

EXPERIMENTAL STUDIES OF SURFACE NUCLEATION AND CRYSTALLIZATION OF GLASSES

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1. INTRODUCTION

Surface crystallization is much more frequent than internal crystallization but, paradoxically, has been much less studied. One possible reason for the lack of detailed studies on the subject is the inherent difficulty of controlling and characterizing the surface properties of glass.

From a technological point of view, the establishment of a firm understanding and the ability to control the kinetics of surface nucleation and growth in glasses may lead to the development of a wide variety of information devices for optical memories and related applications [1]. Additionally, controlled surface crystallization has proved to be quite an effective method of enhancing the strength of glass [2].

The mechanisms of surface crystallization are still a matter of controversy. Several factors which promote free surface crystallization have been alluded in the past and include: cracks or irregularities in the surface, alteration due to chemical reactions with the atmosphere, differences between bulk and surface composition, contamination with solid particles, etc. Most studies carried out so far, however, are qualitative and the relative importance of these potential origins of surface crystallization in various glasses have not been determined.

The relevance of surface crystallization was recognized by the devitrification committee (TC7) of the ICG which started a multinational research effort on the subject in 1989.

The objective of this paper is to review and analyze most of the relevant papers on surface crystallization

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and also to present a few results generated by the TC7 Committee on the subject. The goal is to provide a firmer understanding of the causes for the predilection of glasses to crystallize from the surface rather than in the bulk. In addition, the question of whether or not there is an intrinsic preference for crystallization at the free surfaces will be addressed.

2. SURFACE NUCLEATION

2.1. Effects of Surface Quality, Chemical Composition and Temperature

Only a few comprehensive studies were devoted to heterogeneous nucleation in glass, on crucible walls and on metallic particles, see for instance [3-6], and the subject certainly deserves further attention. In this article, however, I deal only with isothermal studies on free surface crystallization.

Starting in the early thirties, a number of papers of qualitative nature were published concerning the surface devitrification of several glasses.

Observations of crystallization around internal bubbles were specially important because their surfaces are in principle much cleaner than the external glass surfaces. These papers were summarized recently [7] and are listed in Table 1.

Table 1. Surface crystallization studies.

Author	Year	Glass	crystals on bubbles ?
Morey	30	Soda-lime-silica	no
Scott	61	Na ₂ O.2SiO ₂	no
Klingsberg	67	BaO-Al ₂ O ₃ -TiO ₂ -SiO ₂	no
Ernsberger	66	Soda-lime-silica	only on a few bubbles
Mattox	67	CaO-Al ₂ O ₃ -B ₂ O ₃	in those with solid particles
Hishinuma	86	PbO.SiO ₂ , Na ₂ O.2SiO ₂	no

Despite some controversial results, the majority of papers indicate that only those bubbles contaminated with solid particles are preferential nucleation sites. Most studies provided no evidences for nucleation on (clean) bubble surfaces. It should also be emphasized that it is generally accepted by glass technologists, that glasses with dirty surfaces crystallize much easier than those with clean surfaces.

McMillan [8] reviewed his own group's work and demonstrated the effects of surface abrasion upon crystallization in CaO-ZnO-SiO₂ glasses and CaO-Al₂O₃ glasses. For the former glasses, three different surface treatments were employed ;a) 220 grit grinding, b) partial polish and c) "full" polish. After devitrification at 840°C for 10 minutes it was found that glasses given finish a) exhibited the largest number of crystals, while those given finish c) produced the smallest crystallite density. However, the crystal morphologies were the same in all glasses. Differences in crystalline morphology, though, were noted for CaO-Al₂O₃ which received different polishes. No efforts were made to determine the effects of time or temperature.

Zanotto and Basso [9,10] determined the crystallite density, the crystal growth rate and the fractional area crystallized of diopside crystals (MgO.CaO.2SiO₂) on mechanically polished surfaces of an almost stoichiometric diopside glass (T_g=730 °C) subjected to a single stage treatment at 820°C. The number of surface crystals fluctuated around an average value, N_s, which remained constant for treatments between one and four hours. At this point the fraction crystallized reached approximately 0.6 and crystal impingement prevented further measurements. For periods shorter than one hour, the small crystal size rendered the measurements inaccurate. Unfortunately, the nucleation process was completed in the early stages of crystallization (t < 1h) and thus the nucleation rate could not be measured, even with a SEM (perhaps a double stage heat treatment could solve this problem). On the other hand, by using the measured values of the crystal growth rate and assuming that surface nucleation occurred rapidly from a constant number of random sites, N_s (experimentally determined), the time evolution of the fractional area crystallized was calculated by the JMA theory and compared with the experimental values. Figure 1 shows a good agreement between the theoretical and experimental curves, which confirms the proposed nucleation mechanism, ie., heterogeneous nucleation from a fixed number of sites.

Recently, Zanotto [7] summarized his student's measurements, in a wide range of thermal treatments to probe the effects of time and temperature in various soda-lime-silica glasses; a devitrite (Na₂O.3CaO.6SiO₂), a non-stoichiometric devitrite, a float glass and a microscope slide glass. These compositions were

chosen due to their chemical stability (so the surfaces would remain unchanged during the period of study), due to the possibility of crystallizing different phases in the same glass (in order to infer compositional effects), and finally due to their commercial importance.

The average number density of crystals nucleated, N_s , strongly depended on the surface condition (e.g. **fire** versus **mechanically** polished or **as-received** surface, **clean** versus **dirty**), on the chemical composition of the parent glass, and also on the nature of the crystallized phase. However, N_s did **not** depend on heat treatment time or temperature. An important observation is that no crystals formed on several (clean) **fire** polished surfaces. Figure 2 and Table 2 summarize the experimental crystallite densities for the microscope slide and the float glass. As in the case of diopside, the surface nucleation process was finished in the early stages of the transformation, before significant crystal growth to observable sizes took place, and thus the nucleation rates were too fast to be measured in all temperatures (715 to 1000 °C).

In the same year, an independent study was carried out by Muller and Thamm [11] who determined the nucleation density at **fractured** and also at **mechanically** polished cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, $T_g=815^\circ\text{C}$) glass surfaces heat treated from 900°C to 980°C, for periods up to one and a half hours. Figure 3 shows that the scatter in N_s is quite large but no time or temperature dependence is observed, in agreement with the results for diopside and soda-lime-silica glasses [7,9,10].

A very detailed work was recently published by Kalinina et. al. [12] who determined the crystallite density at the surface of a cordierite glass from 140°C to 860 °C, for periods up to 450h, employing a development treatment at 933°C for 1.5h. Two crystal types were observed, hexagonal μ -cordierite crystals and small rhombohedral crystals, of an unknown x-phase. The number density of μ -cordierite crystals were time and temperature independent, confirming the trends observed for the single stage treatments of other studies [7-11]. However, in this case, the surface nucleation rate of the x-phase was determined and presented a clear maximum around 820-830°C, in the neighborhood of T_g , as commonly observed for homogeneous nucleation. As far as I know this is the sole study where surface nucleation rates have been

measured. The identity of the x-crystals and why the surface nucleation rates are sufficiently slow to allow for their measurement are not known at present.

Table 2 summarizes the crystallite densities reported by several authors for different glasses.

Table 2. Surface crystallite densities.

Author	Year	Treatment	Glass	N_s (mm^{-2})
<u>Ground surface</u>				
McMillan	82	840°C / 10min	ZAS	$3 \cdot 10^4$
<u>Polished</u>				
McMillan	82	840 / 10min	ZAS	$1 \cdot 10^3$
Zanotto	86	820 / 0-4h	CMS ₂	$8 \cdot 10^4$
Zanotto	90	700 / 0-24h	NCS	$4 \cdot 10^2$
Zanotto	90	720 / 0-26h	NCS	$3 \cdot 10^2$
Kalinina	90	140-860/450h	M ₂ A ₂ S ₅	$1 \cdot 10^2$
Muller	90	900 / 10 min	M ₂ A ₂ S ₅	$5 \cdot 10^3$
<u>As-received</u>				
Zanotto	90	750-800 / 0-30h	Float	$0-3 \cdot 10^3$ *
<u>Fractured</u>				
Muller	90	900-980 / 0-80min	M ₂ A ₂ S ₅	$2 \cdot 10^2$
<u>Fire-polished</u>				
Zanotto	90	730 / 0-7.5h	NCS	Zero
Yamane	90		GM 30870	"lowest"

* range of values for different crystal phases.

Summarizing, the results of Table 2 and Figure 2 show that the surface crystallite densities strongly depend on the surface condition. The smoother (and presumably the cleaner) the surface the smaller is N_s . Some fire polished specimens and some (as-received) float glasses, with pristine surfaces, did not crystallize at all, while N_s was almost $10^5 / \text{mm}^2$ for some ground and for mechanically polished specimens.

The results of [7-12] also indicate that, in most cases, surface nucleation finishes in the early stages of the transformation, and saturation occurs before any measurement of the heterogeneous nucleation rate can be made, in a wide temperature range, from T_g to T_m (the x-phase was an exception).

A possible explanation for the apparent lack of temperature dependence of the surface nucleation rates is provided by the classical theory, which is capable of describing reasonably well the temperature dependence of homogeneous nucleation rates in glasses

[6]. If one uses the classical equation, and allows the reduced interfacial energy, $\alpha = \sigma N_A^{2/3} V_M^{1/3} / \Delta H_m$ (these parameters were defined elsewhere [6]) to vary from typical values for homogeneous nucleation ($0.4 < \alpha < 0.6$) to the expected small values for heterogeneous nucleation ($\alpha < 0.3$), it is seen that the smaller the value of α , the flatter, and consequently the less dependent on temperature, is the nucleation curve.

Finally, the absence of crystals on some clean, pristine, surfaces and also on most bubble surfaces provide clear evidences that the free surfaces are not preferential nucleation sites, in agreement with the thermodynamic arguments of Uhlmann [17].

2.2. Effects of the Atmosphere

The effects of the surrounding atmosphere on the crystal growth rates are reasonably well documented [8]. However, much less is known about the effects of atmosphere on surface nucleation densities.

A detailed study was performed by Takahashi and Sakaino [13] who measured the crystal growth rates and also the crystallite densities on the surface of a $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass ($T_g = 470^\circ\text{C}$) for a series of heat treatments, from 200 to 500°C in N_2 , CO_2 and water vapor. The number of crystals increased in the following order; in dry N_2 , in H_2O vapor, being much larger in dry CO_2 , with a maximum at $250\text{--}300^\circ\text{C}$. They demonstrated that Na_2CO_3 crystals formed at the glass surface provided active sites for crystallization of sodium disilicate crystals at the development temperature (600°C for 20min).

Partridge and McMillan [14] have shown that atmospheres containing reduced oxygen and water contents inhibit surface nucleation of a $\text{ZnO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ glass.

3. CRYSTAL GROWTH

In the vast majority of experimental studies of crystal growth in glasses, nucleation spontaneously initiates or is induced at the glass surface and the time evolution of the crystallized layer growing towards the specimen center is determined by microscopy techniques. Thus, the growth kinetics refer to molecular rearrangements in the bulk of the glass.

Recently, a different experiment was carried out with an almost stoichiometric cordierite glass supplied by

Shott Glass for the TC 7 Committee members. The full set of results will be presented in a forthcoming congress [15], but a relevant summary is given below. Three types of growth kinetics were determined, i.e., of: i) crystals which nucleated at the surface and grew in the bulk, ii) surface nucleated crystals which grew two-dimensionally on the surfaces, in the early stages of the transformation, and iii) internal crystals, which nucleated on foreign particles, and grew in the bulk. The three types of growth rates were equal, within experimental error, implying that the surface and bulk diffusion processes for growth, and inferentially for nucleation, are similar.

In a previous paper [7] I suggested that the bulk and surface diffusional mechanisms might be different. That suggestion was based on molecular dynamics calculations and also on the observed differences between the activation enthalpies for crystal growth, H_c , and viscous flow, H_η , in a float glass which crystallized from the surface. This matter is clarified in [18] where we demonstrate that the differences in H_c and H_η are genuine for most glasses and not only for those which only nucleate at the surfaces.

4. SUMMARY

Surface nucleation saturates in the early stages of crystallization for most glasses. The nucleation rates are too fast to be measured in wide temperature ranges, from T_g to T_m . This insensitivity to temperature is due to the small values of surface energy.

Nucleation is not observed on pristine, clean, surfaces, as predicted by simple thermodynamic arguments. Surface nucleation is mainly due to impurity particles whose number is inversely proportional to the degree of surface perfection and cleanliness.

There is much scope for further work on surface crystallization.

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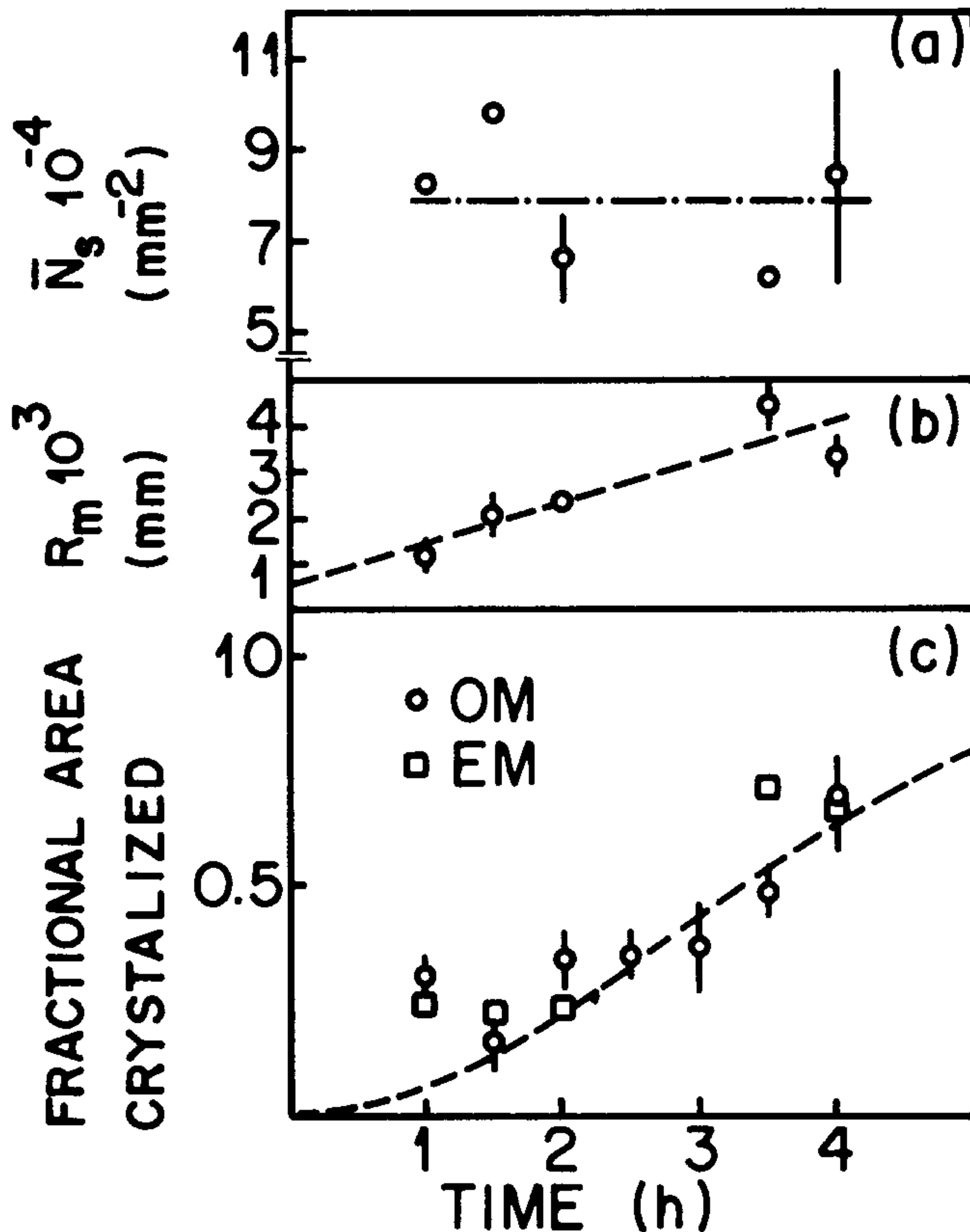


Fig. 1- Surface crystallization of a diopside glass at 820°C. (o) Optical microscopy (□) SEM [10].

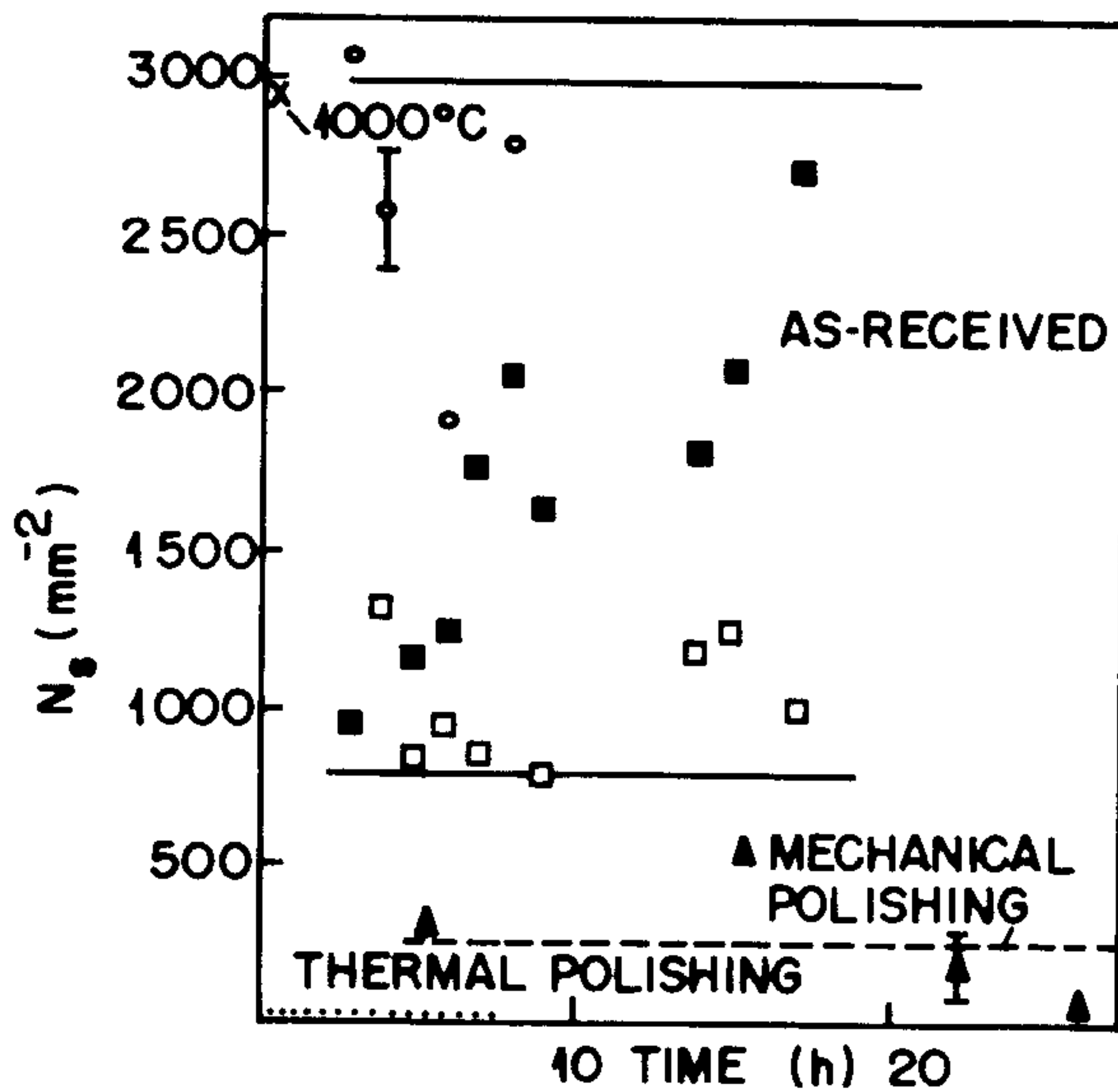


Fig. 2- Crystallite density on the surfaces of a soda-lime silica glass. As-received surfaces: (o) 715°C; (■) 730°C; (□) 735°C; (x) 1000°C [7].

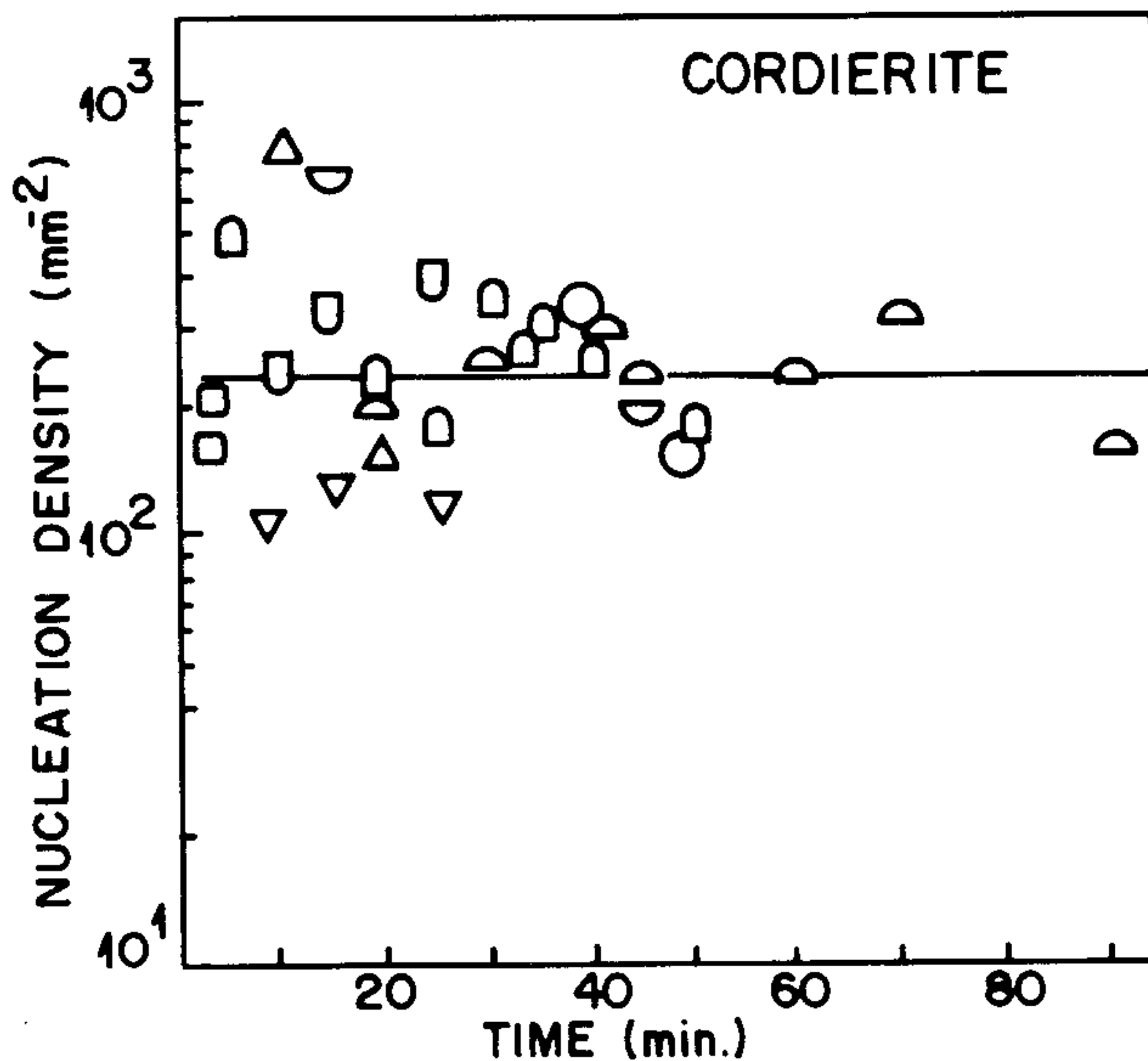


Fig. 3 - Crystallite densities at fractured surfaces of a cordierite glass treated from 900°C to 980°C [11].