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Effect of microgravity on crystallization in heavy metal fluoride glasses processed on the CSAR-I sounding rocket

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Gravity-driven density segregation in viscous glass is believed to trigger homogeneous nucleation during the high-temperature processing of heavy metal fluoride (HMF) glasses. Processing of HMF glasses in microgravity could, therefore, minimize commonly observed micro-crystal formation in these glasses during their heat treatment for fibre drawing. Although, preliminary experiments on parabolic flight aircraft had earlier indicated that gravity enhances and microgravity suppresses crystallization during the processing of HMF glasses, these results were considered inconclusive due to the short processing time of 20 seconds. The CSAR-I sounding rocket provided an opportunity to process HMF glasses over a longer duration of five minutes in microgravity. These experiments indicated that microgravity helps in reducing crystallization in HMF glasses during their heat treatment at 325°C, which is very close to their fibre drawing temperature range of 300–320°C.

1. Introduction

Heavy metal fluoride (HMF) glasses are amongst the most promising fibre materials for future optical communication systems due to their predicted ultra-low optical loss limit of 0.001 dB/km [1]. However, such low losses could not be realized in HMF glass fibres due to excess scattering from micro-crystals formed during bulk glass synthesis and fibre drawing. The lowest reported losses in HMF glass fibres are about 0.65 dB/km [2]. Failure to eliminate undesired micro-crystals, and resulting optical degradation, during the conventional processing of HMF glass fibres has been identified as the limiting factor in further loss reduction in these fibres [3].

The micro-crystals in HMF glasses are formed by heterogeneous and homogeneous nucleation during glass synthesis and fibre drawing. Heterogeneous nucleation is mainly caused by contamination of the glass melt from the processing container, while gravity-driven density segregation in viscous glass on the ground is believed to be the primary reason for homogeneous nucleation in these glasses. Since both these factors cannot be eliminated during the conventional processing of HMF glasses on the ground, the predicted ultra-low losses cannot be realized.

The processing of HMF glass fibres involves two-steps: (i) synthesis of bulk glass preforms by a melt-quenching technique, and (ii) fibre drawing from these preforms at their glass softening temperature where the viscosity is around 10^3–10^4 poise. Therefore, it is essential to minimize micro-crystal formation in HMF glasses during both these process steps. It is difficult to avoid crystal nucleation during the conventional synthesis of HMF glasses, but rapid quenching of the melt is utilized to freeze these nuclei and avoid crystallization. However, reheating of bulk glass preforms to glass softening temperature for fibre drawing creates new nuclei and allows growth of these and pre-existing nuclei. This causes optical degradation in HMF glass fibres.

It is believed that microgravity containerless processing of HMF glass preforms and fibres could minimize formation of these undesired micro-crystals. Synthesis of HMF glasses is yet to be attempted in microgravity. However, containerless synthesis of HMF glasses on the ground by a gas film levitator has produced glass preforms with the lowest concentration of heterogeneous nuclei resulting in very low scattering losses of about 0.015 dB/km [4]. Unfortunately, HMF glass fibres with such low losses have not been realized, presumably due to micro-crystal formation during their heat treatment for fibre drawing.

The focus of our research is on studying the effect of microgravity on micro-crystal formation and resulting optical degradation in HMF glasses during their

heat treatment for fibre drawing. Although our preliminary experiments conducted on the T-33 parabolic flight aircraft had earlier indicated that gravity enhances crystallization in HMF glasses [5], these results were not considered conclusive due to the short microgravity processing time of only 20 seconds available on the aircraft. The CSAR-I sounding rocket flight provided an opportunity to process HMF glass samples in microgravity for a longer duration of five minutes. This paper describes the payload, provides experimental details and presents the results obtained from these experiments.

2. The CSAR-I glass processing payload

A fully automated experimental payload was developed in-house for the processing of HMF glass samples onboard the Canadian Space Agency Rocket-I (CSAR-I). A picture of the CSAR-I glass processing payload with its skin removed is shown in Fig. 1. This payload consisted of three compartments separated by deck plates. The top compartment contained the material processing facility, the middle contained electronic controls and a data-logger, and the bottom contained three sets of high energy density batteries for supplying power to the payload.

The material processing facility consisted of 12 interchangeable resistance heated furnaces capable of achieving 600°C. They were divided into six pairs of annealing and processing furnaces. Each annealing furnace was stacked on top of a processing furnace with a common axial bore to accommodate the sample holder. The sample holders were held along the axes of the furnace pairs with the help of end rods, which were attached to the deck plates through vibration-free mounts. Six gold plated brass sample holders (one per pair of furnaces) were used to hold HMF glass samples. Two samples of about 6 mm (D) $\times$ 25 mm (L) were placed in each sample holder. Three independent drive mechanisms, each coupled to two pairs of furnaces, provided upward and downward movement to the furnaces. Top and bottom limit switches dictated the final positions of the furnaces.

During the CSAR-I experiments, the samples remained stationary while the furnaces moved to position themselves over the samples in the desired sequence. The samples were pre-heated in the annealing furnaces and then introduced into the processing furnaces at the start of the process cycle. They were then transferred back into the annealing furnaces at the end of the five minute processing period.

The electronic control system consisted of twelve temperature controllers, a full telemetry link and an on-board data-logger. The data-logger monitored the following outputs throughout the experiments: 12 furnace thermocouples, 3 bottom and 3 top limit switches, 0-g and 300 sec event relays, and voltages of the three battery banks, and current drawn from these battery banks.

Three sets of high energy density batteries powered the payload internally during the rocket flight, while external batteries powered it during the ground-based operations. One set of batteries powered all the electronic systems, the second powered the motors and controls, and the third set powered all the furnaces. The maximum power requirement during the initial heating of all the twelve furnaces was 43 A at 36 V.

A full ground support system was used for testing and payload operation on the ground. It consists of an experimenter's console, a portable 286 computer, ground power supplies, umbilicals (local and block house), and a high power boom umbilical.

The payload was thoroughly tested and calibrated. Each of the twelve furnaces was calibrated to determine its heating rate, initial temperature overshoot, difference between the furnace temperature and the set point,

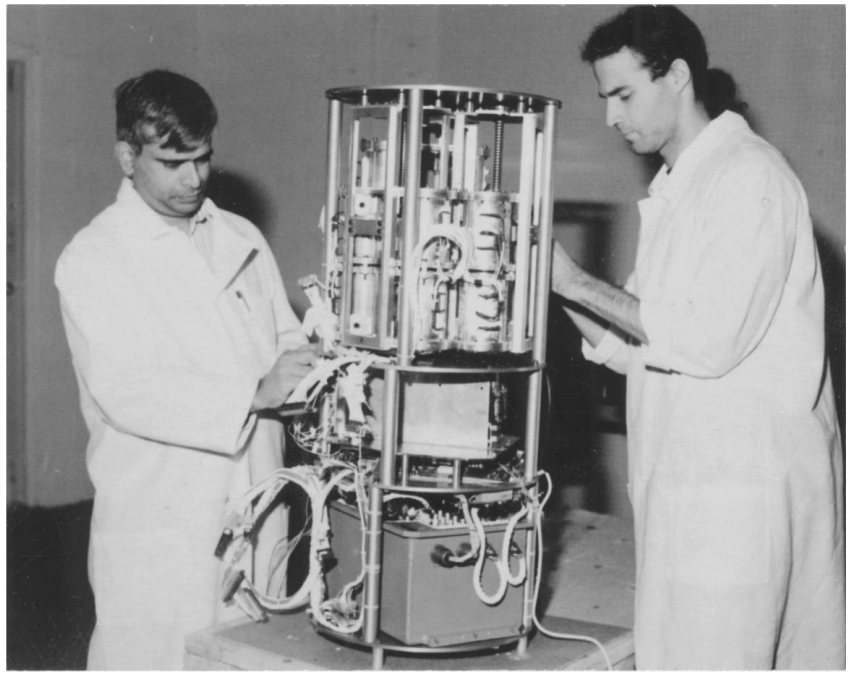


Figure 1 The CSAR-I rocket payload with its skin removed.

axial temperature uniformity inside the furnace and the sample holder, temperature difference between a test sample and the furnace in steady state, and a test sample heating profile during a simulated process cycle.

These tests indicated that the initial heating rate for the furnaces was about 50°C/min. Although the furnaces initially overshot the pre-set temperatures by about 40°C, they stabilized to within ±2°C of the set points in about 25 minutes. The axial temperature uniformity inside the furnace and the sample holder was ±2°C over a 50 mm length in the middle of the furnace. In steady state, the test sample temperature was within ±2°C of the furnace temperature. The test sample heating profile indicated that the sample temperature increased from annealing temperature to the processing temperature gradually and attained the desired value only by the end of the cycle.

3. Experimental details

3.1. Glass synthesis and characterization

HMF glass samples were synthesized by a conventional melt-quenching technique in two glass systems called ZBLAN glass (consisting of ZrF_4, BaF_2, LaF_3, AlF_3, and NaF) and ZBGAN glass (where LaF_3 was replaced with GdF_3). Typically, a 50 g charge was melted in a platinum crucible in a resistance heated furnace in an inert environment, and then quenched and annealed in a pre-heated graphite mould. The compositions of HMF glass samples are given in Table I.

Good quality cylindrical HMF glass preforms of about 6 mm (D) × 60 mm (L) dimensions were produced for this research. The graphite mould left a carbon film on the surface of these preforms, which was removed by mechanical polishing. These preforms were visually inspected to detect bubbles, voids, particulate matter inclusions and crystallization in them. They were then sliced to produce 25 mm long samples for the CSAR-I experiments. Only samples free from any visual defect were used. Their sliced ends were polished to remove mechanical damage. Two HMF glass samples (one ZBLAN and one ZBGAN) were placed in each sample holder with fused silica spacers on either side of these glass samples.

HMF glass samples (10 mm length) were sliced from some of these preforms and used for optical measurements. The end faces and side wall of these samples were polished. Transmission measurement was done over a wavelength range of 0.20–2.8 μm by a Cary 2400 spectrometer, while a Perkin-Elmer FTIR spectrometer was utilized over the range of 1.28–10 μm. A preform analyser from York Technology, Model P102, was used to measure the refractive index in these glasses.

Differential thermal analysis (DTA) plots for HMF glass samples were obtained by a Shimadzu DTA 50 system to determine glass transition, on-set of crystallization and melting temperatures. The sample size was approximately 10 mg, N_2 flow was 40 ml/min, the temperature range was from room temperature to 500°C, and the heating rate was 2–10°C/min.

TABLE I Composition of HMF glasses used in this research (in mol%)

	ZBLAN		ZBGAN	
Raw Materials	L4	L8	G4	G8
ZrF_4	53	50	50	47
BaF_2	20	19	22	21
LaF_3	4	8	—	—
GdF_3	—	—	4	8
AlF_3	3	3	4	4
NaF	20	20	20	20

3.2. CSAR-I glass processing experiments

The CSAR-I sounding rocket mission provided an opportunity to process HMF glass samples in microgravity for a duration of five minutes. Although the rocket was expected to provide between 6–7 minutes of microgravity time, the actual processing time was preset to five minutes. Ground-based reference HMF glass samples were processed a few days prior to the rocket launch at the launch site using the same payload and the same process parameters as those intended for the flight experiments. The payload was programmed to go through a preset sequence of operations.

During the ground-based experiments, six pairs of HMF glass samples in their sample holders were axially mounted inside the six furnace pairs. Each sample holder contained one ZBLAN and one ZBGAN glass sample. The furnaces were then heated for 30 minutes to attain their selected temperatures. The annealing furnaces were set around 200°C to ensure that the glass samples were not subjected to temperatures in excess of 300°C during the pre-heating, since a temperature overshoot of about 40°C was noticed earlier in these furnaces during their pre-heating. The processing temperatures were in the range of 325–400°C. The process was initiated by manually activating the 0-g signal on the ground console and terminated after five minutes by activating the 300 sec signal. The data-logger recorded various outputs which indicated that the payload worked as intended during these experiments.

Another set of 12 HMF glass samples in six new sample holders was then loaded into the payload for the rocket flight experiments. The furnace settings were not disturbed from the ground-based experiments so as to keep them the same during the flight experiments. The payload was then integrated with other payloads and rocket modules for the launch.

The rocket was launched on March 19th, 1992 from the White Sands Missile Range in New Mexico, USA. It carried five research payloads on a two-stage Black Brant-9 launch vehicle built by Bristol Aerospace Ltd. During the countdown period, the furnaces were preheated for 30 minutes using external batteries, but were switched to internal batteries just before the actual launch. The rocket launch was successful and the payload landed safely after the flight. It was recovered in working order without any visible damage.

Microstructural characterization of HMF glass samples, before and after their processing for crystallization studies, was done by a back scattered electron imaging technique using a JEOL-820 scanning electron

microscope (SEM) operated at 15 kV with a beam current of 1–12 nano amperes. The samples were mounted in an epoxy block, lapped perpendicular to their longitudinal axes and then polished on a lead lap using loose diamond and light oil.

4. Results and discussions

4.1. Characteristics of HMF glasses

Good quality HMF glass samples were synthesized for this research. Visually, they appeared clear, transparent and generally free of defects. Tiny bubbles were sometimes seen along the axis in some portions of the glass preforms and these portions were sliced off and discarded prior to sample preparation for further processing or characterization.

Fig. 2 shows an infrared transmission spectrum obtained on a ZBLAN-L4 glass sample. Other HMF glass samples produced similar spectra. The transmission was about 85% in the visible to near infrared region, except for three shallow ionic absorption peaks. The positions of these absorption peaks matched with those reported in the literature for OH^- ions (at 2.8 μm), carbon inclusions (at 3.4 μm) and dissolved CO_2 (at 4.25 μm). The ultraviolet absorption edge was around 0.25 μm, while the infrared absorption edge was around 5.5 μm. The refractive indices measured in these samples varied in the range of 1.486–1.493 depending on the composition. The refractive index was uniform across the length and diameter of each sample.

The DTA plots of HMF glass samples in all four compositions, obtained at a heating rate of 10°C/min, indicated that the glass transition was in a narrow range of 264–269°C, the onset of crystallization was also in a narrow range of 347–354°C, while the melting was in the range of 421–447°C [6].

The heating rate of 10°C/min provided the best DTA plots with least noise, while higher noise at lower heating rate generally made it difficult to precisely detect the beginning of a thermophysical event. It was noticed that while the glass transition and melting temperatures remained practically unaffected as the heating rate was reduced from 10°C/min to 2°C/min, the onset of crystallization temperature decreased by about 20°C. This indicates that the crystallization in these glasses could actually occur around 330°C. The crystallization in these glasses was indeed detected around 320°C during some fibre drawing and glass processing experiments. Since the glass softening temperature in HMF glasses is around 300°C, they have a narrow fibre drawing temperature range of 300–320°C.

4.2. Performance of the CSAR-I payload

The CSAR-I payload performed well during the ground-based experiments as indicated by the data recorded by the on-board data-logger. The telemetry link and on-board data logger independently provided continuous recording of critical events and important parameters throughout the CSAR-I rocket flight. Analysis of this data confirmed that the rocket flight was successful and the payload performed as anticipated [6]. The processing temperatures during the flight matched with those obtained during the ground-based experiments.

Fig. 3 shows the vertical parabolic trajectory recorded for the CSAR-I rocket during the flight. The rocket attained a maximum height of about 246 km and provided a microgravity duration of about 400 seconds. The longitudinal acceleration recorded by the rocket during its flight is given in Fig. 4. It indicates that the payload experienced acceleration levels in excess of 10-g during the rocket launch and re-entry.

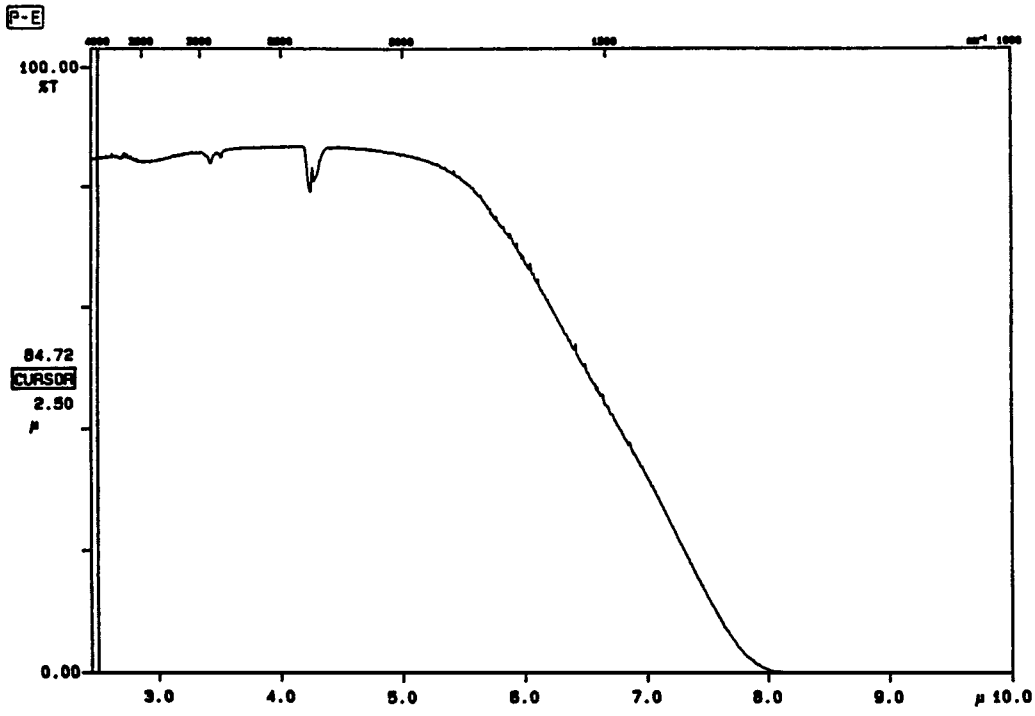


Figure 2 Infrared transmission spectrum of a ZBLAN-L4 glass sample.

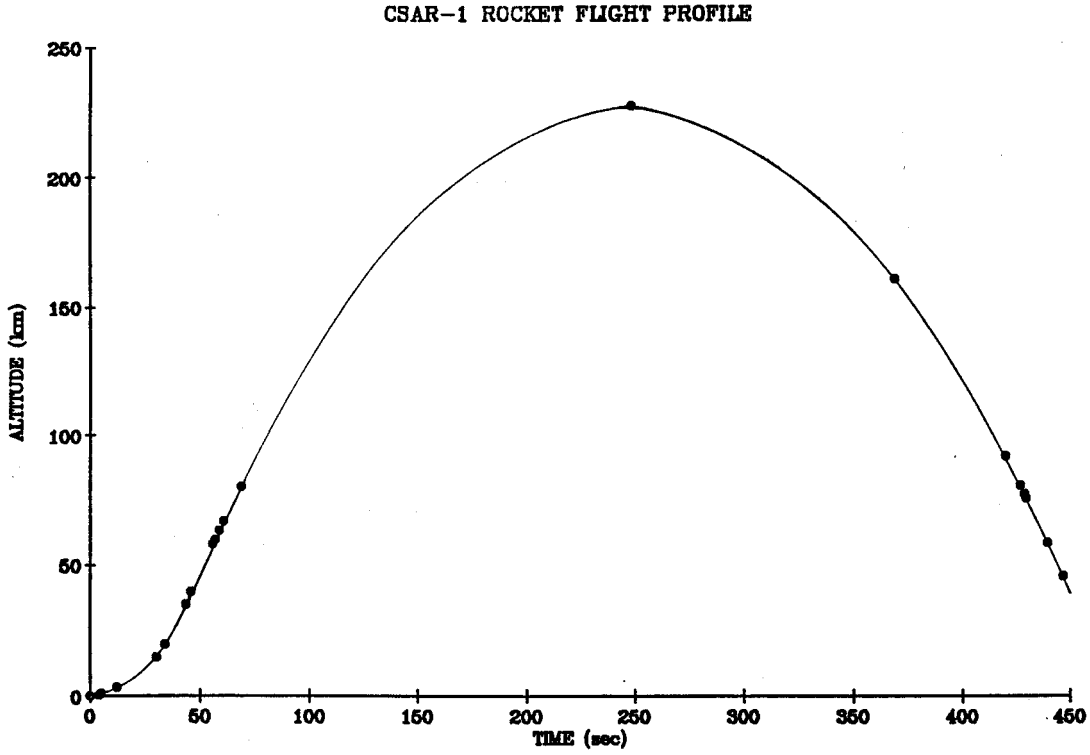


Figure 3 The actual microgravity flight profile of the CSAR-I rocket.

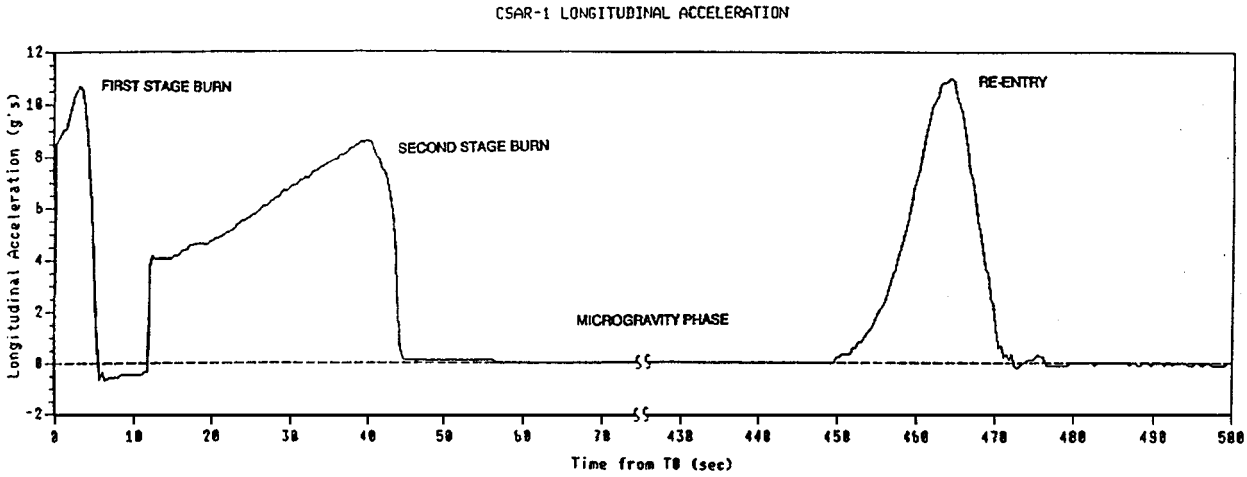


Figure 4 The longitudinal acceleration achieved by the CSAR-I rocket during its flight.

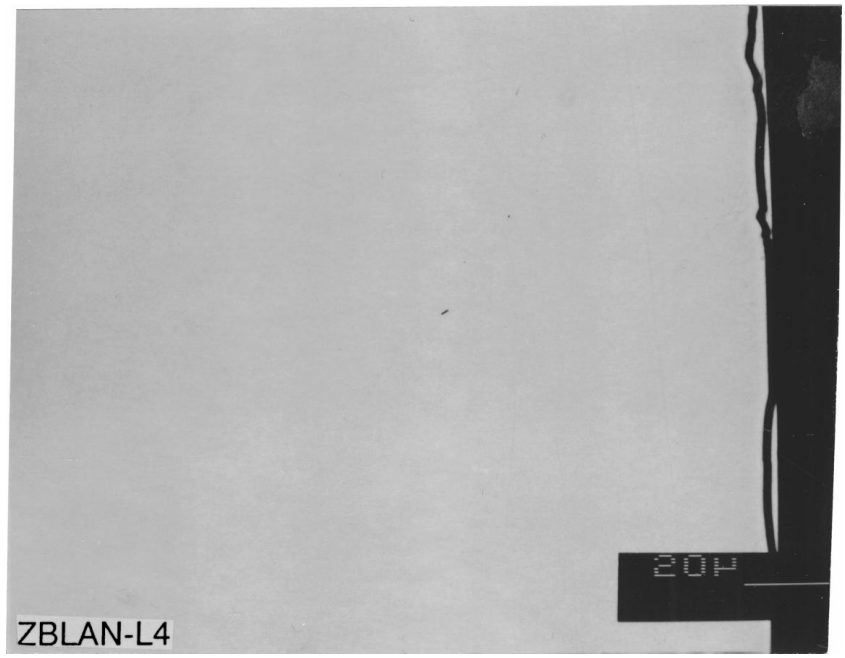
4.3. Effect of microgravity on crystallization

Fig. 5 presents SEM micrographs of HMF glass samples processed in microgravity for five minutes at 325°C. These micrographs correspond to: (a) a ZBLAN-L4 glass sample, and (b) a ZBGAN-G8 glass sample, and show no evidence of any crystallization. On the other hand, HMF glass samples processed at 325°C on the ground for five minutes showed extensive crystallization at the surface. This is shown in Fig. 6 for: (a) a ZBLAN-L8 glass sample, and (b) a ZBGAN-G4 glass sample.

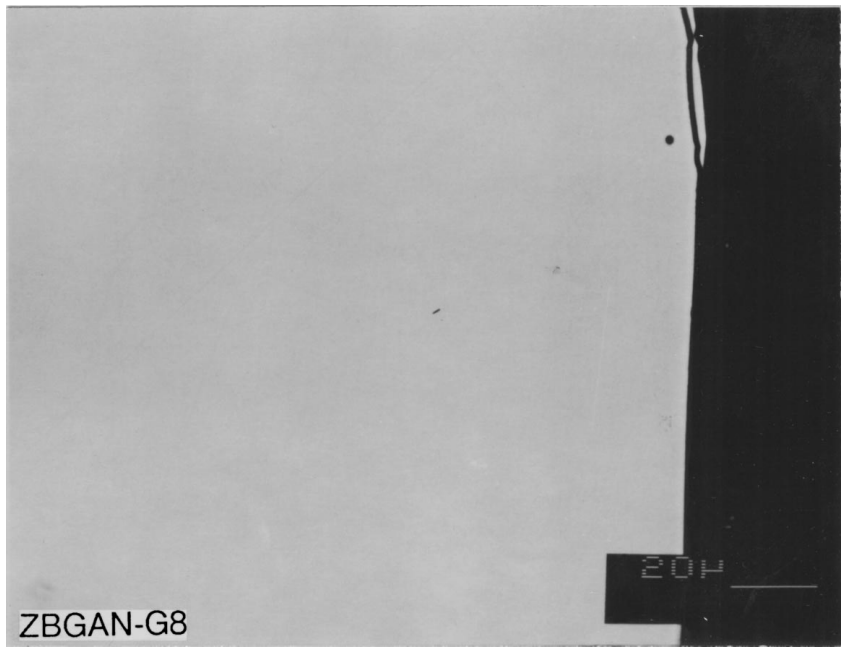
It is to be noted that earlier ground-based crystallization studies on HMF glasses, which were conducted under statistical design at temperatures and durations comparable to these experiments, had indicated that the ZBLAN-L4 glasses produce the highest amount of crystallization amongst the four compositions, while the ZBLAN-L8 and ZBGAN-G8 glasses produce the least amount of crystallization [7].

Since the ZBLAN-L4 glass sample did not crystallize in microgravity while the ZBLAN-L8 and ZBGAN-G4 glass samples developed extensive surface crystallization on the ground, the observed results were due to the difference in gravity levels instead of compositions. The processing temperature of 325°C is very significant for HMF glasses as this is very close to their fibre drawing temperature range of 300–320°C. Thus these results imply that microgravity would help in reducing crystallization, and resulting optical degradation, in HMF glasses during their heat treatment for fibre drawing. This is a very significant finding since it could lead to the realization of predicted low losses in HMF glass fibres.

Although HMF glass samples were processed at four temperatures in the range of 325–400°C during the CSAR-I rocket flight, only the samples processed at 325°C were deemed suitable for interpreting the effect of microgravity. The samples processed at higher temperatures were, unfortunately, exposed to



(a)



(b)

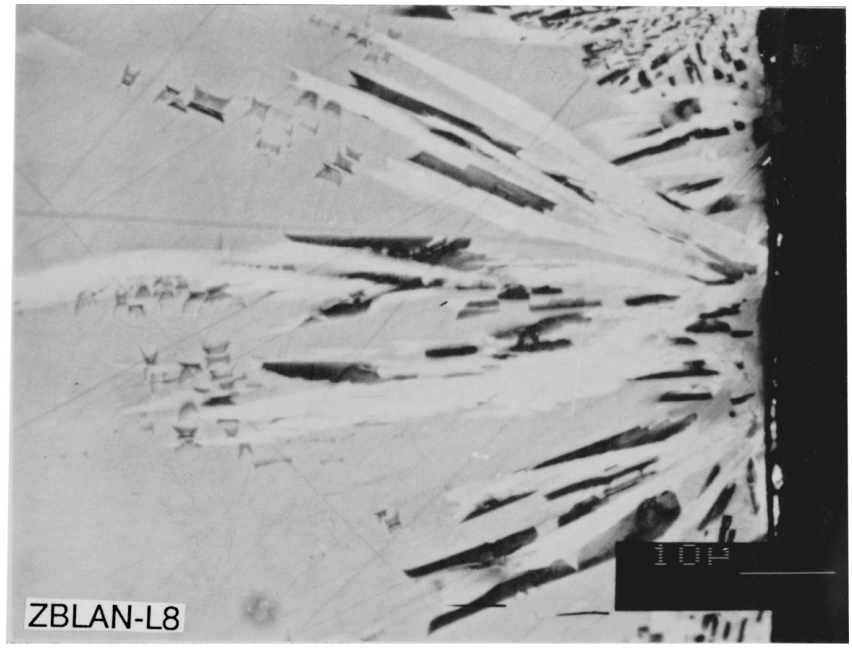
Figure 5 SEM micrograph of HMF glass samples processed at 325°C for five minutes in microgravity on the CSAR-I rocket: (a) ZBLAN-L4 glass, and (b) ZBGAN-G8 glass.

high gravity levels (∼10-g) at high enough temperatures (due to unexpected furnace temperature excursion) during the rocket's re-entry into the earth's atmosphere. This caused extensive crystallization in these samples and made them unacceptable as microgravity processed samples.

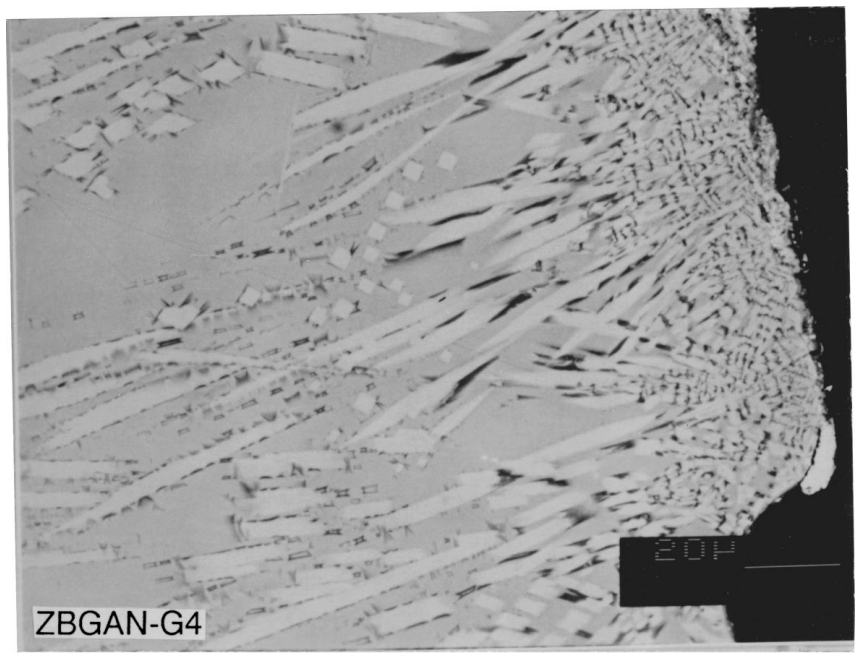
4.4. Effect of high temperature and high acceleration levels during rocket's re-entry

HMF glasses are known to crystallize on the ground around 320°C. Moreover, the results of our earlier experiments on the T-33 parabolic flight aircraft had indicated that higher acceleration (2-g) levels enhance crystallization in HMF glasses [5]. Therefore, care was taken during the CSAR-I experiment planning to ensure that HMF glass samples remained below 300°C during the rocket's re-entry to avoid accidental crystallization upon their exposure to high acceleration levels (in excess of 10-g).

Fig. 7 shows computed sample temperature response curves for two extreme process cycles involving the lowest (325°C) and the highest (400°C) processing temperatures during the CSAR-I experiments. These response curves were computed from the ground-based calibration data and the actual processing and annealing temperatures used during the ground-based and the rocket flight experiments. Rocket's re-entry is also



(a)



(b)

Figure 6 SEM micrograph of HMF glass samples processed at 325°C for five minutes on the ground using the CSAR-I payload: (a) ZBLAN-L8 glass, and (b) ZBGAN-G4 glass.

marked on this figure, which suggested that HMF glass samples would remain below 300°C during the rocket's re-entry and the chances for accidental crystallization due to high acceleration exposure would be minimal.

Unfortunately, this assumption appears to have remained valid only during the glass processing experiments in microgravity at 325°C. An unexpected and sudden rise of temperature (∼35°C) was recorded by the data-logger in all furnaces during the rocket's re-entry. Fig. 8 depicts the temperature of an annealing furnace recorded during the ground-based and the rocket flight experiments, which indicates such a temperature excursion at rocket's re-entry. All furnaces showed similar behaviour.

This temperature excursion would have brought the temperatures of most samples, except those processed at 325°C (since they would have cooled sufficiently), to their crystallization region. The exposure of these samples to high gravity levels at this juncture would cause crystallization in these samples. This was indeed noticed in samples processed at higher temperatures. Fig. 9 shows such a crystallized ZBLAN-L4 glass sample processed at 365°C on the rocket.

The reason for this unexpected temperature excursion is not exactly known, but it may have been caused by hot air entering the payload during the rocket's re-entry. The skin temperature of the rocket is known to increase significantly during its re-entry due to air friction from the atmospheric gases. Since the payload

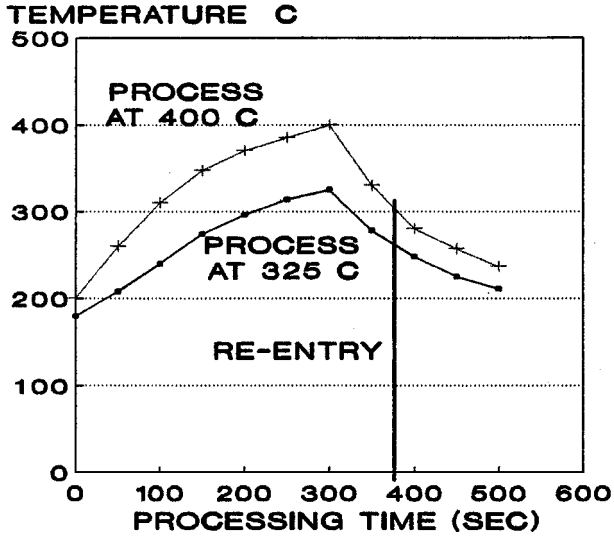


Figure 7 Computed sample temperature vs time profiles at processing temperatures of 325°C and 400°C.

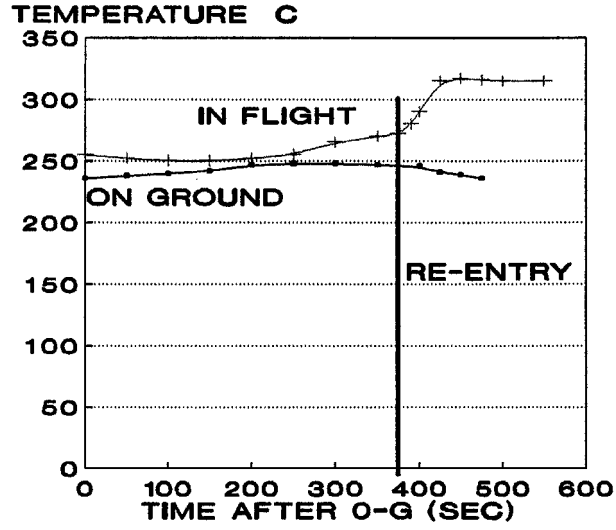


Figure 8 Temperature of an annealing furnace during the ground-based and the rocket flight experiment indicating temperature excursion during the re-entry.

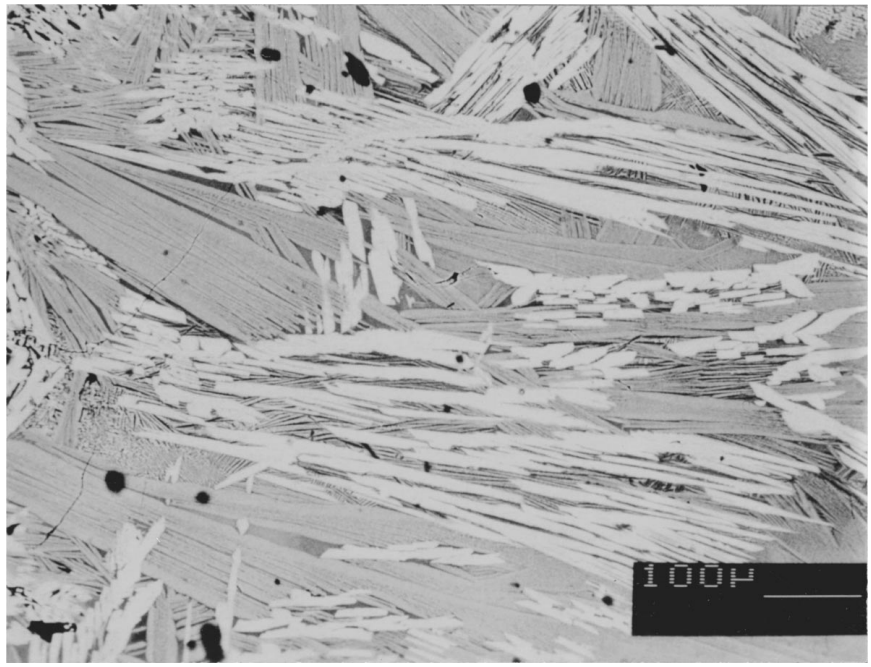


Figure 9 SEM micrograph of a ZBLAN-L4 glass sample processed at 365°C for five minutes on the CSAR-I rocket, which was exposed to high gravity and high temperature during rocket's re-entry.

was not sealed, very hot air would have entered the payload during the rocket's re-entry. Depending on the thermal mass of the furnaces and sample holders, this could have caused the furnace temperature to rise suddenly.

4.5. Comparable independent studies

Encouraged by our results, D.S. Tucker, from Marshall Space Flight Centre of National Aeronautics and Space Administration (NASA), conducted further HMF glass processing experiments using commercial ZBLAN-L4 glass fibres on a sounding rocket in 1996 [8]. A water cooled quench block was used in these experiments to rapidly cool the samples immediately after their processing in microgravity to minimize the effect of high gravity exposure during the rocket's re-entry. These rocket experiments confirmed our earlier findings that microgravity helps in reducing crystallization in HMF glasses during their heat treatment at crystallization temperature. Based on these results, the Space Product Development Division of NASA is developing facilities for HMF glass synthesis and fibre drawing in space with the aim of evaluating the feasibility of commercial production of these low loss fibres in space.

5. Conclusions

The results of these rocket experiments indicate that microgravity helps in reducing crystallization in HMF glasses during their heat treatment to crystallization temperatures, which are very close to the fibre drawing region. This is a very significant finding

which has raised the hope that the use of microgravity during the processing of HMF glass fibres could lead to the predicted low losses in these fibres.

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