions. However, it is this phenomenon that has been observed experimentally and described in the previous section of the paper.

As the decrystallization took place below the solidus temperature of the system involved, for the phenomenon to be elucidated, it is necessary to apply an approach different from the one discussed above. I do not propose here a quantitative theory, but only terms in which the phenomenon can be understood. As it was mentioned above, a glassy system at temperatures falling between T_g and solidus temperature is a metastable liquid at equilibrium. Let us consider the glass-ceramics at those temperatures as a liquid solution, with the microcrystals being a precipitate. In the present case, the precipitate is the microcrystals of $Li_2O{\cdot}SiO_2$ and the solvent is the vitreous constituent of the glass-ceramics. The concentration of Li_2O in the vitreous constituent at the process temperature (560°C) is presumed to be sufficient for the solution to be nearly saturated. (The solution is truly saturated at the temperature (610°C) of the glass-ceramics preparation.)

In those terms, Li-for-Na ion exchange must lead to a disturbance of phase equilibrium in the system, that is, to a disturbance of the equilibrium in the volumes of the liquid and solid phases. Due to the ion exchange process the concentration of Li_2O in the liquid phase (a solvent) becomes lower and that fact gets the solid phase (the microcrystals $Li_2O{\cdot}SiO_2$ as a precipitate) to dissolve, for the Li_2O concentration in the liquid phase is to be kept the same as for the saturated solution. That process must endure till all the crystals have dissolved. The crystallization of the initial glass in the channels should have been considered as the precipitate formation in a general thermal way, that is, without silver particles as the nuclei. Thus, we propose to interpret the effect in the terms of the theory of phase equilibrium in the heterogeneous liquid solutions.

From the viewpoint of the proposed terms, the edge of the decrystallization front can be defined as a place where all the crystals have already dissolved but lithium concentration in the vitreous constituent adjacent to the front is still equal to the one of saturated solution. Other conditions being equal, that concentration at a given temperature is strictly defined by the equilibrium constant. Thus, in all the samples involved one can expect the concentration of lithium cations at the edge of the decrystallization front to be the same. To corroborate this consideration, the pictures of the fringe shift patterns of the vitreous layers at the edges of the samples after processing were taken with Mach-Zehnder interferometer supplied with a microscope.

The refractive index of multialkali silicate glasses is known to depend on the concentrations of the alkali cations contained. Therefore, since the samples are plane-parallel plates with one-dimensional distribution of alkali concentrations extending from the sample edge to the edge of the decrystallization front, the fringe shift patterns of the samples are the contour plots (topological maps) of the index.[4] Using those index plots one can determine the similar plots for the ratio of alkali concentrations in the vitreous layers, for the glass index depends linear on that ratio.[5] Studying the fringe shift patterns in all the processed samples has shown that the number of the fringes in the vitreous layers does not depend on the processing time and is equal to 4·5 for all the samples. Figure 2 shows one of the pictures of the fringe shift pattern in the sample after 5 h processing. The ratio of the concentrations of exchanging alkali ions at the

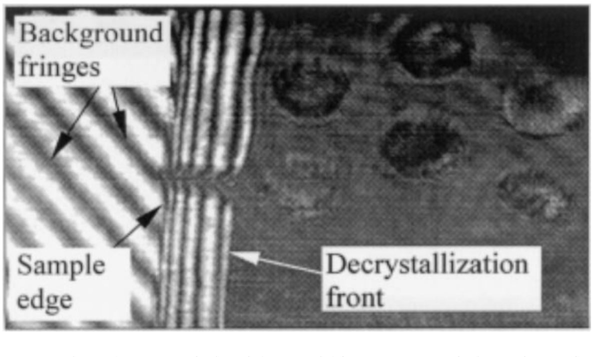

Fig. 2. The picture of the fringe shift pattern of the edge of the sample after 5 h processing taken with a microscope. Mach-Zehnder interferometer is used. There are 4·5 fringes between the sample edge and the edge of the decrystallization front.

interface becomes about unchangeable for a short time interval compared with the total processing times used.[6] Then, there being the same number of fringes in all the samples (after 1·5, 3, and 5 h ion exchange processing), it is possible to state that for all those samples that ratio at the edges of the decrystallization fronts is the same. Allowing for the fact that any sample ought to keep electronutrality in processing, that is, the total alkali concentration is always constant, the lithium (and sodium) concentration at the decrystallization front in all the samples is the same too. (Here, we disregarded the small amount of K_2O contained in the glass, for K cations are of low diffusion mobility.) We suppose that concentration to be the saturated one.

Thus, we know the position at which lithium concentration in all the samples is the same. That position is the edge of the decrystallization front. It gives an opportunity to judge whether the character of the diffusion behavior of the system is of Fickian. For the criterion of that behavior the combination $d/\sqrt{t}$ can be chosen, where d stands for the depth of the vitreous layer upon processing (where lithium concentration is equal to the one of saturated solution) and t-the time of the processing. If the combination does not depend on the processing time, the diffusion process is of Fickian character.[6] The magnitudes of d for the samples after 1·5, 3, and 5 h processing are already mentioned above and are equal to 0·12, 0·19, and 0·27 mm. The calculated meaning of the criterion $d/\sqrt{t}$ for those samples are $1{\cdot}63{\cdot}10^{-3}$, $1{\cdot}83{\cdot}10^{-3}$, and $2{\cdot}01{\cdot}10^{-3}\,\mathrm{mm/s}^{1/2}$, correspondingly. Thus, the criterion depends on time. This means that Fick's diffusion equation cannot be applied in describing the phenomenon, and it is necessary to develop a specific phenomenological model of the diffusion process in glass-ceramics or other partially crystallized glassy media. That model must take into account the kinetics of crystals dissolution, which will result in an additional term, commonly called the power of the source, in the diffusion equation.

5 Conclusion

It is shown that Li-for-Na ion exchange in the glass-ceramic material, with $Li_2O{\cdot}SiO_2$ being the crystals, leads to the ceramics decrystallization. The process is proposed to be interpreted in the terms of the theory of phase equilibrium in heterogeneous liquid solutions, where the vitreous constitute of the glass-ceramics is considered as a solvent and the crystals as a precipitate, which is dissolving in altering solvent composition through the ion exchange process. The decrystallization disturbs Fickian character of the diffusion process and makes one develop a new phenomenological description of the diffusion process with allowance for the process of crystal dissolution.

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