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

Progress Report
for Period December 1, 1976 - November 30, 1977

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ABSTRACT

Modeling of the process of Internal Centrifugal Zone Growth (ICZG) has been completed. Both one-dimensional models (for infinitely long samples and induction coils) and two-dimensional models show similar S-curve instabilities on heating, but the two-dimensional models serve to define the shape of the molten zone. Molten zone shape was found to be a sensitive function of RF skin depth in the solid and induction coil geometry. Changes in these parameters lead to zone shapes which change from convex to concave. Practical guidelines were established for the suitability of the ICZG process by calculating a maximum RF frequency to obtain a suitable surface-to-center temperature difference in the sample and a minimum frequency to avoid heating instabilities. For there to be an allowable frequency range, it is necessary that $2hR_s/k > 1$ where h is the surface heat transfer coefficient, R_s is the sample radius and k is its thermal conductivity; this limits ICZG to poor conductors (non-metals) except for very large samples and forced surface cooling. Experiments on silicon were used to verify the heating instability quantitatively. Internal susceptors were tried to heat oxides at low frequencies but led to local overheating and cracking.

PROGRESS REPORT

I. Technical Progress

The broad technical objectives of this contract are (1) to complete work on the modeling and extension of the process of Internal Centrifugal Zone Growth, and (2) to begin work on basic phenomena related to the solidification of non-metals. In connection with (1), theoretical modeling and experimental work are carried out at Carnegie-Mellon University and related experimental work is carried out in cooperation with Dr. G. W. Clark at the Oak Ridge National Laboratory.

A. Completion of Modeling of ICZG

Modeling of the process of Internal Centrifugal Zone Growth is now complete and has been documented completely in the doctoral thesis of Robert A. Hartzell; the title page, table of contents and abstract of this thesis are an Appendix to this progress report. Some noteworthy highlights are the following:

1. Two-dimensional modeling. The two-dimensional modeling of systems with finite induction coils and sample sizes has shown that the size and shape of the molten zone during ICZG are sensitive to the RF skin depth, δ , in the solid and to the induction coil geometry, but they are insensitive to the activation energy of the electrical conductivity, the RF skin depth in the liquid, and the surface heat transfer coefficient. The most dramatic effect of changing the skin depth δ is the change from a concave (Fig. 1a) to a convex (Fig. 1b) solid liquid interface as δ increases with

power adjusted to give a molten zone of the same maximum radius. The best operating skin depth from the point of view of zone shape is that between the concave and convex shapes; such a "flat" interface would avoid convergence or divergence of the various phases of eutectic-like composites and, hence, would lead to greater lamellar perfection. The effect of induction coil geometry is illustrated in Figs. 2a-d. The length of the molten zone increases with the length of the induction coil as expected. Changes in the diameter of the induction coil lead to changes in the convexity and concavity of the zone and also to changes in the zone length. Thus, both induction coil length and diameter must be varied to obtain a zone of desired length and flatness.

2. Practical guidelines have been established for ICZG and related processes.
 - i) To obtain a sufficiently large surface-to-center temperature difference for inductively heated samples requires a minimum RF skin depth which, in turn, leads to a maximum operating frequency

$$f_{\max} = \frac{16h^2}{\pi\sigma\mu k^2} \quad (1)$$

where h is the surface heat transfer coefficient, σ is the electrical conductivity, μ is the magnetic permeability and k the thermal conductivity (all properties of the solid near the melting point).

- ii) To avoid severe heating instabilities, one needs a maximum value of the RF skin depth of about half the sample radius, R_s .

This leads to a minimum operating frequency

$$f_{\min} = \frac{4}{\pi \sigma \mu R_s^2} \quad (2)$$

- iii) In order for there to be some allowable frequency range, we need $f_{\max} > f_{\min}$ which leads to the condition

$$\frac{2hR_s}{k} > 1 \quad (3)$$

Materials for which condition (3) is violated are unsuitable for ICZG; examples are metals with high thermal conductivities, k , unless the sample radius, R_s , is very large or forced cooling is used to get high values of the surface heat transfer coefficient, h . Even if condition (3) is satisfied, one needs an RF generator capable of delivering the proper power and in the frequency range between $f_{\min}$ and $f_{\max}$, as given by equations (2) and (3). This analysis has been applied to a number of materials for which a sufficient amount of thermal and electrical data exists in the literature and the results are presented in Tables I and II.

3. Experiments were conducted at CMU to test the results of the modeling for a semiconductor and for oxide systems.

- i) Silicon. A quantitative verification of the S-curve instability phenomenon was completed for a one-inch diameter cylinder of silicon at 450 kHz and the results are presented in Fig. 3. Heating with a susceptor enabled the sample to be held at a surface temperature of 1150°C at a current of 26 amps. A slow decrease in current caused a decrease in sur-

face temperature. If the current was restored to 26 amps before the surface temperature dropped much below 900°C, curve 1 was followed and the initial state of the system was restored. If, on the other hand, the current was not restored to 26 amps until the surface temperature dropped to 800°C, cooling continued as per curve 2. Within the accuracy of published data and of our model, our calculations are in accord with a rear knee of the S-curve at a temperature between 800°C and 900°C.

- ii) Oxides. Because we were limited to a 450 kHz RF generator at CMU, we were unable to heat oxide samples directly (note from Table II that the desired frequencies are all in the MHz range). (Experimental work on oxides in cooperation with Oak Ridge was reported in C00-2407-5) Consequently, the apparatus at CMU was used to study the RF coupling to samples with "internal susceptors"; these samples consist of large volume fractions (~25%) of tungsten in CeO_2 , La_2O_3 , ZrO_2 or mixtures of these oxides. Sixteen different samples were tried with results that can be generalized as follows: if the volume fraction of tungsten is too small, significant coupling with the RF field does not occur; whereas, if there is a large enough volume fraction of tungsten to promote significant coupling, the heating is localized to tungsten-rich regions which results in localized overheating and concomitant cracking. These tests indicate that "internal susceptors" are not a suitable substitute for a higher frequency generator.

4. Liaison with Oak Ridge.

Liaison was maintained with Dr. G. W. Clark and Mr. John Holder of Oak Ridge by telephone and by Dr. Clark's participation as an examiner for Mr. Hartzell's doctoral thesis defense at CMU. Oak Ridge has been supplied with copies of the thesis and will be supplied with forthcoming journal articles derived therefrom.

B. Basic Phenomena Related to the Solidification of Non-Metals

As indicated in our Proposed Technical Program for the period 1 December 1976 - 30 November 1977, we had planned to change direction and to embark upon a basic study of phenomena related to the solidification of non-metals. This phase of the work has barely begun but will be one of our main efforts during a three-month no-cost-extension requested from DOE for the period December 1, 1977 to February 28, 1978. This topic will also be the main thrust of our new Proposed Technical Program.

II. Expanded and Contemplated Effort

This research is being conducted by the principal investigator, Professor Robert F. Sekerka and one full-time graduate student, Mr. Robert A. Hartzell. Mr. Hartzell completed research for the Ph.D. degree in September of 1977 and is in the process of being replaced by another student for the remainder of the current contract period and possibly by a postdoctoral fellow thereafter. Percentages of the expended effort are given in tabular form below.

	← Expended →												Anticipated			
	1976		← 1977 →										1978			
	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	
Prof. Sekerka (Principal Invest.)	← 10% →						← 17.5% →			← 25% →						
Mr. Hartzell (Grad. Student)	← 100% →															
New Grad. Student(s)											← 50% →			← 100% →		

As mentioned in section IB above, part of the contemplated remaining effort will be to launch research on basic phenomena related to the solidification of non-metals. The additional objective during this period will be to re-write portions of Mr. Hartzell's doctoral thesis for journal publication.

III. Reports

Progress Report C00-2407-1 } Technical Report C00-2407-2 }	Submitted with first renewal
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Progress Report C00-2407-3	Submitted with second renewal
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Technical Report C00-2407-4 } Progress Report C00-2407-5 }	Submitted with third renewal
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Progress Report C00-2407-6	Submitted herewith
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Additional Documentation: Doctoral Thesis: "Modeling of Internal Centrifugal Zone Growth," by Robert A. Hartzell, Carnegie-Mellon University, September 1977.

Note: Portions of this doctoral thesis will be published in the form of three journal articles now under preparation and with titles as follows:

1. "Instability Phenomena During the RF Heating and Melting of Ceramics," by Robert F. Sekerka and Robert a Hartzell

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

IV. Meetings

Spring meeting of the Metallurgical Society of the AIME, Atlanta, Georgia, March 6-9, 1977 (financed in part by present contract).

ERDA Workshop on Phase Transformations, Lawrence Berkeley Laboratory, April 18-20, 1977 (financed through ERDA independent of the present contract but having to do with related subject matter).

Gordon Conferences on Ceramics, Tilton, New Hampshire, August 1-5, 1977. Invited speaker on "Chemical Potentials and Kinetics of Morphology Changes at Surfaces in Non-Metallic Solids."

Intermat Corporation, Waltham, Massachusetts, September 7-8, 1977 (regarding skull melting of oxides).

Fall meeting of the Metallurgical Society of the AIME, Chicago, Illinois, October 24-25, 1977 (financed in part by present contract).

Materials Research Society, Boston, Massachusetts, November 13-15, 1977.

Fig. 1a

Fig. 1. Surface temperature and isotherms in the cross section of one quadrant of a cylindrical sample during ICZG. Distances are measured in units of the sample radius and temperatures in units of the melting temperature. The hollow squares represent the cross sections of the R.F. induction coil: (a) RF skin depth of 0.2 of the sample radius and resulting concave solid-liquid interface (unit isotherm); (b) RF skin depth of 0.5 of the sample radius and resulting convex solid-liquid interface with much layer zone.

Fig. 1b

Figures (2a-d). Changes in molten zone shape and surface temperature for various sizes and proximities of the RF induction coil. Notation on curves is the same as Figure 1. In all cases, coil current was adjusted to give the same maximum molten zone diameter of 0.8 of the sample radius. Note especially the changes in length and curvature of the zone.

Fig. (2a)

Fig. (2b)

Fig. (2c)

Fig. (2d)

TABLE I

Operating conditions predicted by the theoretical model of ICZG
for non-oxide non-metallic materials.

material	minimum dia., cm	frequency	current amps	power KW
HAFNIUM BORIDE	12.2	490 HZ	4900	281
THORIUM TETRABORIDE	9.6	440 HZ	2300	44
TITANIUM DIBORIDE	7.5	870 HZ	1900	48
TUNGSTEN BORIDE	6.4	2 KHZ	1200	27
ZIRCONIUM DIBORIDE	2.5	10 KHZ	410	9
HAFNIUM CARBIDE	1.4	57 KHZ	200	6
DIMOLYBDENUM CARBIDE	14.1	200 HZ	3100	55
NIObIUM CARBIDE	4.6	110 KHZ	150	23
SILICON CARBIDE	0.9	5200 MHZ	1	1
TANTALUM CARBIDE	3.5	5 KHZ	760	19
THORIUM CARBIDE	1.5	50 KHZ	87	2
TITANIUM CARBIDE	5.8	3 KHZ	860	29
TUNGSTEN CARBIDE	3.9	1 KHZ	1500	55
URANIUM CARBIDE	4.7	5 KHZ	470	11
VANADIUM CARBIDE	10.9	760 HZ	1800	52
ZIRCONIUM CARBIDE	4.0	7 KHZ	650	25
BORON NITRIDE	2.2	8 MHZ	10	4
HAFNIUM NITRIDE	2.4	19 KHZ	290	8
TANTALUM NITRIDE	2.9	13 KHZ	390	12
TITANIUM NITRIDE	2.6	12 KHZ	260	5
CHROMIUM DISILICIDE	105.8	37 HZ	14000	1476
CHROM. MANGAN. SILICIDE	13.4	1 KHZ	390	5
MANGANESE SILICIDE	11.0	10 KHZ	85	2
MANGANESE DISILICIDE	168.8	29 HZ	15000	2062
MOLYBDENUM DISILICIDE	2.4	18 KHZ	160	3
URANIUM TRISILICIDE	5.3	4 KHZ	340	6
CERIUM SULFIDE	1.1	710 KHZ	5	1
LANTHANUM SULFIDE	1.7	560 KHZ	5	1
PRASEODYMIUM SULFIDE	2.0	400 KHZ	8	1
SAMARIUM SULFIDE	4.7	56 KHZ	33	1
BISMUTH TELLURIDE	18.3	970 HZ	220	2
INDIUM TELLURIDE	3.2	1 MHZ	3	1
LEAD TELLURIDE	3.5	270 KHZ	11	1
ZINC ANTIMONIDE	7.9	33 KHZ	22	1
INDIUM ARSENIDE	16.4	61 HZ	1600	6
GERMANIUM	41.5	240 HZ	1300	33
SILICON	23.0	1 KHZ	780	39

TABLE II

Operating conditions predicted by the theoretical model of
ICZG for oxides.

material	sample dia.,cm	frequency	current amps	power KW
ALUMINUM OXIDE	3.0	90000 MHZ	1	2
BERYLIUM OXIDE	3.0	45000 MHZ	1	6
CERIUM DIOXIDE	3.0	450 KHZ	69	13
HAENIUM DIOXIDE	3.0	5 MHZ	22	14
MAGNESIUM OXIDE	3.0	450 MHZ	2	13
SILICON DIOXIDE	3.0	45000 MHZ	1	1
THORIUM DIOXIDE	3.0	45 KHZ	240	16
TITANIUM DIOXIDE	3.0	230 MHZ	1	1
URANIUM DIOXIDE	3.0	5 MHZ	15	7
ZIRCONIUM DIOXIDE	3.0	5 MHZ	16	7

APPENDIX

MODELING OF INTERNAL CENTRIFUGAL ZONE GROWTH

by

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ABSTRACT

The electric and temperature fields within inductively heated materials have been calculated in order to better understand the essential features of the crystal growth process called Internal Centrifugal Zone Growth (ICZG). It has been found that electrical conductivities that increase with temperature like those of oxides are responsible for a heating instability. There has been considerable effort directed towards an increased understanding of this instability, because it is recognized as the root cause of many of the experimental problems associated with this growth technique. Fortunately, the modeling has been able to predict that the instability can be controlled through a judicious choice of RF frequency, sample size, and sample doping. Another area of investigation has been the effect of induction coil geometry and frequency on the shape of the solid/liquid interface, an important consideration in crystal growth. Besides the one- and two-dimensional modeling of steady states, solution of the time-dependent differential equations for the electric and temperature fields, combined with an analysis of the RF generator/sample interaction, has provided considerable information concerning the formation of the initial melt zone, the relationship between generator meter readings and internal heating, and methods of control for future automation. Various predictions of the modeling such as the heating instability and generator/sample interaction have been confirmed by an experimental investigation of internal heating in silicon and ceria-based ceramic-metal composites.

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