Noncontact Temperature Measurement - Requirements and Applications for Metals and Alloys Research

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Temperature measurement is an essential capability for almost all areas of metals and alloys research. In the microgravity environment many of the science priorities that have been identified for metals and alloys also require noncontact temperature measurement capability. For example, in order to exploit the full potential of containerless processing, it is critical to have available a suitable noncontact temperature measurement system. This system is needed to track continuously the thermal history, including melt undercooling and rapid recalescence, of relatively small metal spheres during free-fall motion in drop tube systems. During containerless processing with levitation - based equipment, accurate noncontact temperature measurement is required to monitor one or more quasi-static samples with sufficient spatial and thermal resolution to follow the progress of solidification fronts originating in undercooled melts. In crystal growth, thermal migration, coarsening and other experiments high resolution thermal maps would be a valuable asset in the understanding and modeling of solidification processes, fluid flows and microstructure development. The science and applications requirements place several constraints on the spatial resolution, response time and accuracy of suitable instrumentation.

Introduction

Melts and alloys constitute a critically important category of engineering materials. Many of the applications of metals frequently depend on structure sensitive properties which reflect the microstructural details and processing history of an alloy. The processing of most metals and alloys usually involves a solidification step, during which a gravitational field may have dramatic effects on microstructure and on those properties influenced by microstructure. There are several well established examples of microstructural influences of gravity in the areas of solidification, crystal growth, containerless processing and supercooling of metallic melts. Gravity has a direct bearing on buoyancy induced convection and on the resulting chemical segregation levels produced by solidification. An important component in the progress that has been achieved in controlling solidification processing has resulted from a closer study of the relationships between the liquid transport and the solidification interface. This understanding has resulted from the ability to quantify the conditions at the solidification interface in terms of the relevant compositions of liquid and solid and the interface temperature.

In the microgravity environment there are new opportunities for controlling the solidification process. One of the most important is the minimization of convective flows to allow better control of melt temperature and composition. Similarly, sedimentation types of effects can be reduced considerably. There are also new possibilities for melt processing including containerless processing to avoid the affects of crucible induced contamination of reactive liquids. However, to optimize the advantages and

to realize the new opportunities for processing it is vital to have accurate temperature measurements which because of the new processing routes are also required to be of a non-contact nature.

Non-Contact Temperature Measurement Requirements

Metals and Alloys

In addressing the science priority needs in the metals and alloys discipline a Metals and Alloys Discipline Working Group has been active for the past several years in formulating plans (1). A summary of the key science areas that have been identified by the members of the Discipline Working Group for microgravity processing is presented in Table 1. For the most part, the key science areas relate to liquid processing or the treatment of liquid-solid mixtures and the microstructural consequences of solidification. An important addition refers to measurements of thermophysical properties which are critical to the effective development and testing of solidification models. It should also be emphasized that the science priority areas are continually being examined for revision and updating.

In order to illustrate the non-contact temperature needs in the metals and alloys discipline a full discussion of all the science areas in Table 1 is not required. Instead a few areas will be highlighted to demonstrate the requirements.

Dendritic Microstructures

The phenomena of dendrite coarsening is important in determining the overall solidification microstructure with regard to the microstructural scale. The typical effects involved in coarsening are illustrated in Fig. 1 which comes from the work of Voorhees and Glicksman (2). A series of secondary dendrite arms is illustrated with a distribution in sizes that has

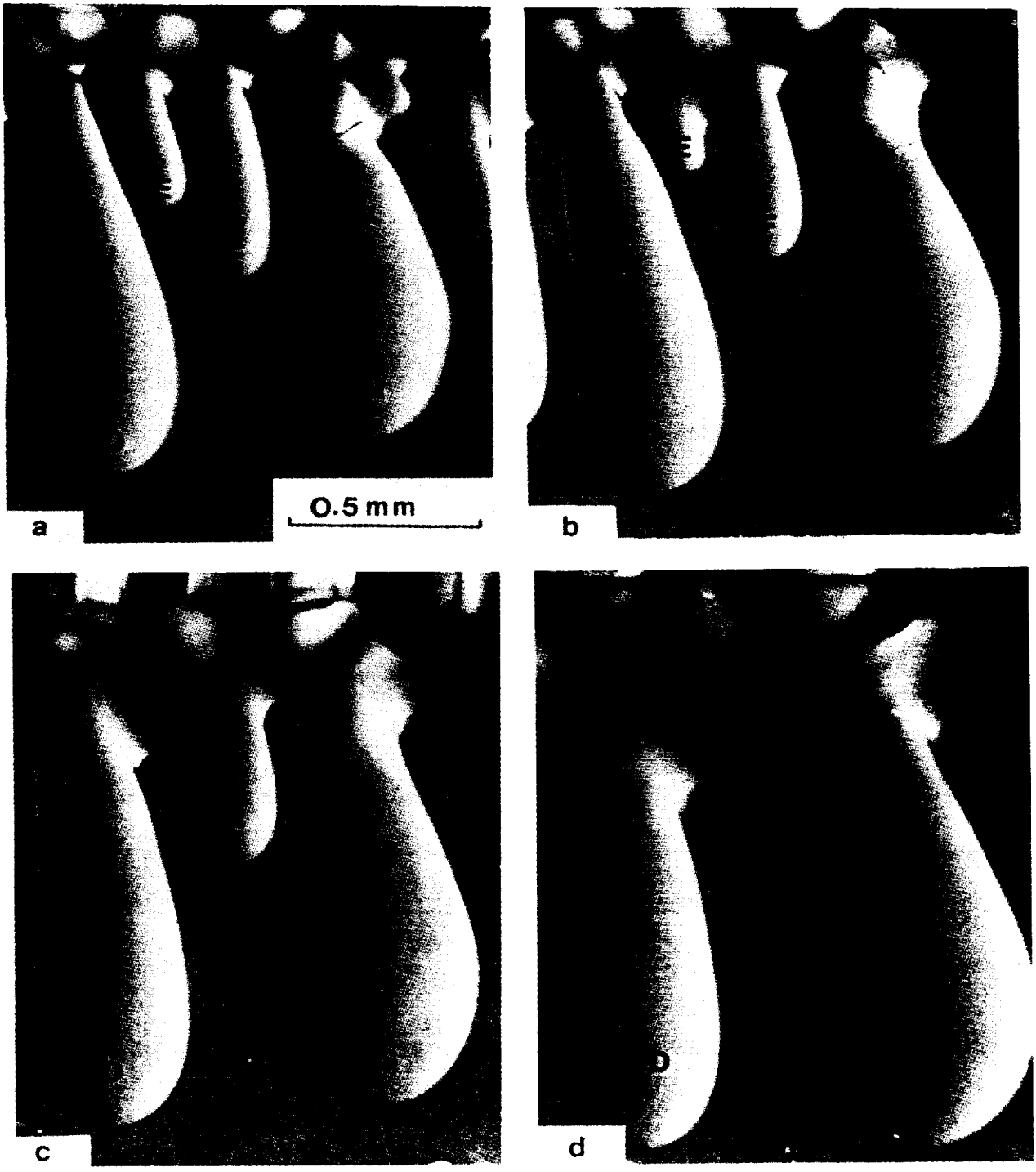


Fig. 1 Sequence of photomicrographs showing dendritic side branches evolving in time (a-d) under nearly isothermal conditions (from ref. 1).

developed as a result of competitive growth due to melting point differences produced by differences in local radius of curvature. To characterize the thermal distribution within such a microstructure is necessary to have the resolution of measurement be of the order of the scale of the microstructural features i.e., secondary dendrite arm spacing. Although in the situation shown in Fig. 1 this scale is rather large, at the early stages of dendritic growth the scale becomes much finer as illustrated in Fig. 2. Furthermore, the sequence of dendritic growth events illustrated in Fig. 2 demonstrate very rapid growth associated with dendrite microstructures. This rapid growth is also related to the fineness of the microstructural scale and exhibits a steep dependence on temperature. In fact, at much larger values of supercooling of the order of 10-100°C, dendrite growth volocities of the order of tens of meters per sec have been recorded (3). Thus, in dendrite coarsening a high spatial and thermal resolution is required due to the microstructural scale and the relatively small temperature differences involved. On the other hand, in the case of dendritic growth, a very rapid temperature response and accurate temperature measurement is required in order to resolve the dependence of dendrite velocity upon undercooling.

Containerless Processing

Containerless processing involves the thermal treatment of a volume of material usually as a liquid in a suspended state free from a supporting vessel. During containerless processing potential contaminants originating from a crucible and possible heterogeneous sites for nucleation catalysis of the liquid that can be associated with a crucible may be avoided. A high purity melt can be maintained even with reactive materials at elevated temperatures. This can allow for the reliable measurement of thermophysical properties and for the study of chemical reactions in liquids which are

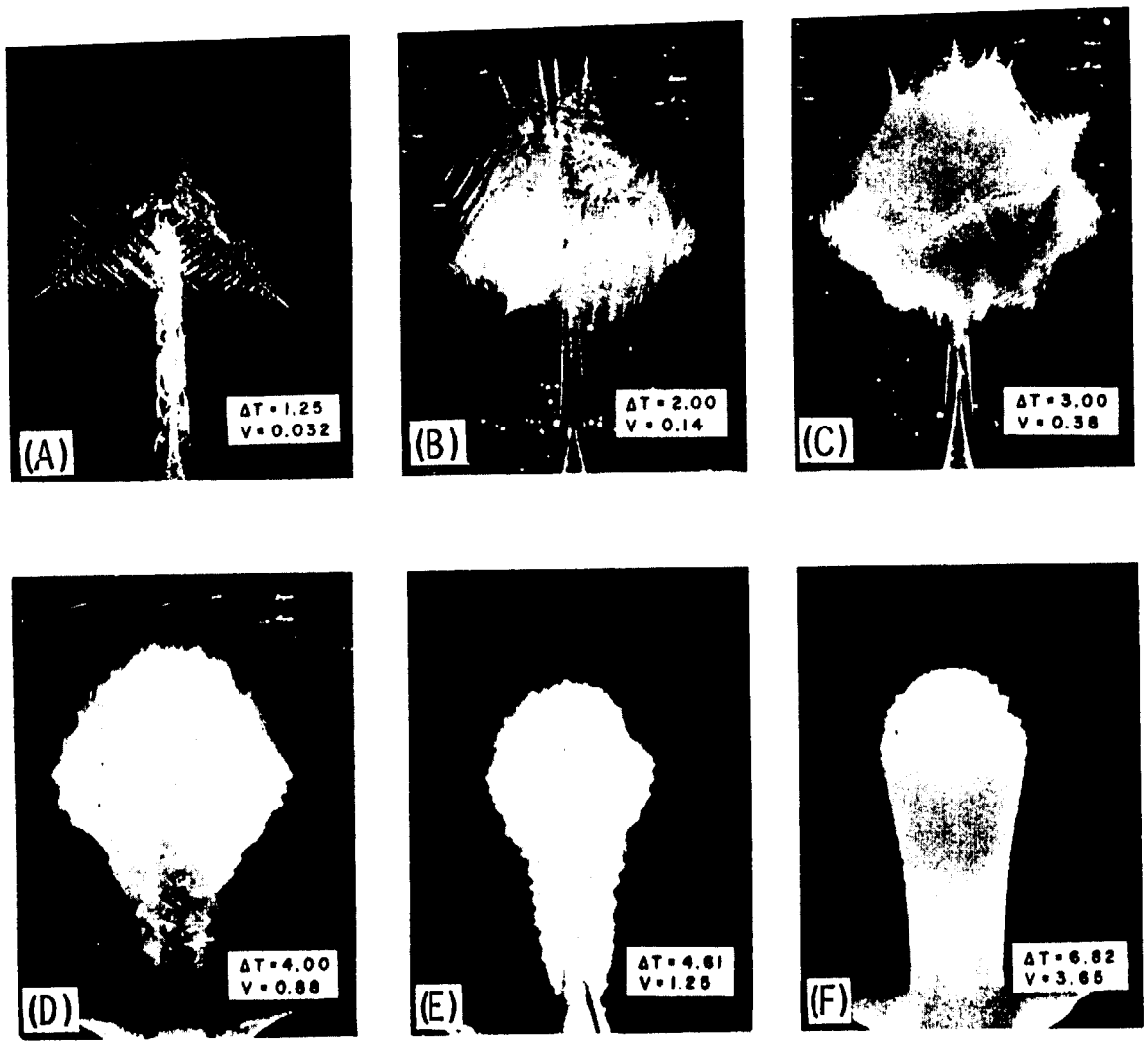


Fig. 2 Sequence of photographs showing dendritic growth at various levels of melt supercooling and steady state growth rates, V.

usually difficult to handle due to their reactivity. The elimination of crucible induced nucleation can lead to large supercooling, to the development of novel solidification microstructures, and to the formation of metastable phases. A microgravity environment facilitates the application of containerless processing and with externally applied positioning fields allows for the treatment of much larger volumes than are possible during ground based processing.

A variety of containerless processing techniques have been developed as illustrated in Fig. 3. In each case a crucible is not used. Instead, either a free fall environment or an environment in which a molten sample is held in position through some externally applied force is used. The containerless processing approach illustrates many of the specific needs of non-contact temperature measurement in the metals and alloys discipline. These requirements can be illustrated by highlighting the conditions involved in drop tube processing. Drop tube processing is a containerless technique in which solidification occurs as a molten sample undergoes free fall through a chamber. While elimination of crucible induced nucleation can encourage liquid supercooling during processing, the presence of catalytic sites associated with internal impurities or the particle coating may limit the level of supercooling obtained during the falling period. With fine droplets nucleation sites may be isolated, allowing most of the particles to supercool more deeply (4). The coating may be modified to alter the catalytic potency of surface nucleation sites through the control of the gas environment during processing. The gas environment also influences the thermal conductivity and the resultant cooling behavior during solidification. High cooling rates can promote alternate microstructure formation during solidification under a

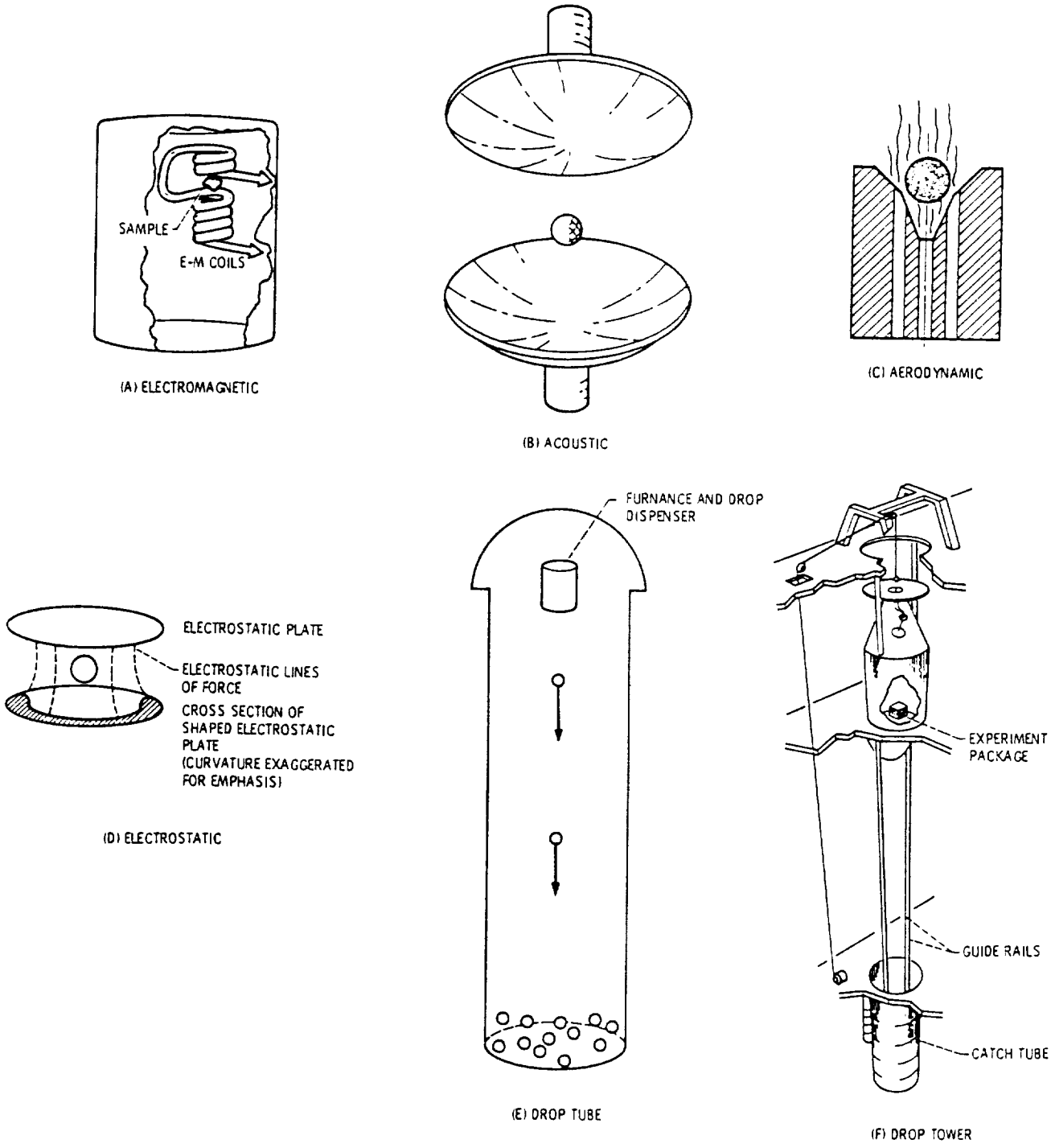


Fig. 3 Illustration of the variety of containerless processing techniques that are available.

containerless condition. Therefore, drop tube processing allows for the study of solidification under conditions of high supercooling during the free fall period which simulates the conditions of the microgravity environment.

While long drop tubes of the order of 100 m allow for the processing of sample diameters in the order of 1 cm, laboratory drop tubes of the order of 3-5 m in length are restricted to smaller diameters of the order of 100-300 microns. In each case however, the temperature requirements are similar in that one would like to measure the temperature continuously during the free fall period. At present, continuous recording of the temperature of a falling particle is not possible. In order to address the problem of temperature measurement, a variety of alternate approaches have been tried and are continually to be developed further. These developments are equally applicable to other forms of containerless processing and have been centered along three main areas. These areas include: the use of internal droplet microstructural information to calibrate the temperature changes during solidification, the application of heat flow analysis combined with droplet structure information to infer some of the thermal history of a sample and the application of some instrumentation combined with heat flow calculations to arrive at an estimate of the thermal history.

Microstructural Evaluation of Thermal History

A useful technique for determining the thermal history of a particle during drop tube processing is to relate the scale of the microstructure to the temperature of the droplet during solidification. A eutectic alloy solidification that results in the formation of a normal type cooperative solidification product is most useful for this purpose. This allows a correlation to be made between eutectic spacing and the undercooling at nucleation. Using thermal analysis of powders, control over the size and

cooling rate allows for different levels of undercooling to be achieved below the eutectic temperature as illustrated in Fig. 4 for a InSb-Sb eutectic alloy (5). Through quantative image analysis, the onset eutectic spacing can then be determined for each undercooling level as summarized in Fig. 5. In agreement with eutectic growth theory, the eutectic spacing, λ, values are related to the initial undercooling ΔT by the following relation;

$$\ell n\ (\lambda) = -3.48 - 1.56\ (\ln\ \Delta T) \qquad (1)$$

Using this expression the undercooling level for samples processed in a drop tube can be assessed. Furthermore, based upon directional solidification data a model was derived to relate the eutectic spacing to the solidification rate and can also be applied to both the thermal analysis and drop tube processed samples. For the InSb-Sb system an increase in undercooling from 0.1-0.2 T_e resulted in a decrease in the onset eutectic spacing from 275-93 nm and a corresponding increase in the initial growth rate 0.23-2.2 cm/sec.

Microstructural examination of the undercooled eutectic powder revealed two well defined morphological regions as illustrated in Fig. 6. A rod type eutectic structure forms upon nucleation at the droplet surface and is maintained with a increase in rod spacing as a re-heating or recalescence occurs due to the release of the heat of fusion during solidification. As growth slows with continued recalescence, external cooling begins to assist in removal of the latent heat and a transition from a rod to lamellar growth occurs which allows for most efficient heat flow. The eutectic spacing for the rod morphology is determined by the initial undercooling and thermal conditions during droplet recalescence, while the lamellar spacing is controlled by heat transfer to the surroundings. The microstructures

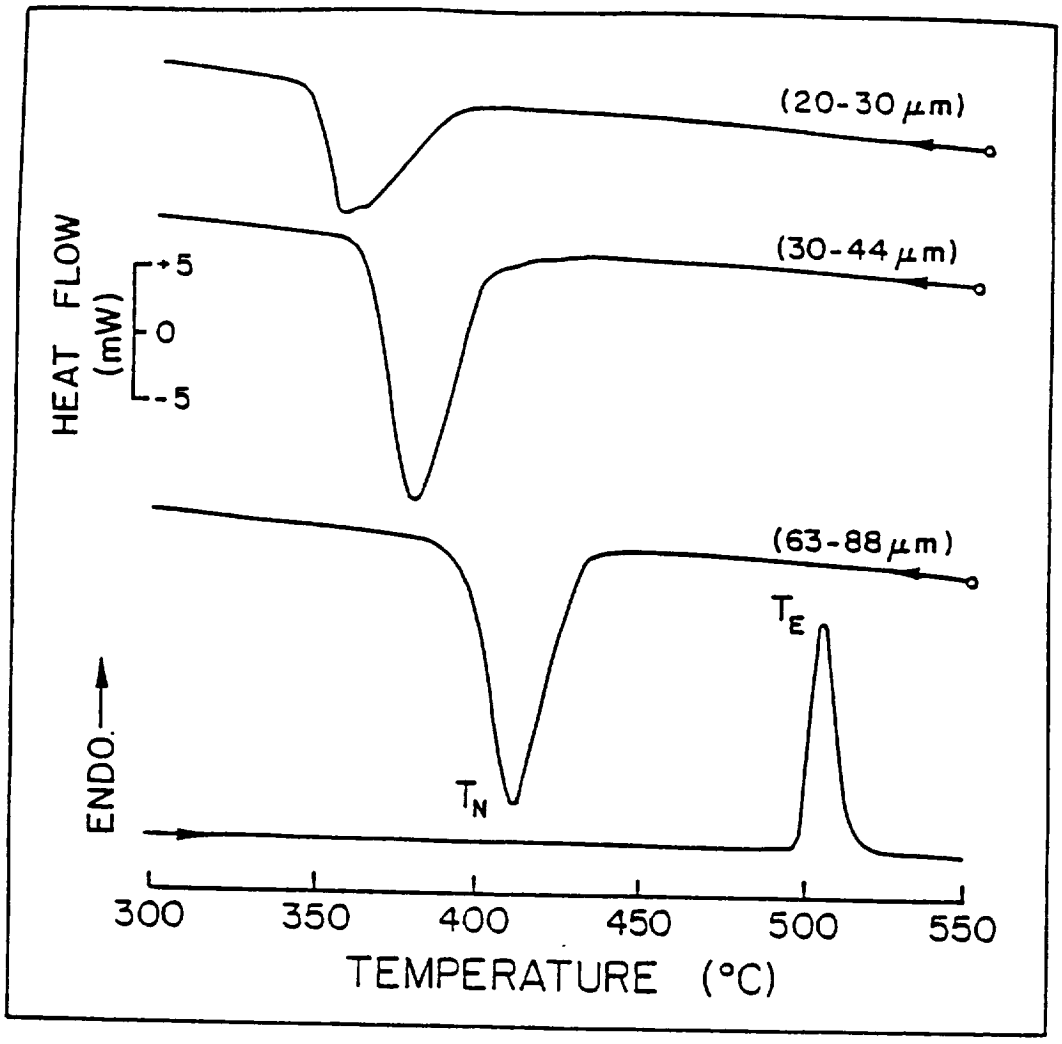


Fig. 4 DTA thermograms indicating the dependence of undercooling on droplet size for a InSb-Sb eutectic alloy.

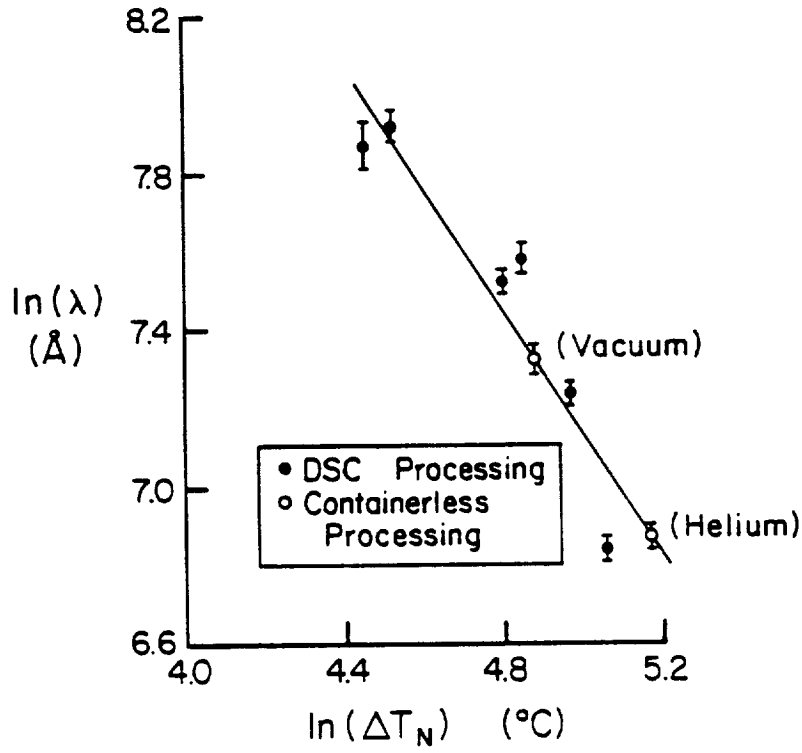
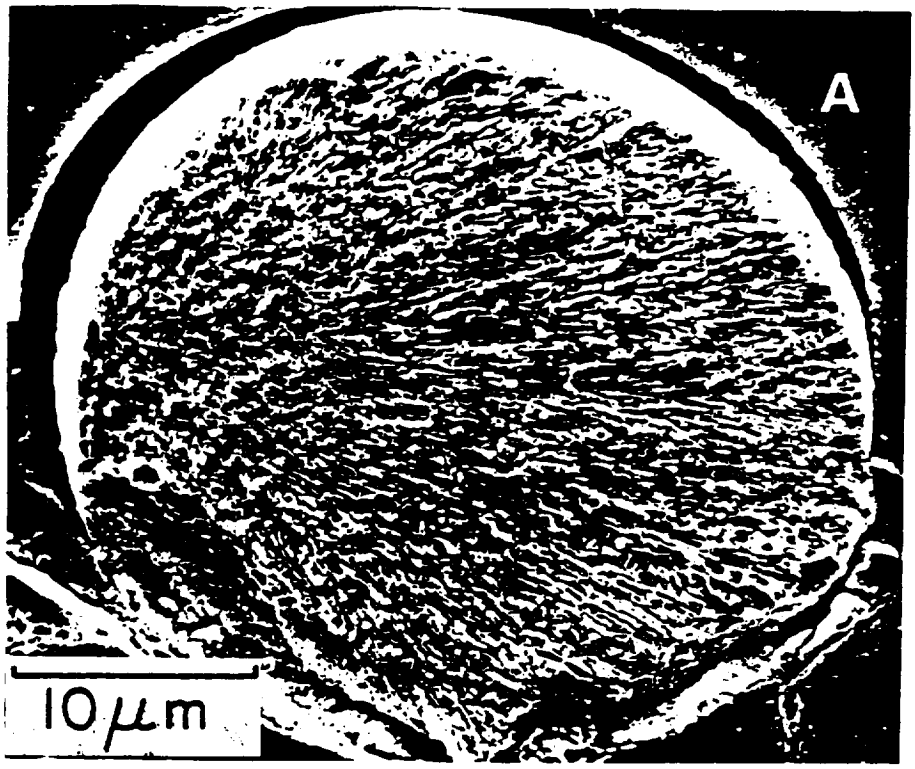


Fig. 5. Variation in onset eutectic spacing with undercooling at nucleation for InSb-Sb eutectic powder.



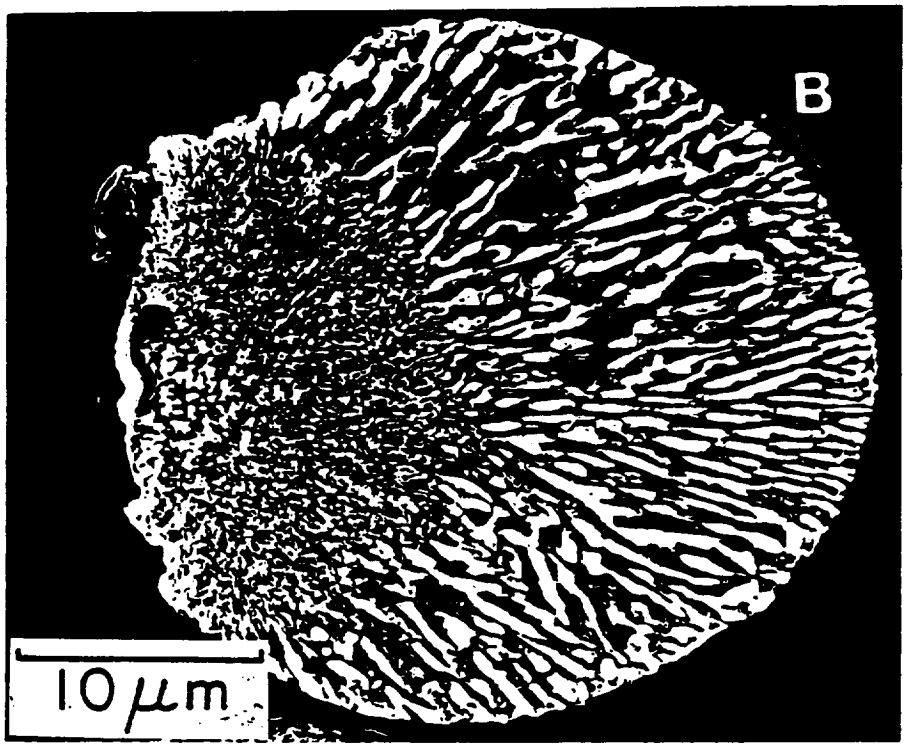


Fig. 6. SEM micrographs illustrating the eutectic structure developed in undercooled InSb-Sb powder, drop tube processed under (a) He gas and (b) vacuum conditions.

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developed in similar size powders by drop tube processing under helium and vacuum conditions are compared in Fig. 6. The rod spacing is much finer for the helium processed sample reflecting an increased level of undercooling and a higher cooling rate. Furthermore, the application of the relation in Eq. 1 to detailed microstructural information on the progress of solidification across the drop allows for the interface temperature to be inferred at different stages of solidification so that a more complete thermal history for the sample may be evaluated. While this approach is quite effective and relies upon a eutectic solidification reaction, the occurrence of eutectics is fairly widespread and represents one of the most interesting solidification type reactions.

Heat Flow Analysis

During drop tube processing the cooling of a liquid droplet is due partially to radiator heat transfer and also to convective heat transfer. The temperature history of a liquid droplet during drop tube processing may be described by the following governing equation (6) as:

$$\frac{dT}{dt} = - \frac{\epsilon A \sigma}{mc} (T^4 - T_w^4) - \frac{hA}{mc} (T-T_a) \qquad (2)$$

where T_a is the gas film temperature, approximately $(T+T_g)/2$, T_g is the gas temperature, T_w is room temperature, t is the time, ϵ is the emissivity of the liquid, A is the surface area of the droplet, σ is the Stefan-Boltzmann constant, m is the mass of the droplet, c is the specific heat of the liquid and h is the heat transfer coefficient.

A finite difference method can be applied to eq. 2 to calculate the liquid droplet temperature as a function of falling distance in the drop tube and is illustrated for an Fe-Ni alloy in Fig. 7. In order to access the undercooling an experimental approach was developed to determine where the falling drop solidifies in the drop tube. A copper substrate was held at fixed distance from the initial drop point. If the drop was molten upon impacting the platform, the shape would be a splat, while if solidification had started before impact a spherical or hemispherical particle would result. By varying the platform height, the position at which solidification occurred could be determined and used with the calculation summarized in Fig. 7 to estimate the undercooling. For the case of an Fe-30 w/o Ni alloy an undercooling of about 120°C below the stable liquidus was attained in a 2 mm drop (Fig. 7). Similar experiments were conducted on Fe-10, 20 and 25 w/o Ni alloys. The undercooling results coupled with the Fe-Ni phase diagram are shown in Fig. 8. For the alloys with 10 and 20 w/o Ni a metastable BCC phase formed, while for alloys of 25 and 30 w/o Ni the stable FCC phase was produced. These results agree well with the calculated metastable phase boundaries. Therefore, the formation of the metastable BCC phase provides a measurement of the minimum undercooling. The consistency between the minimum undercooling estimate, the solidification free fall distance measurement and the heat flow calculation provides support for this approach to the analysis of the thermal history during drop tube processing.

Thermal Measurements

Another example of an attempt to judge the thermal history during drop tube processing has been developed for use with the NASA/MSFC 105 m drop tube (6). As illustrated in Fig. 9, a two color pyrometer is used for initial temperature determination of the sample at the top of the drop tube prior to

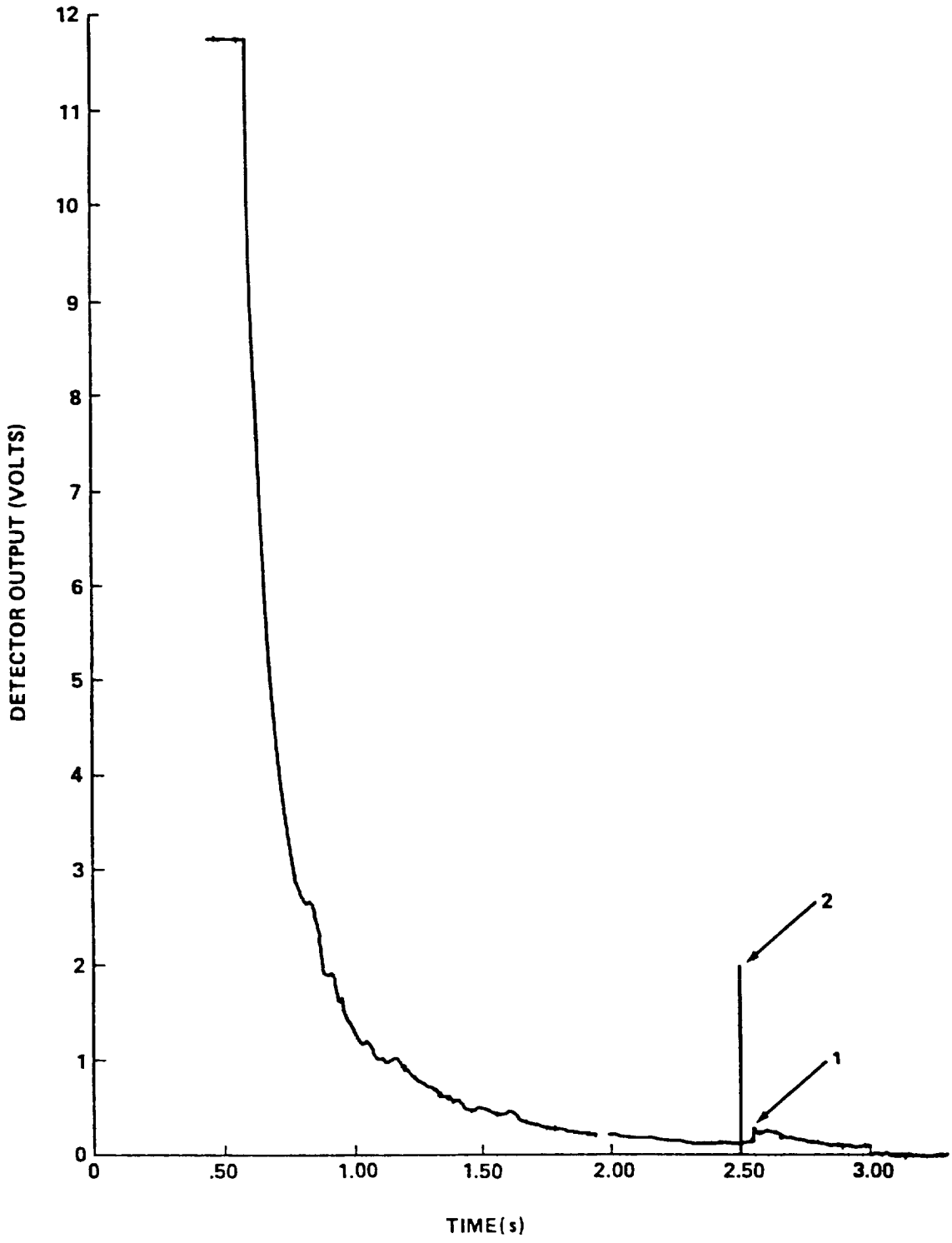

Fig. 7 Schematic illustration of the main components in the NASA/MSFC 105 m drop tube. (From ref. 6).

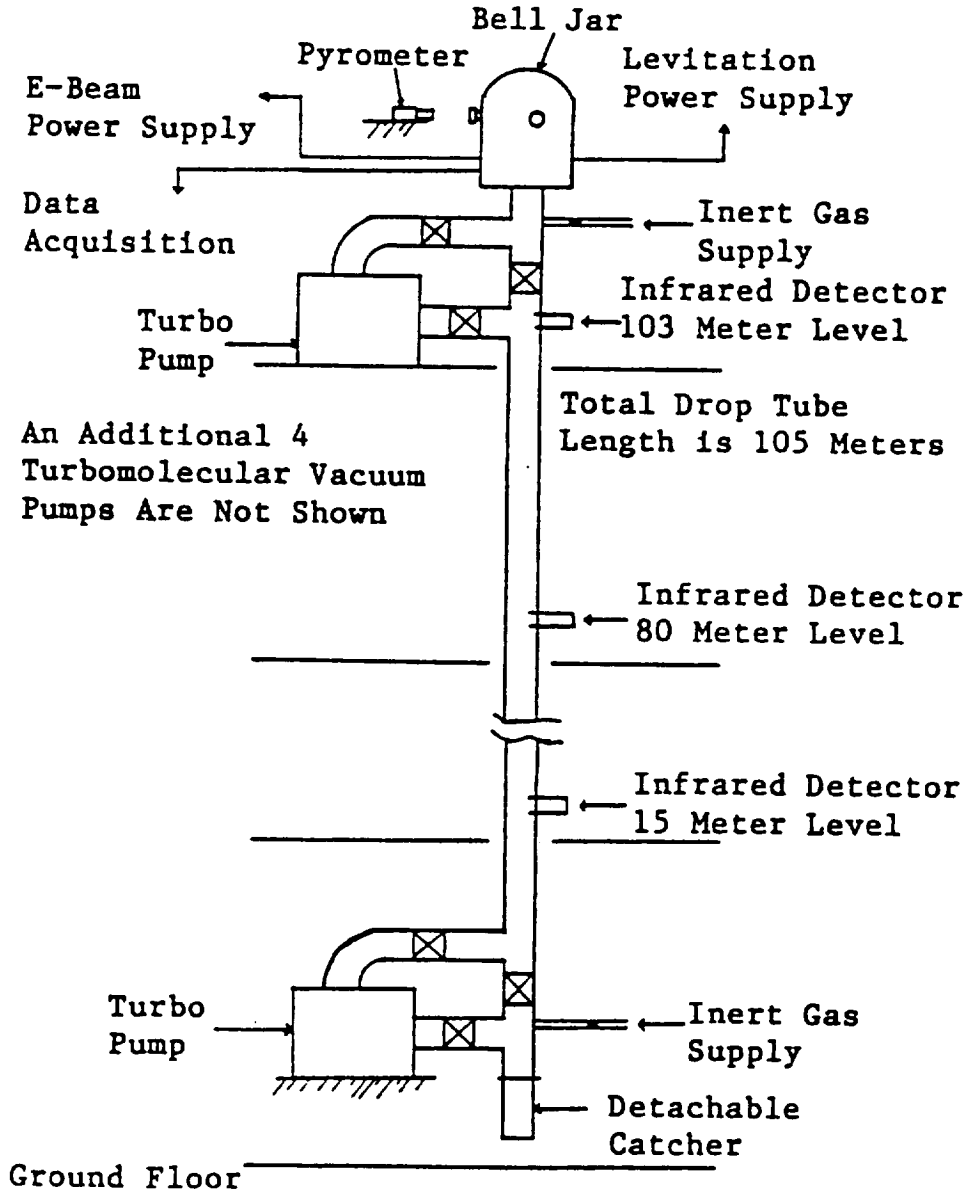

Fig. 8 Computer-stored infrared detector signal for a Nb-Ge alloy drop. (From ref. 6).

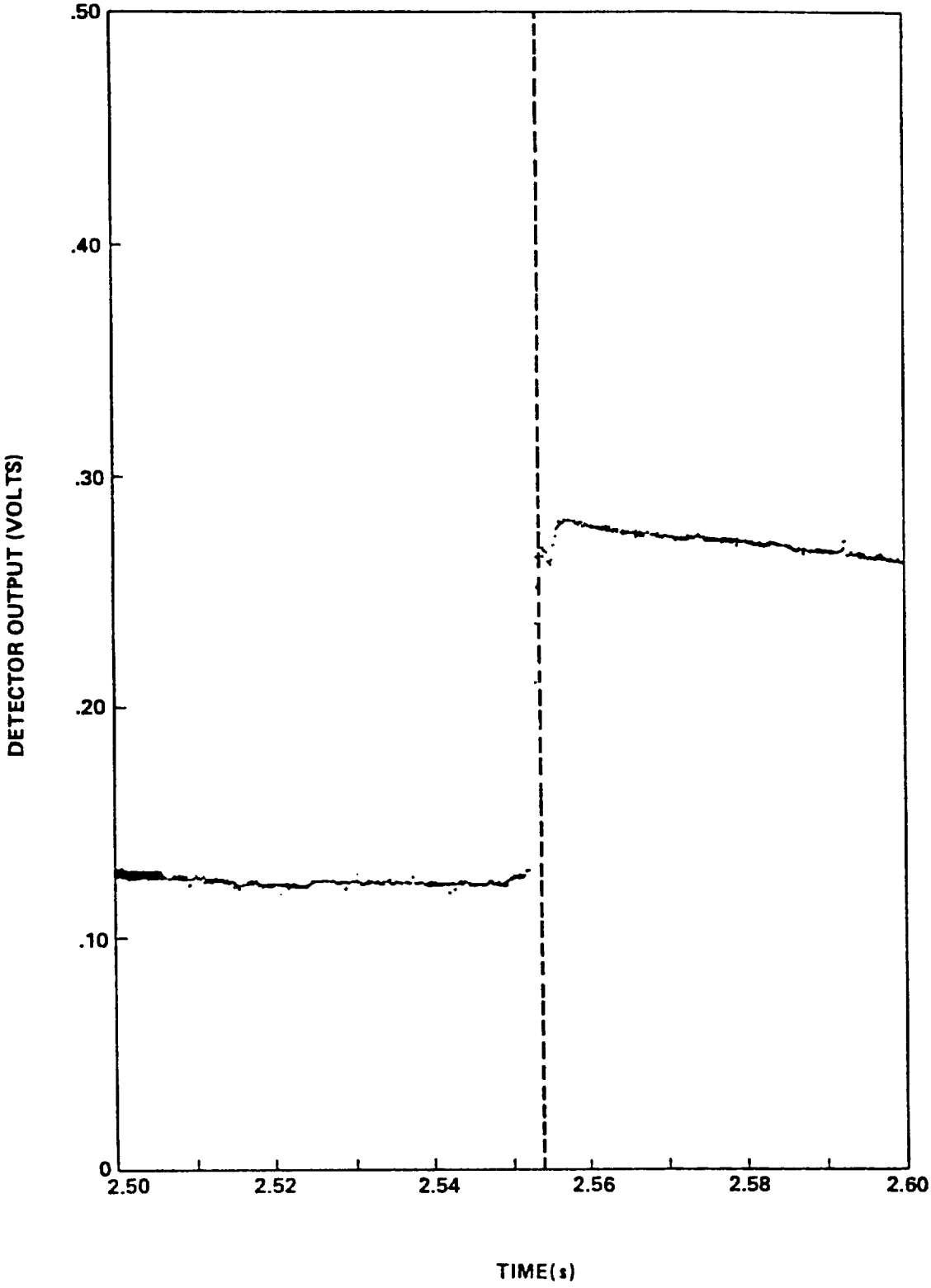

Fig. 9 Expanded recalescence peak for a Nb-Ge alloy drop. (From ref. 6).

release. The samples are allowed to free-fall the entire length of the drop tube. During the fall the recalescence event associated with the nucleation is detected by a series of infrared sensors. With a knowledge of the release temperature at the top of the tube and the cooling time to recalescence which is measured by the infared sensors, the undercooling can be calculated from a heat flow analysis. The uncertainty in the calculations of undercooling for samples processed in this manner is of the order of ± 50°C. Part of the uncertainty in temperature determination is due to incomplete knowledge of the thermophysical properties of liquid metals such as the specific heat. With this approach significant undercooling levels of about 23% of the melting temperature have been obtained for a number of high melting temperature metals and alloys. The example shown in Fig. 10 is for a Nb-Ge alloy drop. In an expanded view shown in Fig. 11, the details of the recalescence event are apparent. The recalescence behavior is an important component of the microstructural development because it relates to the period of rapid crystal growth following nucleation from a highly undercooled state. The details of this process are more clearly illustrated in Fig. 12 which represents results from a Ni-Sn eutectic alloy that was processed with an electromagnetic levitation system (7). The measured time periods for the duration of the recalescence portion of solidification approach milliseconds for this particular alloy and illustrate the high speed response required. When it is considered that only one such recalescence event will occur over the entire length of a long drop tube, the demands on the instrumentation become clear. Perhaps this is the reason that a fully instrumented approach to drop tube processing is not yet available, but certainly is urgently needed for all aspects of research and development in containerless processing.

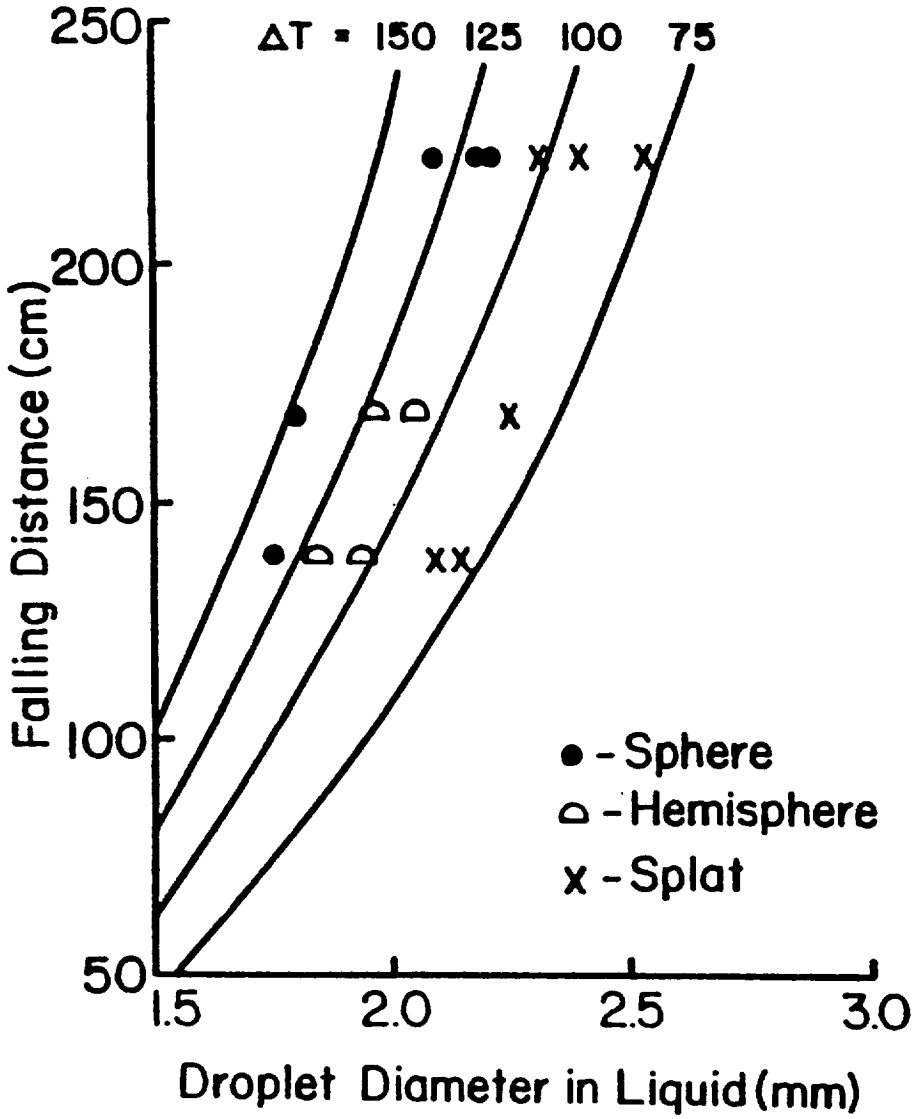

Fig. 10 The calculated undercooling curves during free fall, with droplet shape observation summary (superheat of 200°C).

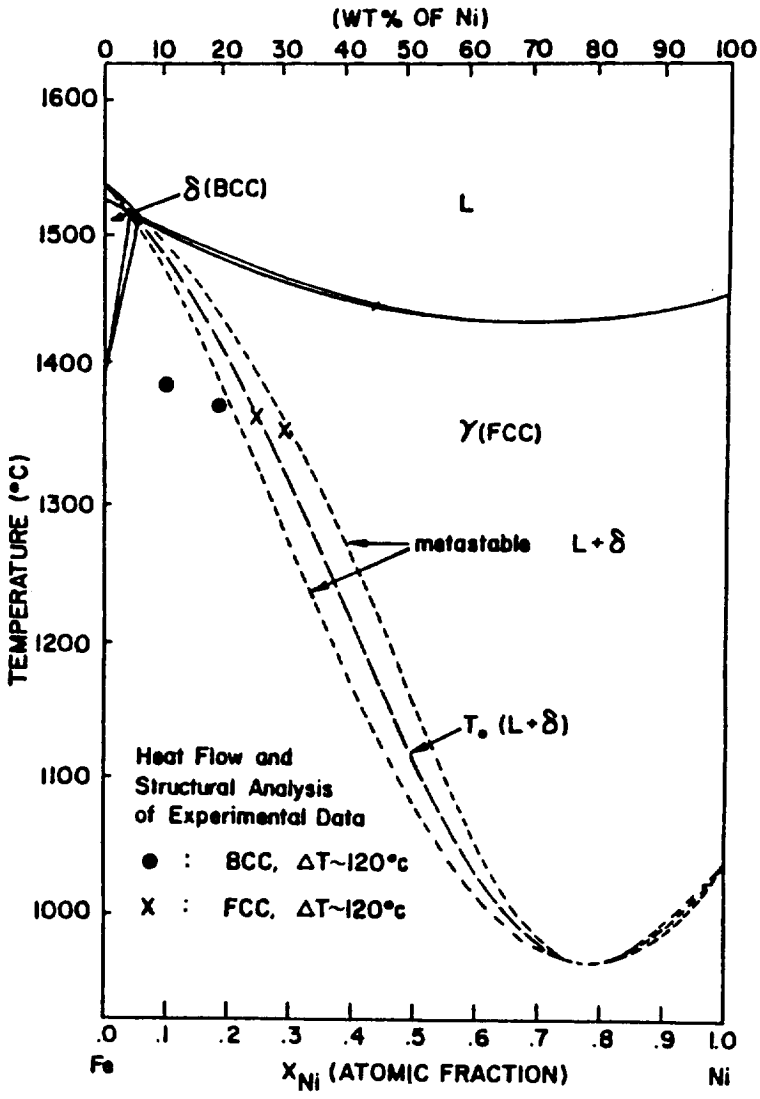

Fig. 11. Fe-Ni phase diagram showing metastable phase boundaries and estimated drop tube sample undercooling values.

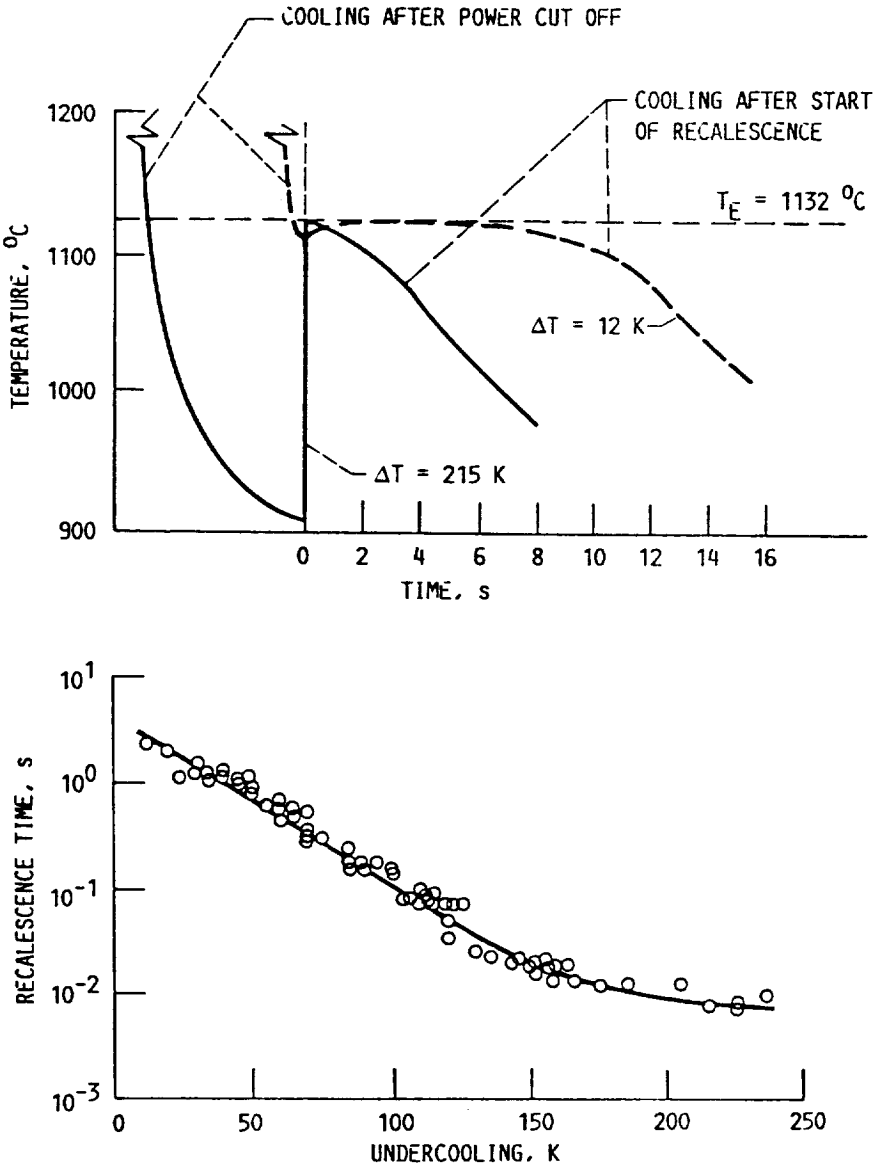

Fig. 12 a) Cooling curves for a eutectic Ni-Sn alloy at two levels of undercooling. b) Recalescence time and initial undercooling for a Ni-Sn eutectic sample. (From ref. 7).

Microstructure Prediction-Design

The overall development of a microstructure depends upon a number of processes occurring both serially and in parallel. For example, nucleation, growth, coarsening, convection, coalescence, and solid state reactions are some of the more significant processes. Ideally one would like to predict the outcome of these unit processes and develop methods for analyzing the resultant microstructure and properties. In a number of physical phenomena related to materials processing it is possible to identify material behavior in terms of a few characteristic parameters which can be expressed in terms of dimensionless groups. Over the range of values that the dimensionless groups are valid, the response of the material can be scaled so that the magnitude of the response at one value is related in some simple way to its response at some other value.

At present the most successful scaling laws are based on diffusional transport and morphological stability. Additional phenomena such as convection and nucleation are also included to complete the modeling of microstructure. For example the expected microstructures for growth conditions encountered in various domains of growth rate-thermal gradient are illustrated in Fig. 13 (8). It is important to note that the structural transitions occur at constant cooling rate which is the product of velocity and thermal gradient. The information provides a design tool for microstructure change. It also illustrates the importance of knowledge of temperature gradient as well as growth rate during solidification processing.

Another case where temperature gradient information is important is in the thermosolutal migration of bubbles and drops. When a system containing a second phase of vapor bubbles or liquid droplets is subjected to a thermal gradient an inbalance of intefacial tension around the drop or bubble will

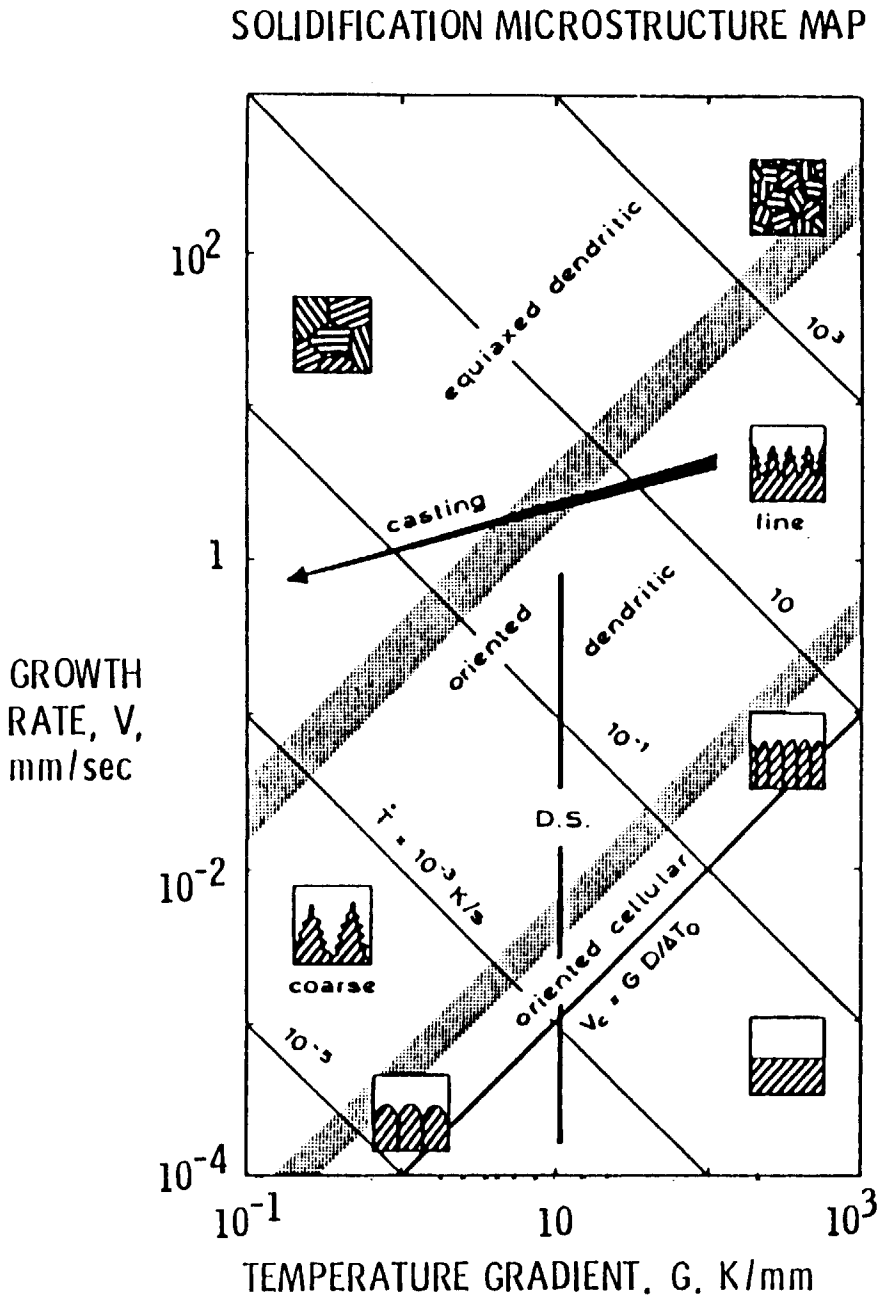

Fig. 13 Illustration of the expected microstructures from growth conditions encountered in various domains of growth rate and temperature gradient. (From ref. 8).

develop because the interfacial energy is a function of temperature. This force inbalance will drive convective flows called Marangoni Convection and is important to understand when a microgravity environment causes a suppression of density driven convection flows.

Summary - Non Contact Temperature Measurement Requirements

Based upon these few illustrations and a number of other important processing operations in the metals and alloys discipline area it is possible to formulate an initial set of recommendations for the types of noncontact temperature measurement capability that is important to support future materials research under microgravity conditions. These recommendations and requirements are summarized in Table 2. The three basic categories involve the ability to measure high temperature and to measure these temperatures with relatively rapid response rates and accommodate a range of heating rates as well as cooling rates encountered in containerless processing and other materials operations. A fine spatial resolution is required along with a rapid response in order to determine with accuracy the thermal gradients involved in processing as well as thermal profiles on relatively fine scale dimensions. With this thermal measurement capability one can not only monitor the growth rate on the average, but also develop thermal maps for the entire microstructural evolution which are needed in order to develop successful models to describe in analytical terms the evolution of microstructure in a microgravity environment.

Acknowledgement

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Table 2

Metals and Alloys

Non-Contact Temperature Measurement

Requirement	Application
*High Temperature	- 500 to 4000 K, with ± 1K resolution (Containerless Processing) (Alloy Solidification) (Phys. Prop. Measurement)
*Fast Response	- Cooling Rates (10^4 - 10^6 K/s) - Recalescence Reheating (10^5 K/s) - Drop Tube Free Fall - Nucleation Undercooling ($T_M - T_N > 100$ K)
*Fine Spatial Resolution	- Temperature Gradients (0.1 K/cm - 10^5 K/cm) - Thermal Profiles in Phase Mixtures and Powders (<1 micron, dT < 1° C 1 - 5 cm^2) - Thermal Maps for Morphological Development and Thermosolutal Flows - Monitor Crystal Growth Rates (10^{-2} cm/s to 100 cm/s)

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Table 1

Metals and Alloys

Science Priority Areas

A. Coarsening and Stability of Two-Phase Mixtures
   - Dendrite Coarsening
   - Ripening and Coalescence
   - Gravitational Settling
   - Liquid Phase Settling
   - Critical Wetting

B. Solidification of Supercooled Metals
   - Dendritic Growth/Diffusion Control
   - Interfacial Control (Kinetics)
   - Nucleation and Formation of Metastable Phases
   - Control of Supercooling
   - Containerless Processing

C. Interfacial Processes
   - Directional Solidification - Phase Spacing/Morph.
   - Particle Pushing
   - Bubble Formation - Porosity Control
   - Thermosolutal Migration of Droplets and Bubbles

D. Scaling Laws
   - Microstructural Prediction/Design
   - Anisotropic Surface Energy Effects and Kinetics
   - Polyphase Solidification

E. Measurements of Thermophysical Properties

F. Deposition and Dissolution of Metals
   - Deposition and Dissolution from Ionic Solutions
   - Vapor Deposition
   - Whisker Growth