

KINETICS OF NUCLEATION AND CRYSTAL GROWTH IN GLASS FORMING MELTS IN MICROGRAVITY

NASA Contract: NAG8-1465

526-76

037-76

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Introduction

This is a flight definition project with the specific objective to investigate the kinetics of nucleation and crystal growth in microgravity for high temperature inorganic oxide melts that have the potential to form glass when cooled. The present project is related to our previous NASA project¹ that was concerned with glass formation for high temperature containerless melts in microgravity. The previous work culminated in two experiments^{2, 3} which were conducted aboard the space shuttle in 1983 and 1985 and which consisted of melting levitated, spherical (6 to 8 mm diameter) samples in a Single Axis Acoustic Levitator (SAAL) furnace at 1500° C.

Of special relevance to the present project was the finding that glass formation for a CaO-Ga₂O₃-SiO₂ composition melted in microgravity was nearly three times more likely than for the same composition melted at 1-g (on earth). This finding was based on the comparison of the critical cooling rate for glass formation (defined as the slowest rate at which a melt can be cooled without crystallizing) for the identical composition measured at 1-g (on earth) with the cooling rate which the containerless melt experienced in micro-g (space), see Fig. 1. The improvement in glass formation for the containerless melt prepared in micro-g was attributed to the suppression of heterogeneous nucleation that usually occurs at the melt-container interface on earth (1-g). Unfortunately, the maximum improvement in glass formation for containerless melts in microgravity could not be determined because of the unplanned termination of the third flight experiment due to the Challenger accident.

A second important finding of equal importance was that the glass obtained from the space melted sample, which had been prepared from a deliberately, chemically inhomogeneous (hot-pressed) sample, was considerably more chemically homogeneous than the control sample prepared on earth (1-g). Melt homogenization or mixing at 1-g is known to be caused primarily by gravity-driven convection. Why a glass prepared in micro gravity, where gravity-driven convection is ideally absent and the melt would be more nearly stagnant, was more chemically homogeneous, remained unclear.

It is interesting to note, however, that similar results have been obtained from other

microgravity experiments^{4,9}, even for glasses processed in containers. The following list summarizes the most important results that have been consistently reported for glass forming melts in microgravity.

- (1) *Glass formation is enhanced for melts prepared in space^{2,4}.*
- (2) *Glasses prepared in microgravity are more chemically homogeneous^{2,8} and contain^{6,8} fewer and smaller chemically heterogeneous regions than identical glasses prepared on earth.*
- (3) *Heterogeneities that are deliberately introduced such as Pt particles are more uniformly distributed^{7,8} in a glass melted in space than in a glass melted on earth.*
- (4) *Glasses prepared in microgravity are more resistant to crystallization^{4,6,9}, and have⁶ a higher mechanical strength and threshold energy for radiation damage.*
- (5) *Glasses crystallized in space have a different microstructure, finer grains more uniformly distributed, than equivalent samples crystallized on earth^{4,8}.*

The preceding results are not only scientifically interesting, but they have considerable practical implications. These results suggest that the microgravity environment is advantageous for developing new and improved glasses and glass-ceramics that are difficult to prepare on earth. However, there is no suitable explanation at this time for why a glass melted in microgravity will be more chemically homogeneous and more resistant to crystallization than a glass melted on earth.

A fundamental investigation of melt homogenization, nucleation, and crystal growth processes in glass forming melts in microgravity is important to understanding these consistently observed, but yet unexplained results. This is the objective of the present research. A lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) glass will be used for this investigation, since it is a well studied system, and the relevant thermodynamic and kinetic parameters for nucleation and crystal growth at 1-g are available. The results from this research are expected to improve our present understanding of the fundamental mechanism of nucleation and crystal growth in melts and liquids, and to lead improvements in glass processing technology on earth, with the potential for creating new high performance glasses and glass-ceramics.

Hypothesis

The solidification of high temperature melts is controlled by the kinetics of nucleation and crystal growth. A melt forms a glass when nucleation and subsequent crystal growth does not occur or can be avoided during cooling the melt. Understanding the kinetics of nucleation and crystal growth for a melt is also the basis for understanding glass formation for that melt. According to the classical theory of nucleation and crystal growth, the volume

fraction, $V_c/V (= x)$, that crystallizes in a melt during cooling can be related to the nucleation rate, I_v , and crystal growth, U as¹⁰,

$$x = 1 - \exp [- (4\pi/3) \int I_v (\int U dt'')^3 dt'] \quad \dots \quad \dots \quad \dots \quad \dots(1)$$

If x in the quenched melt is below the lower detection limit, which is currently about 10^{-6} , the resulting material is considered a glass.

The simplified forms of I_v and U at a temperature T are given in Eqs. 2 and 3,

$$I_v = (n_v D / \lambda^2) \exp (- W^* / kT) \quad \dots \quad \dots \quad \dots \quad \dots(2)$$

$$U = (f D / \lambda) [1 - \exp (V_m \Delta G_v / RT)] \quad \dots \quad \dots \quad \dots \quad \dots(3)$$

where W^* is the thermodynamic barrier for nucleation, ΔG_v is the free energy difference between unit volumes of the crystal and liquid phases, n_v is the number of molecules or formula units of the nucleating phase per unit volume, k is the Boltzmann constant, and λ is a jump distance on the order of atomic dimensions, V_m is the molar volume of the crystal phase, R is the gas constant, and f is an interface site factor which refers to the fraction of sites on the interface to which an atom can attach. For melts with an entropy of fusion of less than $2R$ which is approximately true for most glass forming melts, the site factor f is close to unity. D is the effective diffusion (self) coefficient and is related to the viscosity of the melt, η , at the temperature T as,

$$D = kT / 3\pi\lambda\eta \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots(4)$$

None of the above equations involves gravity (g) *per se*, and it is hard to not clear why the kinetics of nucleation or crystal growth (or, conversely, the kinetics of glass formation) for a melt in microgravity will be different from those at 1-g. However, the experimental results suggest differently.

It is suspected that gravity-driven convection at 1-g introduces a high rate of mass transfer in melts, which could affect the structure of the melt in several ways.

- (1) Materials dissolved from the container walls may continually be convected (carried) into the melt at 1-g thereby, creating chemical inhomogeneities and potential sites for heterogeneous nucleation and crystallization. Due to lack of gravity-driven convection in micro-g, any materials dissolved from the container could be confined to a thin layer at the melt-container interface leaving the bulk of the melt essentially free from these impurities (or nucleation sites). If there is less mixing in a melt in micro-g then the overall nucleation rate is expected to be lower and chemical homogeneity would be better than for a glass melt at 1-g.
- (2) High temperature melts, particularly, multicomponent melts containing two or more

components of differing density can experience localized compositional fluctuations which favors the formation of clustered regions whose chemical compositions differ from the overall composition of the melt. Rapid quenching of a melt freezes these compositionally different (microheterogeneous) regions in the glass, which are potential nucleation sites for crystallization. A higher rate of mass transfer can induce a larger compositional fluctuation in a melt at 1-g forming microheterogeneous regions of larger size and number. As a consequence, a glass prepared on earth can be less chemically homogeneous and have a higher nucleation rate or crystallization tendency compared to the same glass prepared in space.

The above two hypotheses basically imply that the perturbation induced by gravity-driven convection causes the effective diffusion coefficient, D (Eq. 4) to be larger in a melt at 1-g. Experiments show^{11,12} values of D that are 30 to 40% lower for melts in space compared to the best values reported for melts on earth. A lower value of D in space experiments will reduce both the nucleation and crystal growth rates (Eqs. 2 and 3), resulting in an overall increase in the tendency for glass formation (Eq. 1) of the melt compared to that of a melt on earth.

The formation of microheterogeneous regions can be viewed qualitatively as a demixing effect (shown schematically in Fig. 2), which is enhanced by gravity-driven convection. If there is no Marangoni flow, a melt in micro-g would be essentially stagnant and the effect of demixing would be much smaller. The equilibrium level of homogeneity at 1-g can be attained in a shorter time, but it is expected to always be less than what can be achieved in space.

A third hypothesis stems from the reported^{13,14} pseudoplastic character of glassy materials. This means that a glass under an applied stress will have a lower effective viscosity, η (or higher D , Eq. 4), compared to a stress-free glass at the same temperature. In other words, a stressed glass will have a higher tendency for crystallization than an unstressed glass. Since a melt at 1-g is under constant convection compared to a near quiescent melt in micro-g, it is suspected that a glass prepared at 1-g will have a higher stress and will be more susceptible to crystallization than a glass prepared in space.

Experiment

The hypotheses mentioned above, namely, (1) the reduction of nucleation and crystal growth rates, (2) improvement in chemical homogeneity, and (3) reduction of stress for the glasses prepared in space compared to those for the glasses prepared on earth will be tested through flight and ground based experiments. As mentioned before, a lithium-disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ or LS_2) will be used as the test composition.

The flight experiments will include melting an LS_2 composition in sealed platinum capsules

at temperatures between 1100 and 1500° C and cooling the melts at predetermined rates. While a part of the samples will be returned to earth as their as-quenched condition for various property measurements, others will be given a two stage heat treatment in space between 420 and 700° C for 30 min to 12 h for nucleation and crystal growth. Conventional microscopic techniques will be used to determine the rates for nucleation and crystal growth of the glasses as a function of temperature and to evaluate the microstructure of the crystallized samples. These data will be compared with that for the control samples from similar measurements at 1-g.

Differential thermal analysis (DTA) will be used to compare the crystallizing tendency for the space and earth melted glasses. A few selected properties that are likely to be affected by the degree of homogeneity and stress of a glass such as the density, refractive index, and optical transmission in the UV, visible, and IR, will be measured and compared for these glasses. Any difference in the structure of space and earth melted glasses will also be investigated by x-ray photoelectron spectroscopy (XPS), neutron diffraction, and Raman and IR spectral analysis.

Work Performed / Undertaken

The work for this project was started with investigating the effect of melting temperature on the crystallization of an LS₂ glass. Since the microheterogeneous regions discussed earlier form in the liquid state, it is reasonable to expect that melting temperature might have an effect on the size and number of these regions and, hence, on the overall crystallization behavior of the glass. Glasses (50 g) were prepared by melting a homogeneous batch of the LS₂ composition in a platinum crucible at 1450° C for 15 min. The melt was then stirred with an alumina rod and held at temperatures between 1050 and 1450° C at 50° C intervals for 2 h before quenching between steel plates.

A 50 mg sample of each glass with particle size between 425 and 500 μm was analyzed by DTA at a heating rate of 10° C/min. No effect of melting temperature of this LS₂ glass was apparent in the DTA thermograms. The peak temperature of the glass transition endotherm and crystallization exotherm in DTA occurred at 481±1° C and 658±2° C, respectively, for all the glasses melted at different temperatures.

The IR spectra for these glasses as measured by KBr pellet technique from 450 to 2000 nm are also essentially identical and do not show any effect of melting temperature.

The LS₂ glasses prepared by melting at different temperatures are now being used to measure the nucleation and crystal growth rate as a function of temperature using conventional optical microscopy. Neutron diffraction, XPS, and Raman spectra measurements for these glasses are continuing.

References

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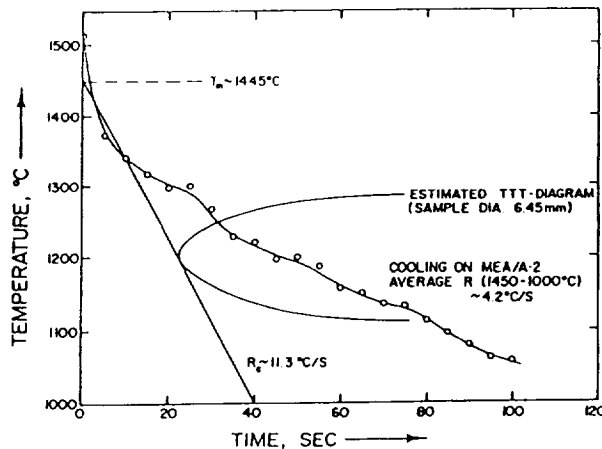


Fig. 1. The TTT diagram for a 25 SiO₂-35.7CaO-39.3Ga₂O₃, mol% glass determined at 1-g and the actual cooling rate used in space experiment (ME A/A-2) for this melt.

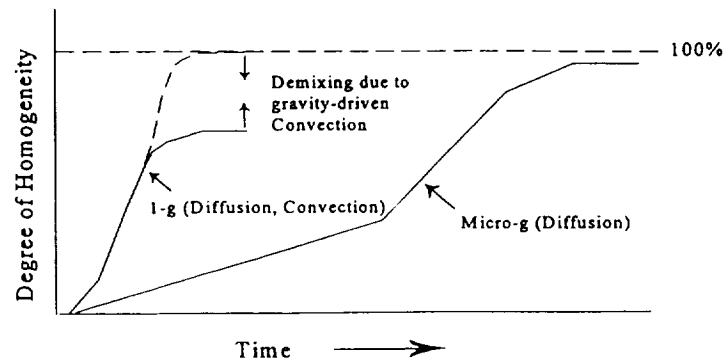


Fig. 2. A most likely situation for melt homogenization in micro-g and at 1-g. At 1-g, the melt may be homogenized in a shorter time, but degree of homogenization will be less due to possible demixing induced by gravity-driven convection.