N O T I C E

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QUARTERLY REPORT NO. 3

TRANSIENT AND DIFFUSION ANALYSIS OF Hg Cd Te

1.0 INTRODUCTION

This is the third report of technical progress on Contract No. NAS8-33698, titled, "Transient and Diffusion Analysis of Hg Cd Te". This report concerns technical work performed between 20 March and 20 June 1980, and includes work being carried out under the increased Scope of Work, "Exhibit B" of the modified contract.

The work during this period has concentrated on the solution of the one dimensional planar interface solidification problem. This problem has been formulated in a most general way and numerical solutions have been obtained. In addition, progress on the design and construction of a high gradient furnace will be reported.

It is useful at this point to review why the one dimensional solidification problem is of interest. Previous work by Tiller and Jackson (1) and Smith, Tiller, and Rutter (2) addressed the problem of solute distribution in a dilute alloy system with constant segregation coefficient and a constant growth rate. By treating the one dimensional planar interface case in three parts, they were able to obtain analytical solutions for solute distribution in the initial transient, steady state region, and final transient. As pointed out in the previous progress report, these solutions do not apply to the Hg Cd Te system due to the following

(NASA-CR-161524) TRANSIENT AND DIFFUSION ANALYSIS OF Hg Cd Te Quarterly Progress Report, 20 Mar. - 20 Jun. 1980 (SEMTEC, Inc.) 27 p HC A03/MF A01 CSCL 20L

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behavior that violates most of the previous works assumptions. In contrast to the dilute alloy system, the Hg Cd Te system has for a initial liquid solute mole fraction of .2(Cd Te) :

- A solute mole fraction in the solid that varies from about .6 for the first to freeze to .2 at steady state.
- A changing interface solidification temperature from 800°C initially to 705°C at steady state.
- Widely separated liquidus and solidus curves with a segregation coefficient k that varies from 2.9 to more than 6 over the approach to steady state growth.

The goal here is to reformulate the problem to allow for changing k and interface temperature. Recent work by Favier (3) has pointed out that the interface velocity cannot remain constant throughout a solidification experiment and that the applied thermal field in effect determines the solidification rate. Favier has solved the one dimensional problem for a rather complicated thermal field but assumed a constant value for the segregation coefficient, thus limiting the applicability of this work to the Hg Cd Te system. In the following sections we will formulate the general problem, indicate a numerical method for solution of the problem and apply the results to experimental solute profiles to determine the effective diffusion constant for Hg Cd Te.

2.2 TRANSIENT ANALYSIS

2.1 ANALYSIS OF THE PLANAR INTERFACE CASE

We wish to formulate the most general one-dimensional solidification problem in keeping with the Bridgam - Stockbarger growth configuration and the HgCdTe solid solution system. We shall make the following assumptions:

I. The thermal and concentration fields considered are one-dimensional.

II. No significant diffusion occurs in the solid.

III. The thermal field is a specified function of the spatial variables and time and does not change as a result of the solidification process. The thermal field is taken to be monotonic in the spacial variable.

IV. The sample movement rate, R, is constant. The growth rate, v, is not necessarily constant.

V. We will deal with a binary or pseudobinary system.

We shall choose spacial variables such that z is measured from a fixed laboratory frame and x is measured in the sample from the first to freeze point (ampoule tip). The variable η is the distance into the liquid from the solid - liquid interface (see Figure 1.).

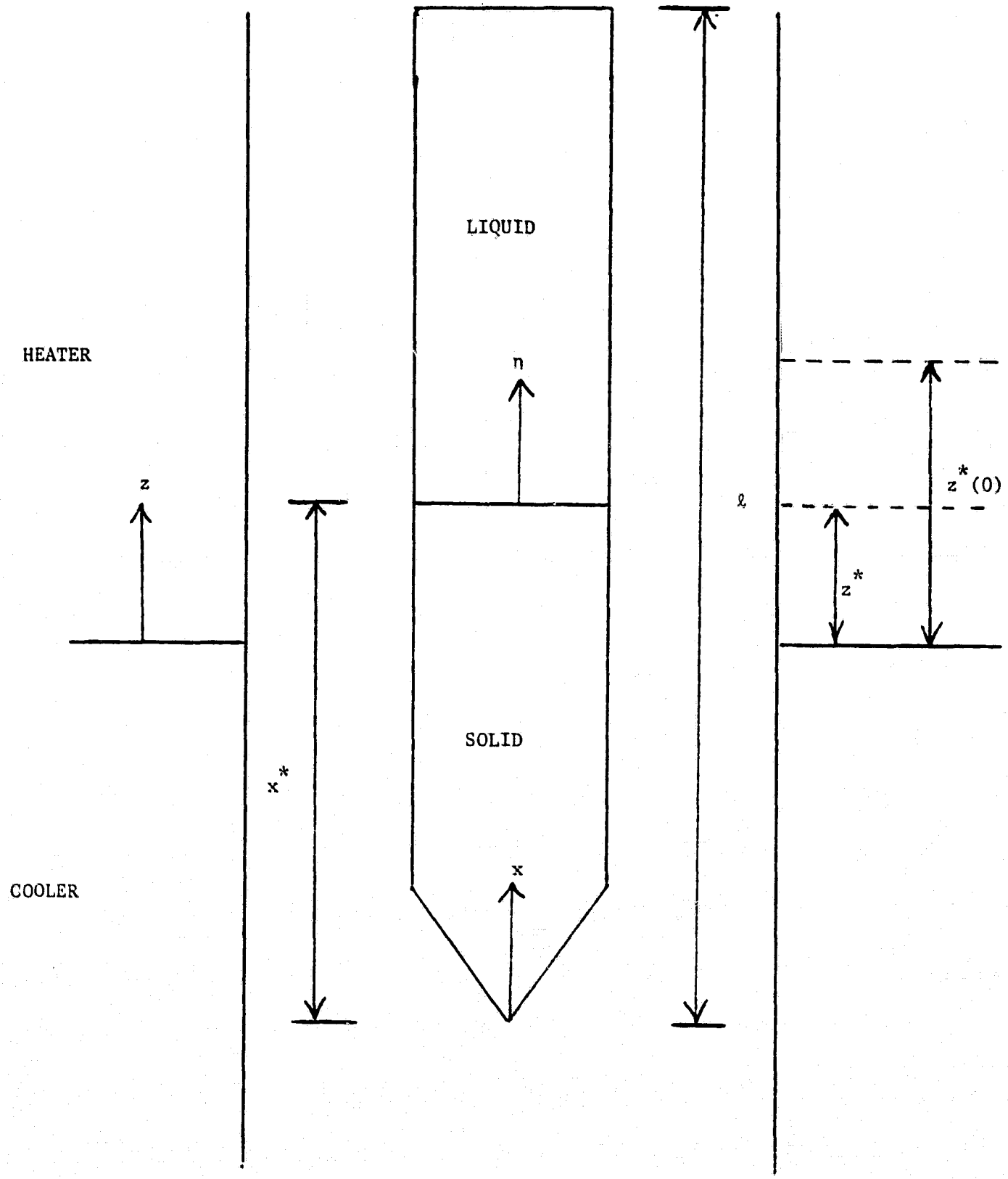

FIGURE 1.

The starred (*) values refer to variables evaluated at the solid-liquid interface. Choose $t = 0$ to be the start of solidification in the tip of the ampoule and $z^*(0)$ the z - coordinate of the ampoule tip at $t = 0$. We may then relate the various coordinate systems by

$$x = z + Rt - z^*(0), \tag{1}$$

$$x^* = z^* + Rt - z^*(0), \tag{2}$$

and

$$\eta = x - Rt + z^*(0) - z^*(t). \tag{3}$$

The total length of the sample is ℓ, and $\eta = \ell' = \ell - x^*$ denotes the end of the ampoule in the η system.

Let $C(\eta,t)$ denote the solute mole fraction in the liquid ahead of the interface. It is more convenient to express the thermal field in the fixed coordinate system, thus,

$$T = T(z,t) \tag{4}$$

and we shall assume a thermal field of the form

$$T = T_o + Gz \tag{5}$$

where G is thus the thermal gradient, assumed to be constant over the region of interest.

We define the liquidus and solidus components of the phase diagram (binary or pseudobinary) by $L(C)$ and $S(C)$ respectively. We have

$$S(0) = L(0) \text{ and } S(1) = L(1). \tag{6}$$

Furthermore, we may define the solid - liquid interface location $z^*(t)$ such that

$$T(z^*,t) = L(C(0,t)) \tag{7}$$

since $\eta = 0$ denotes the interface location in the η system.

Writing the diffusion equation in the z - coordinate system and transforming into the η system gives :

$$D \frac{\partial^2 C(\eta,t)}{\partial \eta^2} + v(t) \frac{\partial C(\eta,t)}{\partial \eta} = \frac{\partial C(\eta,t)}{\partial t} \quad , \eta > 0 \tag{8}$$

with the associated boundary conditions

$$C(\eta,0) = C_o \quad , \tag{9}$$

$$\frac{\partial C(\eta,t)}{\partial \eta} = 0 \quad \text{at } \eta = \ell' \quad \text{for all } t, \tag{10}$$

$$v(t)\ (k(C) - 1)\ C(o,t) = D \frac{\partial C(o,t)}{\partial \eta} \quad , \quad t > 0 \tag{11}$$

The boundary condition in equation (10) is normally written in a slightly different form. If we consider a semi-infinite sample, equation (10) may be written as

$$C(\eta,t) = C_o \quad \text{as} \quad \eta \to \infty \quad \text{for all } t. \tag{12}$$

This form of boundary condition is sufficient for the semi-infinite sample and allows computation of the initial solidification transient and approach to steady state growth. It is our aim here to solve for both the initial and final transients for a finite length sample, hence requiring that the first derivitive of the concentration in the liquid vanish at the far end of the ampoule is necessary to obtain the initial transient, steady state region, and the final transient. Equations

(10) and (12) are obviously equivalent as $\ell \to \infty$.

The boundary condition in equation (11) arises from conservation of total solute and is applied at the interface $\eta = 0$. Here $k(C)$ is the segregation coefficient

$$k(C(0,t)) = \frac{C_S\ (0,t)}{C_L\ (0,t)} \tag{13}$$

where S and L denote the solid and liquid sides of the interface respectively. Note that we have not assumed a constant segregation coefficient, but k depends on $C(0,t)$ and is defined by the phase diagram of the system under study. The growth velocity $v(t)$ is related to the sample pull rate R by

$$v(t) = R + \frac{dz^*}{dt} \quad , \tag{14}$$

where we recall that z^* is defined by equation (7).

In addition to the equations above we shall assume that the system under study is such that we may approximate the segregation coefficient, liquidus portion of the phase diagram, and thermal field by the following:

$$k = \alpha + \beta C + \delta C^2 \tag{15}$$

$$L = T_A + M_A C + \gamma C^2 \tag{16}$$

$$T = T_o + Gz \tag{17}$$

Equations (16) and (17) now allow one to solve for $\frac{dz^*}{dt}$ via equation (7)

$$T(z^*,t) = L(C(0,t)),$$

giving

$$z^*(t) = (1/G)(T_A - T_o + M_A C(0,t) + \gamma\, C^2(0,t)) \quad ,$$

and

$$\frac{dz^*}{dt} = (1/G)(M_A + 2\,\gamma C(0,t))\,\frac{\partial C(0,t)}{\partial t} \quad . \tag{18}$$

In summary, under conditions outlined above we seek to solve

$$D\,\frac{\partial^2 C(\eta,t)}{\partial \eta^2} + (R + \frac{dz^*}{dt})\,\frac{\partial C(\eta,t)}{\partial \eta} = \frac{\partial C(\eta,t)}{\partial t} \; ; \; \eta \to 0 \tag{19}$$

subject to

$$C(\eta,0) = C_o \quad , \tag{20}$$

$$\frac{\partial C(\eta,t)}{\partial \eta} = 0 \quad \text{at } \eta = \ell' \text{ for all } t \geq 0 \quad , \tag{21}$$

$$(R + \frac{dz^*}{dt})(\alpha + \beta C(0,t) + \delta\, C^2(0,t) - 1)C(0,t) = D\,\frac{\partial C(0,t)}{\partial \eta}$$

$$\text{at } \eta = 0 \quad . \tag{22}$$

The numerical approach to the solution is oulined in the next section.

2.2 NUMERICAL APPROACH

The differential equation and boundary conditions outlined in the previous section can be viewed as an initial value problem in time and a boundary value problem in the spatial variable. This set of equations may be solved by finite difference techniques, but we consider a different approach to be more appropriate. The algorithm chosen will be outlined below.

Let the incremental time and spatial steps be Δt and $\Delta\eta$ respectively. We will assume that at some time t_o, the values of $C(\eta,t)$ have been determined for $t \leq t_o$ and all η. The goal is to then compute $C(\eta,t')$, where $t' = t_o + \Delta t$ for all η. Assume a value for the concentration at the interface at $t = t'$, say

$$C(0,t') = C^* \quad , \tag{23}$$

where C^* is a trial value. We then compute

$$\frac{\partial C(0,t')}{\partial t} = \frac{C^* - C(0,t_o)}{\Delta t} \quad . \tag{24}$$

This allows us to determine the interface velocity v by

$$\frac{dz^*}{dt} = (1/G)(M_A + 2\ \gamma C(0,t'))\ \frac{\partial C(0,t')}{\partial t} \tag{25}$$

and

$$v = R + \frac{dz^*}{dt} \quad . \tag{26}$$

The first derivitive in η may be found from the boundary condition (Equation (22)) as

$$\frac{\partial C(0,t')}{\partial \eta} = (1/D)(R + \frac{dz^*}{dt})(\alpha + \beta C(0,t') + \delta C^2(0,t')-1)C(0,t')) \tag{27}$$

The second derivitive of C in η is found via the diffusion equation (Equation (19)) giving

$$\frac{\partial^2 C(0,t')}{\partial \eta^2} = (1/D)\left(\frac{\partial C(0,t')}{\partial t} - \left(R + \frac{dz^*}{dt}\right) \frac{\partial C(0,t')}{\partial \eta} \right) \tag{28}$$

We then may use a Taylor series expansion to obtain our desired results.

$$C(\Delta\eta,t') = C(0,t') + \frac{\partial C(0,t')}{\partial \eta}\Delta\eta + \frac{\partial^2 C(0,t')}{\partial \eta^2} \frac{\Delta\eta^2}{2} \tag{29}$$

as the value for the concentration at $\eta=\Delta\eta$ in front of the interface at $t = t'$.

So far we have simply computed $C(\eta,t)$ at the first spatial increment away from the interface. We now wish to propagate this value out in η until the end of the ampoule is reached ($\eta = \ell'$) and test to see if the boundary condition

$$\frac{\partial C}{\partial \eta}(\eta,t') = 0 \text{ at } \eta = \ell' \tag{30}$$

is met. The solution may be propagated to $\eta' = 2\Delta\eta$, the next spatial step, by first calculating

$$\frac{\partial C(\Delta\eta,t')}{\partial t} = \frac{C(\Delta\eta,t') - C(\Delta\eta,t_o)}{\Delta t} \quad . \tag{31}$$

We then may use a Taylor series expansion and the diffusion equation to obtain

$$\frac{\partial C}{\partial \eta}(\Delta\eta,t') = \frac{\partial C(0,t')}{\partial \eta} + \frac{\partial^2 C(0,t')}{\partial \eta^2}\Delta\eta \tag{32}$$

$$\frac{\partial^2 C}{\partial \eta^2}(\Delta\eta,t') = (1/D)\left(\frac{\partial C}{\partial t}(\Delta\eta,t') - \left(R + \frac{dz^*}{dt}\right) \frac{\partial C(\Delta\eta,t')}{\partial \eta}\right). \tag{33}$$

We note here that the value of the interface velocity $R + \frac{dz^*}{dt}$ does not change as we increment the spatial variable. A second expansion leads to the desired results

$$C(\eta',t') = C(\Delta\eta,t') + \frac{\partial C(\Delta\eta,t')}{\partial\eta}\Delta\eta + \frac{\partial^2 C(\Delta\eta,t')}{\partial\eta^2}\left(\frac{\Delta\eta^2}{2}\right) \tag{34}$$

The process from equation (31) to equation (34) is repeated for the next spatial step $3\Delta\eta$, ect. until $\eta = \ell'$, the end of the ampoule at this time step. A test is made to see if the boundary condition (Equation (30)) is satisfied. If not, a new trial value of C^* is selected and the entire process involving equations (23) to equation (34) is repeated until the boundary condition is satisfied.

We began this explanation by assuming all of the $C(\eta,t)$ were known at some $t = t_o$. The initial value boundary condition, $C(\eta,0) = C_o$, allows one to take $t_o = 0$ and proceed in a straightforward manner to calculate $C(\eta,t)$ for any t. At each time step, after the value of $C(0,t) = C^*$ has been found that satisfies the boundary condition in Equation (30), we may then proceed to obtain the solute concentration in the solid.

The interface position, measured from the tip of the ampoule, is given by x^* (Equation (21)) where we note that $z^*(t)$, and thus x^*, is determined by the thermal field and the liquidus curve of the phase diagram evaluated at $C(0,t)$. The solute concentration in the solid $C_s(x^*)$, is defined by

$$C_s(x^*) = k(C(0,t))C(0,t) \tag{35}$$

where k is assumed to be known via Equation (15). After the solid concentration is determined at a position x^*, the remaining amount of liquid to be solidified is found as

$$\ell' = \ell - x^* . \tag{36}$$

The time is incremented by Δt, and the entire processes repeated to give new values of $x^*(t)$, $C_s(x^*)$, ect., until the end of the ampoule $\ell' = 0$ is reached. In the following section, representative plots of these variables and fits to actual experimental data will be presented.

2.3 RESULTS

In this section we will present typical results obtained from the previous analysis. Figure 2 is a plot of the mole fraction of Cd Te in the solid versus the length of the sample measured from the first to freeze tip. This curve is calculated assuming a sample pull rate of .1116 cm/hr for a value of the diffusion constant of 5×10^{-5} cm^2/sec. The length of the sample was taken to be 18 cm. Data necessary to fit the liquidus portion of the phase diagram and the segregation coefficient was supplied by Dr. S.L. Lehoczky of MacDonald Douglas Research Laboratories in St. Louis, Missouri and his co-workers. The thermal gradient was assumed to be a constant $200^{\circ}C$/cm over the region of interest. In figure 2 we note the initial transient characterized by decreasing Cd Te content as the diffusion layer in the liquid was being built up; the steady state region in which the solid is of uniform composition, and the final transient in which the solute is depleted in the remaining liquid resulting in a decreasing solid solute composition.

We may now compare calculated curves such as figure 2 to the experimentally determined composition profiles obtained by density measurements or X-ray microprobe analysis. The fit to the liquidus curve and segregation coefficient are determined by the plase diagram, so the diffusion constant is the only free parameter in analysing the composition profile. Figure 3 is the same theoretical data as in figure 2, plotted on an expanded split scale. In this case we have included experimental composition profile data by Lehoczky, et. al.of MDRL for Hg Cd Te crystal grown at a pull rate of .1116 cm/hr. The two theoretical curves

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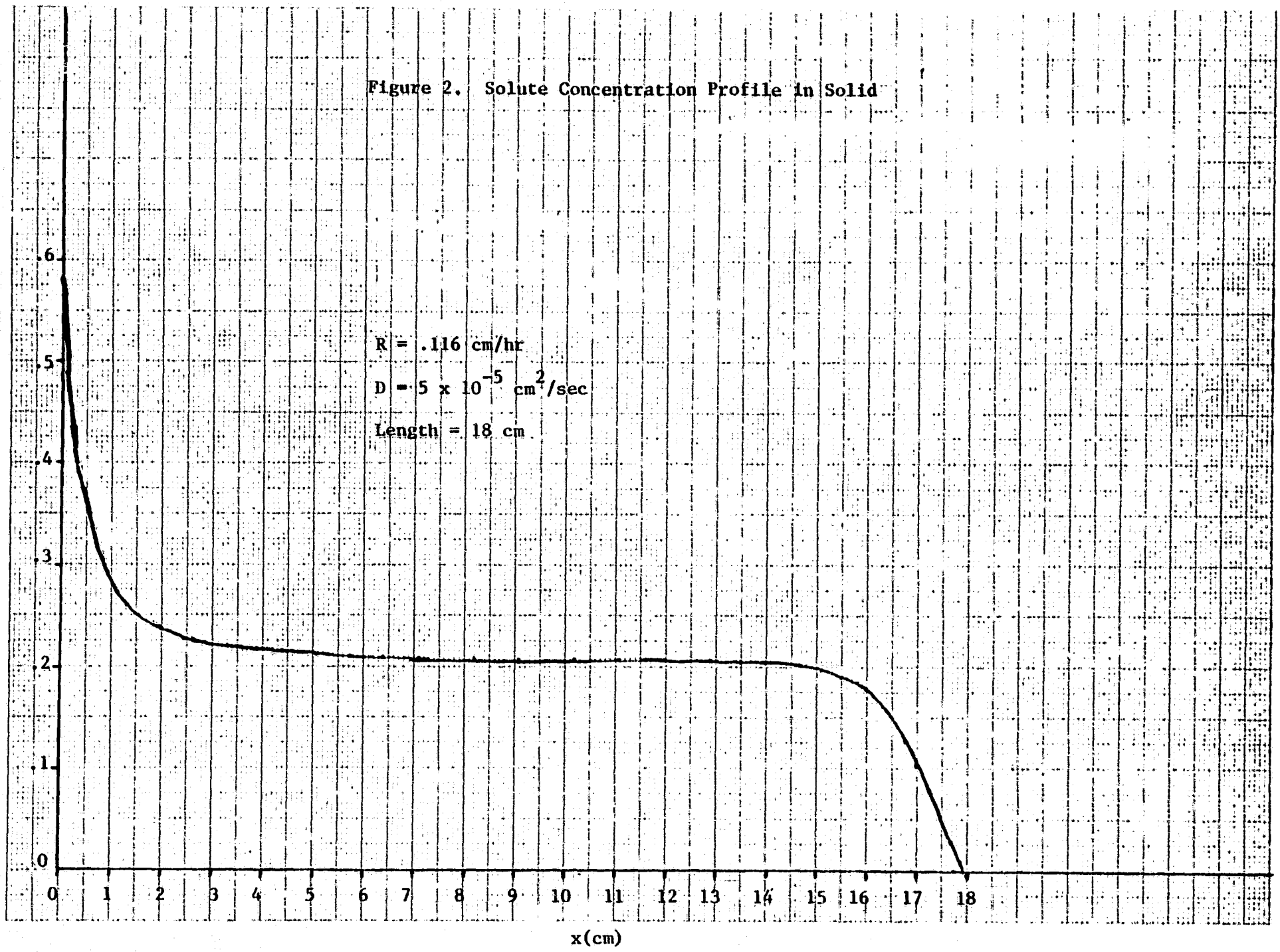

Figure 2. Solute Concentration Profile in Solid

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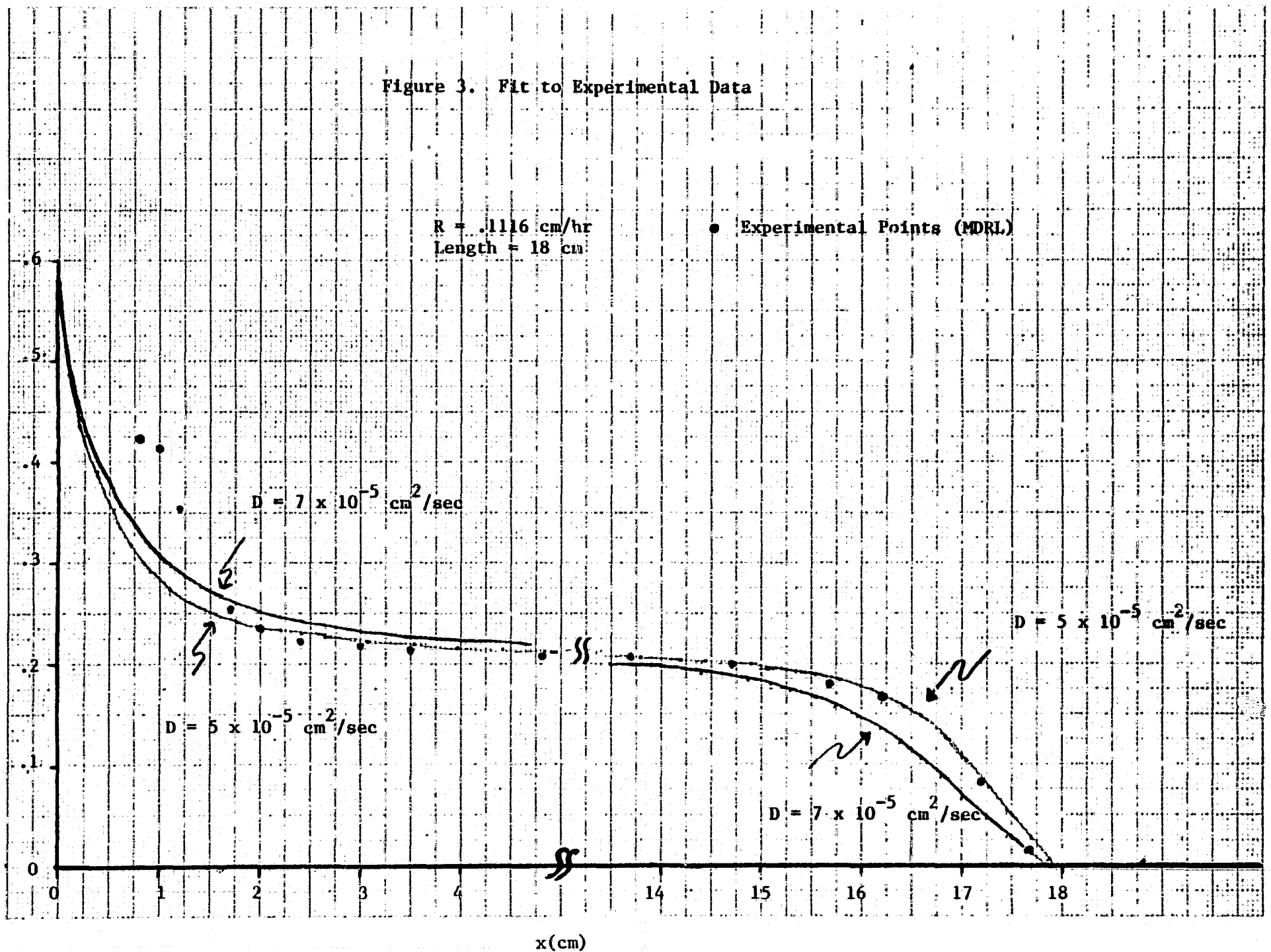
Figure 3. Fit to Experimental Data



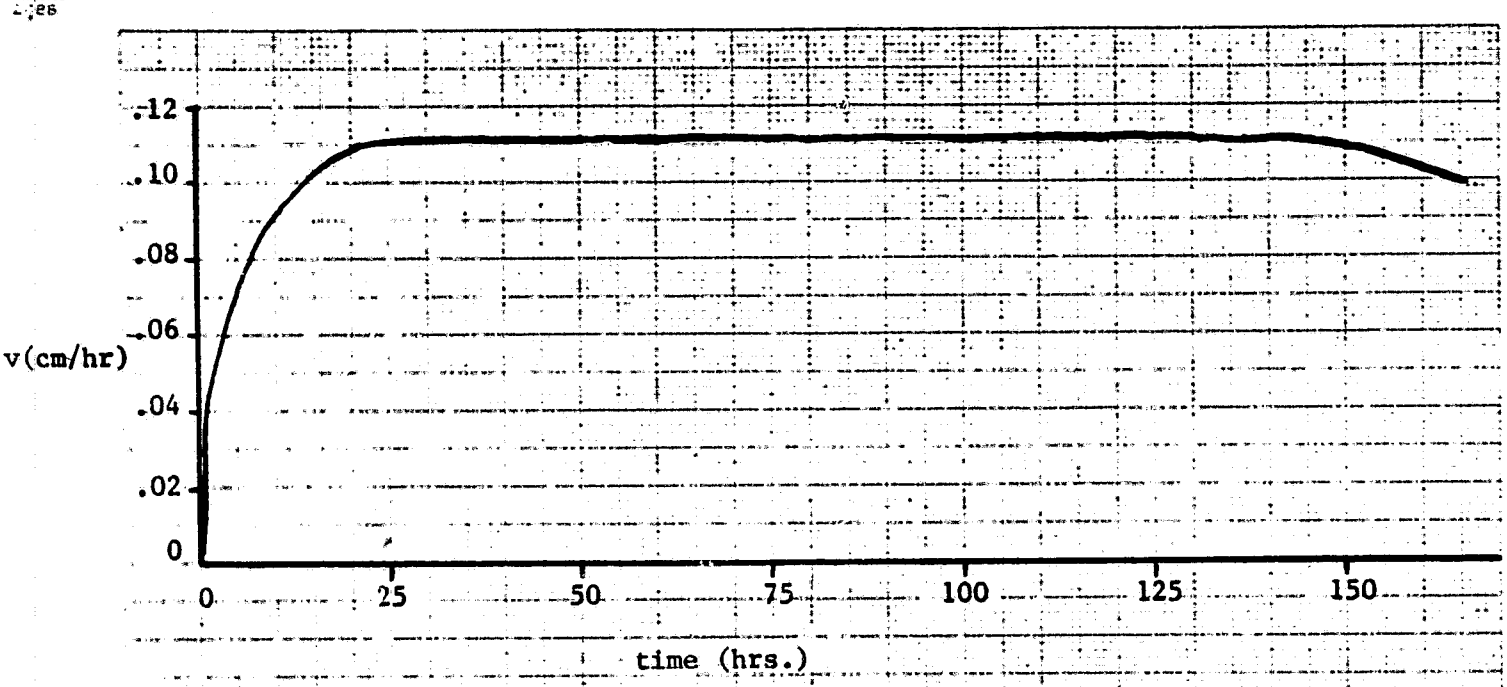


Figure 4. Interface Velocity vs. Time

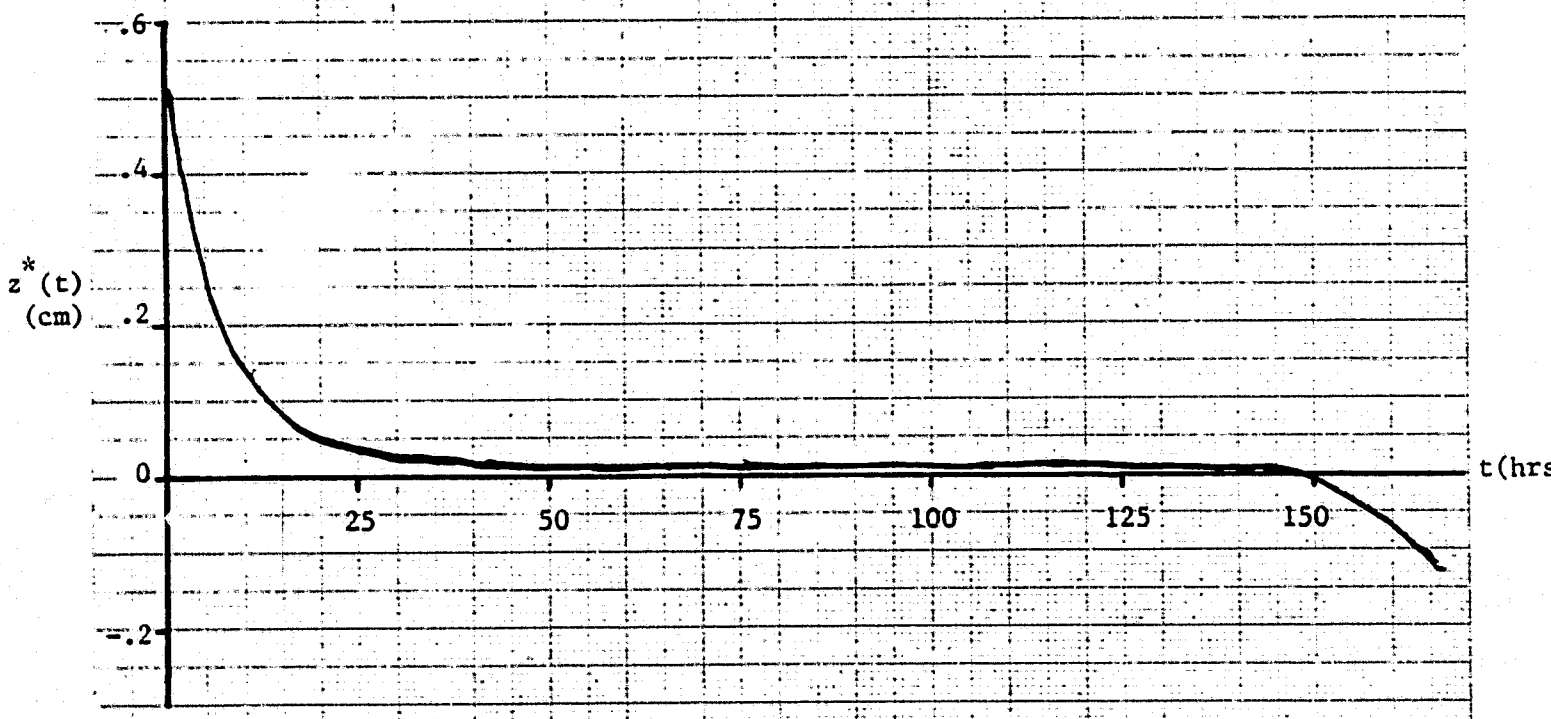


Figure 5. Inteface Location vs. Time

are for values of the diffusion constant of 5×10^{-5} cm^2/sec and 7×10^{-5} cm^2/sec. We note that the agreement between experiment and theory is quite good in this case, with the best fit obtained for $D = 5 \times 10^{-5}$ cm^2/sec. The first three experimental points lie well off the theoretical curve. The most likely explanation for this is that in this region, the crystal is solidifying within the conical ampoule tip and thus a one dimensional calculation does not adequately reflect initial solidification conditions. We also note that the sensitivity to the diffusion constant is good enough to allow determination of the diffusion constant to approximately 15% if the scatter in the experimental data is small.

One of the primary goals of this study was to analyze the solidification process in Hg Cd Te so that growth conditions may be optimized. Figures 4 and 5 are an example of the value of this analysis in choosing proper growth conditions, and are calculated for the same parameters as the previous graphs. In the plot of interface velocity versus time, we see that it requires almost 25 hours of growth before the growth rate is equal to the sample pull rate. Of more practical use is figure 5 which gives the interface location $z^*(t)$ as measured in the coordinate system fixed to the furnace mid-plane. We see that for the assumed mid-plane temperature of 700^oC and thermal gradient of $200^oC/cm$, the initial solidification begins well into the hot portion of the heater and gradually drops down into the mid-plane of the heater as steady state growth is achieved. As solute is depleted near the end of the ampoule, the interface drops into the cold end region. In a real furnace system,

there is only a small region over which a planar isotherm, and thus a planar interface, will exist. A shifting interface as illustrated by figure 5 implies that the furnace settings must be changed in time to insure that the planar isotherm is also the solidification temperature if we are to obtain a planar interface. Calculations such as these may be coupled to thermal analysis computations to find the appropriate furnace settings as a function of time to achieve optimized growth conditions for Hg Cd Te.

Acknowledgements -- SEMTEC would like to thank Dr. S.L. Lehoczky and Dr. F. Szofran of MacDonald Douglas Research Laboratories for the use of their phase diagram and composition profile data. The work at MDRL is partially funded under NASA contract NAS8-33107.

3.0 HIGH GRADIENT FURNACE

3.1 HOT ZONE

The hot zone of the high gradient furnace will consist of a thin walled metal tube that is heated by passing low voltage high current AC power through the tube. The furnace is being designed to run in air or vacuum by constructing two interchangable tubes, one of tantalum and one of Inconel 600. The tantalum tube would require a pressure of 10^{-6} torr because of the high temperature oxidation properities of tantalum. A tube constructed of Inconel 600 high temperature stainless steel will be used in vacuum and also tried in air.

The tantalum tube assembly is a modified tantalum oversheath for thermowells manufactured by Thermo/Co. of Houston, Texas. The tube is 12" long with flanges welded on both ends. It is produced from stock 5/8" I.D. .015" wall Fansteel tantalum.

The Inconel 600 tube was constructed from a 1" rod stock because of delivery lead time and size availability of the tubing. The 1" x 12" rod stock was drilled to .75" I.D. then the wall was turned to 0.010". A flange of 347 stainless steel 0.5 mm thick from Goodfellow Metals of Cambridge, England was welded to the tube ends for power connections and support.

To estimate the amount of power needed to raise the tube heaters to 1000°C only the resistivity and surface areas need be known.

Using the following equations:

$$R = \rho L / 2\,\pi r_o t \tag{1}$$

$$A_t = 2\,\pi r_o L \tag{2}$$

$$I = \sqrt{\frac{\varepsilon \delta A_t T^4}{R}} \tag{3}$$

$$v = IR \tag{4}$$

where: A_t = surface area

r_o = outside radius

L = length

R = resistivity

ρ = wall thickness

I = current

ε = emissivity

δ = Stefan-Boltzman constant

T = temperature

v = volts

t = wall thickness

the amount of current needed for the .015" wall 5/8" I.D. tantalum tube heater is ≈ 400 amps at 3.25 volts. On the other hand, the 0.010" wall 3/4" I.D. Inconel tube will require ≈ 360 amps at 7.5 volts. These current values are in the range of available transformers and are not difficult to obtain.

3.2 ADIABATIC ZONE AND GAS INLET

The design of the adiabatic zone has been changed from that discussed in the second Quarterly Report. Instead of the layered metal strips, a ceramic block with a thin stainless steel insert in the center will be tested. This is designed to give a greater flexibility with the sizes of adiabatic zones that can be used. The ceramic will hopefully provide a sufficient amount of insulation between the hot and cold zones.

The design of the gas inlet for the withdrawing of heat from the sample in the cold end has also been changed to aid in the testing of the high temperature furnace. The inlet has been made removable so that the furnace can be operated with and without the extra cooling.

3.3 COLD END HEATER

A modified Applied Test Systems (ATS) series 3110 laboratory furnace will serve as the cold end heater. The furnace has a 3/4" I.D. with a 9" heated length. With the axial insulation removed from the ATS furnace, the tube furnace is easily mounted to the ATS furnace. This stackability of the ATS furnace, gas inlet, adiabatic zone, and the tube furnace leads to an efficient and stable arrangement.

3.4 STATUS

Design changes have been finalized and drawings are completed. Raw materials have been received and machining is in its final phase. Assembly and system check out will be performed in the next phase of the high gradient furnace project.

PROBLEMS

There were no problems of a technical nature that would impact performance in this reporting period.

PLANS FOR THE NEXT QUARTER

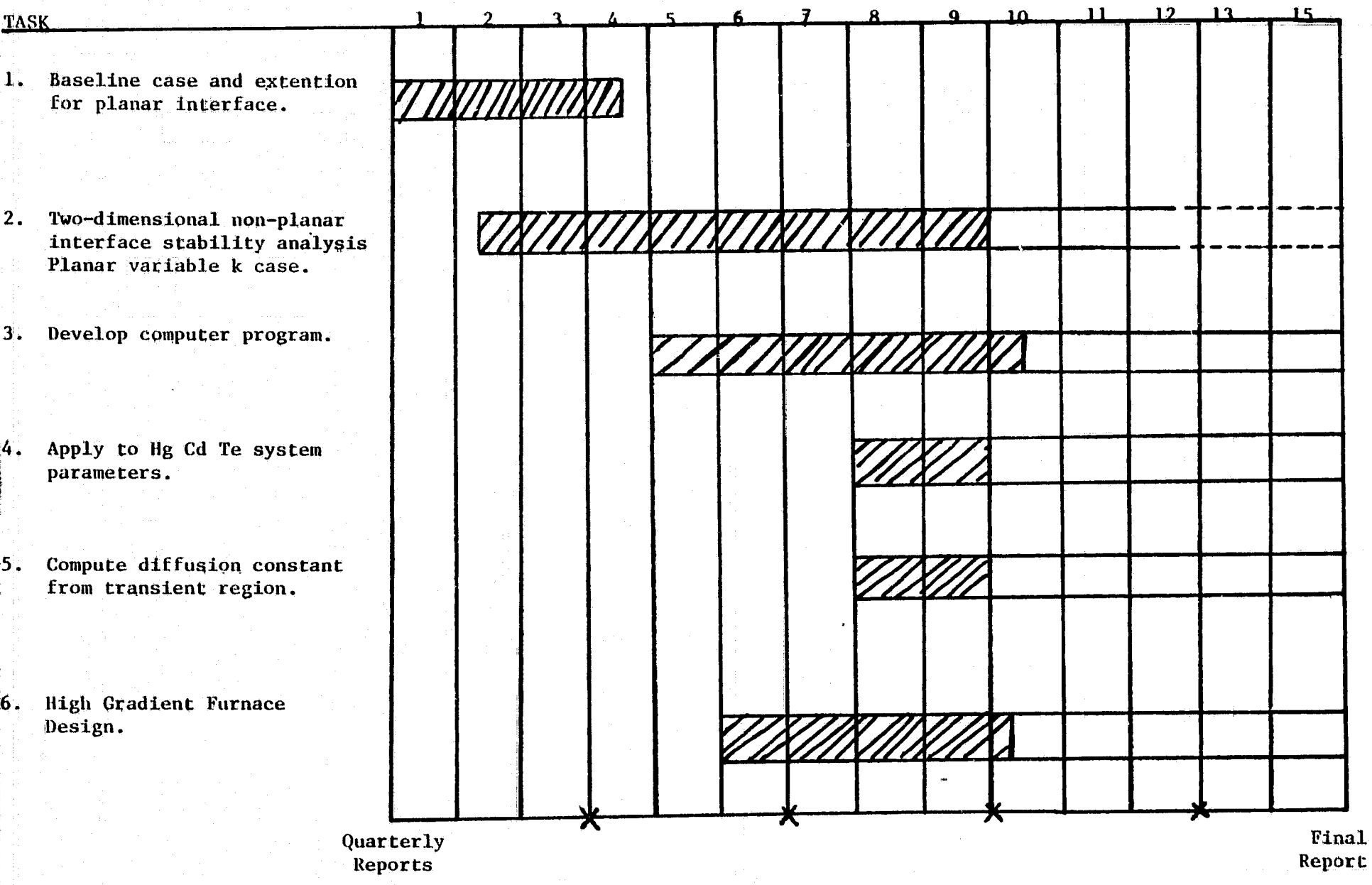
In the next quarter, the results of the solution to the one dimensional solidification problem will be applied to derive furnace settings, ampoule length and sample pull rate for optimum growth conditions. The diffusion constant will be determined from experimental data. In addition, the two dimensional diffusion problem will be examined in an effort to couple fluid flow and diffusion into the interface stability problem.

Work on the high gradient furnace will continue, with testing expected to be completed near the end of the next reporting period.

SCHEDULE AND FINANCIAL PERFORMANCE

The following pages present schedule and financial data current up to this quarter. Additions to and redirection of emphasis have modified the schedule somewhat.

PROGRESS AS OF 20 JUNE 1980



FINANCIAL REPORT

CONTRACT NAS8-33698

The period of performance, including Amendment No. S/A 2 (CPFF), is to November 28, 1980.

Total Estimated Cost	$ 57,121.00
Fixed Fee	4,101.00
Total Sum Allotted	61,222.00
Total Direct Labor Expended through 6/12/80 (Voucher 19)	$ 17,273.00
Direct Materials	862.22
Materials Overhead	86.22
Overhead	14,336.68
Travel	246.05
G&A	4,778.38
Total	$ 37,582.65
Total Estimated Cost for Completion through 28 Nov. 1980	$ 19,538.35
Total Amount Billed through 6/12/80 (Voucher 19)	37,582.65
Amount Received through 6/20/80 (Vouchers 1-18)	35,147.54
Fee billed through 6/20/80	1,460.03

Estimated progress on technical work is 65% of work completed.

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1. W.A. Tiller and K.A. Jackson, Acta Met. 1 (1953) 428.
2. V.G. Smith, W.A. Tiller, and J.W. Rutter, Can. J. Phys. 33 (1955) 723.
3. J.J. Favier, J. Crystal Growth 49 (1980) 373.