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

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Introduction

This flight definition project has the specific objective of investigating the kinetics of nucleation and crystal growth in high temperature inorganic oxide, glass forming melts in microgravity. It is related to one[1] of our previous NASA projects 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 (at 1500º C) and cooling levitated 6 to 8 mm diameter spherical samples in a Single Axis Acoustic Levitator (SAAL) furnace.

Compared to other types of materials, there have been relatively few experiments, 6 to 8, conducted on inorganic glasses in space. These experiments[2 – 11] have been concerned with mass transport (alkali diffusion), containerless melting, critical cooling rate for glass formation, chemical homogeneity, fiber pulling, and crystallization of glass forming melts. One of the most important and consistent findings in all of these experiments has been that the glasses prepared in microgravity are more resistant to crystallization (better glass former) and more chemically homogeneous than equivalent glasses made on earth (1g). The chemical composition of the melt appears relatively unimportant since the same general results have been reported for oxide, fluoride and chalcogenide melts. These results for space-processed glasses have important implications, since glasses with a higher resistance to crystallization or higher chemical homogeneity than those attainable on earth can significantly advance applications in areas such as fiber optics communications, high power laser glasses, and other photonic devices where glasses are the key functional materials.

The classical theories for nucleation and crystal growth for a glass or melt do not contain any parameter that is directly dependent upon the g-value, so it is not readily apparent why glasses prepared in microgravity should be more resistant to crystallization than equivalent glasses prepared on earth. Similarly, the gravity-driven convection in a fluid melt is believed to be the primary force field that is responsible for melt homogenization on earth. Thus, it is not obvious why a glass prepared in space, where gravity-driven convection is ideally absent, would be more chemically homogeneous than a glass identically prepared on earth. The primary *objective* of the present research is,

To obtain experimental data for the nucleation rate and crystal growth rate for a well characterized silicate melt (lithium disilicate) processed entirely in space (low gravity) and compare these rates with the nucleation and crystal growth rates for a similar glass prepared identically on earth (1g).

The nucleation and crystal growth rates for a melt prepared in space have never been measured directly, but such data are expected to explain (at least partially) these puzzling, but extremely interesting results that have great scientific and practical relevance to the development, manufacturing, and use of inorganic glasses, glass-ceramics, the new bulk metallic glasses (BMG), and other solids derived from a melt.

Hypothesis

The reason why space glasses appear to be more resistant to crystallization than identical glasses prepared on earth is not known at this time, but "shear thinning" is suspected to be a likely reason. "Shear thinning" is the reduction in viscosity, which occurs with increasing shear rate in non-Newtonian liquids at a constant temperature as shown in Fig. 1. Such a reduction in viscosity with increasing shear rate has been reported for several commercial glasses[12 - 14], including the lithium disilicate (LS_2) composition[15, 16] that will be used in our space experiments. The reported[16] decrease in viscosity with increasing shear rate for a LS_2 glass is shown in Fig. 1. We believe that the gravity-driven convection that is normally present to some degree in a melt on earth will be much smaller or ideally absent in a nearly stagnant (quiescent) melt in space. A more quiescent melt in space should experience a smaller (or negligible) shear rate and, consequently, have a higher viscosity (less shear thinning) than a melt on earth at the same temperature as schematically shown in Fig. 2. A higher viscosity for the space glass would be expected to make it more resistant to crystallization because of the smaller nucleation and crystal growth rates, see Fig. 2.
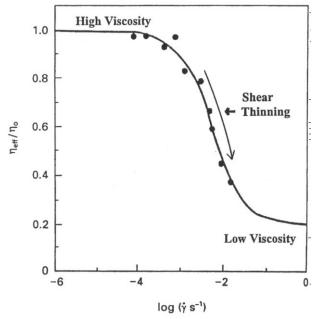

Fig. 1. Change in the effective viscosity (η_{eff}) with shear rate γ for a $Li_2O.2SiO_2$ glass at 483^0 C ($\eta \sim 2.24 \times 10^{10}$ Pa.s). From ref. 18

Ground-Based Work on Shear Thinning
A. Modeling
Computer modeling for the rates of fluid flow and shear across a LS_2 melt contained in a platinum capsule of the same shape and size (cylindrical, 2.5 cm long and 1.0 cm in diameter) as those proposed for the flight experiments were performed in collaboration with Drs. N. Ramachandran of USRA and E. Ethridge of MSFC, NASA. The calculations were carried out using a FIDAP fluid dynamics package (Fluent Inc., version 8.0, 1998) assuming the platinum cylinder containing the melt was heated in such a way that a

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thermal gradient existed at its two ends. The curved wall of the cylinder was assumed to be insulating and the gravity acting in a transverse direction to the thermal gradient. The results show that the shear rate decreases linearly with decreasing gravity for a constant temperature gradient across the melt and increases with increasing temperature gradient, see Fig. 3. This means that the shear rate for a glass prepared in space ($< 10^{-4}$ g) will be at least four orders of magnitude less than that in the same glass prepared at 1g. Data for glasses such as LS_2 indicate that a reduction of four orders of magnitude in the shear rate for the space glass could cause the viscosity to increase from 2 to 10 times. Such an increase in viscosity could decrease the crystallization tendency (or increase the glass forming tendency) by factors from 16 to 10,000 compared to an identical glass prepared on earth.
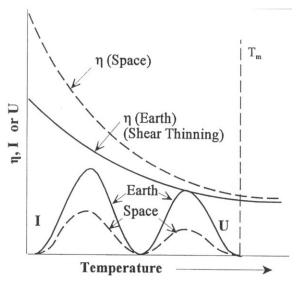

Fig. 2. Schematic representation of the anticipated viscosity (η), nucleation rate (I), and crystal growth rate (U) for a melt in space and for the identical melt on earth based on "shear thinning".
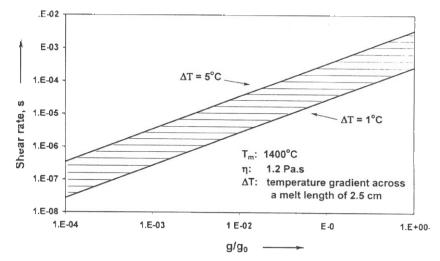

Fig. 3. Calculated shear rate for a $Li_2O.2SiO_2$ melt as a function of gravity.

B. Experiment

Experiments to verify the shear thinning hypothesis were performed by (isothermally) heating bent LS_2 glass fibers at temperatures (350 to 400⁰ C) well below the temperatures for nucleation (425 to 500⁰ C) and crystal growth (> 570⁰ C) for this glass. The glass fibers, ~ 150 μm diameter and 12 cm long, were

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bent and held between two fixed holes, ~ 2.5 cm apart, on a refractory block as shown schematically in Fig. 4. The flexural stress at the tip of the bent fibers will be the highest, estimated about 0.5 GPa in the present case. Straight glass fibers of the same LS_2 composition, which were not subjected to any kind of stress, were also heated simultaneously for comparison. The refractory block holding the glass fibers was inserted in a furnace already equilibrated at a preset temperature and held there for various times between 10 min and 4 h.
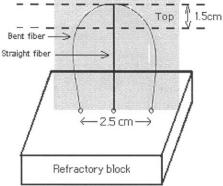

Fig. 4. Schematic of heat-treatment experiments of bent and straight $Li_2O.2SiO_2$ glass fibers.

When released after the heat treatment, the bent fibers were found to deform permanently as shown in Fig. 5 for the fibers heated at 370^0 C, and the deformation increased with increasing time for heat treatment. This 370^0 C temperature is much lower than the glass transition temperature (~ 460^0 C) for this glass, where viscosity is expected to be larger than 10^{14} Pa.s. The permanent deformation of the glass fibers indicates that a fluid flow might have been occurred, at least at the tip of the bent fibers, even at 370^0 C. This means that with the application of a bending stress, the viscosity of the glass decreased from its value of stress-free condition, which is a manifestation of shear thinning.
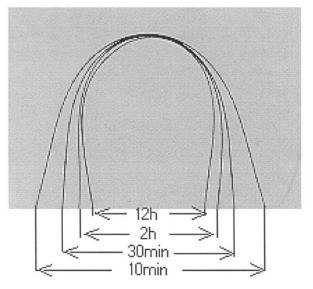

Fig. 5. Permanently deformed $Li_2O.2SiO_2$ glass fibers after heat-treatment at 370^0 C for the times shown.

Results from differential thermal analysis (DTA) also showed, Fig. 6, that the crystallization peak for the sample prepared from the tip of the bent fibers that were heated at 370^0 C for 3 h, was larger and occurred

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at a lower temperature than those for the sample prepared from the identically heat treated straight fibers. Clearly, the tip of the bent fibers, where the bending stress was the highest, contained a higher number of nuclei than the stress-free, straight fibers. It is to be noted that the 370^0 C heat treatment temperature is about 55^0 C lower than the onset temperature ($\sim 425^0$ C) for nucleation for this LS_2 glass, and no nuclei is expected to form when the glass is heated at 370^0 C. However, the DTA results in Fig. 6 indicate the formation of additional nuclei at the tip of the bent glass fibers, presumably due to a lowering of viscosity caused by the applied bending stress in this region of the fibers.
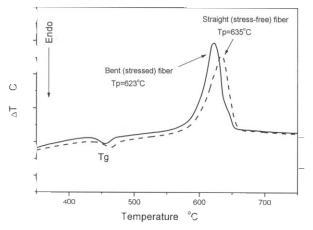

Fig. 6. Differential thermal analysis of the bent (stressed) and straight (stress-free) $Li_2O.2SiO_2$ glass fibers after heat-treatment at 370° C for 3 h.

Similar heat treatment experiments conducted for bent and straight LS_2 glass fibers at 450^0 C for 8 h, show visible crystallization at the tip of the fibers, see Fig. 7. This 450^0 C temperature is about 120^0 C lower than the onset temperature for crystallization for this glass, and, as expected, no such crystallization was observed on the stress-free, straight fibers, Fig. 8, which received a simultaneous and identical heat treatment as the bent fibers.

The above experiments clearly demonstrate that the tendency for nucleation and crystal growth in a LS_2 glass is increased when it is subjected to an external stress, and shear thinning, i.e., a decrease in viscosity with increasing stress, is suspected to be a reason for this. Further investigations for a quantitative determination of the nucleation and crystal growth rates as a function of stress at a constant temperature, as function of temperature at a constant stress, and the mechanism of stress relaxation for these LS_2 glass fibers are continuing.

Plans for Flight Experiments
The overall plan for the flight experiments will be to measure, for the first time, the nucleation rate (I) and the crystal growth rate (U), each at three different temperatures, for a $Li_2O.2SiO_2$ (LS_2) glass prepared completely in space, see Tables 1 and 2. The glasses prepared in space will be made by remelting a glass prepared on earth. A glass cylinder contained in a doubly sealed platinum cylinder (2.5 cm long and 1.0 cm in diameter) will be melted at 1400° C for 3 h and quenched to glass at an appropriate cooling rate. After melting and cooling, the encapsulated glass samples will be given a nucleation heat treatment at either 440, 455, or 470° C for 1 to 5 h and a crystal growth heat treatment at 590, 610, or 630° C for 10 to 30 min. The samples heat treated in space will be analyzed on earth to determine I and U which will be compared with the I and U values for glasses melted and heat treated (for nucleation and crystal growth) identically on earth.

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The traditional method[17, 18] , which requires measuring the number or size of crystals by optical microscopy on polished sections of the heat treated samples, will generally be used to determine I and U. A newly developed alternative method[19, 20] which uses differential thermal analysis (DTA) and which has several advantages (faster, smaller amount of samples, less complexity for sample processing) over the traditional method will also be used for measuring I and U.
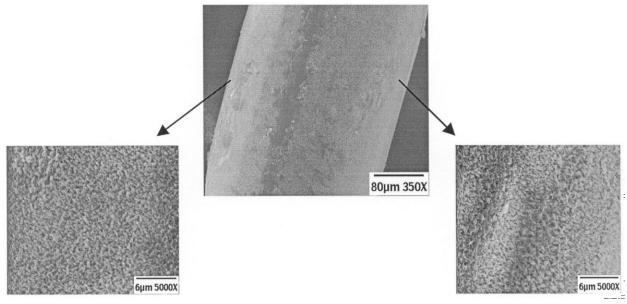

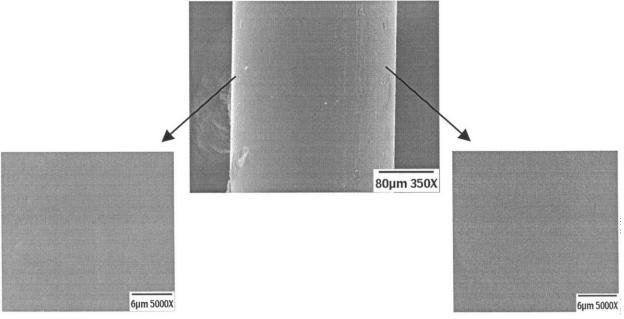Fig. 7. Crystallization in $Li_2O.2SiO_2$ bent (stressed) glass fibers when heat-treated at 450^0 C for 8 h.

Fig. 8. A $Li_2O.2SiO_2$ straight (stress-free) glass fiber after heat treatment at 450^0 C for 8 h (the same heat-treatment as received by the bent fiber in Fig. 7). The 450^0 C is about 120^0 C lower than the onset temperature for crystallization of this glass, and, as expected, no visible crystallization was observed in this stress-free fiber.

Some of the glass samples melted in space in platinum capsules will be returned to earth in their as-quenched condition (i.e., without any heat treatment for nucleation and crystal growth in space) for

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structural evaluation, measuring specific properties, and determining the concentration of quenched-in nuclei (N_q) in these glasses (samples in the bottom row of Tables 1 and 2). A comparison of N_q in the space and earth melted glasses will provide qualitative information on the degree of chemical homogeneity in these glasses. A glass containing a colored (blue) spot on its surface (sample B in Tables 1 and 2) will also be remelted in space for assessing the extent of fluid flow in high temperature melts in microgravity. Any movement of the blue spot in the melt will leave a blue trail in the melt.

Table 1. Experimental plans for measuring nucleation rate (I) for a LS_2 glass in space (samples are doubly sealed in platinum capsules).

Sample Type	Melting in Space Temp./Time	Nucleation Temp. °C	Time, Hour 1	3	5	Crystal Development Temp./Time
A	1400 °C/3h	440	√	√	√	
		455	√	√	√	
		470	√	√	√	600 °C/20 min
A	None (Melted on earth)	440	√	√	√	
		455	√	√	√	
		470	√	√	√	
A,B	1400 °C/3h	None (A-N, B-N)				None

Table 2. Experimental plans for measuring crystal growth rate (U) for a LS_2 glass in space (samples are doubly sealed in platinum capsules).

Sample Type	Melting in Space Temp./Time	Nucleation Temp./Time	Crystal Growth Temp. °C	Time, Min. 10	20	30
A	1400 °C/3h	455 °C/30 min	590	√	√	√
			610	√	√	√
			630	√	√	√
A	None (Melted on earth)	455 °C/30 min	590	√	√	√
			610	√	√	√
			630	√	√	√
A,B	1400 °C/3h	None	None (A-N, B-N)			

A, Glass premelted on earth.
B, Glass premelted on earth with a colored spot.
A-N, B-N: Melted in space, but no nucleation or crystal growth heat treatment in space.

Comments
If the values for I and U for the LS_2 glass prepared in microgravity are indeed found to be smaller than the glass made on earth, then our understanding of the fundamental processes for nucleation and crystal growth in glasses will be greatly improved. The classical equations for I and U may need to be modified to account for differences in gravity through the viscosity term in these equations. This enhanced understanding of the

fundamental mechanisms for glass formation, nucleation, and crystallization could lead to improvements in present-day glass processing technology on earth, thereby, improving our ability to produce glasses of higher quality and improved properties.

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