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FLIGHT I TECHNICAL REPORT FOR EXPERIMENT 74-37
CONTAINED POLYCRYSTALLINE SOLIDIFICATION IN LOW-G**

by

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ABSTRACT

A 5×10^{-3}M solution of fluorescein in cyclohexanol was directionally solidified in a standard 10 x 10 x 45mm UV silica cuvette, using a bottom thermoelectric chilling device. Progress of the experiment was monitored by time lapse photography. During flight (SPAR I) the camera malfunctioned and only one quarter of the expected data were collected. Comparison of flight and ground specimens indicated that: (1) The dark green layer observed ahead of the solid-liquid interface; which is most likely the solute-enriched zone, appears to be wider in the flight specimen; (2) Parasitic nucleation ahead of the solid-liquid interface in the flight sample led to an irregularly shaped interface, smaller grain size, equiaxed grain morphology and a larger average macroscopic growth rate; (3) The formation of equiaxed grains ahead of the solid-liquid interface in the flight specimen may be attributed to ordered islands within the liquid, which survived remelting because of the low degree of superheating ($\simeq 1.5°C$), did not settle because of reduced gravity and acted as nuclei during cooling.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

I. INTRODUCTION

This experiment is designed to investigate the effect of a low gravity environment on the columnar-to-equiaxed transition in polycrystalline metallic solidification. One portion of the experiment (Part A) will involve production of casting under low gravity conditions; the other portion, Part B, is an attempt to measure the effect of reduced gravity on the width of the solute enriched zone ahead of the solidification interface. Part A will be performed in SPAR IV; Part B was performed on SPAR I and is the subject of this report.

This study was prompted by the unexpected occurrence of fine grained equiaxed microstructures in the Skylab M551 experiment (Ref. 1) and in a drop tower metals melting experiment (Ref. 2). The significant effect of microstructures on the mechanical properties of castings and weldments cannot be overemphasized.

The unique and severe restrictions of the sounding rocket as a research vehicle and the desire to glean as much information as possible from a 300s experiment led us to the choice of low melting point low entropy of fusion, organic materials as models for metallic solidification. These materials have been used successfully in the past and have the advantages of low melting point, ease of handling, and transparency (Ref. 3). Thus the experiment can be performed quickly, with low power requirements and can be observed directly with the aid of a camera. The general plan for Part B was to observe the buildup of a colored solute in transparent solvent ahead of the solidification interface.

II. PROCEDURE

A. BENCH TESTS

The optimum conditions for this experiment were established in the laboratory, using bench top simulations. The system cylohexanol-fluorescein was selected because its melting point, 22°C, made it very convenient from an apparatus design point of view and because it had been used successfully in the past for a similar demonstration (Ref. 3).

The desired experimental conditions consisted of a visually observable solute-enriched layer ahead of a stable, mascroscopically linear, solidification interface, producing directionally solidified crystal. There conditions were obtained using a 5×10^{-3}M solution of fluorescein in cyclohexanol contained in a standard 10 x 10 x 45mm UV silica cuvette and solidified from the bottom by a thermoelectric chill. The solidification rate was approximately 10 μm/s and optimum lighting was found to be reflected illumination by a tungsten filament microscope illuminator. Optimum photographic conditions were obtained by using a 35mm Nikon F camera with a 55mm Micro lens and extenders to increase the magnification to 1.5X. The lens had a filter whose transmission peaked at 540nm; the wavelength of maximum fluorescence of the fluorescein, and Tri-X film was used. These experimental conditions were described in a document submitted to MSFC on 1 July 1975 (Ref. 4). A photograph taken in this manner is shown in Figure 1. A dark band, which in reality is green, is visible ahead of the interface. Microscopic observations led us to conclude that this band is not a Becke line. It could, therefore, be assumed that it is the solute-enriched layer.

The experimental parameters described above were found to be of critical importance for a successful observation of the solute enriched zonc. The solidification rate was chosen to be as slow as practically possible. The distribution of solute in the solute-enriched zone depends on the characteristic diffusion distance, $D_L R$; where D_L is the diffusivity of solute in the liquid and R is the growth rate. The width of this zone, δ, may be taken approximately equal to D_L/R. Assuming $D_L \approx 10^{-5} cm^2/s$ and R=10 μm/s, δ is approximately 100μm, an observable valve. Lower growth rates would lead to a larger δ, but might render observation inadequate in the allowed 300s time allowed.

Visual observation of the solute-enriched layer was found to be very sensitive to the lighting conditions. Optimum conditions would have required excitation by long wavelength UV and observation of the emitted fluorescent radiation. When this was attempted the intensity was too low for photographic recording at the minimum shutter speed of 1/4s. This minimum speed was imposed by the motor drive of the camera. The observation that

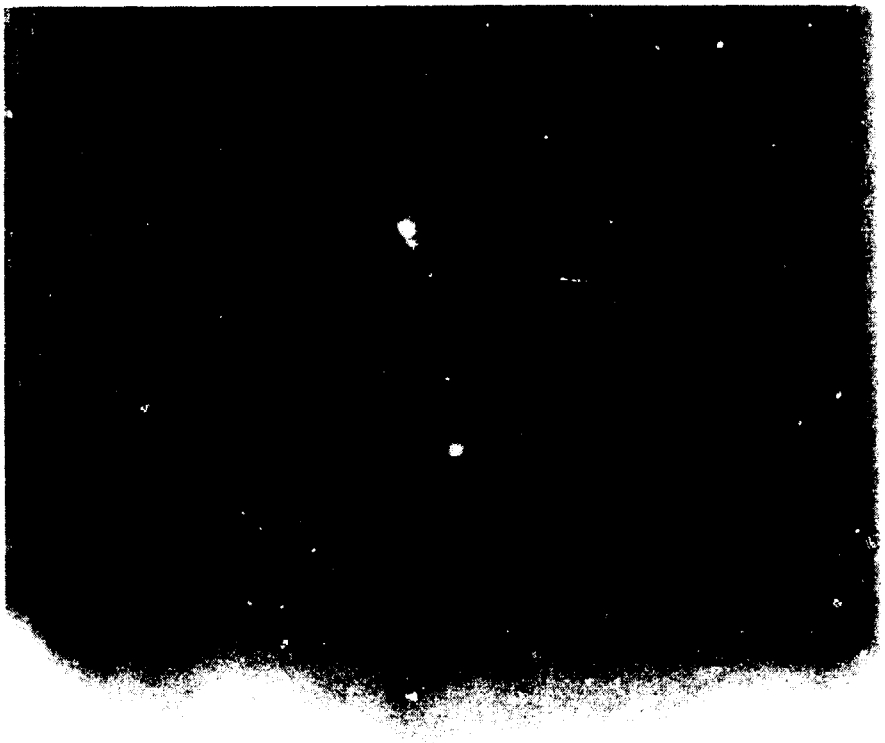

Figure 1 Solidification of cyclohexanol-fluorescein GBS June 1975

tungsten illumination produced more intense fluorescence was puzzling, and fluorescence spectometry we conducted on the solution to clarify this point. We found that in addition to an excitation peak in the long UV region there was another excitation peak centered on 430 μm. This explained our observations.

B. GROUND BASE SIMULATIONS

An apparatus for the performance of this experiment was designed and built by MSFC, as shown in MSFC drawing number 95M31400. The heart of the unit is the cuvette/heat sink assembly which is shown in Figure 2 and consists primarily of an aluminum block, a thermoelectric cooling device, and the silica cuvette. In order to provide one-gravity baseline data, attempts were made to perform the experiment in the laboratory using the flight hardware. Despite our best efforts we were not able to successfully perform a valid ground base simulation before the apparatus was installed in the rocket payload. This was due to many reasons. When the equipment was first delivered it did not function properly and when it was eventually functioning correctly the data did not show the desired effects. The major problems with obtaining data were an improperly positioned light source, poor background, and too rapid solidification. Final adjustments and modifications indluding inversion of the cuvette assembly, installation of a resistor to slow the rate of solidification, and a change to color film were made very shortly before launch. It was found that the rate of solidification was relatively insensitive to external pressure between 10^{-2} and 760 torr.

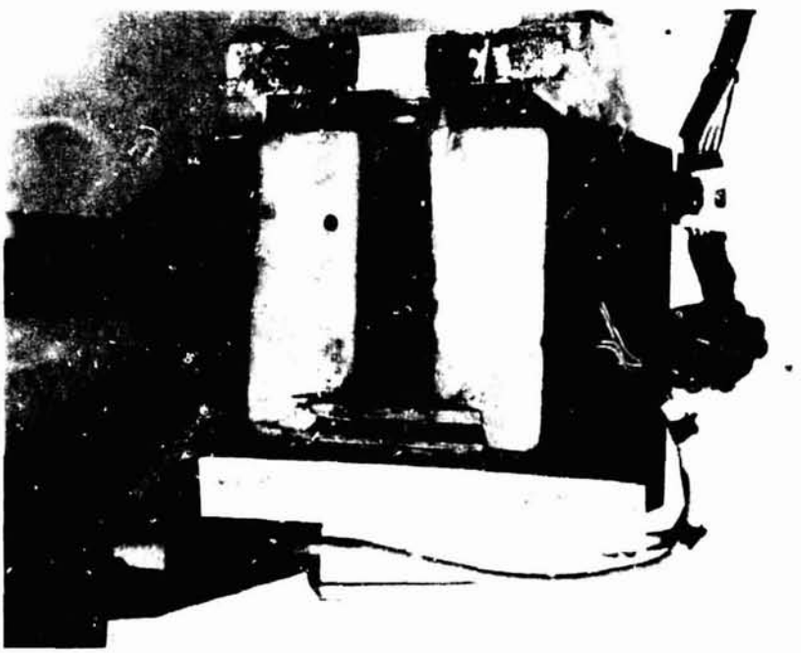

Figure 2 Flight cuvette/heat sink assembly

The modifications to the flight hardware resulted in seemingly valid observations of a solute-enriched zone as shown in Fig. 3, which was taken using the flight cuvette installed in a mockup apparatus in the laboratory. Subsequent ground base simulation (GBS) tests performed in the flight apparatus in the rocket payload on 7 and 9 December 1975 shown in Figs. 4 and 5. All of these films show a deeper green layer ahead of the interface, as confirmed by several observers in addition to the PI. Thus, the experiment was ajudged ready to launch.

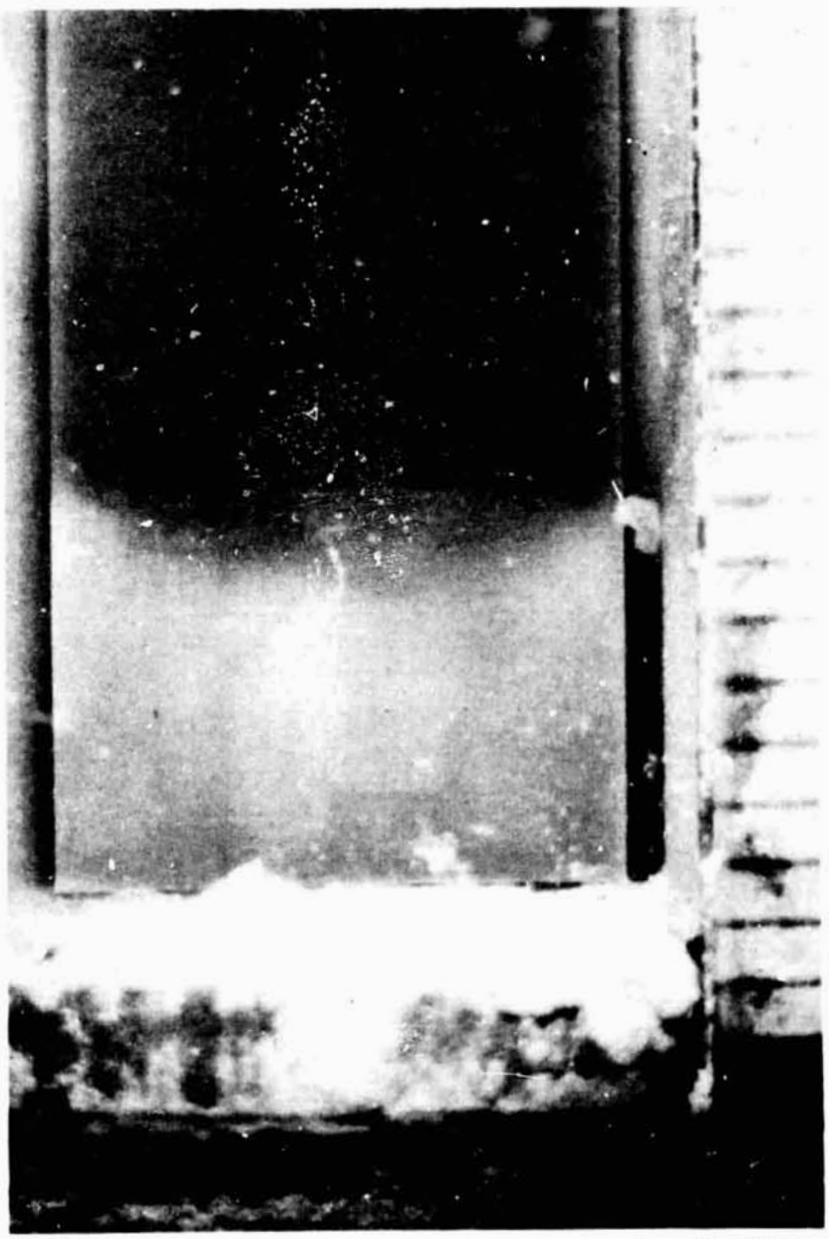

Figure 3 Solidification of cyclohexanol-fluorescein, GBS, November 1975

Figure 4 Solidification of cyclohexanol-fluorescein, horizontal all systems test 7 Dec 1975

Figure 5 Solidification of cyclohexanol-fluorescein, vertical all systems test, 9 Dec 1975

III. RESULTS

The expected flight data were to have consisted of a sequence of 220 pictures showing the progress of solidification and the buildup of the solute-enriched layer. The pictures were to be taken at one second intervals. Unfortunately, during flight, the government furnished (GFE) camera for this experiment malfunctioned. We obtained four test exposures before lift-off followed by 13 exposures which seem to have been taken at the beginning of the low gravity interval and 56 exposures which were probably taken toward the end of the cooling sequence. The first 13 low-g frames show that no cyrstallization had yet occurred; this is consistent with our ground base results in which the first solid is observed at approximately 20 seconds. The 56 subsequent frames show approximately 6mm of solid present; this solid continued to grow as the film sequence progressed. As is visible in Fig. 6, the morphology of the solid cyclohexanol and the shape of the interface in the flight specimen are significantly different from those of the ground base specimens.

The interface is seen to be much more irregular, there are several crystallites which have nucleated in the liquid ahead of the interface, the grain size is smaller, the grain morphology is columnar, and the green solute-enriched zone is less distinct. Upon receipt of the data, we began a series of experiments to determine to what extent these were genuinely gravity-related effects.

The telemetered thermal data portrayed a slightly different thermal history than had been obtained in the ground base simulation, as shown in Fig. 7, where the flight data are plotted as symbols and the GBS data as lines. It was thought that the different thermal history might be related to the low gravity observations, thus the cooling parameters were varied in order to match the flight data. The resulting curves are shown in Fig. 8. Simulations performed with this thermal history were no different than in our previous attempts.

The relevant observations from pertinent tests are shown in the following Table. These tests were a systematic attempt to determine why the flight experiment displayed different growth morphology and nucleation characteristics. No explanation was found.

The Table also shows that we always observe a linear interface in GBS tests, whereas the flight experiment showed an irregular interface. Looking at the sequence of pictures it can be seen that the irregularity of the interface in the flight specimen is caused by entrapment of crystals growing in the liquid ahead of the interface.

Figure 6 Solidification of cyclohexanol-fluorescein, flight test, 11 Dec 1975

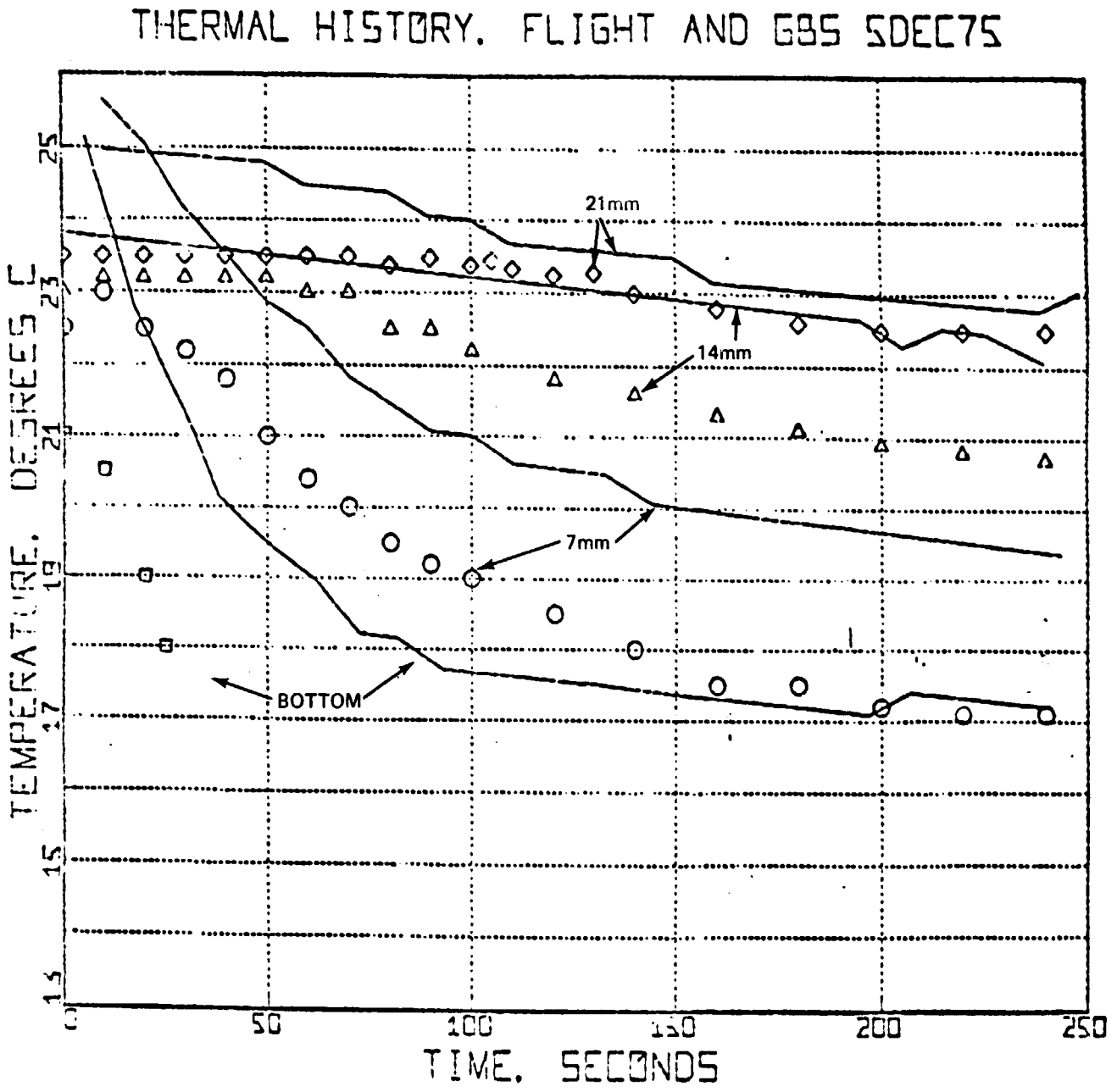

Figure 7 Thermal histories of a typical pre-flight GBS (solid lines) and the actual flight test (symbols)

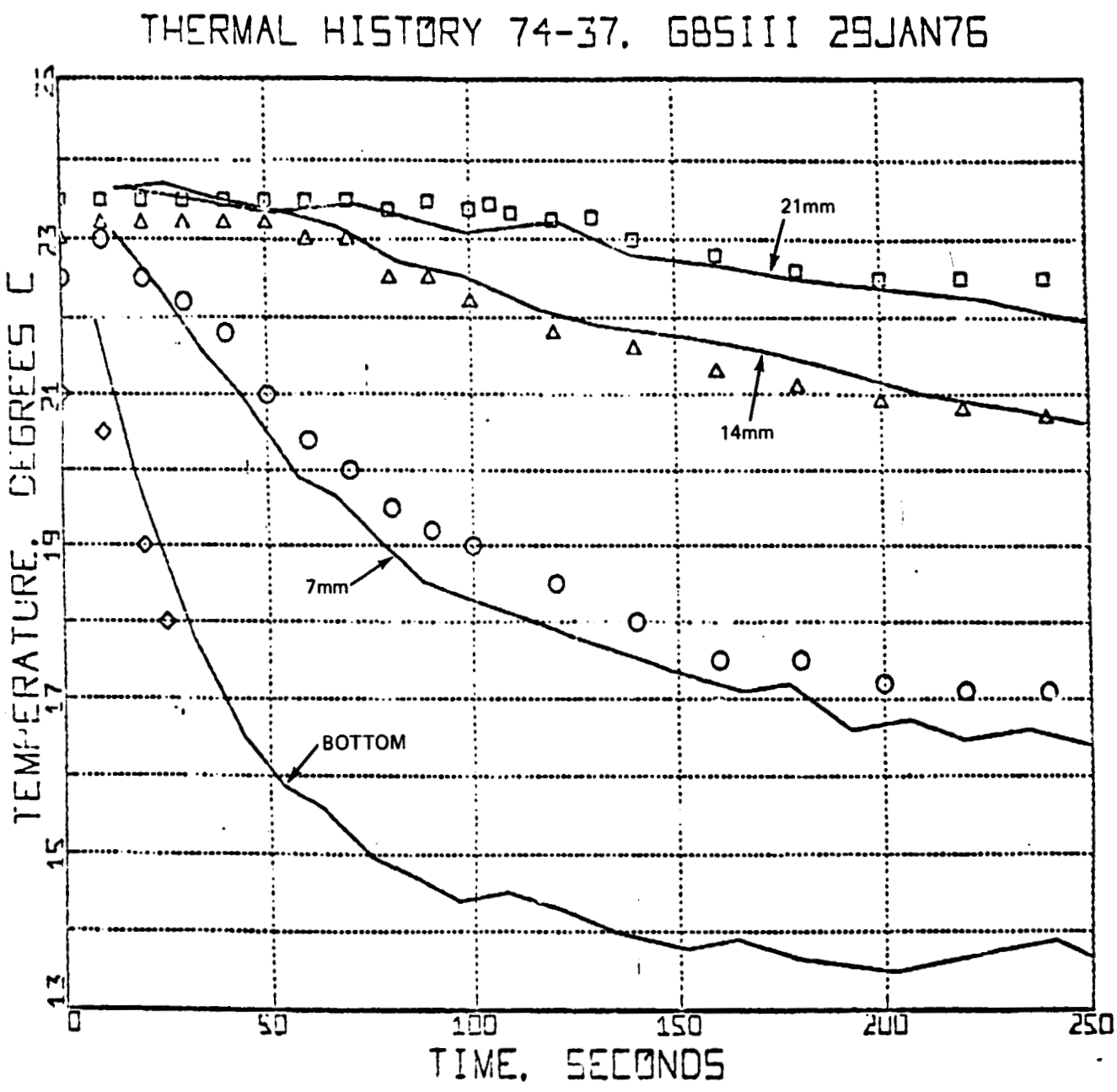

Figure 8 Thermal histories of a typical post-flight GBS (solid lines) and the actual flight test (symbols)

TEST OBSERVATIONS

Test	Interface	Grain Size *(mm)	Grain Morphology	Nucleation+ Events $\underline{n}$ $d_{max}(\mu m)$	Green± Band (μm)	Bubbles
GBS 5 Dec. 75	Linear	-	Columnar	- -	-	None
Horiz 7 Dec. 75	Linear	2.5	Columnar	0 -	120-180	≃4 mm Dia.
Vert 9 Dec. 75	Linear	2	Columnar	3 450	70-140	None
Flight 11 Dec. 75	Irregular	1.2	Equiaxed	15 900	300-600	≃4 mm Dia.
GBS I 18 Dec. 75	Linear	3.5	Columnar	0 -	60-120	None
GBS II 18 Dec. 75	Linear	3.5	Columnar	0 -	60-120	None
GBS I 28 Jan. 76	Linear	2.5	Columnar	1 400	60-120	None
GBS II 28 Jan. 76	Linear	2	Columnar	0 -	60	None
GBS II 29 Jan. 76	Linear	2	Columnar	0 -	60-100	Simulated
GBS IV 29 Jan. 76	Linear	2.5	Columnar	1 600	75-150	Simulated

* In the case of Columnar Microstructures the smaller dimension (width) is reported

\+ Occuring in the liquid ahead of the interface during the 220s interval. The flight data was taken during a 60s interval. n is the total number of nucleii observed, d is the distance ahead of the interface.

± Visual observations from films, a dash indicates that no film record was made.

A columnar grain morphology was observed in all except the flight test. Likewise, nucleation ahead of the interface was rarely observed except in the flight test. Repeated nucleation ahead of the interface naturally leads to an equiaxed microstructure. The maximum distance from the interface to a nucleus in the liquid is also reported in the Table. It is seen that the flight test showed nucleation at a much greater distance into the liquid than any of the GBS tests. It should be noted that the 15 nucleation events in the flight sample occurred during 56 seconds of observation whereas all of the other tests were observed for a full 220s.

Column 3 of the Table shows that the grain size obtained in the low-gravity test was significantly smaller than that obtained in the GBS tests.

In several tests, including the flight test, a 4mm diameter bubble was present at the bottom of the cuvette. It was thought that the bubble might have sufficiently perturbed the heat and fluid flow to cause spurious results. In order to evaluate this possibility a 4mm diameter thin-walled glass sphere was installed in the bottom of the cuvette for several GBS tests. The presence of this simulated bubble had no significant effect on solidification, as shown in the last two rows of the Table. Further, the original bubble was present in the horizontal GBS and had no significant effect on solidification. Thus, the bubble did not affect the flight test results.

The average growth rate was deduced from measurements of the interface position as a function of time. Data from two GBS and the flight test are shown in Fig. 9. Since the origin of time of the flight data cannot be located it has been placed arbitrarily at t=80s. The slopes of the curves give average growth rates. In general, the GBS tests gave average growth rates of 20 to 30μm/s whereas the flight test showed a growth rate of 60μm/s. This is simply explained as being due to nucleation ahead of the interface. Those nucleii which are situated ahead of the interface grow in all directions. If the dendrite tip velocity remains the same as that in columnar growth, then the average macroscopic interface velocity would be twice as high. Thus, this observation is taken as indicating that the dendrite tip velocity is pratically constant in all of these tests.

Column 6 of the Table lists visual observations of the width of the darker green solute-enriched layer which is seen ahead of the interface. These values were obtained by looking at the original films on a lightbox and visually estimating the width of the deeper green layer, using a 7X magnifier and reticule. The reticule was calibrated in units of 0.1mm and the film magnification was typically 1.6X, thus the smallest division represented approximately 60 μm. In general, the green band was observed to be about 60 to 120μm wide,

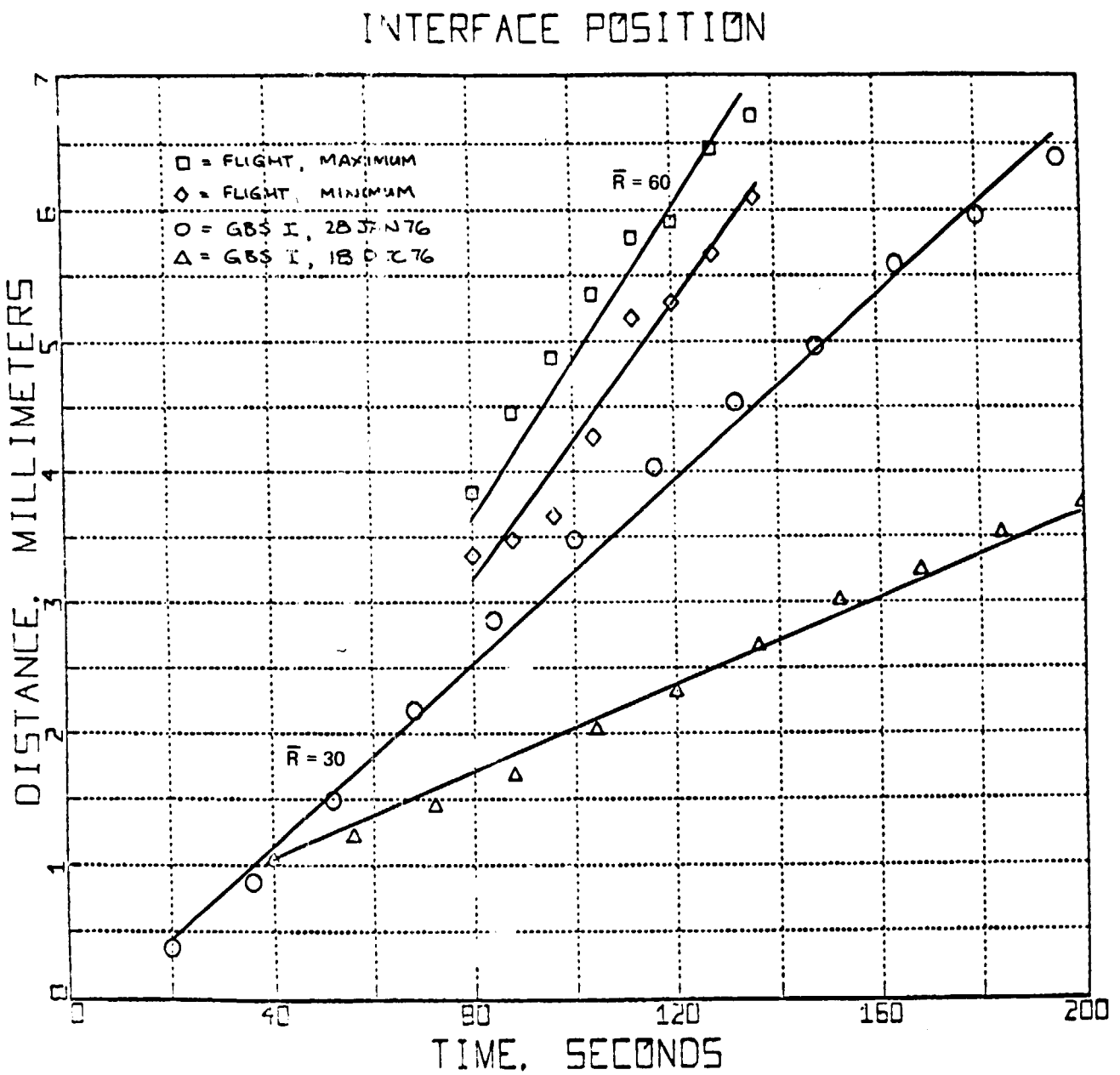

Figure 9 Interface position as a function of time for two GBS tests and the flight test

but in the flight test it appeared to be larger by a factor of 5. We attempted to quantify this subjective observation.

Several of the films were analyzed using a Joyce-Lobel scanning microdensitometer. The instrument was set up to traverse from the crystal into the liquid. The spot size was approximately 15 μm on the film to be measured; this corresponds to about 10 μm linear distance on the actual specimen. Traverses were made using a green filter, thus only the green emulsion of the film was scanned, or without a filter in which case all three emulsion layers contributed to the observed density. Figure 10 shows a trace obtained from frame 674-1 of the vertical test in which a pronounced green layer was visible to the eye. No evidence of the solute-enriched zone is present in the trace. Figure 11 shows a simular trace which was made through a grain boundary groove in which a distinct, thick green band was visible. Again, no evidence for the green band was found. In no case were we able to make an objective, repeatable measure of the width of the green band. The human eye is unusually sensitive to color and can detect in the region of 10^7 shades of color; a microdensitometer does not approach this sensitivity. This is a possible explanation for this problem. However, it is well known that a human observer is highly prone to suggestion and under difficult observational conditions the eye often detects nonexistent objects. Numerous attempts were made to confirm these observations by impartial observers; in all cases the observers claim to have seen the green layer. If the darker green layer is, in fact, the solute-enriched zone ahead of the solid-liquid interface, it can be concluded that it is wider in the flight specimen.

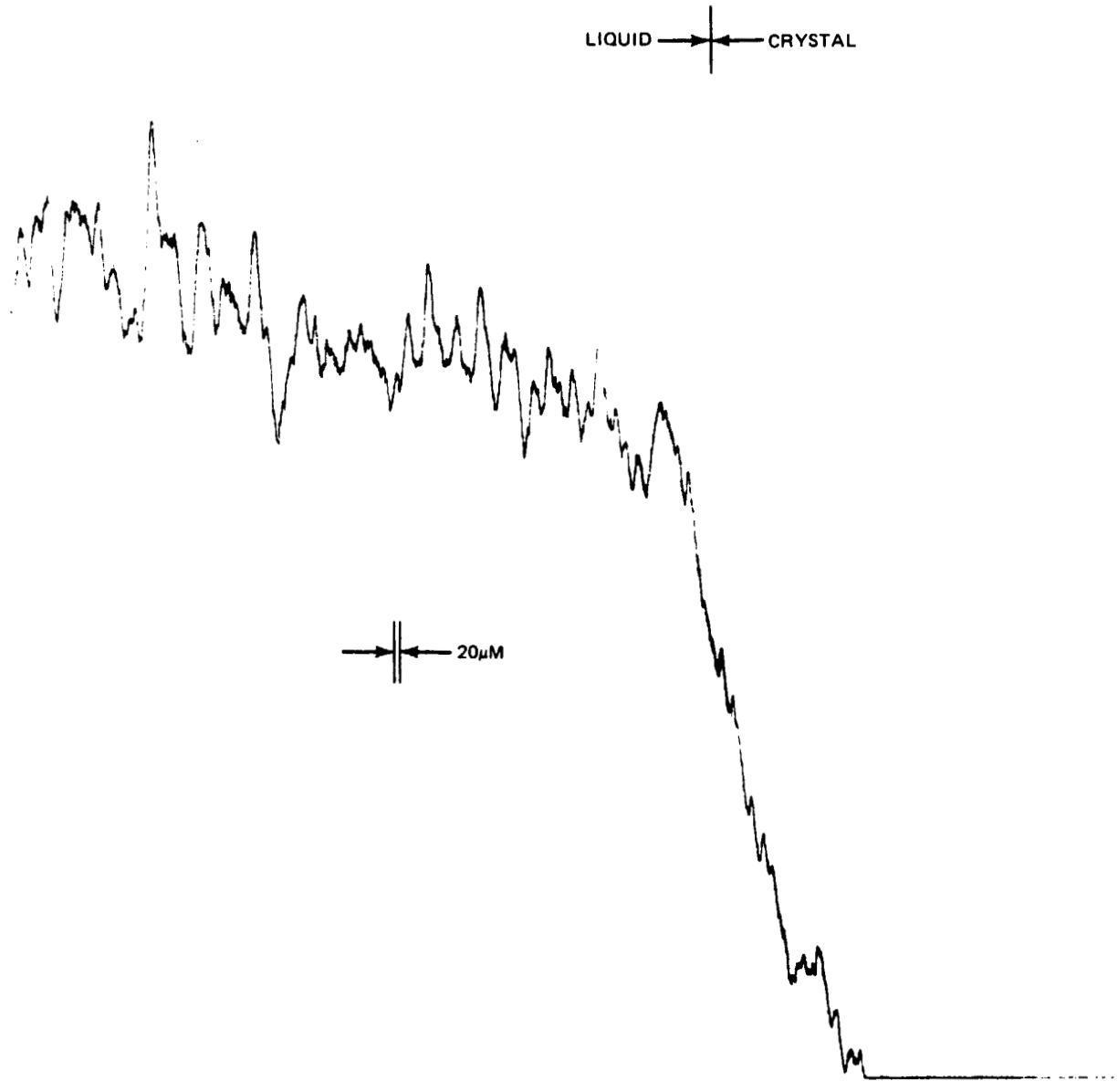

Figure 10 Microdensitometer trace from frame 674-1, vertical test, flat position of interface. Optical density (ordinate) is plotted against distance (abscissa)

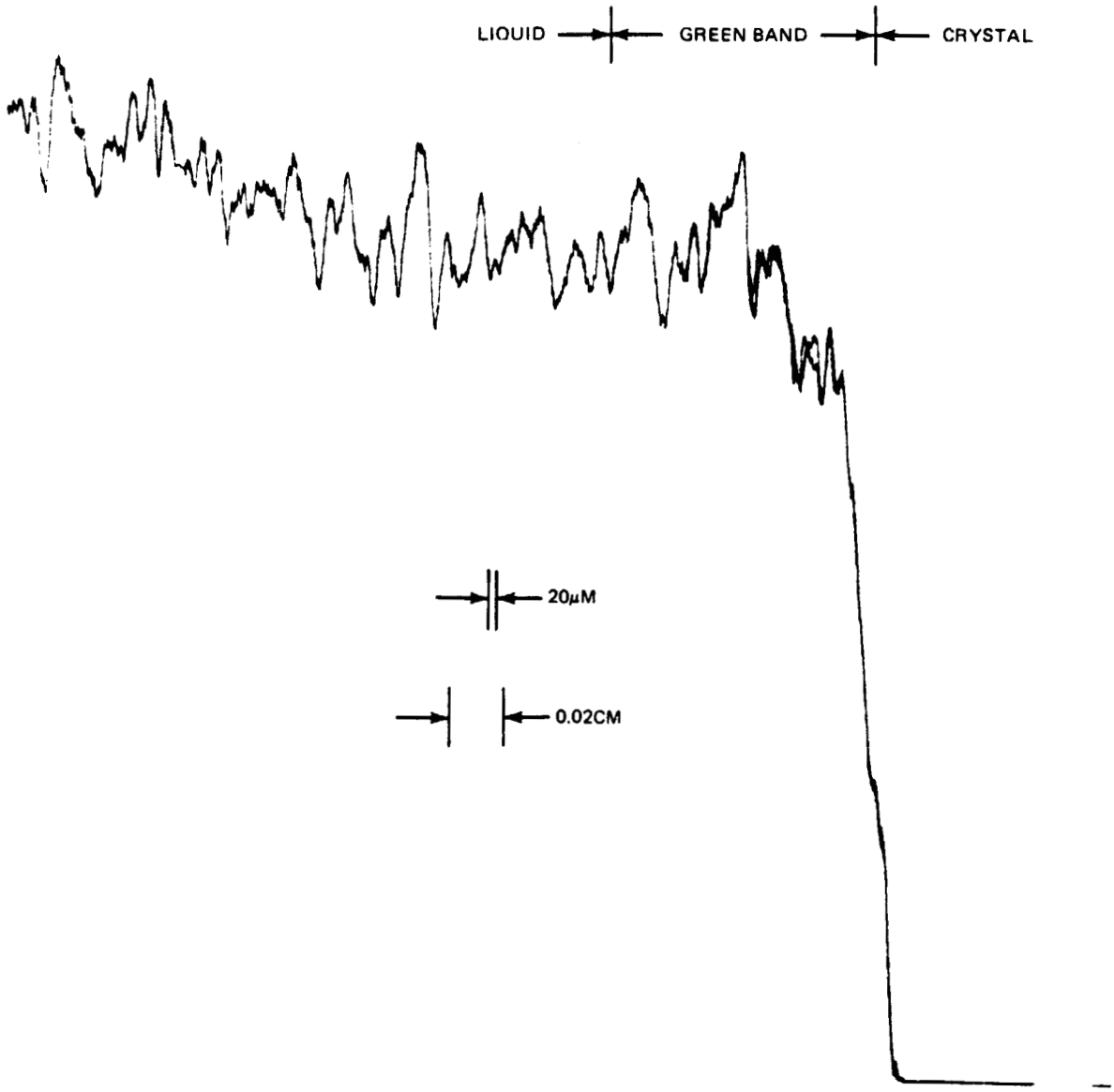

Figure 11 Microdensitometer trace from frame 674-1, vertical test grain boundary groove. Optical density (ordinate) is plotted against distance (abscissa)

IV. DISCUSSION

The darker green layer ahead of the solid-liquid interface is presumably the solute-rich zone, which appears to become wider in the flight specimen. Because of inadequate sensitivity of a Joyce-Lobel scanning microdensitometer, the detection of this zone and accurate measurement of its thickness was not possible.

Parasitic nucleation, or nucleation ahead of the interface, was the key feature of this experiment. This led to an irregular interface, a small grain size, an equiaxed grain morphology, and a large average macroscopic growth rate. This is in contrast to terrestrial experiments in which nucleation ahead of the interface was rarely observed and in which we observed a linear interface, larger grain size, columnar morphology, and a smaller growth rate. The terrestrial experiments were performed with three different orientations of the gravitational vector.

It is believed that all of the possible experimental reasons that this might be a spurious observation were eliminated. The most obvious possibility was a different thermal history between GBS and flight; this was quickly eliminated.* The next possibility considered was an impurity effect, but the same cuvette, unopened, was used for the horizontal, vertical, flight and 28th of January tests so that contamination can also be ruled out. The perturbation introduced by the bubble was shown to be minimal by comparison to the 7th of December flight and 29th of January tests. Bench tests to determine whether launch-induced fluid motion could lead to parasitic nucleation were negative; it was not possible to cause nucleation ahead of the interface even by violently shaking the cuvette assembly for one minute before the bench test. Another possibility is that the solution was not adequately superheated before launch; this could result in the presence of numerous small ordered islands which would act as nuclei. The rocket was kept in thermostatically controlled environment of 23.3 to 23.6°C overnight before launch, which is approsimately 1.5°C above the liquidus temperature. Some ordered islands might have survived remelting, presumably because of the low superheating, might not have settled, and then acted as nuclei during cooling. Thus the formation of parasitic equiaxed grains, observed ahead of the solid-liquid interface in the flight specimen, could be explained.

*Latest telemetry data, provided by MSFC, show significantly different thermal histories (See Appendix).

V. CONCLUSIONS

1. The darker green layer observed ahead of the solid-liquid interface is most likely the solute-enriched zone and appears to become wider in the flight specimen.

2. The irregular shape of the interface in the flight specimen, the smaller grain size, the equiaxed grain morphology, and the larger average macroscopic growth rate are attributed to parasitic nucleation ahead of the solid-liquid interface.

3. The formation of parasitic equiaxed grains ahead of the solid-liquid interface in the flight specimen may be attributed to ordered islands within the liquid, which survived re-melting because of the low degree of superheating ($\sim$1.5° C), and did not settle because of reduced gravity and acted as nuclei during cooling.

VI. REFERENCES

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APPENDIX

On 5 March 1976 we received revised telemetry data from MSFC. The new data contains revised values for the bottom themistor readings; these are plotted in Fig. A-1 along with the thermal data from GBS II of 28 January 76. Note that the new telemetry data portray a flight thermal history that is radically different from any of the previous GBS tests. It is thought that this different thermal history may be, at least in part, responsible for the anomalous flight observations.

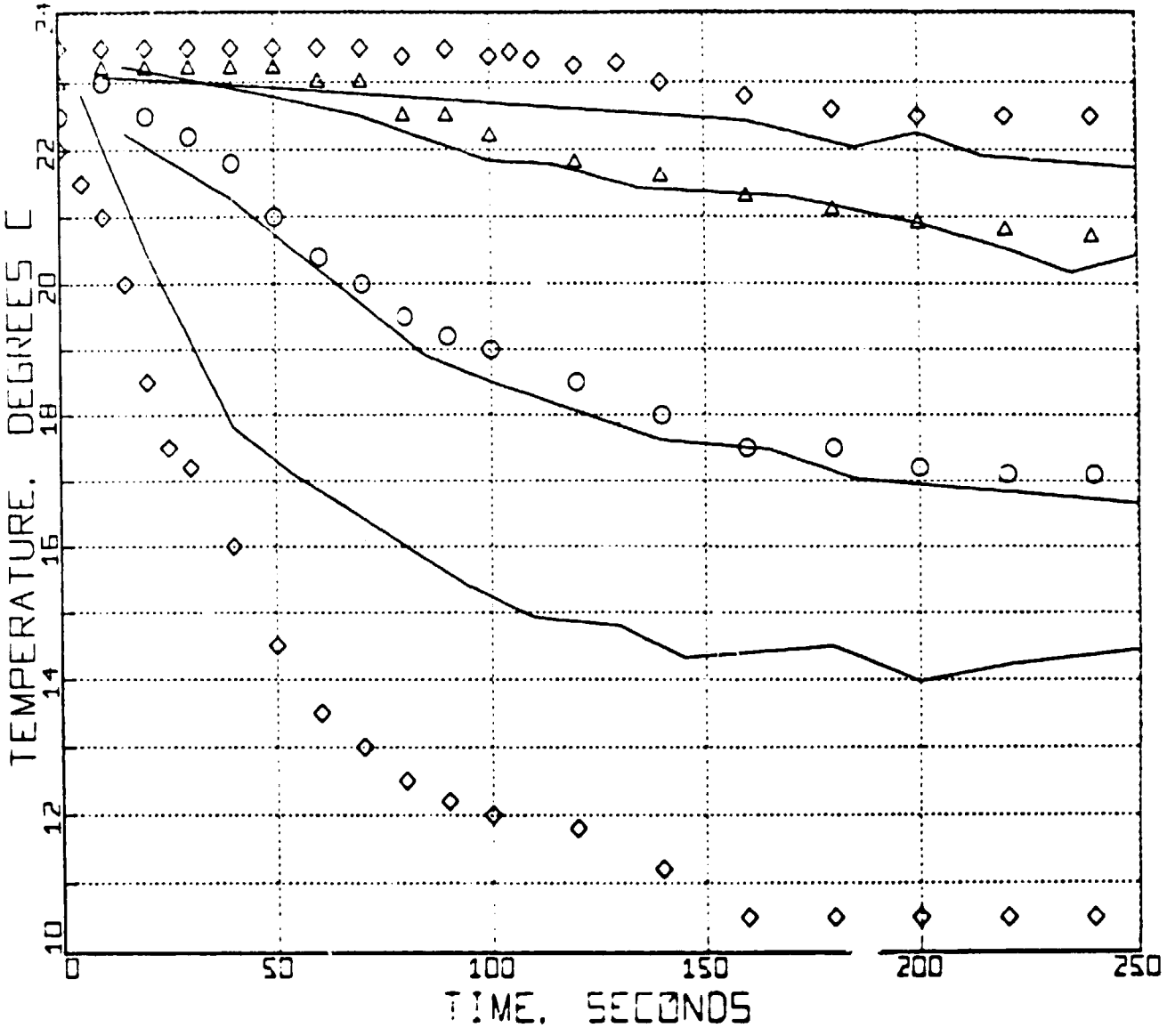

Figure A-1 Revised Thermal History of the Actual Flight Test (Symbols)