

# Advances in Nucleation and Crystallization in Glasses

**SYMPOSIUM OF THE GLASS DIVISION  
OF THE AMERICAN CERAMIC SOCIETY**

**Special Publication No. 5**

# Advances in Nucleation and Crystallization in Glasses

**SYMPOSIUM OF THE GLASS DIVISION  
OF THE AMERICAN CERAMIC SOCIETY**

**April 26-28, 1971**

Edited by

**L. L. HENCH**  
University of Florida  
Gainesville, Florida

and

**S. W. FREIMAN**  
Naval Research Laboratory  
Washington, D. C.

**Special Publication No. 5**

© COPYRIGHT 1971 BY  
THE AMERICAN CERAMIC SOCIETY, INC.  
65 CERAMIC DRIVE, COLUMBUS, OHIO 43214

Printed in the United States of America



## FOREWORD

The papers in this volume were presented at the Glass Division Symposium, "Nucleation and Crystallization—Revisited," held at the 73rd Annual Meeting of the American Ceramic Society, April 26-29, 1971, Chicago, Illinois.

Ten years have passed since the "Symposium on Nucleation and Crystallization in Glasses and Melts" was published by the American Ceramic Society in 1962. During that period, the number and variety of industrial and consumer products manufactured by the crystallization of glass have become extensive. These products include radomes, cookware and dinnerware, telescope mirror blanks, building materials, cements and coatings, to mention only a few. The large number of patents in the field indicates how many types of glasses can be converted into glass-ceramics and the wide range of useful properties that such materials possess. The technology necessary to produce this wide variety of glass-ceramic materials has been made possible by extensive scientific research performed throughout the world during this period. It is this research that forms the basis for the present volume.

The format of this volume is the presentation of a keynote review of progress in each of the areas of nucleation, crystallization and applications to glass-ceramics. Each keynote review is followed by papers emphasizing the viewpoint of various laboratory groups active in the field, integrating recent results into their general approach to the problem. Finally, each section of the book contains specific new research contributions, thus yielding both a historical as well as a journalistic perspective to the proceedings. All papers were given technical reviews through regular Society review procedures.

It is with special pleasure that the editors acknowledge the contributions from several international laboratories. We also wish to express sympathy to the Bulgarian Academy of Sciences on behalf of the American Ceramic Society with relation to the untimely death of Dr. Svetoslav D. Toshev, one of the contributors to this volume.

The editors express particular appreciation for the direction and assistance provided by Dr. Daniel Stewart, 1970-71 program chairman of the Glass Division, throughout the organization and administration of the Symposium. It was through his suggestion that the Symposium was organized. Grateful acknowledgement is also expressed to Miss Margie Reser, Mr. James Welch and Dr. Lowell Swarts for their guidance and assistance in the many administrative matters encountered throughout the course of preparing this proceeding.

A Review  
Donald N. Thissen

Kinetics of Overall Crystallization  
Melts in Terms of the Nonsteady State  
of Nucleation

J. Cutler and P. Zaslavsky

Crystal Growth in Network Liquids by  
Rearrangement

A. R. Cooper

L. L. Hench

S. W. Freiman

## CONTENTS

|   | Page |
|---|------|
| - NUCLEATION -  |      |
| Nucleation in Glass—A Review<br><i>J. J. Hammel</i>   | 1    |
| The Kinetics of Nucleation and the Formation<br>of Glass-Ceramic Materials<br><i>I. Gutzow and S. Toshev</i>  | 10   |
| Use of Pair Correlation Functions in the Study<br>of Phase Separation Kinetics<br><i>P. K. Gupta and A. R. Cooper</i>                                   | 24   |
| Scattering Characteristics of a Classically<br>Nucleated and Coalesced Microstructure<br><i>D. T. Sturgill</i>  | 33   |
| Effects of Oxide Nucleating Agents on Phase<br>Separation of Simple Glass Systems<br><i>Minoru Tomozawa</i>   | 41   |
| Alternative to the Random Network Structure for Glass:<br>Nonuniformity as a General Condition<br><i>Rustum Roy</i>                                     | 51   |
| X-Ray Diffraction Analysis of Structural Changes<br>in Vitreous Silica<br><i>C. V. Gokularathnam, R. W. Gould, and L. L. Hench</i>                      | 61   |
| Nucleation and Crystallization in $ZrO_2$ -Nucleated<br>Glass-Ceramic Systems<br><i>G. F. Neilson</i>   | 73   |
| $TiO_2$ and $ZrO_2$ as Nucleants in a Lithia<br>Aluminosilicate Glass-Ceramic<br><i>D. R. Stewart</i>   | 83   |
| - CRYSTALLIZATION -   |      |
| Crystal Growth in Glass-Forming Systems—<br>A Review<br><i>Donald R. Uhlmann</i>  | 91   |
| Kinetics of Overall Crystallization of Undercooled<br>Melts in Terms of the Nonsteady State Theory<br>of Nucleation<br><i>I. Gutzow and D. Kaschiev</i> | 116  |
| Crystal Growth in Network Liquids by Structure<br>Rearrangement<br><i>A. R. Cooper</i>  | 123  |



|   |     |
|---|-----|
| Analysis of Diffusion Controlled Crystal Growth<br>in Multicomponent Systems<br><i>A. R. Cooper and P. K. Gupta</i>   | 131 |
| Spherulitic Crystallization in Glasses<br><i>S. W. Freiman, G. Y. Onoda, Jr., and A. G. Pincus</i>  | 141 |
| Crystallization of $\text{Li}_2\text{O-SiO}_2$ Glasses<br><i>Anthony R. West and Fredrik P. Glasser</i>   | 151 |
| Determining the Suitability of Nucleating Agents<br>for Glass-Ceramics<br><i>R. L. Thakur</i>   | 166 |
| Crystallization Temperature—A New Parameter to<br>Characterize Noncrystalline Oxide Materials<br><i>Takeshi Takamori and Rustum Roy</i>                         | 173 |
| Crystallization of $\text{SrB}_4\text{O}_7$ from Its Melt<br><i>Suzanne R. Nagel and C. G. Bergeron</i>   | 183 |
| Effect of Melt Composition on the Crystal Growth<br>Kinetics of $\text{PbB}_4\text{O}_7$<br><i>R. J. Eagan and C. G. Bergeron</i>                               | 191 |
| The Effect of Water and Impurities on the Crystal<br>Growth Rate of Lead Tetraborate from Its Melt<br><i>R. J. Eagan and C. G. Bergeron</i>                     | 202 |
| - APPLICATIONS -  |     |
| Applications of Glass-Ceramics<br><i>Alexis G. Pincus</i>   | 210 |
| The Constitution, Microstructure and Properties of<br>Glass-Ceramics<br><i>P. W. McMillan</i>   | 224 |
| Structure, Properties, and Applications of<br>Glass-Ceramics<br><i>George H. Beall</i>  | 251 |
| The Crystallization of some Ceramic Coatings<br><i>R. A. Eppler</i>   | 262 |
| Anomalous Properties of Glass-Ceramics<br><i>G. M. Muchow</i>   | 272 |
| Morphology of Partially Crystallized $\text{B}_2\text{O}_3\text{-BaO-Fe}_2\text{O}_3$ Glass<br><i>M. Fahmy, M. J. Park, M. Tomozawa, and<br/>R. K. MacCrone</i> | 276 |
| Subject Index   | 284 |
| Author Index  | 286 |

## NUCLEATION IN GLASS—A REVIEW

J. J. HAMMEL

PPG INDUSTRIES, Inc.

Glass Research Center

Pittsburgh, Pennsylvania

### Abstract

Theoretical and experimental advances in nucleation in glass since the 1961 symposium on "Nucleation and Crystallization in Glasses and Melts" are reviewed. The theoretical aspects of nucleation of gases, crystals, and phase separation are considered. Transient effects which in the past have generally been neglected along with entropy and interfacial energy changes on cooling through the glass transition can be major factors in the general absence of homogeneous nucleation in glass. Nucleation rates for phase separation have been measured and the occurrence of spinodal decomposition in glass is discussed. Recent mechanisms proposed to explain the catalyzed crystallization of glass are reviewed and the most recent experiments on the role of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{P}_2\text{O}_5$  are covered.

### Introduction

This paper will cover a brief review of studies of nucleation in glass made just prior to and at the time of the 1961 symposium on "Nucleation and Crystallization in Glasses and Melts" and some of the most pertinent work since the symposium. Most of the observed nucleation occurs above the glass transition so strictly speaking we will not be describing nucleation from glass but from glass-forming liquids. However, since the expression nucleation from glass is less cumbersome it will be used interchangeably.

### A Brief Summary of the 1961 Symposium

Just a few years prior to the 1961 symposium on "Nucleation and

Crystallization" Stookey<sup>1</sup> discovered that certain glasses containing nucleating agents could be cooled and formed to a desired shape. These same glasses could be subsequently heat treated to a fine grained glass-ceramic having useful properties. A great flurry of activity followed to determine the mechanism of formation of these glass-ceramics. This led to the 1961 symposium which was devoted almost exclusively to glass-ceramics. In glasses containing  $\text{TiO}_2$  as a nucleation catalyst it was generally agreed that  $\text{TiO}_2$  led to a liquid unmixing which will be referred to as phase separation. Maurer<sup>2</sup> demonstrated that light scattering centers in a  $\text{TiO}_2$  containing glass went from isotropic to anisotropic. This was evidence that the scattering centers were initially amorphous before becoming crystalline. Ohlberg, Golob, and Strickler<sup>3</sup> examined two glasses containing  $\text{TiO}_2$  and found by electron microscopy that crystallization began at the interface of phase separated droplets. In one case it appeared that the droplets crystallized first, these in turn catalyzed the crystallization of the matrix; in the other case the matrix crystallized prior to the droplet crystallization. Vogel and Gerth<sup>4</sup> looked at a variety of glass compositions and gave considerable electron microscopy evidence for phase separation preceding internal or bulk crystallization.

Hillig<sup>5</sup> examined the crystallization in glasses of the  $\text{BaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$  and the  $\text{BaO} \cdot \text{TiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  systems and interpreted his results on the basis of a homogeneous nucleation mechanism. However, he proposed that phase separation could indirectly lead to crystallization by the formation of unstable phases which could nucleate homogeneously. He also proposed that certain components could act as surfactants, i.e., concentrate at the liquid-crystal interface, and reduce the interfacial



energy. This in turn would substantially lower the work of formation of a critical nucleus. Finally, he showed the importance of transient times in nucleation in glasses. Transient times are times required to reach a steady-state nucleation.

Fine-grained glass-ceramics can also be produced by dissolving slightly soluble components in the melt at high temperatures and then precipitating them at lower temperatures. These in turn heterogeneously nucleate the main crystalline phase; the size of the colloidal precipitate and its cell dimensions being important considerations. Earlier, Maurer<sup>6</sup> had found that  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  crystals would not nucleate in  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  glasses until precipitated gold particles reached approximately 80Å. He showed that the large radii of curvatures associated with very small particles could produce large strain energies in the nucleating crystals. The larger the particles the less the strain energy and hence the less the work required to form a nucleus of critical size. Vogel<sup>7</sup> and Rindone<sup>8</sup> showed the importance of epitaxy and matching crystal cell dimensions for heterogeneous nucleation by colloidal precipitates. Locsei<sup>9</sup> showed that iron and manganese sulfide in concentrations of 4 to 5% will precipitate and heterogeneously nucleate crystallization internally. Finally, Roy<sup>10</sup> proposed that nucleation can be accomplished by the glass separating into SRO phases (Short Range Order phases). Here he emphasizes that glass does not have any one structure but is a "family of structures with different types of short range order."

Do we have a better understanding of nucleation in glass-ceramics and nucleation in glasses in general than we had ten years ago? Before answering this question let's take a brief overall view of nucleation in glass, both theoretical and experimental.

#### Nucleation of Gases from Glass

The nucleation events in glass will be broken down into three areas:

- (1) nucleation of gases from glass;
- (2) nucleation of liquids from glass;
- and (3) the nucleation of crystals from glass.

Homogeneous formation of vapor nuclei from a liquid subjected to a negative pressure is given by the following:

$$I = N\gamma_0 \exp[-(\Delta G_a + W^*)/kT] \quad (1)$$

where  $\Delta G_a$  is the activation energy for transport across the liquid-vapor interface,  $N$  is the number of liquid molecules per cc. and  $\gamma_0$  the fundamental jump frequency (from kinetic theory).<sup>11,12</sup> Since under the high hydrostatic tensions required to nucleate vapor bubbles the vapor pressure term is negligible and the work term simplifies to

$$W^* = \frac{16\pi\sigma^3}{3p^2} \quad (2)$$

Where  $\sigma$  is the surface tension of the liquid and  $p$  is the internal pressure, in this case tension or negative pressure of the liquid. Fisher<sup>13</sup> calculated, for water, a negative pressure of approximately  $1.3 \times 10^3$  atmospheres to form one bubble in a period of  $10^3$  seconds. What does this all mean with respect to the homogeneous nucleation of dissolved gases in glass? Glasses have surface tensions and  $\Delta G_a$ 's higher than water, thus making it even more difficult to nucleate vapor. However, since in glass our general concern is the nucleation of dissolved gases and not glass vapor the pressure term should be converted to activities. Therefore, the work term for dissolved gases becomes

$$W^* = \frac{16\pi v^2 \sigma^3}{3(kT \ln a^*/a_0)^2} \quad (3)$$

where  $v$  is the molecular volume,  $a^*$  is the critical saturation activity and  $a_0$  the normal saturation activity.  $a^*/a_0$  is defined as the critical supersaturation ratio for homogeneous nucleation. The activities are related to concentrations through an activity coefficient. Equations (1) and (3) show that relatively large supersaturations are required to form gaseous phases in glass.

According to Cable,<sup>15</sup> who has done considerable work on the formation of bubbles in glass, it is very likely that the nucleation of gas bubbles is all heterogeneous, occurring during melting and at the glass refractory interface and requiring only small supersaturations. Heterogeneous nucleation of gases can be described using the following equations:

$$W^* = \frac{16v^2\sigma^3 f(\theta)}{3(kT \ln a^*/a_0)} \quad (4)$$

where  $f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^{2/4}$  and  $\cos \theta$  is given by  $(\sigma_{SL} - \sigma_{SG}) / \sigma_{LG}$ .  $\theta$  is the contact angle and  $\sigma_{SL}$ ,  $\sigma_{SG}$ , and  $\sigma_{LG}$  are the interfacial energies between the solid-liquid, solid-gas, and liquid-gas, respectively. The lower the contact angle ( $0^\circ$  equals complete wetting) between the gas and solid surface in the presence of the liquid the more effective the nucleating surface. Also, experimentally it has been found that the poorer the wetting, i.e., the higher the interfacial energy, between the liquid and solid surface the more effective the nucleating surface.<sup>13</sup> It can also be shown theoretically that any cavities, irregularities or protrusions on the solid would be very good nucleation sites for gases.<sup>13</sup>

#### Nucleation of Crystals From Glass

Nucleation of crystals from glass can be described in two ways—self-crystallization and precipitation. For self-crystallization the work term becomes:

$$W^* = \frac{16\pi v^2 \sigma_{LS}^3 T_m^2}{3\Delta h_f^2 \Delta T^2} \quad (5)$$

where  $\sigma_{LS}$  is the liquid-crystal interfacial energy,  $\Delta h_f$  the heat of fusion and  $\Delta T$  the degree of undercooling. For single component glasses  $T_m$  would be the melting temperature and for multicomponent glasses one would use the liquidus temperature.

For precipitation,

$$W^* = \frac{16\pi v^2 \sigma_{LS}^3}{3(kT \ln a^*/a^0)^2} \quad (6)$$

where  $a^*$  is the critical saturation activity and  $a^0$  is the normal saturation activity. Here again, as was the case with dissolved gases, the activities are related to concentrations through activity coefficients. Equation 6 can be used to describe the precipitation of slightly soluble components which precipitate as crystals, e.g., the heavy metals gold, silver, platinum, copper, etc., metal sulfides, certain fluorides, and others. It is generally agreed that the precipitation of these occurs by a homogeneous mechanism,<sup>16</sup> however, the homogeneous nucleation of self-crystallization is the exception rather than the rule.

Let's take a closer look at the chief factors which effect homogeneous nucleation of self-crystallization. On Fig. 1 is a plot of the log of the volume fraction of crystals versus temperature for a typical soda-lime glass.<sup>17</sup>  $\alpha$  is the ratio of the interfacial energy to the heat of fusion which Turnbull found to be roughly constant for a given type liquid.<sup>18</sup>  $\Delta S_f$  is the entropy of fusion and is equal to  $\Delta h_f/T_m$ . The average entropy of fusion for alkali silicates is approximately 8 entropy units, being smaller for lithia silicates than soda silicates.<sup>19</sup>  $10^5$  seconds, which was approximately, one day was taken as the time of the hypothetical experiment at each temperature. It is seen that detectable crystallization, which is controlled by nucleation, is very sensitive to changes in  $\alpha$ . Small increases in the interfacial energy will cause large changes in detectable nucleation.

When using reasonable estimate of  $\sigma_{LS}$  and known values of  $\Delta h_f$  these calculations suggest that homogeneous nucleation should occur in some silicates.<sup>17</sup> The fact that homogeneous

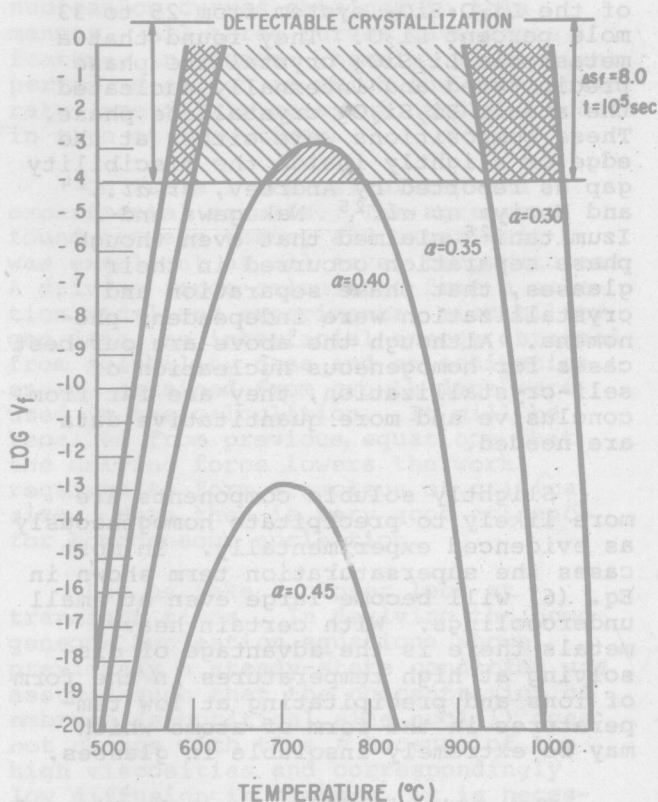


FIGURE 1  
A plot of log volume fraction of crystals versus temperature for a soda-lime glass showing the effects of small changes in liquid-crystal interfacial energy on detectable crystallization.<sup>17</sup>



nucleation is rarely observed could be due to the following: (1) transient effects were not taken into account; (2) the decrease in entropy difference between the supercooled liquid and crystal was not included in the calculations; and (3) the expected rapid increase in  $\sigma_{LC}$  as the glass transition is approached was not included.

As reported in the literature the  $BaO \cdot SiO_2$  and the  $Li_2O \cdot SiO_2$  systems are probably our best cases for homogeneous nucleation of self-crystallization. MacDowell<sup>20</sup> found internal nucleation which he described as homogeneous in compositions from 33 to 40 mole percent  $BaO$ . Seward, Uhlmann, and Turnbull<sup>21</sup> found a miscibility gap in the high  $SiO_2$  end of the binary which extended to approximately 33 mole percent at 800°C. It appeared that when MacDowell did his work he was not aware of this metastable miscibility gap since Seward, *et al.* reported their findings at a later date. However, MacDowell claimed he could not detect any phase separation in his glasses.

Hench, Freiman, and Kinser<sup>22,23</sup> investigated crystallization in glasses of the  $Li_2O \cdot SiO_2$  system from 25 to 33 mole percent  $Li_2O$ . They found that a metastable  $Li_2SiO_3$  crystalline phase precipitated and internally nucleated the stable  $Li_2Si_2O_5$  crystalline phase. These compositions were either at the edge or slightly inside the miscibility gap as reported by Andreev, *et al.*,<sup>24</sup> and Moriya *et al.*<sup>25</sup> Nakagawa and Izumitani<sup>26</sup> claimed that even though phase separation occurred in their glasses, that phase separation and crystallization were independent phenomena. Although the above are our best cases for homogeneous nucleation of self-crystallization, they are far from conclusive and more quantitative data are needed.

Slightly soluble components are more likely to precipitate homogeneously as evidenced experimentally. In most cases the supersaturation term shown in Eq. (6) will become large even at small undercoolings. With certain heavy metals there is the advantage of dissolving at high temperatures in the form of ions and precipitating at low temperatures in the form of atoms which may be extremely insoluble in glasses.

The mechanism for the nucleation of heavy metal sulfides and some fluorides is less clear. It is generally agreed, however, that both have steep solubility-temperature curves in silicate glasses and according to Hinz and Kunth<sup>27</sup> both

sulfides and fluorides possess large regions of immiscibility in these glasses. Whether they precipitate homogeneously as crystals or as liquids and then crystallize is not evident from the literature.

The work term for heterogeneous nucleation of self-crystallization which is the most general case is given by

$$W^* = \frac{16\pi v^2 \sigma_{SL}^3 T_m^2}{3\Delta h_f^2 \Delta T^2} f(\theta) \quad (7)$$

where  $f(\theta)$  has been defined previously and  $\cos \theta = (\sigma_{SL} - \sigma_{SP}) / \sigma_{LP} \cdot \sigma_{SL} \sigma_{SP}$  and  $\sigma_{LP}$  are the interfacial energies between the solid-liquid, solid-impurity surface and liquid-impurity surface, respectively. Here again the lowering of the interfacial energy depends on how well the impurity surface wets the nucleating phase in the presence of the liquid. The better the wetting the more effective the impurity surface. Instead of using the idea of contact angles between surfaces it is perhaps easier to visualize if the concept of strong or weak interactions across the surface is used. Turnbull and Vonnegut<sup>28</sup> claim that the ability of a substrate to act as an effective nucleating site depends on the percent registry defined as  $\delta = (a_s - a_c) / a_s$ , where  $a_s$  and  $a_c$  are interatomic distances of the substrate and nucleating crystal, respectively. Of course the lower the registry the greater the interaction between surfaces. For  $\delta$  values of less than 20 percent nucleation is thought to be possible.

Good examples of heterogeneous nucleation are the photosensitive glasses. A heavy metal, e.g., Au, Ag, Cu, etc., is reduced by radiation, homogeneously precipitated, with the precipitate or colloid heterogeneously nucleating the main crystalline phase. As mentioned earlier the size of the colloidal precipitate and its crystal chemistry are important. Very small particles produce large strain energies due to large radii of curvatures; the crystal chemistry effects the degree of interaction across the interface.

Other compounds which could range from very slightly soluble to fairly soluble could also act as heterogeneous nucleation agents. In general, very slightly soluble compounds might precipitate as crystals which in turn could nucleate the bulk crystallinity, e.g., some heavy metal sulfides and

some fluorides. In the more general situation, in which solubility is relatively good, the compound is more likely to precipitate as a liquid, crystallize and in turn nucleate the bulk crystallinity. Examples would be  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{Cr}_2\text{O}_3$ , to name a few of the better nucleation catalysts. All of these except  $\text{ZrO}_2$  show large regions of immiscibility in silicates.<sup>27</sup> Nielson<sup>29</sup> has described the role of  $\text{ZrO}_2$  in the catalyzed crystallization of  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  glasses.

#### *Nucleation of Liquid from Glass and Spinodal Decomposition*

The separation of liquids from glass, generally referred to as phase separation, can occur by two mechanisms; homogeneous nucleation or spinodal decomposition. It is highly unlikely that phase separation would occur heterogeneously since interfacial energies are already very low. From measurements of solubility as a function of droplet size an interfacial energy of 4.6 erg/cm<sup>2</sup> between a nearly pure silica droplet and a soda-lime rich phase was estimated.<sup>30</sup>

Probably the greatest activity and the largest advances in nucleation in glass since 1961 has been in the area of phase separation. Subliquidus miscibility gaps and/or phase separation were found in the  $\text{B}_2\text{O}_3 \cdot \text{SiO}_2$ ,<sup>31</sup>  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ,<sup>32,33</sup> alkali borates<sup>34</sup> and silicates,<sup>24,35</sup>  $\text{PbO} \cdot \text{B}_2\text{O}_3$ ,<sup>36</sup>  $\text{BaO} \cdot \text{SiO}_2$ ,<sup>21</sup> soda-lime silicates,<sup>37</sup> and others.<sup>38,39,40</sup> Cahn proposed that in addition to nucleation and growth, phase separation could occur by a mechanism of spinodal decomposition.<sup>41</sup> With spinodal decomposition there is no surface energy barrier to nucleation and the separations are only limited by diffusion. This was a new and certainly a challenging concept to the glass scientist. Electron micrographs were certainly consistent with the occurrence of spinodal decomposition as were the earliest low angle X-ray studies.<sup>35,42,43,44</sup>

Low angle X-ray studies in the  $\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  system by Zarazycki and Naudin<sup>45</sup> represent the best evidence for spinodal decomposition in glasses. Several workers have performed low-angle X-ray studies on glasses in the  $\text{Na}_2\text{O} \cdot \text{SiO}_2$  system. Tomazawa, MacCrone, and Herman<sup>46</sup> recently reported that their earlier agreement with theory and also that of Neilson's may have been fortuitous due to phase separation even in the most rapidly cooled samples. Cahn's equations

used to compare theory and experiment cover only the earliest stages of separation. Their samples probably represented later stages. Andreev, *et al.*,<sup>47</sup> who also did low angle X-ray work on glasses in the  $\text{Na}_2\text{O} \cdot \text{SiO}_2$  system, reached the same conclusion on phase separation in their quenched glasses. They also noted that Zarazycki and Naudin started with a much lower level of phase separation making their results more reliable. Therefore, evidence for spinodal decomposition in glasses is not conclusive and more data are needed.

In contrast the evidence for homogeneous nucleation is excellent. The most comprehensive and conclusive evidence for homogeneous nucleation is the work on nucleation of phase separation from a soda-lime glass.<sup>30</sup> In this study, particle size distributions were obtained from electron micrographs of glass samples heat treated at various times and temperatures below the miscibility gap. Knowing the number and size of the particles in a given interval and their growth rate it was possible to extrapolate back to the time when the particles were formed. Figure 2 shows nucleation curves obtained in this manner. All three curves have three features in common: namely, a transient period, a period in which the nucleation rates are fairly constant, and a decrease in rate at long times.

On Table 1 are calculated and experimental results. The agreement found between theory and experiment was excellent at all seven temperatures. A driving force calculated from a solution model and experimental miscibility gap data, an interfacial energy obtained from solubility data and an activation energy obtained from growth data were used in the calculation. It will be recalled from previous equations that the driving force lowers the work required to form a nucleus of critical size. Here then is very good evidence for homogeneous nucleation.

Let us take a closer look at transient times. In deriving the homogeneous nucleation equations shown previously a steady-state condition was assumed such that the concentration of embryos (subcritical size nuclei) does not change with time. Because of the high viscosities and correspondingly low diffusion in glasses, it is necessary to take into account the time required to reach the steady-state condition which is given by:

$$I(t) = I_0 \exp(-\tau/t), \quad (8)$$



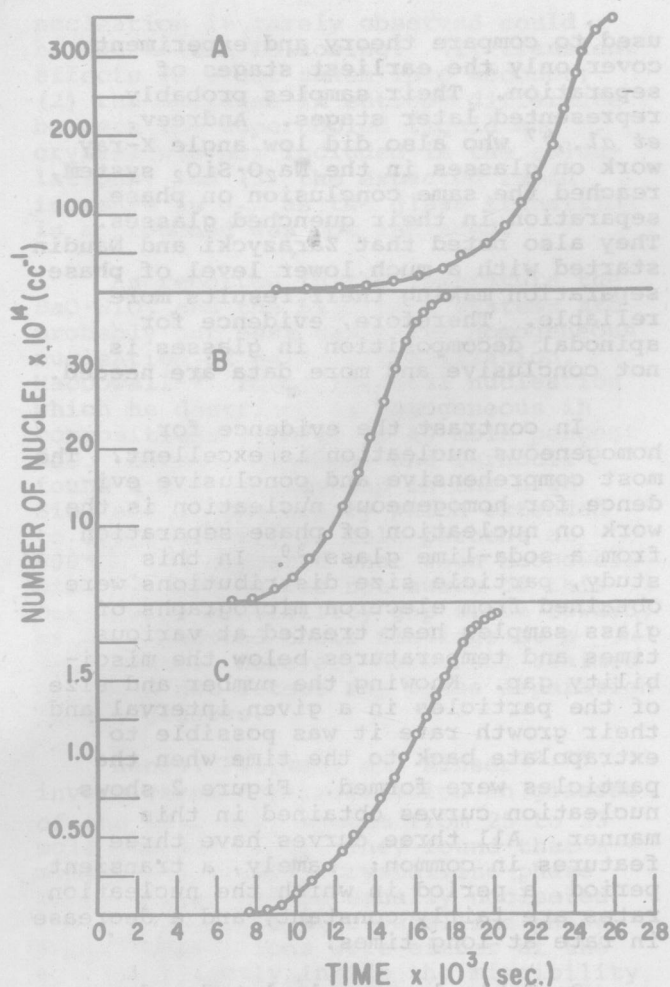


FIGURE 2

Experimental nucleation curves at three temperatures for a soda-lime glass. The curves show transient times, relatively steady state nucleation, and a decrease in rates at longer times.<sup>30</sup>

Where  $\tau$  is called the incubation time and  $I_0$  is the steady-state nucleation rate. The results shown in Fig. 2 were compared with a  $\tau$  derived by Collins<sup>48</sup> and an induction time  $\bar{t}$  derived by Hillig.<sup>5</sup> Hillig's expression is not a true incubation time since in his derivation he did not take into account the inherent instability of the nucleus. To give some idea of the parameters included in an induction or incubation time, Hillig's expression is included and is given by

$$\bar{t} = \frac{V_L^2 r^*^2}{4DV_m^2 X^2} \quad (9)$$

Where  $r^*$  is the size of the critical nucleus,  $D$  is the diffusion coefficient

and  $V_L$ ,  $V_m$ , and  $X$  are the molar volume of the glass and precipitating phase and mole fraction of precipitating phase, respectively. The other derived expressions for  $\tau$  are more complicated.<sup>49,50</sup>

On Table 2 experimental and calculated results are compared. The agreement is very good especially when compared with Hillig's equation. More recently Russell<sup>51</sup> derived an incubation time and compared his expression at 625°C with Hammel's data. Russell calculated an incubation time of  $5 \times 10^3$  seconds which compared to an experimental result of  $10^4$  seconds. He described this as excellent but perhaps fortuitous agreement between theory and experiment.

#### Phase Separation in Controlled Crystallization of Glass

The prevailing ideas on the mechanism of formation of glass-ceramics and the role of phase separation at the time of the 1961 nucleation and crystallization symposium have been discussed. A few of the more significant advances made since then will be described.

Cahn<sup>52</sup> showed that under certain conditions thermodynamics forbids the formation of the stable or crystalline phase prior to phase separation. Using the concept of a metastable liquidus, he found two regions below the monotectic which require phase separation before crystallization can proceed. One of these is the region above the metastable liquidus and the other is the region beneath the spinodal. Although his results show that in certain cases phase separation must precede crystallization, they do not predict whether crystallization will occur.

Barry,<sup>53</sup> *et al.* extended the concept, first proposed by Hillig, that  $\text{TiO}_2$  acts as a surfactant. They included a more detailed mechanism with experimental support. Their experiments were on glasses of the  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  system with varying amounts of  $\text{TiO}_2$ . They concluded: (1)  $\text{TiO}_2$  does not promote nucleation either by inducing phase separation or by epitaxial growth on lithium titanate crystallites and (2)  $\text{Ti}^{+4}$  ions cause a redistribution of non-bridging oxygen ions to the periphery of completely bridged network regions which become the nuclei for crystallization. In this sense  $\text{TiO}_2$  functions as a surface-active agent.

Doherty,<sup>54</sup> *et al.* experimented with a  $\text{MgO} \cdot \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  glass con-

TABLE 1  
Nucleation Data for a Soda-Lime Glass

| Temperature<br>(°C) | r*<br>(Å) | Nuclei (cc <sup>-1</sup> sec <sup>-1</sup> ) |                      |                      |
|---------------------|-----------|--|----------------------|----------------------|
|                     |           | A <sub>0</sub>                               | I (calc)             | I (meas)             |
| 601                 | 21.5      | $3.3 \times 10^{38}$                         | $7.2 \times 10^{11}$ | $6.0 \times 10^{12}$ |
| 608                 | 23.0      | $4.3 \times 10^{38}$                         | $2.5 \times 10^{11}$ | $7.5 \times 10^{11}$ |
| 610                 | 23.5      | $4.7 \times 10^{38}$                         | $1.8 \times 10^{11}$ | $6.4 \times 10^{11}$ |
| 620                 | 26.2      | $5.8 \times 10^{38}$                         | $6.4 \times 10^{10}$ | $6.2 \times 10^{10}$ |
| 625                 | 28.7      | $6.9 \times 10^{38}$                         | $1.1 \times 10^{10}$ | $2.4 \times 10^{10}$ |
| 630                 | 30.0      | $7.7 \times 10^{38}$                         | $5.2 \times 10^9$    | $3.3 \times 10^9$    |
| 640                 | 34.2      | $9.9 \times 10^{38}$                         | $1.9 \times 10^8$    | $2.4 \times 10^8$    |

Source: Data from Hammel, 1967.

taining up to 5% TiO<sub>2</sub>. They found that phase separation preceded the formation of a large number of 50Å titania-aluminate crystals. These crystals were the heterogeneous nuclei for the crystallization of the remaining glass.

Phillips and McMillan<sup>55</sup> made a number of Li<sub>2</sub>O·SiO<sub>2</sub> glasses containing one percent P<sub>2</sub>O<sub>5</sub>. The primary effect of adding P<sub>2</sub>O<sub>5</sub> was to bring about extensive two-phase separation into a discontinuous SiO<sub>2</sub>-rich phase and a continuous Li<sub>2</sub>O-rich phase. As a result of the phase separation a large number of potential growth sites are provided

at the phase boundary. This, together with the reduction in crystal growth rate, resulted in a fine-grained high strength structure characteristic of phosphate-nucleated glass-ceramics.

Perhaps the effect of phase separation on the formation of fine-grained glass-ceramics was best summarized by Uhlmann during a recent discussion.<sup>56</sup> He said: (1) phase separation can result in a larger driving force for nucleation than previously existed; (2) it can produce interfaces which could act as preferred sites for nucleation; (3) the separation

TABLE 2  
Calculated and Experimental Transient Times for a Soda-Lime Glass

| Temperature<br>(°C) | $\bar{t}$ (exp.)<br>(sec) × 10 <sup>4</sup> | Calculated Transient Times                    |   |
|---------------------|---|---|---|
|                     |   | $\bar{t}$ (Hillig)<br>(sec) × 10 <sup>4</sup> | $\tau$ (Collins)<br>(sec) × 10 <sup>4</sup> |
| 601                 | 2.1   | 1.20  | 19.3  |
| 608                 | 1.6   | 0.87  | 14.1  |
| 610                 | 1.0   | 0.81  | 13.2  |
| 620                 | 1.1   | 0.56  | 9.3   |
| 625                 | 1.0   | 0.51  | 7.9   |
| 630                 | 0.75  | 0.41  | 6.6   |

Source: Data from Zettlemoyer, 1969.



can result in an appreciably higher atomic mobility than previously existed; and (4) the interfacial regions between the separated phases may be enriched in some component, providing a locally larger driving force for nucleation or a locally higher mobility. Although any one or a combination of the above may be operating it was his feeling that an increase in atomic mobility was by far the most important. This is certainly consistent with theory which stresses the importance of mobility in both the transient time and steady-state nucleation.

#### Miscellaneous Nucleation Phenomena

Yamamoto, *et al.*,<sup>57</sup> found that pressure up to 65 kilobars prior to and during the heating of glasses had a pronounced effect in enhancing the precipitation of noble metal colloids. Uhlmann, Hays, and Turnbull<sup>58</sup> showed theoretically increasing pressure could increase homogeneous nucleation.

Finally, crystallization of AgCl and AgBr precipitates in glass was studied as a function of particle size and undercooling.<sup>59</sup> Using homogeneous nucleation theory and the Turnbull criterion for detectable nucleation, liquid-crystal interfacial energies of 67.5 and 51.0 ergs/cm<sup>2</sup> were obtained for AgCl and AgBr, respectively.

In conclusion, due to the experimental difficulties associated with obtaining good nucleation data we must rely heavily on theory to give us the answers. However, the theory that is now available generally is not directly applicable because of the assumptions made in its derivation and the complexity of glass, especially near the glass transition. It may very well be that the structural changes which occur during glass formation are the most important considerations. Theory does not take into account structural changes. If advances are to be made the theory must be modified to include the more practical nucleation problems or our experimentalists must develop more innovational techniques. These are both challenging goals.

#### References

1. S. D. Stookey, *Corning Glass Works*, U.S. Patent 2,920,971, January 12, 1960.
2. R. D. Maurer, "Symposium on Nucleation and Crystallization in Glasses and Melts" (M. K. Reser, G. Smith, and H. Insley, eds.), American Ceramic Society, Inc., Columbus, Ohio, 1962, p. 97.
3. S. M. Ohlberg, H. R. Golob, and D. W. Strickler, *ibid.*, p. 55.
4. W. Vogel and K. Gerth, *ibid.*, p. 11.
5. W. B. Hillig, *ibid.*, p. 77.
6. R. D. Maurer, *J. Chem. Phys.*, **31**, 444 (1959).
7. W. Vogel and K. Gerth, "Symposium on Nucleation and Crystallization in Glasses and Melts" (M. K. Reser, G. Smith, and H. Insley, eds.), American Ceramic Society, Inc., Columbus, Ohio, 1962, p. 11.
8. G. E. Rindone, *ibid.*, p. 63.
9. B. P. Locsei, *ibid.*, p. 71.
10. R. Roy, *ibid.*, p. 39.
11. D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17**, 71 (1949).
12. D. Turnbull, *Solid State Physics*, Vol. 3, Academic Press, New York, N.Y. (1956).
13. J. C. Fisher, *J. Appl. Phys.*, **19**, 1062 (1948).
14. A. C. Zettlemoyer, *Nucleation*, Marcel Dekker, Inc., New York, N.Y., 1969, p. 239.
15. M. Cable and C. G. Rasul, *J. Amer. Ceram. Society*, **50**, 530 (1967).
16. R. D. Maurer, *J. Appl. Phys.*, **29**, 1 (1958).
17. A. C. Zettlemoyer, *Nucleation*, Marcel Dekker, Inc., New York, N.Y., 1969, pp. 489-525.
18. D. Turnbull, *Physics of Non-Crystalline Solids*, Amsterdam, North Holland Publishing Co., 1965, p. 41.
19. F. D. Rossini *et al.*, *Selected Values of Chemical Thermodynamic Properties*, U.S. Department of Commerce, National Bureau of Standards, 1952.
20. J. F. MacDowell, *Proc. Brit. Ceram. Soc.*, **3**, 229 (1965).
21. T. P. Seward III, D. R. Uhlmann, and D. Turnbull, *J. Amer. Ceram. Soc.*, **51**, 634 (1968).

22. S. W. Freiman and L. L. Hench, *J. Amer. Ceram. Soc.*, **51**, 382 (1968).
23. D. L. Kinser and L. L. Hench, *J. Mater. Sci.*, **5**, 369 (1970).
24. N. S. Andreev, D. A. Goganov, E. A. Porai-Koshits and Yu. G. Sokolov, in *Structure of Glass*, Vol. 3, Part 1, Proc. of the Third All-Union Conf. on the Glassy State, Moscow-Leningrad, 1963, pp. 47-52.
25. Y. Moriya, D. H. Warrington, and R. W. Douglas, *Phys. Chem. Glasses*, **8**, 19 (1967).
26. K. Nakagawa and T. Izumitani, *Phys. Chem. Glasses*, **10**, 179 (1969).
27. W. Hinz and P. Kunth, *Glastechn. Ber.*, **34**, 431 (1961).
28. D. Turnbull and B. Vonnegut, *Ind. Eng. Chem.*, **44**, 1292 (1952).
29. G. Neilson, "Symposium on Nucleation and Crystallization" - Revisited, Chicago, 1971.
30. J. J. Hammel, *J. Chem. Phys.*, **46**, 2234 (1967).
31. R. J. Charles and F. E. Wagstaff, *J. Amer. Ceram. Soc.*, **51**, 16 (1968).
32. D. Ganguli and P. Saha, *Mat. Res. Bull.*, **2**, 25 (1967).
33. J. MacDowell and G. Beall, *J. Amer. Ceram. Soc.*, **52**, 17 (1969).
34. R. R. Shaw and D. R. Uhlmann, *J. Amer. Ceram. Soc.*, **51**, 377 (1968).
35. J. J. Hammel, Proc. VII International Congress on Glass, Brussels, Belgium, paper 36 (1965).
36. D. J. Liedberg, C. G. Ruderer, and C. G. Bergeron, *J. Amer. Ceram. Soc.*, **48**, 440 (1965).
37. S. M. Ohlberg, H. R. Golob, J. J. Hammel, and R. R. Lewchuk, *J. Amer. Ceram. Soc.*, **48**, 331 (1965).
38. W. Vogel, Proceedings of the III All-Union Conf. on the Glassy State, Leningrad, Vol. 2 (1959). Translated from Russian, Consultants Bureau Enterprises, Inc., New York (1960).
39. B. R. Sastry and F. A. Hummel, *J. Amer. Ceram. Soc.*, **42**, 81 (1959).
40. B. Phillips and R. Roy, *Phys. Chem. Glasses*, **5**, 172 (1964).
41. J. W. Cahn, *Acta. Metallurgica*, **9**, 795 (1961).
42. J. W. Cahn and R. J. Charles, *Phys. Chem. Glasses*, **6**, 181 (1965).
43. M. Tomozawa, H. Herman and R. K. MacCrone, Proceedings of the International Symposium on the Mech. of Phase Transf. in Crystalline Solids, Monograph No. 33, British Institute of Metals, London (1969).
44. G. F. Neilsen, *Phys. Chem. Glasses*, **10**, 54 (1969).
45. J. Zarazycki and F. Naudin, *J. Non-Cryst. Solids*, **1**, 215 (1969).
46. M. Tomozawa, R. K. MacCrone and H. Herman, *Phys. Chem. Glasses*, **11**, 136 (1970).
47. N. S. Andrew, G. G. Boiko and N. A. Bokov, *J. Non-Cryst. Solids*, **5**, 41 (1970).
48. F. C. Collins, *Z. Elektrochem.*, **59**, 404 (1955).
49. R. F. Probst, *J. Chem. Phys.*, **19**, 619 (1941).
50. A. Kantrowitz, *J. Chem. Phys.*, **19**, 1097 (1951).
51. K. C. Russell, *Acta Met.*, **17**, 1123 (1969).
52. J. W. Cahn, *J. Amer. Ceram. Soc.*, **52**, 118 (1969).
53. T. I. Barry, D. Clinton, L. A. Lay, R. A. Mercer, and R. P. Miller, *J. Materials Sci.*, **4**, 596 (1969).
54. P. E. Doherty, D. W. Lee, and R. S. Davis, *J. Amer. Ceram. Soc.*, **50**, 77 (1967).
55. S. V. Phillips and P. W. McMillan, *Glass Tech.*, **6**, 46 (1965).
56. D. R. Uhlmann, discussion remarks, *Trans. Faraday Soc.*, **11B** (1970).
57. T. Yamamoto, H. Yamamoto, and S. Sakka, *Phys. Chem. Glasses*, **11**, 11 (1970).
58. D. R. Uhlmann, J. F. Hays, and D. Turnbull, *Phys. Chem. Glasses*, **7**, 159 (1966).
59. J. J. Hammel and T. E. McGary, International Symposium on the Reactivity of Solids, J. W. Mitchell, Ed. (6th; 1968), J. Wiley, N.Y. (1969).



## THE KINETICS OF NUCLEATION AND THE FORMATION OF GLASS-CERAMIC MATERIALS

I. GUTZOW AND S. TOSCHEV  
Institute of Physical Chemistry  
Bulgarian Academy of Sciences  
Sofia 13, Bulgaria

### Abstract

The kinetic theories of homogeneous and heterogeneous transient nucleation are reviewed. Comparison of theory with nonsteady state nucleation and catalyzed crystallization in  $\text{NaPO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7$  model glasses doped with Ir, Pt, Rh, Au, and Ag showed that the activity of the metal catalysts varied markedly. Effectiveness of the catalysts can be related more closely to thermal expansion strains developed during cooling than to matching of crystalline lattices.

### Introduction

Phase formation is the basic physical process in the preparation of glass ceramic materials. Stookey<sup>1,2</sup> was the first to treat this process as heterogeneous nucleation taking place at active cores. The latter are either deliberately introduced in the melt prior to crystallization or subsequently created as a result of some thermal pretreatment of the glass. This very fruitful idea was accepted by most of the later workers in the field<sup>3-5</sup> providing at the same time a firm basis for the solution of numerous technological problems. It was believed<sup>1-3,5</sup> that the ability of the cores to catalyze nucleation in glasses was closely related to the structural matching between the substrate and the precipitating phase in the sense of Dankov's concepts.<sup>1,2,6</sup>

On the other hand Vogel<sup>7,8</sup> and other investigators drew attention to the role of liquation (liquid-liquid separation) phenomena in the formation of glass ceramic materials. Liquation, being typical for most of the multicomponent glassforming systems complicates considerably the mechanism of the basic crystallization process. As the mutual

influence of liquation and crystallization has been critically surveyed by Tashiro<sup>9</sup> we shall abstain from a detailed discussion of this topic. It should only be added that liquation phenomena hampered considerably the understanding of the crystallization mechanism in glasses which are of technological interest. For this reason our investigations were carried out with simple model glasses exhibiting no tendency to liquation.

As far as the theoretical interpretation of nucleation kinetics is concerned it must be pointed out that the cited works<sup>1-6</sup> treat nucleation as a virtually steady state process in terms of the classical concepts of Volmer<sup>10</sup>, Becker and Döring<sup>11</sup>, and Kaischew and Stranski<sup>12</sup> developed nearly thirty-five years ago. A little later Zeldovich<sup>13</sup> and Frenkel<sup>14</sup> showed that transient effects are inherent in the very physical nature of nucleation. Their analysis implied that at constant supersaturation a steady state nucleation rate  $I_0$  is established only upon the expiration of a certain time interval  $\tau$  termed usually as induction time.

The significance of such induction times in solid state transformations was emphasized by Turnbull<sup>15</sup>, while Hillig<sup>16</sup> was the first to approach the crystallization of glasses from this point of view. However, the Zeldovich-Frenkel treatment as well as that of the subsequent authors involved the assumption that each molecule of the initial phase arriving at the surface of an embryonic cluster can be incorporated without additional constraints. Such a model is applicable to the condensation of droplets and to liquation in glass forming systems. In these instances the theory predicts very low  $\tau$ -values ( $\tau = 10^{-7} - 10^{-8}$  sec in homogeneous nucleation of droplets from vapors).

From this standpoint liquation in melts should be perceptibly delayed only

in the vicinity of the vitrification temperature  $T_g$  when the viscosity approaches  $10^{12} - 10^{13}$  poises. Such effects were experimentally observed by Hammel and Ohlberg.<sup>17,18</sup> It was shown in the meantime<sup>19-21</sup> that when crystalline nuclei form, the impediments associated with the incorporation of the building units of the mother phase in the new phase clusters can bring about a considerable enhancement of the induction time, i.e., the observed time lags should be much longer than those expected in the above mentioned situations with isotropic phases. Theoretical estimations indicate that the induction times in glass forming melts leading to the separation of crystalline phases should become perceptible when the viscosity approaches  $10^5 - 10^6$  poise, increasing enormously in the vicinity of  $T_g$ .<sup>20</sup> Hence, transient effects can be very essential and even decisive in the nucleation kinetics of glass forming systems and in the formation of glass-ceramic materials.

The present paper reviews recent theoretical and experimental work carried out in this laboratory on nucleation in glasses. The attention is accentuated to quantitative considerations thus affording the possibility of outlining a new approach to the problem of catalyzed crystallization of glasses.

### Basic Equations

Zeldovich and Frenkel<sup>13,14\*</sup> derived the following differential equation describing in generalized form the kinetics of nucleation

$$\frac{\partial I(g, t)}{\partial g} = -\frac{\partial X(g, t)}{\partial t} = -\frac{\partial}{\partial g} \left[ D(g) N(g) \frac{\partial}{\partial g} \left( \frac{X(g, t)}{N(g)} \right) \right] \quad (1)$$

Here  $I(g, t)$  is the time-dependent rate of formation of clusters containing  $g$  atoms,  $X(g, t)$  is the actual concentration of the clusters at time  $t$ .  $N(g)$  is the equilibrium distribution function of the clusters and  $D(g)$  is the molecular flux toward the cluster of size  $g$ . With appropriate initial and boundary conditions<sup>22,23</sup> an approximate solution to Eq. (1) can be written after Zeldovich as

$$I(t) = I_0 \exp \left( -\frac{t}{\tau} \right) \quad (2)$$

\*See also reference 22.

where  $I(t)$  and  $I_0$  denote the momentous and stationary rates of formation of critical nuclei respectively. A more accurate expression for  $I(t)$  derived recently by Kashchiev<sup>23</sup> reads

$$I = I_0 \left( 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -n^2 \frac{t}{\tau} \right) \right) \quad (3)$$

Equations (2) and (3) are presented graphically in Fig. 1. The stationary nucleation rate is defined by (see, e.g., reference 24)

$$I_0 = D_K N_1 \Gamma \exp \left( -\frac{A_K}{kT} \right) \quad (4)$$

where  $N_1$  is the concentration of single molecules,  $A_K$  is the work of formation of critical nuclei built of  $g_K$  atoms and  $\Gamma$  is the so called nonequilibrium Zeldovich factor

$$\Gamma = \left( \frac{A_K}{g_K^2 3\pi kT} \right)^{1/2} \quad (5)$$

The flux  $D_K$  can be expressed by the surface area  $S_K$  of the critical nucleus, the collision rate  $Z$  and the dimensionless kinetic factor  $Z'$  accounting for the incorporation hindrances across the critical nucleus phase boundary<sup>20</sup>

$$D_K = S_K Z Z' \quad (6)$$

The magnitude of  $Z'$  is of primary importance for the value of the induction

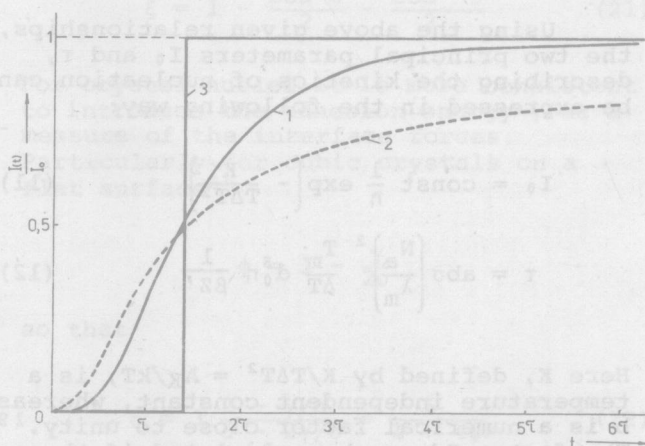


FIGURE 1  
 $I(t)$  plots in transient nucleation. (1) after Eq. (3), (2) after Eq. (2), and (3) after the approximate presentation (17).



time  $\tau$  which according to Eqs. (2) or (3), is a fundamental characteristic of the kinetics of nucleation. As a matter of fact, the theory predicts<sup>22,23,25</sup> that

$$\tau = \frac{a}{\Gamma^2 D_K} \quad (7)$$

a being a numerical coefficient of the order of unity. In undercooled melts  $Z$  can be expressed by the viscosity  $\eta$  of the ambient medium<sup>19,26</sup>

$$Z = \frac{\beta kT}{d_0^3 \eta} \quad (8)$$

The work of formation of spherically shaped critical nuclei is

$$A_K = \frac{16}{3} \pi \frac{\sigma^3 v_m^2}{\Delta \mu^2} \quad (9)$$

where the thermodynamic driving force of the crystallization process  $\Delta \mu$  is approximately proportional to the undercooling in accordance with an equation proposed years ago by J. J. Thomson

$$\Delta \mu \approx \frac{\lambda_m}{T_m} \cdot \Delta T \quad (10)$$

The meaning of the notations used so far is the following:  $\beta$ —steric factor of the order of 0.1–0.01,<sup>26</sup>  $\sigma$ —interfacial energy at the crystal/melt boundary,  $v_m$ —molar volume of the crystal,  $\lambda_m$ —heat of fusion,  $T_m$ —melting point,  $d_0$ —a quantity close to the molecular spacing in the melt.

Using the above given relationships, the two principal parameters  $I_0$  and  $\tau$ , describing the kinetics of nucleation can be expressed in the following way:

$$I_0 = \text{const} \frac{1}{\eta} \exp\left(-\frac{K}{T\Delta T^2}\right) \quad (11)$$

$$\tau = \text{ab}\sigma \left(\frac{N_a}{\lambda_m}\right)^2 \frac{T_m}{\Delta T} d_0^5 \eta \frac{1}{\beta Z'} \quad (12)$$

Here  $K$ , defined by  $K/T\Delta T^2 = A_K/kT$ , is a temperature independent constant, whereas  $b$  is a numerical factor close to unity.<sup>19</sup> The factor  $Z'$  can be calculated if the cluster growth law is known.<sup>19,20</sup> An approximate relation is  $Z' = (Z'_\infty)^3$  where  $Z'_\infty$  is determined by the linear rate of

growth of the macrocrystal  $V_\infty$  at the same supersaturation

$$Z'_\infty = V_\infty \left[ Z d^3 \left( 1 - \exp\left(-\frac{\Delta \mu}{kT}\right) \right) \right]^{-1} \quad (13)$$

Hence, data pertaining to the crystal growth in the same melt can be used to evaluate  $Z'$  ( $d$  is the lattice spacing). The limitations of this method are thoroughly discussed.<sup>20</sup> It follows for instance that under typical conditions

$$\frac{\tau \text{ crystalline phase}}{\tau \text{ isotropic phase}} = 10^4 - 10^6$$

Once  $I_0$  and  $\tau$  are known, the kinetics of the nucleation process can be quantitatively evaluated. The number of the nuclei formed within the time interval  $0, t$  per unit volume of the melt will be

$$N(t) = \int_0^t I(t) dt \quad (14)$$

or by taking into account Eq. (2)

$$N(t) = I_0 t \left\{ \exp\left(-\frac{t}{\tau}\right) + t \text{Ei}\left(-\frac{t}{\tau}\right) \right\} \quad (15)$$

Expression (15), wherein  $\text{Ei}$  is the integral exponential function is schematically presented in Fig. 2. When the induction time can be ignored, Eq. (15) reduces to

$$N(t) = I_0 t \quad (16)$$

It follows from the last equation that the time needed to form one nucleus on an average is equal to the reciprocal of the steady state nucleation rate, i.e.,  $t_1 = 1/I_0$ . The same is true for the mean time of expectation  $\bar{t}$  required for the appearance of the first nucleus, i.e.,  $\bar{t} = t_1$ . No simple relationship between  $t_1$ ,  $\bar{t}$ , and  $I_0$  exists in the transient case described by Eq. (15); moreover  $t_1 \neq \bar{t}$ .<sup>27</sup>

A further approximation to Eq. (15) which proved to be sufficiently good<sup>28,29</sup> can be written as (see Fig. 2)

$$N(t) = \begin{cases} 0 & 0 \leq t \leq b\tau \\ I_0(t - b\tau) & b\tau < t < \infty \end{cases} \quad (17)$$