

Letter to the Editor**Surface nucleation in a diopside glass**

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The kinetics of nucleation and growth of diopside crystals ($\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$) on the surface of a diopside glass at 820°C were studied. The largest crystal size, crystal number density per unit area and fractional area crystallized were measured in both optical and SEM micrographs. It was concluded that surface nucleation occurs very rapidly from a random number of active sites. The General Theory of Transformation Kinetics describes well the case of fast heterogeneous nucleation from a constant number of sites at the glass surface.

Several types of phase transformations occur by nucleation and growth of second phases. The kinetics of such processes are usually described by a theory derived by Kolmogorov [1], Johnson and Mehl [2] and Avrami [3–5] in the late 1930s, known as the General Theory of Transformation Kinetics [6]. This theory is intensively used to infer the mechanism of phase transformations in metals, polymers and inorganic glasses [7–12].

Recently the theory was rigorously tested, without any adjustable parameter, with two glasses which nucleate homogeneously: $\text{BaO} \cdot 2\text{SiO}_2$, which shows spherulitic crystallization [13], and $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, which shows single crystals [14]. It was concluded that, if proper precautions are taken in the measurement and analysis of both crystal nucleation and growth rates, the theory predicts well the glass–crystal transformation.

The purpose of this letter is to present a test for the (expected) validity of the General Theory for the case of heterogeneous crystal nucleation in glass, specifically for nucleation at the glass/air surface.

The most universal form of the theory for the fraction transformed, α , is

$$\alpha = 1 - \exp(-\alpha'), \quad (1)$$

where α' is the fictitious fraction transformed, which is calculated by neglecting impingement effects, allowing each crystal to nucleate and grow inside the previously born crystals. This quantity can be calculated if the nucleation, $I(t)$, and growth rate, $U(t)$, time functions are known at the temperature of interest.

One hundred grams of an almost stoichiometric $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$ (diopside) glass, with 1 wt% Al_2O_3 to minimize spontaneous devitrification, was melted at 1450°C for 5 h in a platinum crucible. This particular composition was chosen because only surface nucleation is observed in this glass [15,16] and, due to its excellent resistance to atmospheric attack, surface modification is minimized during the period of study.

Thin specimens were obtained by quenching the molten glass between two steel plates. One surface of each specimen was polished to optical quality, cleaned with acetone, and then the specimens were heat treated at $820 \pm 2^\circ\text{C}$ from 1 to 4 h. Chemically etching with a 0.2% HF–0.1% HCl solution for 30 s was enough to reveal the microstructures of the partially crystallized materials. The samples were photographed with an Olympus optical microscope ($40\times$ objective lens) and also with a Cambridge Stereoscan SEM under $4000\times$

magnification. Approximately 200 crystals were counted and measured per specimen to determine the average number of crystals per unit area, \bar{N}_s , the maximum edge size, $R_m(t)$, and the fractional area crystallized, $\alpha(t)$.

Figure 1 shows a typical SEM micrograph of surface crystals (diopside) in the diopside glass. The time dependence of the average number of crystals per unit area, \bar{N}_s , maximum edge dimension, $R_m(t)$, and fractional area crystallized are shown in figures 2(a), (b) and (c) respectively.

There is a large statistical scatter around a mean value of $N = 78\,900$ crystals/mm²; however, this value does not depend on the heat treatment time, at least up to 4 h at 820°C. Therefore, nucleation occurs rapidly from a fixed number of (unknown) sites in the very early stages of crystallization.

Figure 2(b) shows that the growth rate $U = dR_m/dt = 2.48 \times 10^{-7}$ mm/s, is constant up to 4 h at 820°C. The extrapolated straight line gives a positive intercept, indicating that nuclei or active particles of about 0.5 μm existed at the original glass surface.



Fig. 1 Square diopside crystals on the surface of diopside glass heated at 820°C. Bar indicates 1 μm.

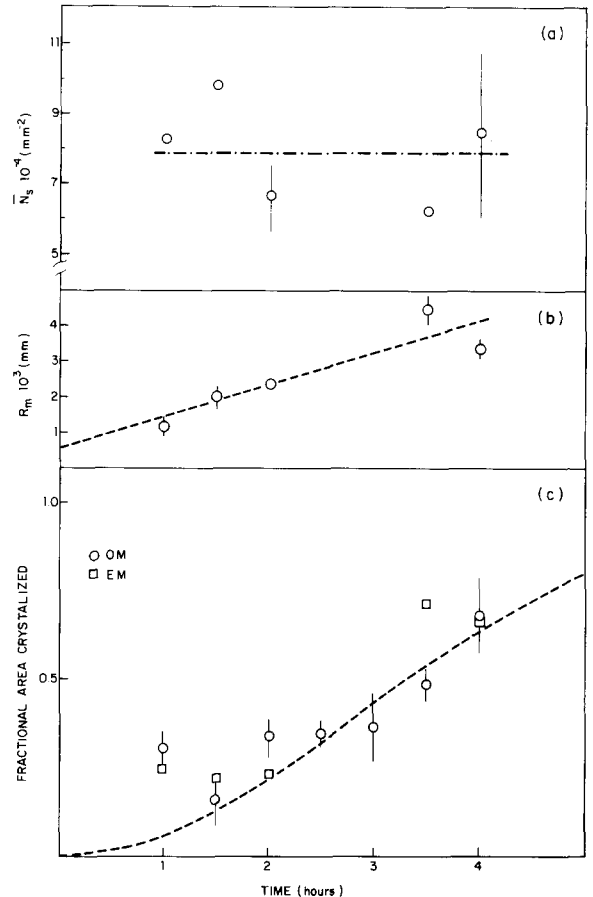


Fig. 2. Time dependence of (a) the average number of crystals per unit area, \bar{N}_s , and (b) maximum edge size, R_m . Figure 2(c) refers to the fractional area crystallized, α , determined by optical microscopy (\circ) and by electron microscopy (\square). The dotted line is the theoretical curve calculated by eq. (4).

For the special case under study, i.e. fast nucleation of square shaped crystals from a fixed number of sites at the glass surface, N_s , the fictitious fractional area transformed, α' , is

$$\alpha'(t) = N_s R^2(t), \quad (2)$$

where $R(t)$ is the edge size.

If the growth rate, U , is time-independent, the edge dimension can be related to the heat treatment time, t , by the simple relation

$$R(t) = Ut. \quad (3)$$

Therefore, the actual fractional area crystallized is easily computed by the combination of equations (1–3):

$$\alpha'(t) = 1 - \exp(-N_s U^2 t^2), \quad (4)$$

and can be compared with experimental values.

The evolution of the fractional area crystallized, shown in fig. 2(c), is reasonably well described by eq. (4), calculated using the experimental values of N_s and U .

The overall behavior is similar to that reported for the volume nucleation in a nearly stoichiometric $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glass [14]. In the present case, however, the statistical scatter in N_s and α are much more pronounced due to the heterogeneous nature of surface nucleation.

In summary, this result supports our previous work on surface nucleation kinetics [17] where it was concluded that surface nucleation occurs very rapidly from some random number of active (impurity) sites. The General Theory of Transformation Kinetics describes well the case of instantaneous heterogeneous nucleation from a constant number of sites at the glass surface.

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