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CHARACTERIZATION OF THE GENERAL PURPOSE RESEARCH FURNACE FOR LOW-G DIRECTIONAL SOLIDIFICATION EXPERIMENTS

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ABSTRACT

Preliminary tests have shown that it is possible to control the temperature settings in NASA's General Purpose Research Furnace in such a manner as to obtain a constant rate of movement of a high temperature isotherm down the length of the furnace. These tests also showed that a temperature gradient on the order of 40° C/cm could be obtained in the furnace while moving the particular isotherm of interest, i.e., 900° C. This provides the possibility of performing directional solidification experiments in the furnace on a MEA flight in the low gravity environment provided by the Shuttle. A functional dependency of growth rate on perturbations during the growth has been derived and shows the importance of avoiding non-steady growth rates and changing temperature gradients.

1. INTRODUCTION

The low gravity environment afforded by the Space Shuttle offers a unique opportunity to study the effects of convection upon the compositional homogeneity in electronic crystals grown from the melt. By conducting

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experiments on Earth in a 1-g environment and comparing these to identical experiments carried out in the low-g environment of space where the effects of gravity driven convection will be different, these effects can perhaps be separated from the other convective driving forces which may be present during the crystal growth process. However, great care must be taken to minimize the influence of extraneous effects which may also affect the crystalline quality and the compositional homogeneity of the crystal.

The General Purpose Research Furnace (GPRF) is a three zone furnace developed by NASA for flight on the Space Shuttle to conduct experiments in materials science in the Materials Experiment Apparatus (MEA) test series. One of the experiments to be carried out during the flight of STS-15 in 1984 will be the directional solidification of a crystal of lead-tin-telluride (LTT). Directional solidification can be achieved by either moving the furnace and the sample relative to each other or by ramping a temperature gradient through the furnace at a constant rate. Since the GPRF was designed as a stationary furnace with no moving parts, it is necessary to characterize the temperature profiles of the furnace and to develop a procedure whereby the temperature controls of the three zones can be ramped down such that a solidification front passes down the specimen at a constant growth rate with a sufficiently high temperature gradient to avoid constitutinal supercooling. This paper will present a brief review of past solidification experiments in space, a description of the GPRF, the goals of the solidification experiment, and the ground-based studies currently being carried out to optimize the experiment to be performed in the MEA-A2.

2. BACKGROUND

2.1 Previous Experiments

Previous experiments in directional solidification have been carried out and are described very well in Materials Processing in Space(1) by Naumann and Herring. Perhaps the most informative set of experiments in this area have been those of Gatos and Witt in the Skylab and Apollo-Soyuz (ASTP) flights.(2,3) In the Skylab experiments on InSb, they found no evidence of the growth striations which are always present in Earth grown crystals. In addition, they showed that the distribution of a highly dilute solute in the space grown crystals could be explained by a diffusion controlled growth process as described by the theory of Smith, Tiller and Rutter (STR).(4) In the ASTP experiment on germanium, they added an interface demarcation technique which permitted a detailed microscopic investigation of the growth. They found an asymmetric interface shape which they could only attribute to an asymmetric temperature distribution in the furnace. This temperature distribution would not support a planar interface during the growth. However, on a macroscopic scale, the compositional variations in the germanium crystals doped with gallium could still be described by the STR theory if the solute distribution were perturbed somewhat by the interface curvature. As was the case for the InSb, they found no evidence of the growth striations which were found in the Earth grown samples. In a different Skylab experiment (M563),(5) Wilcox attempted the solidification of the compound semiconductor $In_{(1-x)}Ga_xSb$. Resultant crystals all exhibited properties which indicated unstable growth, probably due to uncontrolled growth rates and inadequate temperature gradients. Gatos and Witt showed that the growth rate during the ASTP experiments were constantly changing when the hot zone of the furnace was ramped down at a constant rate. The same procedure was used in the Skylab experiments; therefore, the growth rates were most likely continuously changing in these tests also. Walter (Exp # M560)$^{(1)}$ grew InSb in a containerless configuration and found that the crystals grew with a faceted surface. In contrast to the Gatos and Witt experiments, doping striations were found in these crystals. No generally accepted explanation has been given for these different results.

2.2 Thermosolutal Convection

Free convection is mass transport induced in a fluid when density differences exist in the presence of an acceleration field (e.g., gravity). In a binary or multicomponent semiconductor materials system, the density of the liquid phase is a function of temperature and composition. Motion arising from temperature and compositional variations (thermosolutal convection) will always be present in crystal growth from a melt in a 1-g environment.$^{(6)}$ The extent to which it will play a role in the low gravity environment has yet to be established. Theoretical calculations using numerical techniques indicate that it will play a significant role in space processing; however, the experiments of Gatos and Witt seem to indicate that convection is not a controlling mechanism of the segregation in their samples. However, results from other space experiments seem to imply that convection is taking place.$^{(1)}$ Recent calculations by Coriell and Sekerka$^{(7)}$ (CS) and Carlson et al.$^{(8)}$ show that a curved interface shape will affect the solute distribution as suggested by Gatos and Witt.

3. EXPERIMENT

3.1 MEA and the GPRF

The Materials Experiment Apparatus (MEA) is shown in figure 1. This self-contained structure serves as a carrier for up to four experiment packages and provides power, sequencing, control, data acquisition and heat rejection. Its purpose is to allow relatively simple experiments to be carried out during Shuttle flights on a space available basis. One of the experimental packages scheduled for the STS-15 flight will contain a GPRF with a capability of achieving temperatures in excess of 1000° C. A schematic of a furnace module contained in this facility is shown in figure 2. There are three heaters in the furnace and a water-cooled heat extractor which contacts the end of the cartridge. The software is programmed to bring the separate heaters to any desired temperature. Careful selection of temperature profiles will allow the movement of a particular isotherm down the length of the furnace at a fixed rate. In the Skylab and ASTP furnace, which had a hot zone, a heat leveller region and a cold zone, the hot zone of the furnace was ramped down at a constant rate. The data of Gatos and Witt showed that this resulted in a continuously varying growth rate that increased monotonically throughout the controlled growth time frame. The effects of a varying growth rate and temperature gradient on crystal composition will be discussed in a later section of this paper.

3.2 Description of the Experiment.

The purpose of this experiment is to determine the effects of gravity driven convection upon the growth by directional solidification of a compound semiconductor. This is to be done by comparing the compositional distribution of a sample which has been directionally solidified in the low-g environment of space with that of a sample similarly grown in the 1-g environment of Earth. The material chosen for this crystal growth was lead-tin-telluride (LTT). LTT is a compound semiconductor that can be considered a binary mixture of lead-telluride molecules and tin-telluride molecules. The pseudobinary phase diagram shows that the two materials are fully missicible. A mixture of 20% tin-telluride and 80% lead-telluride was chosen for this experiment. This choice of material, which solidifies in a temperature range around 900° C, dictates the temperature at which the gradients in the GPRF should be determined. The thermophysical properties of the material which are important for the theoretical calculations have recently been measured.(6) LTT is subject to thermosolutal convection when grown in the Earth's gravity field and cannot be grown without convection. If no convection were present the percentage of tin along the growth axis of the crystal should be approximately that shown by the diffusion controlled growth curve (Fig. 3). If the melt is fully mixed during growth, the compositional profile should look like the mixed curve which is the normal freezing curve in the theory first proposed by Pfann.(9) If some convection is present, the results would lie somewhere between these two cases. The compositional profile could also be affected by other factors such as constitutional supercooling, interface curvature, asymmetric temperature gradients, varying growth rates, and perhaps even Marangoni convection. To minimize the effects of these factors, it is essential to optimize the choices of parameters such as temperatue gradient, growth rate, and thermal coupling between the furnace and the sample.

3.3 Ground Based Tests.

The suitability of the GPRF as a directional solidification furnace had to be evaluated. To do this, the first question to be answered was whether the furnace is capable of producing a sufficiently high temperature gradient to avoid constitutional supercooling in LTT. It is then important to know if the three zones of the furnace can be controlled to maintain a stable temperature gradient at the solidification interface while moving the solidification temperature isotherm down the length of the furnace at a constant rate. It is also important to know the radial thermal gradients for a sample in a flight-type configuration.

3.3.1 Boron Nitride Sample

Since the fabrication of a LTT sample is quite time consumming and the sample can only be solidified once without the risk of ampoule breakage (which could result in corrosion of the interior of the furnace), it was decided to make most of the characterization tests with relatively inert materials which have similar thermal characteristics to the LTT. The first series of tests were caried out on a boron-nitride (BN) sample which contained six thermocouples (Fig. 4). The sample was a solid rod of BN containing six thermocouples (TC's) to measure the axial temperatures in a hole drilled down the center. The controls for the hot zone and the middle zone of the furnace were set at 1000° C and allowed to stabilize. The temperatures of all of the TC's were then recorded and the temperature of the middle zone was ramped down in 5° C increments and allowed to stabilize before the next set of TC data was recorded. The axial thermal gradients in the furnace were obtained from these data and were found to be near 20° C/cm in the temperature range near 900° C (Fig. 5). Using temperatures measured by the control thermocouples for the three zones and a thermal conductivity of 0.3 W/cm-C in the direction parallel to pressing and 0.2 W/cm-C in the perpendicular direction, the temperature profiles of the furnace for the axial center position and along the outside edge of the sample were calculated using the thermal model developed by Carlson. This calculation modeled the furnace in two different ways. The first was to have three discrete zones of constant furnace wall temperature and the second was to use the setpoint temperatures of the three zones and calculate a temperature profile along the wall of the furnace. Using these profiles, the calculated temperatures were compared to those measured by the

TC's. These calculations indicated that the radial gradients were of an acceptable level ($< 3^o$ C/cm) to go to the next set of evaluation tests.

3.3.2 Fused-Silica Sample.

The next sample to be tested was a fused silica (FS) with six TC's placed in the positions shown in figure 6. This sample was used to measure both radial and axial temperature profiles. Fused silica has a thermal conductivity of about 2.1 X 10^{-2} W/cm-C which is more comparable to LTT (3.2 X 10^{-2} W/cm-C for the solid and 6.5 X 10^{-2} W/cm-C for the liquid). The thermal gradients for the FS were about 40^o C/cm for the axial gradients and about 4^o C/cm for the radial gradients in the cooler zone of the furnace. Figure 7 shows typical temperature measurements for the TC's in this sample. In this case the control TC's for all three zones of the furnace were set for 1000^o C and allowed to stabilize. The temperature of the cold zone was then stepped down in 5^o C increments until it no longer had an effect on the temperature distribution, i.e., the temperatures in the sample were controlled only by the two upper zones with no power input to the cold zone. The temperature of the middle zone was then stepped down in 5^o C increments until it similarly had no effect. Finally, the temperature of the hot zone was ramped down until TC #4 was much less than 900^o C. From these data the position of the 900^o C point in the sample was calculated from a simple curve fit between the data points. From this a change in the x position of the 900^o C temperature for each change in furnace setting was calculated and plotted as a function of the set point temperature of the controlling heater zone. For these temperature gradients the growth rate needed to avoid constituional supercooling in LTT is about 0.36 cm/hr. A time table was then deduced from this plot to program the software to control the set points for the various furnace zones such that a constant rate of movement would be obtained for the 900^o C temperature.

Figure 8 shows a portion of the curve for the 900° C position as a function of time taken from the data obtained when the time program was run. As is seen in that figure, the rate in this part of the furnace is very nearly constant as was the case over the entire range covered by the thermocouples. This data is preliminary and more verification tests are needed. The next set of runs on the fused silica sample will be with the TC's positioned in the upper end of the sample to determine the thermal profiles in the upper end of the furnace. The next step will be to calculate the thermal profiles using the Carlson program and compare the results to confirm the validity of the theoretical calculations.

3.3.3 Lead-Tin Telluride Samples.

Finally, a series of samples of LTT such as that shown in figure 9 will be tested as final verification. Preliminary tests on a sample such as this showed that the furnace is capable of producing the required temperature gradients in LTT.

4. FURNACE PERTURBATION ANALYSIS

It was shown by Gatos and Witt that the growth rate and the thermal gradients in the Skylab and ASTP furnace were constantly changing. Those kinds of complications are being minimized in these tests. However, to a certain extent they are unavoidable, and it is important to examine the influence they might have on the experiment. Successful experimental conditions require a constant growth rate of the crystal. Growth occurs when the liquidus temperature, T_1, advances from a given axial position, Z_1, to an adjacent position, $Z_1 + dz$, down the ampoule in a finite time, dt. In order for this to occur the temperature at $Z_1 + dz$ must drop by an amount, Gdz in time dt, where G is the temperature gradient at the interface. That is:

$$\frac{dT}{dt} = -G \frac{dz}{dt} \tag{1}$$

The growth rate, R, defined as dz/dt, is then equal to r/G, where r = dT/dt, is the rate at which the temperature of a given position is changed. Hence, the growth rate is controlled by both the temperature gradient and the rate at which the furnace is cooled.

Changes in either the temperature gradient or the cooling rates will produce undesirable changes in the growth rate. Furthermore a change in cooling rates between two points will produce a time dependent temperature gradient change between those points.

The change in furnace conditions that will be considered are as follows:

ΔG_o = error in temperature gradient due to possible difference in the thermal contact between the ampoule and the heat sink from run to run. (i.e. ΔG_o represents a difference in the anticipated gradient from that actually achieved in a run), and

Δr_i = a step change in the temperature rate of change in the material at the position of the i^{th} thermocouple.

Variation in the temperature rate of change may arise due to changes in thermal contact between the sample, the ampoule and/or the cartridge as well as from an uncertainty in the effect that changing the furnace temperature will have on the sample temperature. The effects that ΔG_o and Δr_i will have on the gradient and temperature rate of change between the i^{th} and i^{th} + 1 position are:

$$dG = \Delta G_o - \frac{\Delta r_i \, \Delta t}{Z} \tag{2}$$

and

$$\Delta r = \left(1 - \frac{z}{Z}\right) \Delta r_i \tag{3}$$

where Δt = the time after the rate change, Δr_i occurred

z = distance from the i^{th} position

Z = distance between the i^{th} and $i^{th} + 1$ positions

Using equations (2) and (3), the effect of the changes in G and r on growth rate can be calculated by taking the total differential of R. This can be shown to be:

$$dR = -\frac{1}{G} \left[\left(1 - \frac{z}{Z} - R \frac{\Delta t}{Z}\right) \Delta r_i + R \, \Delta \, G_o \right] \tag{4}$$

Likewise the stability of the constitutional supercooling condition (CSC) is calculated to be:

$$d\left(\frac{G}{R}\right) = \frac{2}{R} \, dG_o + \left[\frac{1}{R^2}\left(1 - \frac{z}{Z}\right) - \frac{2}{R} \frac{\Delta t}{Z}\right] dr_i \tag{5}$$

Therefore, it can be seen that both the growth rate and the interfacial stability as determined by the CSC are directly affected by perturbations to the temperature gradient and the rate of cooling in the furnace. This points out the importance of knowing the values for G and r during the growth and the importance of minimizing any perturbations that may occur during the flight experiment.

5. CONCLUDING REMARKS

Preliminary tests have shown that it is possible to control the temperature settings in the GPRF in such a manner as to obtain a constant rate of movement of a high temperature isotherm down the length of the furnace. These tests also showed that a temperature gradient on the order of 40° C/cm could be obtained in the furnace while moving the particular isotherm of interest, i.e., 900° C. This provides the possibility of performing directional solidification experiments in the furnace on a MEA flight in the low gravity environment provided by the Shuttle. Further tests will be required to determine the temperature profiles and the control parameters required for the lead-tin-telluride material which has been chosen as the material to be investigated. Finally, a functional dependency of the growth rate on perturbations during the growth has been derived and shows the importance of avoiding non-steady growth rates and changing temperature gradients.

6. REFERENCES

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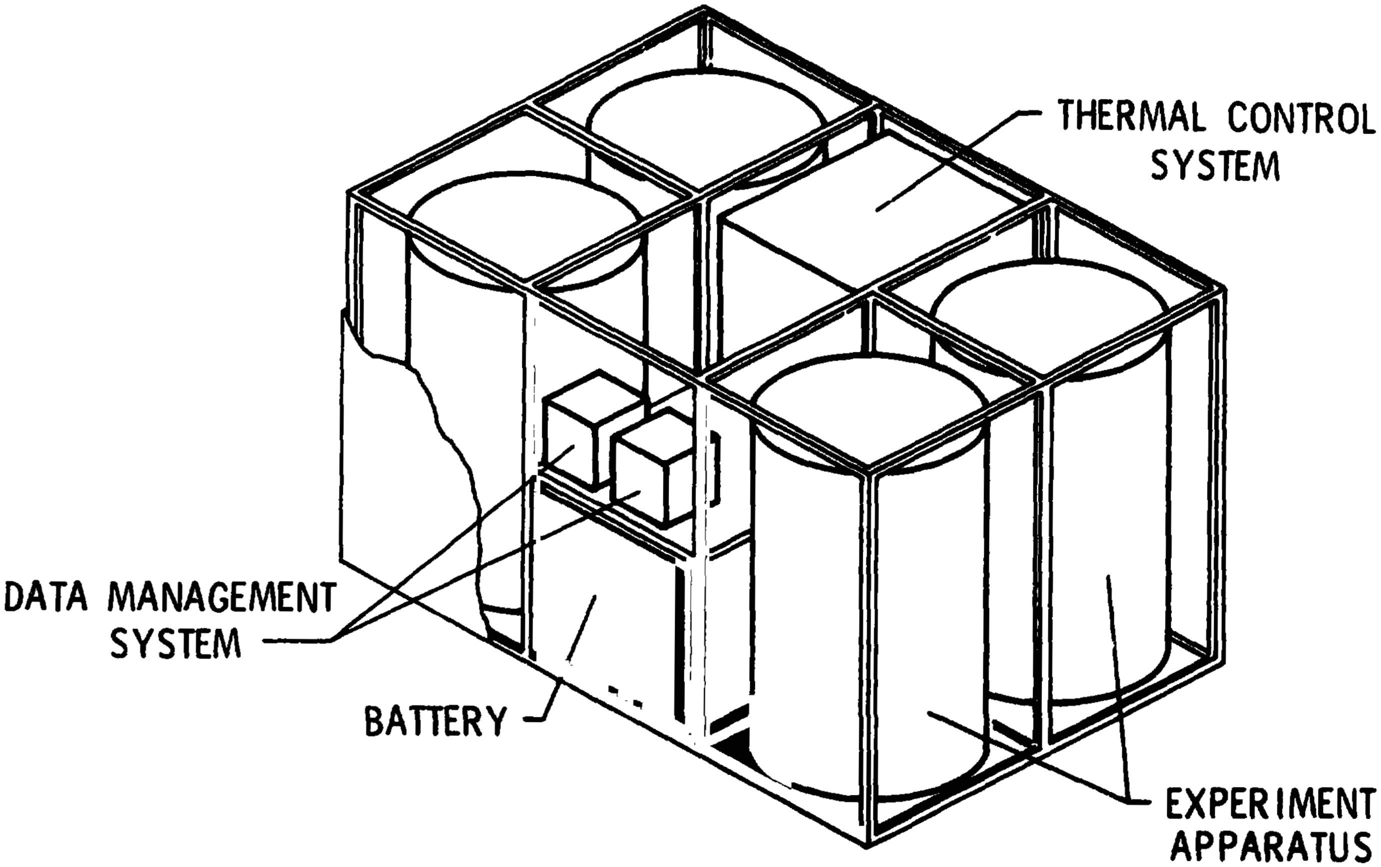
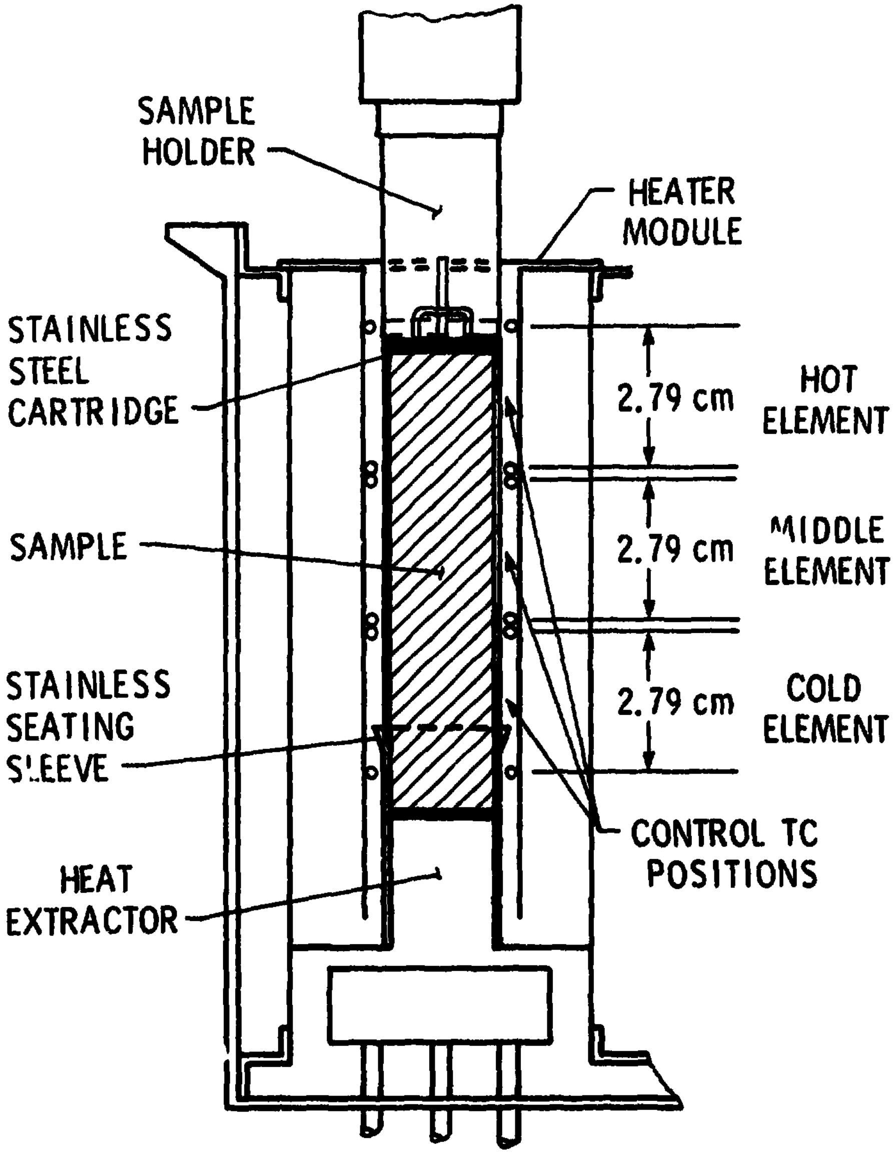
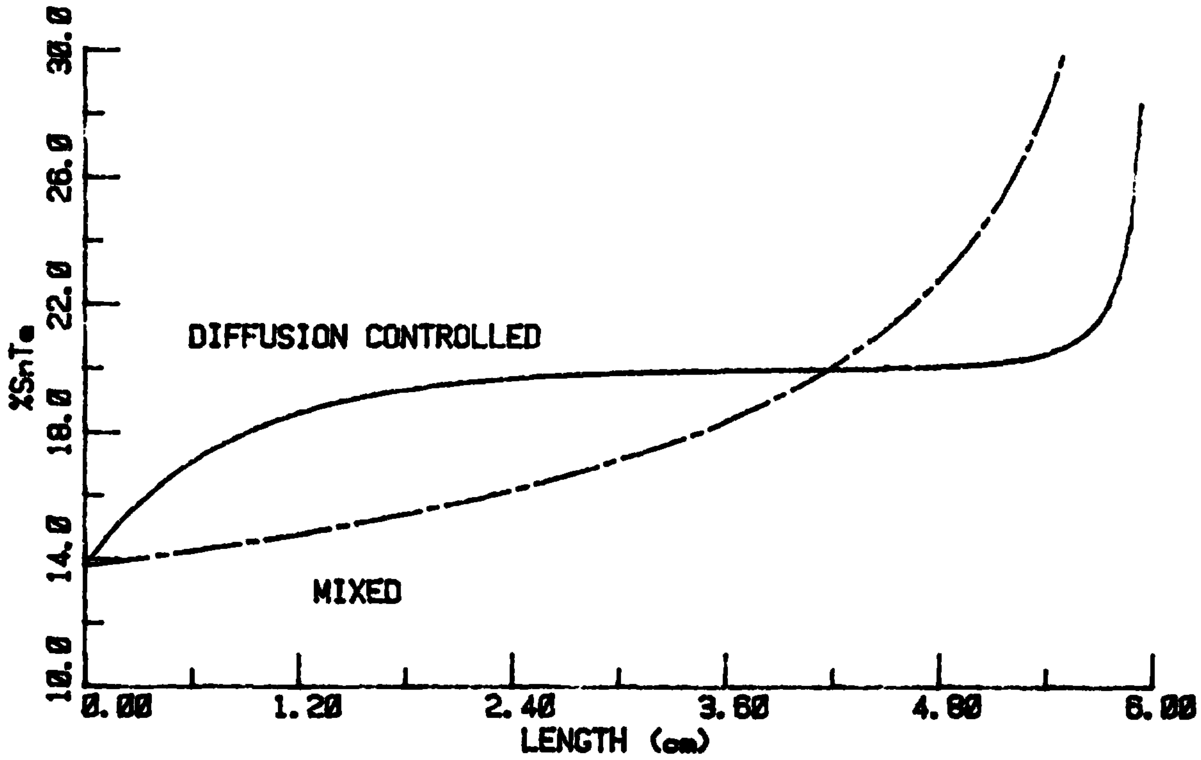


1. Materials Experiment Apparatus (MEA)



2. Schematic of the furnace module in the GPRF showing relative positions of the heater elements, the heat extractor, the positioning sleeve and the sample.



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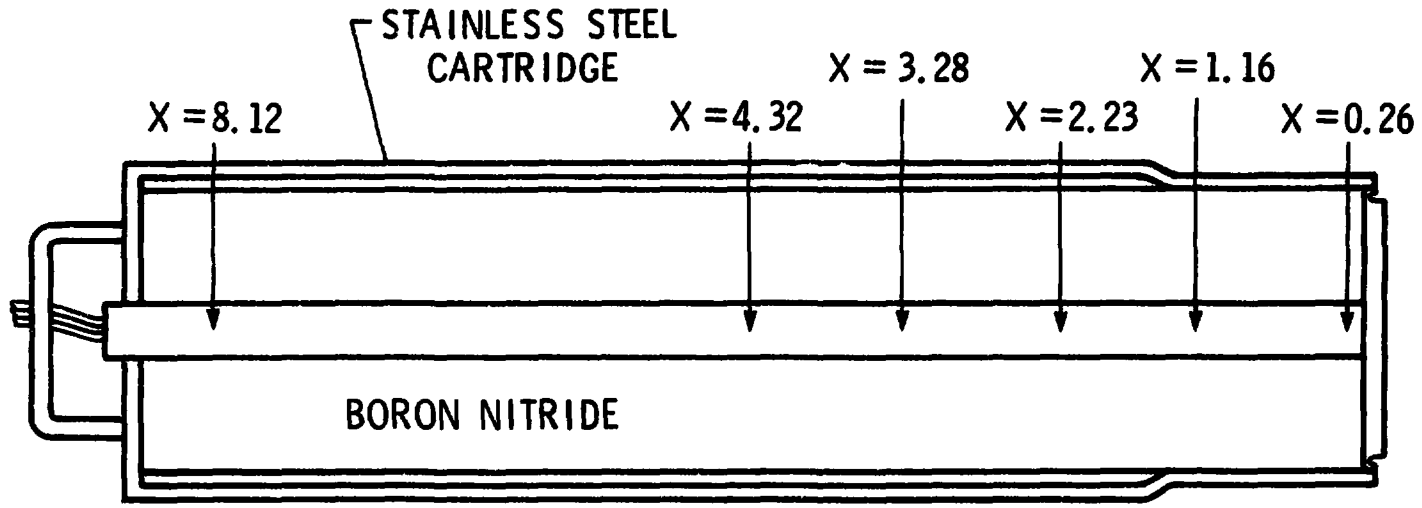
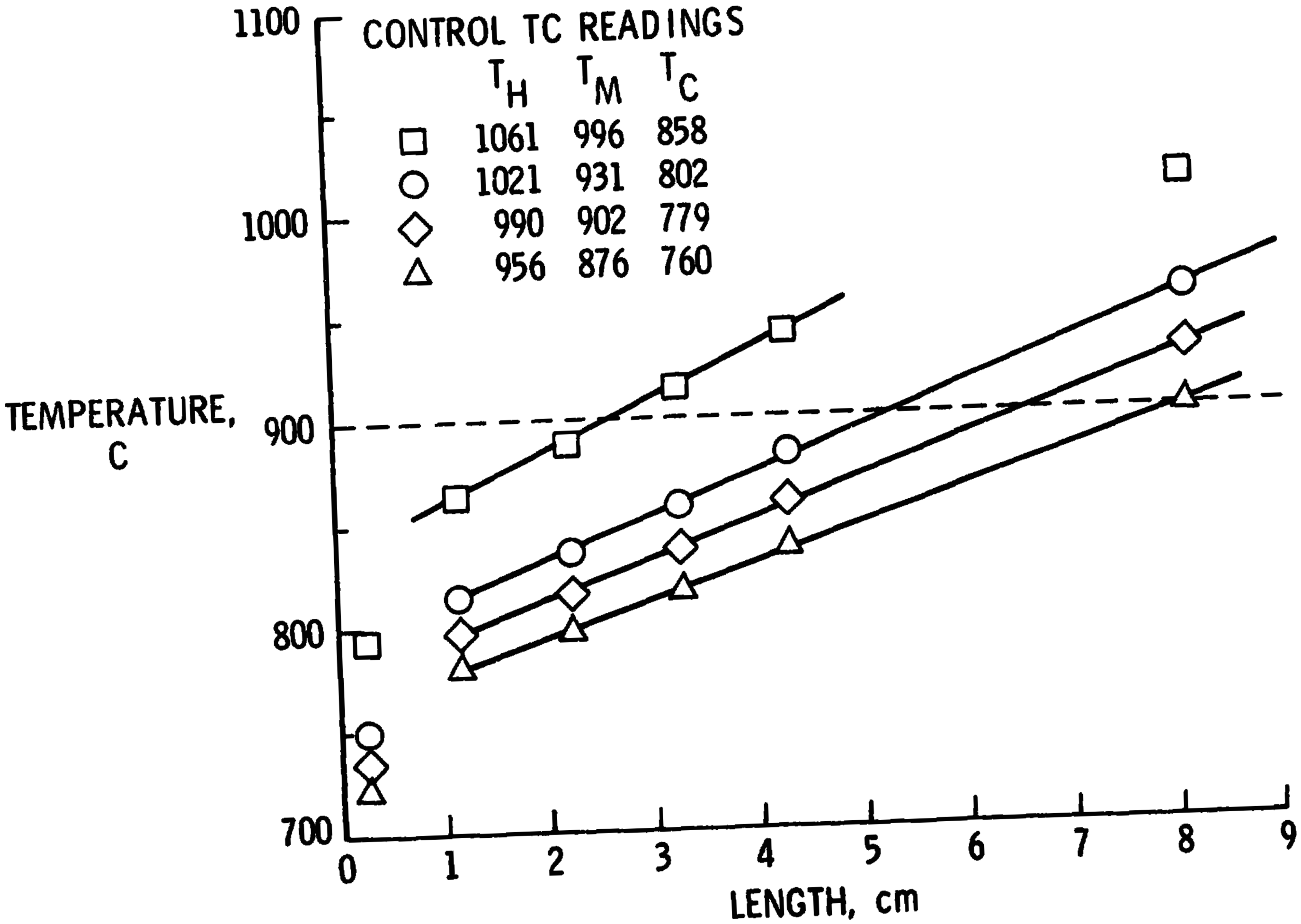
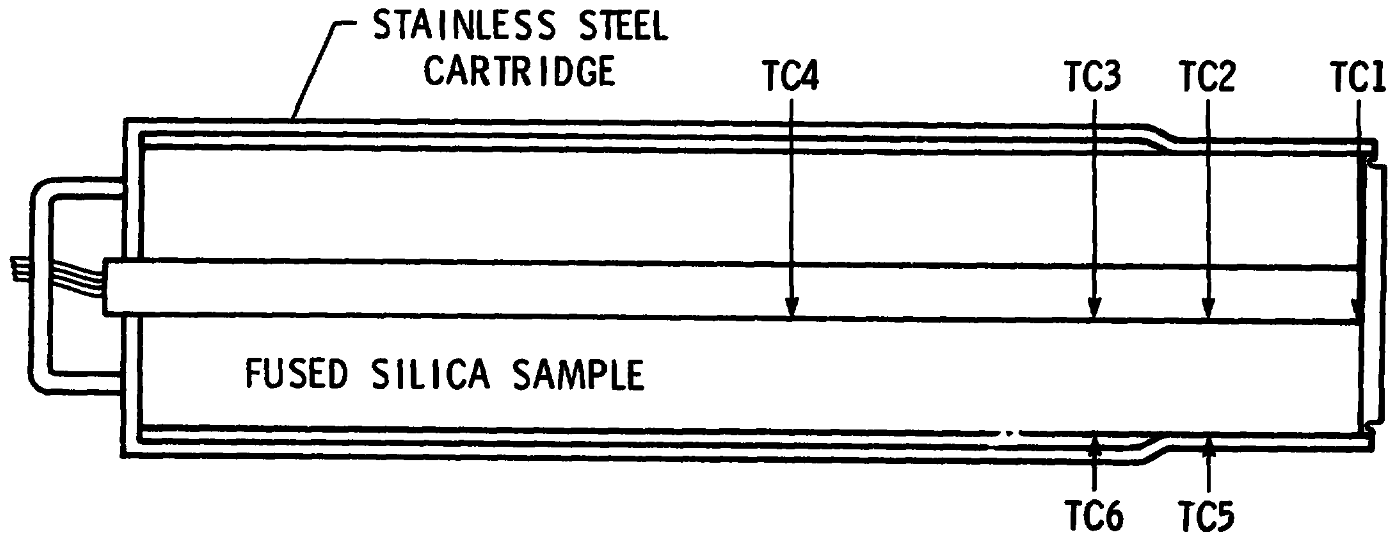


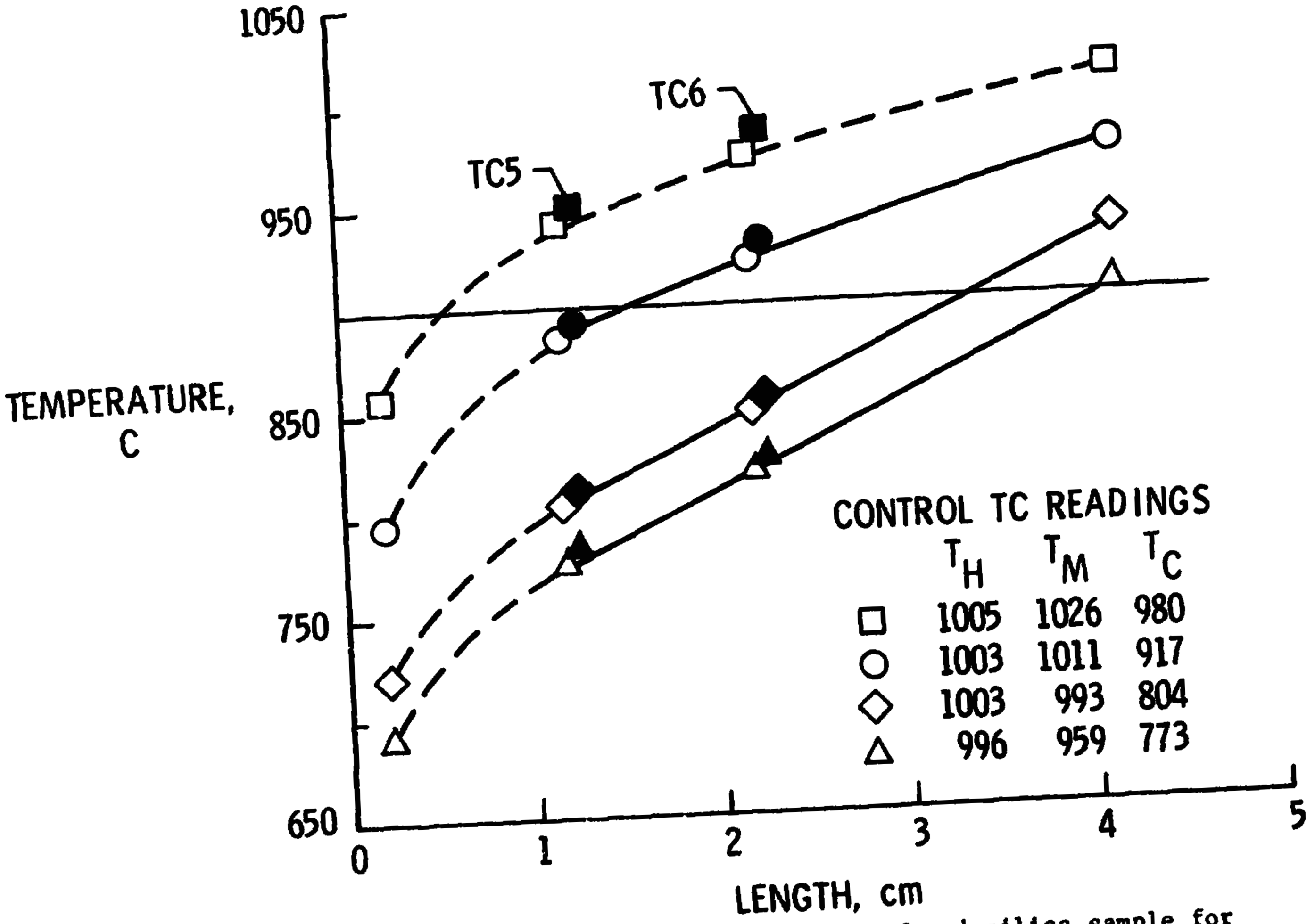
4. Cartridge for the boron nitride sample showing thermocouple placement. Dimensions are in cm.



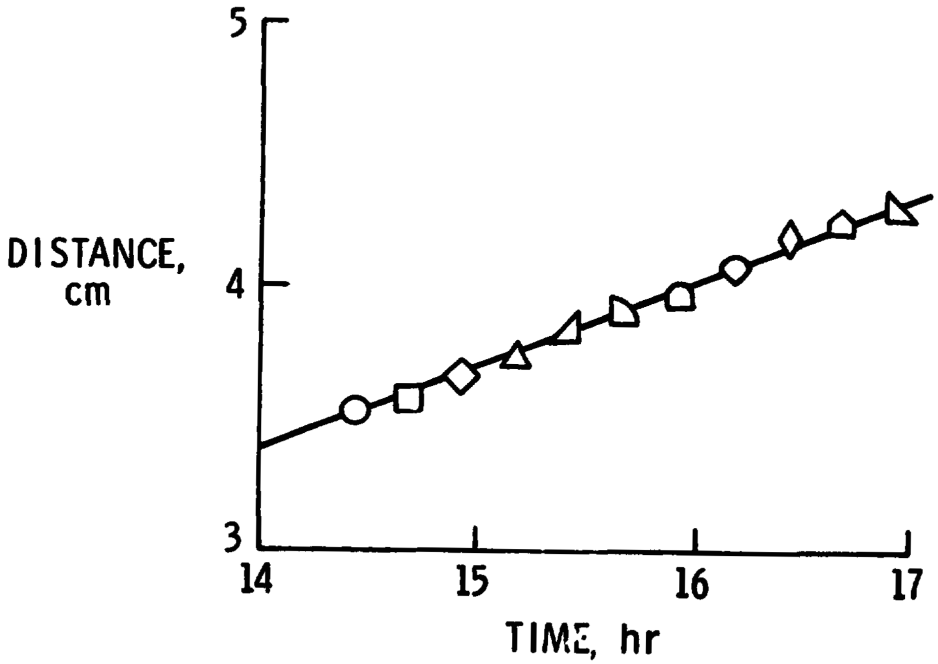
5. Typical temperature profiles in a boron nitride sample for different furnace settings.



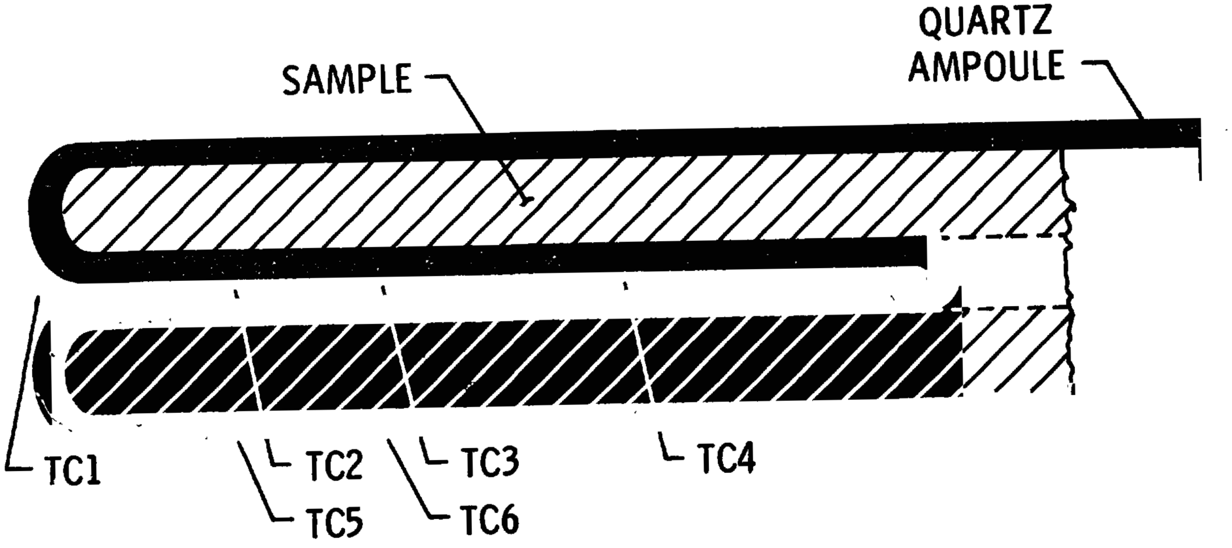
6. Schematic of the fused silica sample showing thermocouple placement.



7. Typical temperature profiles in the fused silica sample for various furnace settings. The darkened symbols indicate the temperatures for thermocouples 5 and 6 which are along the outside of the sample rather than along the axis. Therefore, they give an indication of the small radial temperature gradients.



8. Interface position as a function of time showing the constant rate of change of the 900° C temperature for this region of the furnace.



9. Schematic of a fused silica ampoule containing a lead-tin-telluride sample used for furnace evaluation. Thermocouple positions are indicated. The capillary is in the center of the sample.