

Surface crystallization kinetics in soda–lime–silica glasses

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A review of previous research on surface nucleation in glasses demonstrates that these are mostly qualitative and that strong discrepancies exist regarding the nucleation mechanism. In this article, the surface crystallization kinetics of several glasses – a $\text{Na}_2\text{O} \cdot 0.3\text{CaO} \cdot 0.6\text{SiO}_2$ (devitrite), a non-stoichiometric devitrite, and two commercial soda–lime–silica (a float and a microscope slide) glasses – were determined in a wide range of temperatures and time. An analysis of the average number of crystals per unit area, N_s , crystal growth rates and viscosity data indicates that the surface nucleation rates are very high and that crystallization arises from a fixed number of special sites, N_s . The number of crystals nucleated strongly depends on the surface condition (e.g., fire polished versus mechanically polished or as-received; clean versus dirty), on the chemical composition of the parent glass, and also on the nature of the crystallizing phase. However, N_s does not depend on time or temperature. The experimental evidence indicates that the surfaces ‘per se’ do not alter the thermodynamic barrier for nucleation (the interfacial energy or the chemical potential). The enhanced nucleation rates at the external surfaces are the result of the catalytic effect of some (unknown) solid impurity particles and faster surface diffusion rates.

1. Review of previous work

A summary of previous research on surface nucleation is given below. Tabata [1] studied surface crystallization in several glasses – flint, borosilicate and soda–lime–silica – by optical microscopy and concluded that the degree of crystallization is related to surface defects such as cracks and craters.

Morey [2] studied 87 soda–lime–silica compositions and did not observe crystallization around internal bubble surfaces. He assumed that surface crystallization was due to compositional variations caused by selective volatilization from the external surfaces.

Swift [3] demonstrated that soda–lime–silica glass specimens with dirty surfaces had a much higher degree of crystallization than cleaner specimens.

Scott and Pask [4] suggested that the surface crystallization of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glasses was due to $\text{Na}(\text{OH})$ crystals which developed by reaction with water vapor. Specimens heat treated in dry air or vacuum did not crystallize. Internal bubbles were also crystal free.

Klingsberg [5] concluded that bubbles act as nucleation sites for the crystallization of $\text{BaAl}_2\text{Si}_2\text{O}_8$ (Celsian) in a $\text{BaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$ glass. However, no evidence was provided for nucleation on all bubbles.

Neely and Ernsberger [6] melted soda–lime–silica glasses at low temperatures and observed that crystal nucleation occurred only on a few bubbles, but not in all of them. Internal crystallization was increased in specimens doped with (undissolved) powdered garnet or alumina. Glasses melted at higher temperatures, where the powders dissolved, showed only surface crystallization. The authors suggested that the external surfaces crystallize easily due to selective evaporation and contamination with solid particles.

Bergeron and De Luca [7] detected crystallization of PbTiO_3 on the external surface and also on some internal bubbles in a $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2$ glass. After a treatment at 400°C for 4 h, crystallization appeared in bubbles that were previously crystal free. They concluded that crystals grew preferentially at bubble surfaces.

Mattox [8] reported that bubbles containing graphite particles (from the mould) crystallized

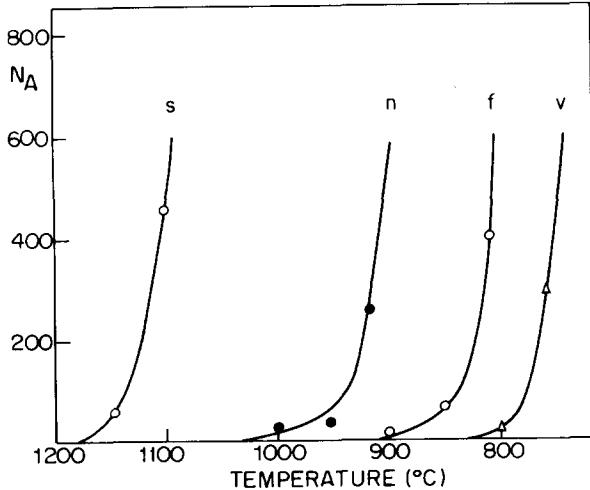


Fig. 1. Nucleation of $\text{BaO} \cdot 2\text{SiO}_2$ crystals on a crucible wall [9]. s, scratched surface; n, normal surface; f, flame-polished surface; v, volume nucleation.

preferentially in a $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glass. He comments, however, that the precise detection of contamination in the devitrification centers is difficult due to crystal growth which hides the former.

Burnett and Douglas [9] determined the nucleation rates of $\text{BaO} \cdot 2\text{SiO}_2$ spherulites in a $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$ glass. The number of spherulites initiated from the Rh/Pt container surface was investigated after the molten glass was quenched directly to the heat treatment temperature. After quenching to room temperature, the glass was knocked out of the crucible, and the number of spherulites with centers at the surface was counted. Figure 1 shows the numbers of crystals on the crucible wall after a 10 min heat treatment. These are compared with the numbers observed for volume crystallization in curve v. Electron microscopy showed that nucleation occurred preferentially along lines, implying that scratches in the container surface provided active sites. A flame-polished crucible surface is compared with a normal surface and a very scratched surface in curves f, n and s, respectively. The scratched crucible surface shows a greatly increased nucleation rate. It should be stressed, however, that these results do not refer to nucleation on the free glass surfaces.

Strnad and Douglas [10] studied the crystallization kinetics in three compositions of the $\text{Na}_2\text{O}-$

$\text{CaO}-\text{SiO}_2$ system with 55, 57.5 and 60 mol% SiO_2 . Figure 2 summarizes the experimental results for the surface nucleation rate, I_s , and the internal nucleation rate in glasses 57.5 and 60.0 after a development treatment at 850°C . As far as I know, this was the sole set of quantitative results on surface nucleation kinetics in oxide glasses and shows that smaller undercoolings are required to induce surface nucleation than internal nucleation. It also shows that I_s increases for higher undercoolings and depends on the chemical composition of the parent glass.

Bansal and Doremus [11] determined the crystallization on mechanically polished surfaces of a Sr-Ba-La-F glass heat treated at a range of temperatures from 322 to 390°C . Spherical crystals appeared rapidly and grew to $10\ \mu\text{m}$, when corrugated regions emerged and covered most of the surface. No quantitative determinations were made. However, the number of crystals appeared to be time and temperature independent.

Zanotto et al. [12] determined the detailed kinetics of both crystal nucleation and liquid phase separation in a series of $\text{BaO}-\text{SiO}_2$ glasses. They established that there is no relation between the surface area of the amorphous droplets and the internal crystal nucleation rate, I , and that I is affected only by the compositional changes caused

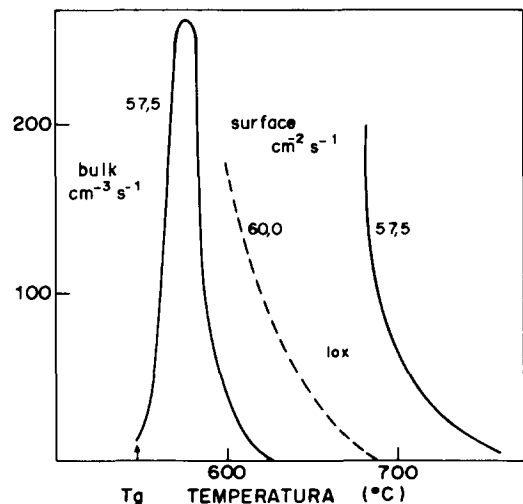


Fig. 2. Surface and internal nucleation rates in $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ glasses. The scale for the surface nucleation rates is one tenth of that shown on the y-axis [10].

by phase separation. Therefore, the surfaces of amorphous droplets do not catalyze nucleation.

Hishinuma [13] carried out an extensive experimental program with the aim of detecting internal nucleation in $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{PbO} \cdot \text{SiO}_2$ glasses. Crystallization was detected only on the external surfaces and none at the (internal) bubble surfaces. In addition, $\text{PbO} \cdot \text{SiO}_2$ glasses previously etched by HF did not present any evidence of surface crystallization.

Recently, Zanotto and Basso [14] studied an almost stoichiometric diopside glass, heated at 820°C from 1 to 4 h, and concluded that the nucleation rate of diopside crystals was undetectably high and occurred from a fixed number ($80\,000/\text{mm}^2$) of particular sites on the external glass surface.

Therefore, except for the studies reported in refs. [10] and [14], which were quantitative, research on surface nucleation kinetics has been mainly qualitative and controversial. For instance, Klingsberg [5] and Bergeron and DeLuca [7] concluded that bubble surfaces are privileged nucleation sites, while most authors agree that only those containing some sort of solid particles are active [2,4,8,13]. In ref. [10], the authors concluded that the number of surface crystals increases with the temperature of treatment, while in refs. [11] and [14] a constant number of sites, independent of time and temperature, was observed. Thus the objective of this paper is to determine *quantitatively* the surface nucleation kinetics in several glasses, in a wide range of temperatures, and to relate the kinetics to the chemical composition of the both parent glass and crystal phases, as well as to the surface condition of the parent glass. Soda–lime–silica glasses were chosen because of their chemical stability, the possibility of nucleating more than one phase in the same glass and finally because of the commercial importance of understanding and controlling devitrification in these glasses.

2. Experimental work

In this research several soda–lime–silica systems were studied, a $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ (de-

vitrite), a non-stoichiometric devitrite, a float glass and a microscope slide glass. Most data were gathered with the last two glasses.

2.1. Float glass

Table 1 presents the chemical analysis of the float glass used here, produced by CEBRACE-Brazil, together with a similar glass, produced by Pilkington Brothers, UK, studied by 13 laboratories in a round-robin test organized by the ICG. This last material had a liquidus temperature in between 995 and 1010°C . The primary devitrification products were devitrite and/or β -Wollastonite.

In this work, a total of 380 specimens were heat treated (in triplicate) at 750 , 775 and 800°C for periods of up to 65 h. Above 800°C , the glasses were too soft and they warped with treatment. A different set of specimens was used for each time period. Three phases were identified by XRD and EDS analysis – devitrite, diopside and tridimite. A fourth, unknown, phase, appeared during some treatments. The microstructures were analyzed by standard ceramographic procedures by means of optical micrographs.

The following parameters were determined: N_s , the average number of crystals per unit area; D_M , the largest dimension of the crystal; and the fractional area crystallized. Figure 3 shows a typical plot of number of devitrite crystals/ mm^2 for glasses treated at 750 , 775 and 800°C .

For the three temperatures, there is a large scatter in N_s , much more pronounced than that normally observed for internal nucleation, which is typically less than 20% [15]. It should also be

Table 1
Chemical compositions (wt%) of two float glasses

	This work	ICG glass
SiO_2	74.91	71.80
Na_2O	10.51	13.60
CaO	9.25	8.78
MgO	3.61	3.76
Al_2O_3	0.94	1.01
K_2O	0.47	0.60
Fe_2O_3	0.30	0.10
SO_3		0.26

stressed that for all temperatures and for most heat treatment times, at least one specimen (among the three treated together) did not show any crystals. A third important observation is that N_s does not depend on time or temperature, i.e. the values of N_s are scattered from 0 to 2600/mm² for all heat treatments.

Figure 4 shows the variation of the largest diameter of the devitrite crystals with time and temperature. The crystal growth rate (dD_M/dt) seemed to be approximately constant (at least at 775 and 850 °C). From an Arrhenius plot, the apparent activation enthalpy for crystal growth, H_c , is 135 kJ/mol. Fractional areas transformed of up to 65% (after 50 h of treatment) were measured [16].

In addition to devitrite, diopside crystals were detected at 775 °C and 800 °C. The overall behavior was similar to devitrite; however N_s varied from 0 to 500/mm², i.e. the number of sites was smaller than for devitrite. Both phases presented similar sizes for a given heat treatment implying that the growth rates were similar. A third phase, tridimite, appeared in much smaller numbers but

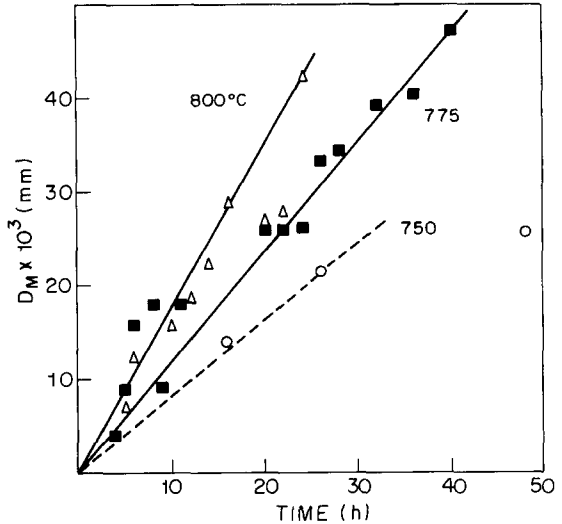


Fig. 4. Largest diameter of devitrite crystals at the surface of the float glass [16] at (Δ) 800 °C, (■) 775 °C and (○) 750 °C.

with crystal sizes about 20 times larger than those of the other two phases.

Experiments designed to verify the effect of possible compositional variations between the two faces of the float glass did not reveal any significant difference in N_s . Further experiments with glass specimens for which N_s was zero (after an initial treatment at 750 °C) demonstrated that they only nucleated after polishing and then heat treating again at 800 °C. Scratching the surfaces of zero N_s samples and heating at 800 °C for 10 h healed the scratches but did not result in nucleation. Finally, only three specimens crystallized among the five that were mechanically polished and tested at 800 °C for 2 h.

2.2. Microscope slide glass

An experimental research program, similar to that described above, was carried out with a commercial microscope slide glass. The effect of the external surface condition was tested by using three types of specimens: as-received, mechanically polished, and fire-polished specimens that were treated from 715 to 1000 °C, for time periods of up to 30 h. In this case, only devitrite crystallized for periods up to 15 h when a second, unidentified, minor phase appeared.

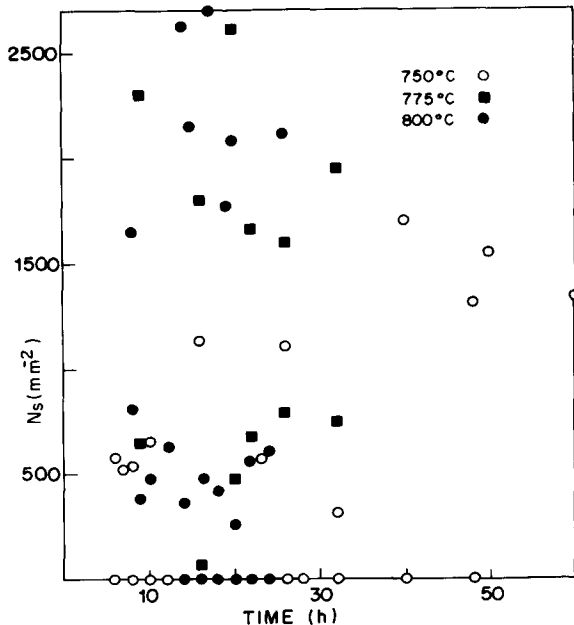


Fig. 3. Average number of devitrite crystals per mm² as a function of heat treatment time at 750, 775 and 800 °C [16].

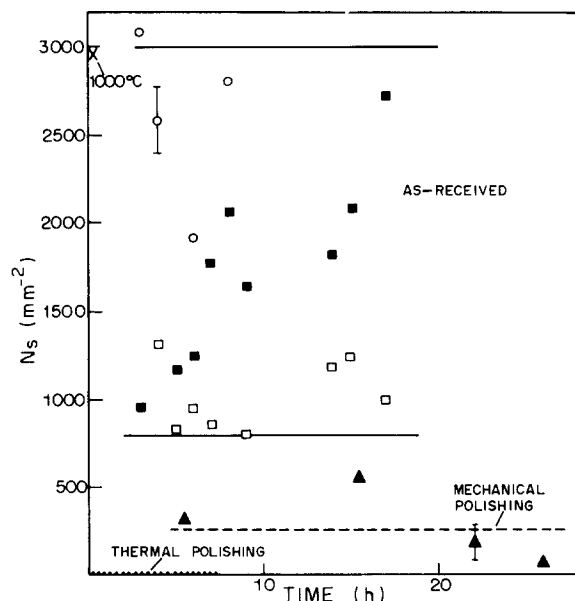


Fig. 5. Average number of devitrite crystals per mm^2 on a commercial microscope slide glass. \blacktriangle , mechanical polishing. As-received: \circ , 715 °C; \blacksquare , 730 °C; \square , 735 °C; \times , 1000 °C.

Figure 5 summarizes the variation of N_s with time, temperature and surface treatment. As for the float glass, there is a large scatter in the experimental values. However, for a given surface condition, these values are fairly insensitive to

variations in heat treatment from 715 to 1000 °C, from 3 to 30 h! The dominant effect is clearly the surface condition. For specimens with as-received surfaces, N_s varied from 800 to 3000/ mm^2 , while for mechanically polished surfaces N_s was significantly smaller, i.e. 100 to 600/ mm^2 . Specimens tested above the melting point of devitrite (1047 °C), i.e., at 1100 °C for 15 min before heat treatment (fire-polished specimens), did not nucleate at 730 °C up to 7.5 h.

The crystal growth rates were time independent at 730 and 735 °C. Fractional areas crystallized up to 85% were covered with the range of treatments employed.

Other systems such as an almost stoichiometric devitrite, and a stoichiometric devitrite, NC_3S_6 , were also studied. A summary of the experimental values of N_s obtained with all systems studied by the author's research group is presented in table 2.

3. Discussion

The experimental results described above allow one to infer the effects of temperature, time, surface condition and chemical composition on the number of active surface nucleation sites, N_s .

Table 2
 N_s values for several glasses

Glass	Surface ^{a)}	Treatment	N_s (mm^{-2})	Crystal
Diopside	MP	820 °C-4 h	$(6-10) \times 10^4$	Diopside
NC_3S_6	MP	700 °C-	10^5	Devitrite
Non-stoich. devitrite	MP	700 °C-24 h	50-100	β -wollastonite
	MP	700 °C-24 h	50-100	Tridimite
	MP	700 °C-24 h	150-700	Devitrite
Mic. slide	MP	720 °C-26 h	100-600	Devitrite
	AR	715 °C/1000-30 h	800-3000	Devitrite
	FP	730 °C-7.5 h	0	-
Float	AR	750 °C/800-60 h	300-3000	Devitrite
	AR		50	Diopside
	AR		25	Unknown
	AR		10	Tridimite
	some specimens		0	-

^{a)} MP, mechanically polished; AR, as-received; FP, fire-polished.

For all glasses studied, the nucleation rates were very fast, reaching saturation quite early in the transformation, and could not be experimentally determined. The number of active sites, N_s (but not the nucleation rates), were time and temperature independent for a wide range of heat treatments covering fractional areas crystallized from 5 to 85%.

It is quite clear, however, that the surface condition has a pronounced effect on N_s . For instance the number of devitrite crystals in a microscope slide glass varies from zero, for fire-polished surfaces, to 3000/mm² for as-received surfaces. That was also observed for a float glass, where specimens with (presumably) virgin surfaces did not show any nucleation, while N_s was as 2600/mm² in others. Mechanical polishing improves the surface condition (makes cleaning easier) of as-received specimens and diminishes the nucleation tendency. Finally, it should be stressed that the number of nucleating sites are much increased on 'dirty' surfaces. This last point agrees with previous studies.

The chemical compositions of the parent glass and also that of the crystallizing phase have a strong effect on the number of crystals nucleated. Thus, for a given surface condition and crystal phase, e.g. for mechanically polished surfaces, the average number of devitrite crystals was $> 10^5$ /mm² in a stoichiometric devitrite glass, 50–100/mm² in a non-stoichiometric devitrite glass, and 100–600/mm² in a commercial soda-lime-silica glass. A different phase in the same parent glass also nucleated with distinct efficiencies. For instance in a float glass (as-received surface), N_s was 300–3000/mm², 50/mm², and 10/mm² for devitrite, diopside and tridimite crystals, respectively, whereas in an almost stoichiometric diopside glass, the number of diopside crystals was approximately 80 000/mm².

For the heterogeneous nucleation rate, I_s , which is obviously the case here, one may write

$$I_s \approx n_s f \nu \exp\left(\frac{-G_d}{RT}\right) \exp\left(\frac{-gF(\theta)\sigma^3}{RTG_v^2}\right), \quad (1)$$

where n_s is the total number of 'formula' units of crystallizing phase/unit area, f is a constant fac-

tor, ν is the vibration frequency, G_d is the activation energy for molecular transport, g is a geometrical factor, $F(\theta)$ is a function of the contact angle θ , σ is the interfacial energy and G_v is the driving force/unit volume. For nucleation induced by N_s identical particles, $fn_s = N_s$.

Unfortunately, I_s could not be measured in this study because it is very high. Consider the possible effects of the relevant parameters on I_s . The number of nucleating sites was clearly dependent on the presence of some sort of impurities, as demonstrated by the strong dependence of N_s with the degree of surface perfection and of cleanliness. The large scatter in N_s is further evidence of surface contamination. The influence of the chemical composition of both parent glass and crystal phase on N_s indicates that impurities are not equally efficient for the nucleation of different phases. Stoichiometric diopside and devitrite glasses presented the highest number of surface crystals.

The possible lowering of the surface energy at the external surface was analyzed by Uhlmann [17], based on his experimental observations on the melting of quartz and albite crystals. He proposed that the absence of a nucleation barrier for melting at the external surfaces (almost no superheating was required) and the complete wetting of the crystal surface by the melt implies that

$$\sigma_{cv} > \sigma_{cl} + \sigma_{lv}, \quad (2)$$

where σ refers to the interfacial energy and c , v and l to the crystal, vapor and liquid, respectively. If relation (2) applies as well at temperatures below the melting point, then the external surfaces of liquids should not be preferred sites for crystal nucleation since such nucleation would imply

$$\sigma_{cv} < \sigma_{cl} + \sigma_{lv}. \quad (3)$$

In other words, eq. (3) must be satisfied for nucleation at the free glass surfaces; however, it is contrary to eq. (2) which was experimentally established.

In this work no nucleation was observed on a clean, fire-polished surface in a clear experimental confirmation of Uhlmann's arguments. The absence of nucleation on bubble surfaces, reported by several authors, reinforces this conclusion.

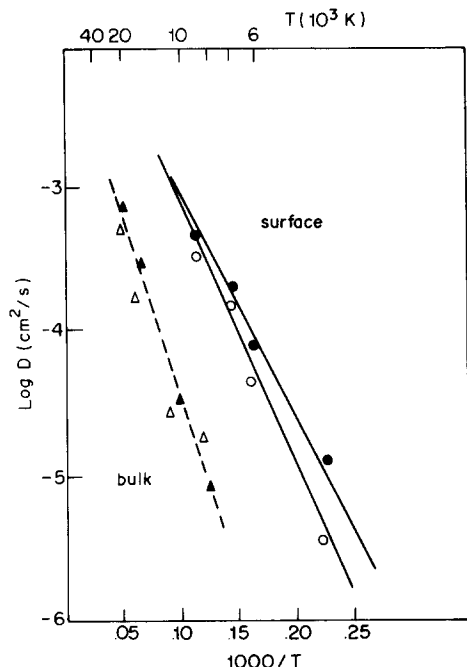


Fig. 6. Calculated surface and bulk diffusion rates of Si and O in silicate glass [18]. Oxygen: \blacktriangle , bulk; \bullet , surface. Silicon: \triangle , bulk; \circ , surface.

Another possibility for preferential nucleation at external surfaces is an increased mobility of ionic species at glass surfaces and consequently an enhanced kinetic term in eq. (1). This point has been demonstrated by the MD calculations of Garofalini and Canover [18] for SiO_2 glass. They concluded that the diffusion coefficients for Si and O at the surface (top 5 Å) are about one order of magnitude greater than those in the bulk. The activation enthalpies of the surface species are 350 and 420 kJ/mol for O and Si; these are lower than the reported value of 590 kJ/mol for each specie in the bulk (fig. 6).

An additional enhancement of mobility is also possible. The catalytic effect of OH-groups is well known [19]. Several authors demonstrated that the overall crystallization rates (bulk and surface) are much increased when glasses are heat treated in a H_2O rich atmosphere. The external surfaces are obviously in closer contact with H_2O than the interior and thus the surface is most likely to suffer such catalyses.

Further evidence for increased diffusion rates at external surfaces is furnished by the crystal growth behavior. The apparent activation enthalpy for the crystal growth of devitrite at the float glass surface is 135 kJ/mol, while that for viscous flow is 290 kJ/mol in the same temperature range (750–800 °C) [16]. This indicates that surface growth is not controlled by viscous flow as observed for internal growth in some glasses. More detailed studies are being carried out in the present author's laboratory to check this important point.

4. Conclusion

The surface nucleation kinetics in several silicate glasses strongly depend upon the number of certain (as yet unknown) foreign particles, which in turn depend on the degree of surface perfection. The nucleation efficiency of such particles is a function of both parent glass and crystallizing phase. The free glass surfaces are not preferred nucleation sites. The surface nucleation rates are too high to be measured by the usual technique. The fast nucleation rates are due to the catalytic effect of the foreign particles, which lower the interfacial free energy, and are also due to the increased atomic mobility at the free glass surface.

Much more work is needed to identify the active contamination particles and to determine the actual surface nucleation rates.

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It is the purpose of this report to assist in the design and interpretation of a systematic work on surface crystallization kinetics now being carried out by the Devitrification Committee of the ICG, TC7. The author acknowledges the collaboration of the TC7 chairman Dr Pannhorst and of Professor Höland and Dr Szabo.

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