MASTER

KINETICS, MORPHOLOGY AND THERMODYNAMICS
OF THE SOLID-LIQUID TRANSITION OF NON-METALS

MASTER

Progress Report

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ABSTRACT

Some of our previous work on Internal Centrifugal Zone Growth has been documented. New calculations have been made to show that for large RF skin depths, the temperature of the sample depends in a systematic way on only three dimensionless parameters; these characterize the RF power level, the surface heat transfer coefficient, and the ambient temperature. Critical values are given for the ambient temperature below which curves of sample temperature versus RF power level are S-shaped. Based on this improvement in understanding, our previous numerical results, valid for arbitrary skin depths, are being prepared for publication.

Work continues toward the measurement of the solid-liquid surface tensions of non-metallic materials via the grain-boundary groove technique. Degassed samples of GeO_2 have been obtained, but the necessary temperature caused damage to the quartz tube in our present apparatus, thus necessitating a new design. While the new apparatus is under construction, sodium sulfate will be used as a prototype material to enable work on the optical system. Use of an astronomical telescope in conjunction with the optical viewport leads to poor image quality so we are considering the substitution of a microscope with a large working distance. Previous difficulties with numerical calculation of the temperature profiles in the system have been alleviated by using finer grid sizes for the finite difference scheme.

Further effort has been expended in cooperation with Professor Mullins to form the basis of new work on the application of Onsager's theory of reciprocity to transport phenomena in solids.

PROGRESS REPORT

I. Technical Progress

Work conducted under the auspices of the present contract can be categorized under two main headings which have also served as titles for the contract:

- A. Generalization of Internal Centrifugal Zone Growth of Metal-Ceramic Composites (Previous Title)
- B. Kinetics, Morphology and Thermodynamics of the Solid-Liquid Transition of Non-Metals (Present Title)

Recent developments have led us to propose new work to be conducted under the following title:

- C. Applications of Onsager's Reciprocity Theory to Transport Phenomena in Solids (Future Title)

Work performed under A and B is summarized below; work contemplated under C is contained in the Proposed Technical Program.

A. Internal Centrifugal Zone Growth (ICZG)

The broad technical objectives of this work were (1) to develop a realistic model of a crystal growth process known as Internal Centrifugal Zone Growth and (2) to utilize the predictive capacities of the model to improve the present ICZG process and to extend the use of the ICZG process in general. Both theoretical (mostly computer-aided modeling) and experimental work were carried out at Carnegie-Mellon University; some experimental work was carried out at the Oak Ridge National Laboratory in cooperation with G. W. Clark and J. D. Holder.

The work on ICZG has been completed and is documented as follows:

Doctoral Thesis: "Modeling of Internal Centrifugal Zone Growth,"
by Robert A. Hartzell, Carnegie-Mellon University, September 1977.

"Eutectics of LaCrO_3 and YCrO_3 with W, Mo and Cr," by J. D. Holder, R. A. Hartzell and G. W. Clark, submitted to J. American Ceramics Society --- preprint appended (Appendix A).

During the past seven months of the present contract period, some effort has been devoted to better understand the basic instability phenomenon reported in Hartzell's thesis. This has resulted in the following publication:

"Instability Phenomena During the RF Heating and Melting of Ceramics," by R. F. Sekerka, R. A. Hartzell and B. J. Farr, to be submitted to J. Crystal Growth, preprint appended (Appendix B).

This paper documents the basic instability phenomenon of the Hartzell thesis but also contains some new calculations performed by a graduate student, B. J. Farr, during the summer of 1979 in order to better understand Hartzell's computer calculations on the basis of a simpler analytical model. The new work leads to definite calculations of the process parameters that correspond to the stability-instability demarcation for large RF skin depths.

Two more papers are in the process of preparation to complete publication of the Hartzell thesis. These are

"Modeling of Internal Centrifugal Zone Growth of Ceramics and Ceramic-Metal Composites I: Mathematical Models," by Robert A. Hartzell and Robert F. Sekerka.

"Modeling of Internal Centrifugal Zone Growth of Ceramics and Ceramic-Metal Composites II: Practical Results," by Robert A. Hartzell and Robert F. Sekerka.

These two papers are essentially in rough draft form. A rough draft of paper I, written by R. A. Hartzell, is appended (Appendix C); it needs to be rewritten to exclude (pages 1-7) the material already covered in the Sekerka - Hartzell - Farr paper and to concentrate more on the mathematical aspects of the computer modeling (expansions of pages 7-9) as documented in the thesis for both one and two dimensional modeling. Paper II is intended for the experimentalist who is not interested in the details of the modeling; it is essentially a rewritten version of one of our progress reports (see Appendix D) properly referenced to paper I and to the Sekerka - Hartzell - Farr paper.

B. Kinetics, Morphology and Thermodynamics of the Solid-Liquid Transition of Non-Metals

The broad objectives of this work are (1) to design and build apparatus for the measurement of the solid-liquid surface tension of non-metallic materials, (2) to measure the solid-liquid surface tension of a few non-metallic materials, (3) to model mathematically the solid-liquid surface tension of non-metals and (4) to determine, and possibly modify, the role that solid-liquid surface tension and other parameters play in causing ceramics to solidify with a coarse-grained structure.

During the last seven months we have made further progress in the measurement of the solid-liquid surface tension of non-metallic materials via the grain boundary groove technique; however, we continue to be plagued by two difficult experimental problems, namely, the growth of crystals of GeO_2 and the functioning of the optical viewport. The procedures and apparatus are described in our previous progress report, COO-2407-7, a portion of which is appended (Appendix E).

1. Crystal Growth

In order to degass samples of GeO_2 , powder was melted under vacuum in a quartz tube and held for a few hours at 1150°C . This produces clear samples, presumably free of porosity. However, the quartz tube recrystallized and collapsed, thus necessitating a new design for our apparatus. We now plan to use a T-shaped inconel tube in a split furnace with the main stems of the T forming the optical viewport as shown in Figure 1a.

Samples of GeO_2 cooled from the degassing temperature appear to be glassy as tested by X-ray analysis. So far, this seems to be a difficult substance from which to grow crystals.

While our new apparatus is being constructed, we are gaining experience by exploration of another substance, sodium sulfate (melting point 887°C , $\frac{\Delta S}{k} = 2.5$) that has a reasonable vapor pressure and can be handled in quartz tubes. So far, we have been able to melt and resolidify this substance and are currently attempting to devise an optical system to view its solid-liquid interface.

2. Optical Systems

We have attempted to view the solid-liquid interface via a Quasar astronomical telescope according to the configuration illustrated in Fig. 2 of our previous report COO-2407-7. The optical image has poor resolution in part because of vibrations associated with the prism and the telescope; we are investigating the possibility of heavier supports for these elements. In addition, the image quality suffers from the reduced aperture of the viewport (about 1" dia.) com-

Fig. 1a. Split furnace with T-shaped tube

Fig. 1b. Auxilliary light port for materials with lower melting points.

pared to the telescope (about 7" dia.). We have, therefore, considered abandoning the telescope in favor of a microscope fitted with a "relay lens" to increase its working distance to about 6 to 10", hopefully sufficiently large to allow cooling of the microscope in order to prevent damage from the hot sample and furnace. In the case of lower melting point materials, there is insufficient radiation from the sample to enable it to be viewed optically by self-generated light; in such a case we plan to use a tube with an additional light port as illustrated in Fig. 2b.

We have attempted some experiments in the cylindrical configuration depicted by Fig. 3 of our previous report COO-2407-7. Unfortunately, NaCl, melted in quartz tubes sealed under vacuum, reacts with the quartz to the extent that transparency is lost. We have, therefore, switched to AgCl which has a melting point of 455°C, and has a low vapor pressure ($<10^{-8}$ atm. at its melting point compared with 10^{-3} atm. for NaCl). This material might even be suitable for the horizontal boat method under an inert atmosphere.

3. Calculation of the Temperature Profiles in the Sample

Further progress has been made in the numerical calculation of temperature profiles for a partially melted sample in contact with a boat; the relevant geometry is depicted in Fig. 4 of our previous report COO-2407-7. In our previous numerical calculations, we had difficulty with the boundary conditions, particularly at the triple junction where the solid, liquid and boat meet each other. This has been resolved by setting the temperature at the triple junction equal to a conductivity weighted average of the temperatures at the four

nearest neighboring points and reducing the grid size in the finite difference scheme. For small enough grid sizes, the truncation errors associated with seemingly different, but supposedly equivalent, forms of the boundary conditions do not lead to significantly different results. We are now embarking on a systematic parametric study of the system for various conductivity ratios, sample thicknesses, and boat sizes.

C. Applications of Onsager's Reciprocity Theory to Transport Phenomena in Solids

Further effort has been expended in cooperation with Professor Mullins to form the basis of new work on the application of Onsager's theory of reciprocity to transport in solids. This is discussed in the Proposed Technical Program to which is appended the following publication:

"Proof of the Symmetry of the Transport Matrix for Diffusion and Heat Flow in Fluid Systems," by R. F. Sekerka and W. W. Mullins.

II. Expended and Contemplated Effort

This research is being conducted by the principal investigator, Professor Robert F. Sekerka, one full-time postdoctoral fellow, Dominique J. Billard, with the assistance of one graduate student, B. J. Farr, during the summer. Percentages of the expended effort are given in tabular form as follows:

III. Meetings Attended

Department of Energy, Germantown, Maryland, May 17, 1979, Seminar and discussions with R. Gottschall.

Knoxville, Tennessee, June 4-5, 1979, Conference on Structural Ceramics.

Preprints Removed