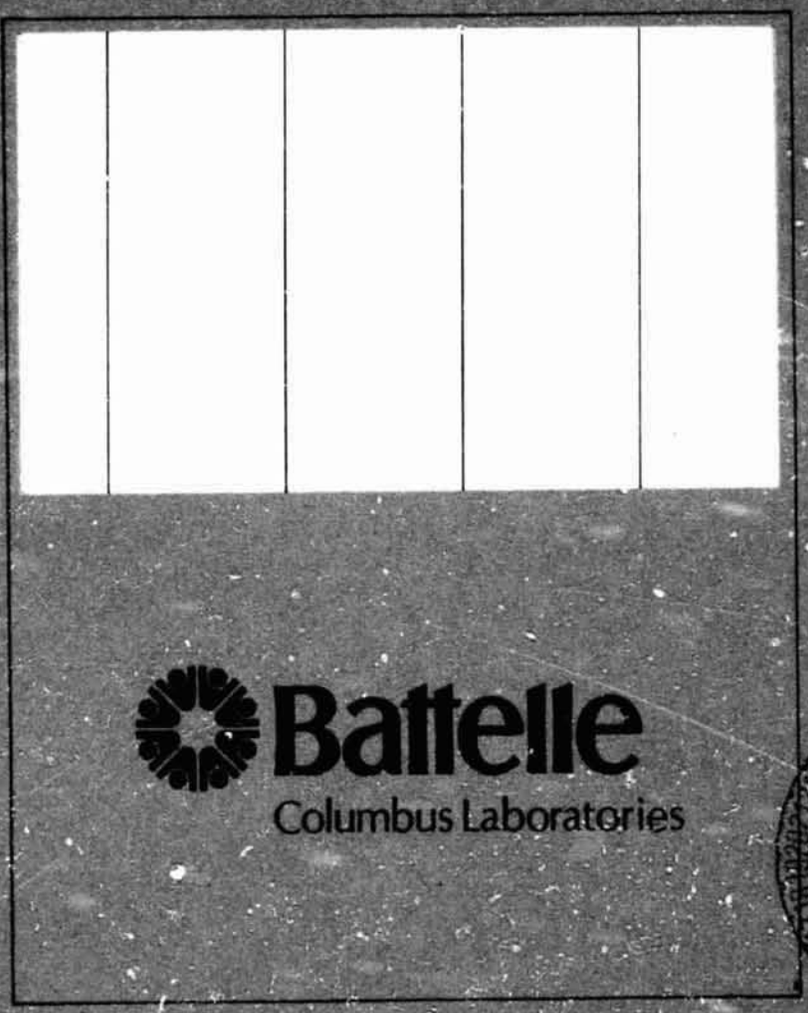
RESEARCH REPORT



Battelle

Columbus Laboratories

FINAL REPORT

on

UNDERCOOLING OF MATERIALS DURING SOLIDIFICATION IN SPACE

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER

April 18, 1975

by

D. P. Moak, N. M. Griesenauer, and S. H. Gelles

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BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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SECTION 1.0 SUMMARY

1.1 Introduction

The undercooling of molten materials below the equilibrium solidus temperature is an interesting and useful phenomenon.

The solidification of undercooled melts of metals and alloys results in pronounced desirable effects in microstructural features, such as refined grain size, refined dendrite morphology, and decreased microporosity which, in turn, affects mechanical and physical properties. Segregation in resultant undercooled ingots is considerably decreased and homogenization kinetics are greatly increased. The effects on microstructural features and segregation within ingots that have been undercooled are of greatest interest and possible commercial usefulness. Many pure metals and alloys of various types have been undercooled to various degress, but essentially none much beyond about 0.2 of the absolute melting temperature.

It is known that the elimination of gravity can result in the elimination of convection in the melt, which in turn may influence the undercooling behavior of a melt. It is important to determine the effects

of gravity (and subsequent convection) on the nucleation and undercooling behavior to better understand the phenomena and to provide experimental support to the thesis that alloys whose components differ significantly in density and whose liquidus and solidus compositions differ greatly during normal solidification can be solidified into fine-grained, homogeneous ingots. Such ingots would exhibit a great reduction in the amount of the low-melting regions resulting from "coring" during normal solidification. Many commercially important high-temperature alloys are inhibited in their use because of gravity-induced segregation during normal solidification. The study of the segregation in such alloys in ingots solidified from an undercooled melt in 0 g could provide added understanding of the effects of gravity on solidification phenomena and undercooling behavior.

1.2 Objective

The general objectives of this program were

(1) To determine the theoretical and actual extent of undercooling
(2) To specify those material properties determining the ability to undercool
(3) To investigate the effects of gravity and its absence on undercooling
(4) To illustrate experimentally the properties of materials affected by solidification subsequent to undercooling
(5) To specify materials most benefitted by undercooling in 0 g
(6) To prepare a comprehensive and self-inclusive 5-day test program for the preparation of unique high-temperature alloys by undercooling
(7) To illustrate experimentally the properties of the material affected by solidification subsequent to undercooling in the 5-day program

(8) To aid in incorporating the 5-day experiment both physically and functionally into CVT testing (Concept Verification Testing)

(9) To characterize and determine the source of variation in undercooling behavior.

The first five of these objectives were addressed to some extent during the Fiscal Year 1973 program on this same subject. The results of these studies are given in the Fiscal Year 1973 Interim Report.[1]*

The results reported herein have been obtained since that report was issued.

1.3 Program Approach

The program approach employed originally addressed three major tasks.

Task 1. Materials Selection and Properties Affecting Undercooling

Materials in the categories of pure metals, alloys, and compounds are to be studied. Specifically, their commercial and scientific value is to be considered, as well as past experience in their undercooling. A correlation between material properties and the ability to be undercooled is to be attempted. The material properties influencing undercooling behavior are to be reviewed, specified, and categorized.

Task 2. Experimental Studies

The terrestrial-based limits of undercooling for selected materials in the three categories--pure metals, alloys, and compounds--are to be characterized as a function of undercooling.

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* References are listed on page 63.

Initial plans included levitation-melting experiments on pure nickel, pure cobalt, and cobalt - 1 percent tin to determine the actual extent of undercooling attainable. Glass-slag envelope experiments to undercool Monel metal, Type 440C alloy steel, and a compound, PbTe, were scheduled to study important properties of the resultant undercooled specimens.

In the course of the program, some modifications of the above plans were found necessary. The development of these changes is documented in the subsequent Technical Discussion of this report.

Task 3. Materials Most Benefitted by Solidification in 0 g

Those materials most benefitted by solidification in 0 g are to be specified. To be included will be predicted ability (theoretical and/or experimental) to undercool and an assessment of the enhanced properties expected as a result of the amount of undercooling.

The following three additional tasks were incorporated into the program in March, 1974.

Task 4. CVT: Low-Temperature Alloy

Aid is to be provided in defining the experimental procedure and posttest analysis for a Concept Verification Testing (CVT) experiment of a low-temperature alloy prepared by undercooling to various extents prior to solidification.

Task 5. CVT: High-Temperature Alloy

Information as required to support the experimental definition, assembly, checkout, and operation of a 5-day General Purpose Laboratory (GPL) test on a unique high-temperature alloy prepared by undercooling is to be developed. This is to include specifying a material that will yield significant information in the allotted test-time period. A characterization procedure for studying significant properties is to be outlined.

Task 6. CVT Participation

This task is to provide for the actual participation by BCL personnel in the 5-day CVT experiment. Involved is to be a preliminary checkout of the experiment, participation in posttest analysis of the specimens, and establishment of laboratory procedures.

As a result of undercooling consistency problems encountered in backup experiments preliminary to the CVT experiments, an additional task was added.

Task 7. Investigation of the Inconsistency of Undercooling

This task has the following objectives:

(1) To select system(s) in which the greatest consistency in undercoolings can be achieved
(2) To investigate the sources of any inconsistencies
(3) To establish the statistical nature of undercooling in the system of our choice at BCL and in CVT experiments to be conducted at MSFC
(4) To design low-g experiment(s) aimed at determining the effect of convection currents and other gravity-driven processes on undercooling.

1.4 Summary of Results

Classical homogeneous nucleation theory predicts that the maximum undercooling attainable for metals is about 0.2 to 0.3 T_m, where T_m is the absolute melting temperature. Experiments on finely divided metal droplets tend to confirm the theory.[2] For glasses or polymers in which the diffusion coefficient decreases rapidly with temperature or for systems in which atomic or molecular transfer across the liquid-embryo interface is difficult, large undercoolings are expected.

Heterogeneous nucleating agents present as foreign particles in the otherwise homogeneous molten material or as phases that form during cooling or that are introduced by the container material limit the degree to which a molten material can be undercooled.

The limitation depends on the effectiveness of the nucleating agent which, in turn, depends primarily on the interfacial energy relations between the liquid and nucleating (catalyst) agent, σ_{LC}; the liquid and solid, σ_{LS}; and between the solid and nucleating agent, σ_{SC}. The contact angle, θ, made between the solid and nucleating agent in the presence of the liquid will determine the ease of the nucleation process. The contact angle for a planar nucleant surface is given by the relation

$$\sigma_{LC} = \sigma_{SC} + \sigma_{SL} \cos \theta \quad .$$

When θ is small ($\sigma_{SC} << \sigma_{LC}$), i.e., when there is good wetting between the nucleating solid and the nucleant, the nucleation barrier free energy will tend toward zero, and very small undercooling will accompany solidification. On the other hand, if θ is very large, approaching 180 degrees, the amount of undercooling will approach that theoretically predicted for homogeneous nucleation. Lattice mismatch between the nucleant and solid is also a factor that has been treated in the literature. If the disregistry is large, the nucleating agent will be ineffective, and larger undercoolings are necessary for the critical nucleation event.

Levitation melting experiments resulted in attainment of maximum undercoolings as follows:

Material	Undercooling	
	ΔT, C	$\Delta T/Tm$
Ni	245	.14
Co - 1Sn	250	.14
Type 304 Stainless Steel	195	.11

Levitation experiments with complex superalloys, such as IN-100 and Inconel 718, supported earlier findings that these alloys could not be undercooled by more than a few degrees.

A series of slag-envelope experiments with Type 304 stainless steel was made. The resultant specimens were metallographically examined, and a linear decrease in secondary dendrite arm spacing (DAS) with degree of undercooling was noted. At a comparable degree of undercooling, it was found that the structure of the stainless steel was considerably finer when undercooled under levitation as opposed to slag-envelope experiments. The levitation specimens were much smaller and thus the measured differences point out the significance of "local solidification time".

Numerous slag-envelope experiments were conducted in an attempt to undercool a steel suitable for property evaluation. The steels investigated include Types 440C, 4340, and 8615.

In no case was a significant degree of undercooling observed. In many cases violent bubbling, suggesting gaseous reaction products, was observed. In several experiments a portion of the charge was actually pushed up in the glass liner so that a 2- or 3-layer ingot resulted. It is postulated that the carbon in the steel reacts with the quartz crucible to give gaseous reaction products of both SiO and CO.

Experiments with Monel 400 (Ni - 32 wt % Cu - 2 wt % Fe) resulted in undercoolings of up to 110 C. Significant structural refinement was noted at this degree of undercooling when compared to specimens that had not been undercooled. Other glass-envelope experiments with a pure Ni-30Cu alloy resulted in undercooling levels up to 80 C. Room-temperature tensile tests were conducted on samples of this alloy, undercooled 0 and 80 C, and showed significant increases ($\sim$ double) in ductility for the specimen undercooled 80 C with the strength level essentially unchanged.

Preliminary design of a 5-day Concept Verification Testing (CVT) experiment in the General Purpose Laboratory (GPL) at MSFC was completed. Narloy Z (Cu - 3 wt % Ag - 0.4 wt % Zr), an alloy of current interest to NASA as a liner material for the Space Shuttle, was tentatively chosen for these experiments because it has a melting temperature within the range of current GPL capabilities.

Preliminary experiments with the alloy resulted in very limited undercooling. Even after removal of the zirconium, and eventually the silver, substantial undercooling was not achieved.

At this point in the program, a study was initiated to determine the source of inconsistencies in the undercooling effects. Basically two different alloys were investigated, Ag - 5 wt % Cu produced by a glass-slag melting technique[3,4] or by vacuum-induction melting and Cu - 5 wt % Ag prepared by the glass-slag technique.

The Ag - 5 wt % Cu alloys were also made the subject of consistency studies in connection with CVT experiments conducted by Dr. M. H. Johnston at MSFC. Fifteen specimen having various fabrication histories and contained in capsules of design developed on the present program were supplied to MSFC for the CVT experiments.

A system was designed and assembled for automatic cycling four samples simultaneously through melting and solidification and continuously monitoring of temperature. As many as 146 cycles were carried out on a Ag - 5 wt % Cu alloy, whereas a maximum of 35 cycles were carried out on the Cu - 5 wt % Ag alloys.

The maximum undercooling achieved in the Ag - 5 wt % Cu alloys was 57 C. The specimens had to be precycled at least 29-66 times before appreciable undercooling was achieved (> 20 C). Intermediate annealing at 1000 C appeared to promote the undercooling process.

In the limited experimentation conducted thus far, there appears to be little difference between the undercooling behavior of Ag - 5 wt % Cu alloys prepared by the glass-slag technique and those prepared by vacuum-induction melting. This is in contrast to the observations of Powell[3] and Powell and Hogan[4] that undercooling is most readily achieved in systems in which oxygen has been introduced (glass-slag technique). The behavior of the vacuum-induction-melted samples was very reproducible and provided somewhat higher maximum undercoolings (57-58 C) than the glass-slag samples (43-50 C).

The Cu - 5 wt % Ag alloys were produced by the glass-slag technique but with the variation that the copper was added either as a

few relatively large pieces or as many small pieces. All samples were subjected to 35 cycles and showed large undercoolings (> 20 C) after only a few cycles (2-8). A maximum undercooling of 97 C was achieved. A difference in behavior was noted between samples produced from the large and small pieces. Those from the large pieces showed similar behavior, a wild cyclical fluctuation in ΔT between a minimum of 20-30 C and a maximum of 60-70 C. Those made from the smaller pieces showed less of the fluctuations, but the individual samples within the lot behaved quite differently in terms of the maximum degree of undercooling (35 versus 97 C) and the equilibrium temperature.

The results obtained thus far on the Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys can be grossly interpreted in terms of the presence in the molten bath and the removal by the glass slag of heterogeneous nucleation agents of as yet unknown identity and origin. Their identity and relation to the degree of undercooling will contribute to the understanding of the heterogeneous nucleation process and its relation to undercooling.

It is important that 0-g experiments, when they are conducted to determine the effect of gravity on the nucleation and undercooling processes, be applied to materials that display a consistent degree of undercooling so that the influence of gravity is not masked by variations in the undercooling behavior. Preconditioning the samples by cycling and/or thermal treatments appears to be a way of establishing a fairly stable level of undercooling. There is one problem yet to be solved, however, and that concerns capsule survival during cool-down from the conditioning treatment. A design must be developed which will allow the samples to be cooled to room temperature and then reheated in the same capsule rather than the reencapsulation procedure now followed. The latter procedure destroys the beneficial effects of preconditioning.

A 0-g study on the undercooling of bulk samples will, in most likelihood, be a study of heterogeneous nucleation in 0 g since it is doubtful that all heterogeneous nucleating agents are removed from a bulk sample. Homogeneous nucleation could be studied on isolated droplets which have high probabilities of being free of foreign particles.

1.5 Conclusions and Recommendations

(1) The main obstacle to achieving a large degree of undercooling is the presence of heterogeneous nucleating agents. These vary in effectiveness depending on interfacial relations and lattice match with the nucleating solid.

(2) The glass environment of slag-envelope experiments may significantly influence the ability of a material to be undercooled. Several types of interaction have been observed experimentally.

(3) The theoretical limit of undercooling (0.2-0.3 of the absolute melting point) has not been obtained experimentally either by levitation or slag-envelope techniques for any material evaluated thus far in this program. Heterogeneous nucleating agents are probably still present in all these materials.

(4) A significant reduction in the secondary dendrite arm spacing (DAS) has been noted with several alloys as the degree of undercooling is increased.

(5) The carbon content of a steel significantly influences its ability to be undercooled because of interaction effects with the slag.

(6) The ductility of Ni - 30 Cu is greatly increased as the degree of undercooling is increased.

(7) The minor (0.4 wt %) zirconium addition to Cu - 3 Ag alloy may inhibit undercooling by reducing other oxides in the experimental environment and forming zirconium oxide which may act as a nucleating agent.

(8) Very high purity copper was not undercooled successfully in slag-envelope experiments.

(9) Significant undercoolings can be achieved in Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys after sufficient "conditioning" of the melt by cycling through melting and solidification and by thermal treatments.

(10) The "conditioning" process appears to remove heterogeneous nucleation agents from the melt by reaction with the glass slag.

(11) No significant effect of sample preparation history (glass-slag versus vacuum induction melting) was found on the Ag - 5 wt % copper alloys. The behavior of the vacuum induction melted alloys was more consistant.

(12) A difference in the undercooling behavior of Cu - 5 wt % Ag was noted depending on the manner in which copper was added to the alloy during production by the glass-slag technique.

(13) The effect of gravity on the nucleation and undercooling processes is not clear with the exception of the anticipated benefit expected from containerless processing. The homogeneous nucleation process may be more difficult at 0 g because of the absence of gravity-driven agglomeration processes.

Future work in exploring undercoolings should be directed toward understanding the processes that determine the degree to which undercooling can occur. Thus, it is mandatory that both homogeneous and heterogeneous nucleation be better understood both from a theoretical and experimental viewpoint.

From the experimental viewpoint, continuing the investigation into the change in undercooling with "conditioning" treatment and

investigating the type and distribution of particulate matter causing the changes in undercooling behavior should provide us with two beneficial effects:

(1) It should provide us with first-hand data on the effectiveness of a particular kind and shape of heterogeneous nucleating agent in catalyzing the solidification process

(2) It should provide us with information for increasing the degree of undercooling in a given material and thus offer a way for improving the properties of the material.

Little work has been done in measuring changes in physical properties on the solid resulting from solidification below its equilibrium melting point. Such work should be done in order to better understand the full potential of undercooling for producing superior materials either on earth or at 0 g.

No experiments have at yet been done at 0 g to see whether changes in undercooling behavior occur because of the absence of net gravitational forces. We would recommend that such an experiment be conducted in glass-slag envelopes on well-conditioned samples. Additional capsule development will be necessary, however, before consistant samples can be obtained.

It is also recommended that the type of classical experiments of Turnbull and Cech[2] on undercooling of fine droplets be repeated at 0 g. Many of the droplets solidify only after homogeneous nucleation so that the effects of gravity on this process should be measureable.

SECTION 2.0 TECHNICAL DISCUSSION

2.1 Task 1. Materials Selection and Properties Affecting Undercooling

Materials in the three categories of interest were selected. These include the pure metals and alloys, cobalt, cobalt/1 wt % tin, and pure nickel. The first two of these were investigated to some extent in FY 1973. Commercial alloy materials for study include Monel, Type 304 stainless steel, and Type 440C stainless steel. These are important alloys, and the respective properties of corrosion, structure, and mechanical properties are to be related to the degree of undercooling in Task 2.

PbTe was chosen as a compound of interest and undercooling was to be related to its electrical characteristics. As suggested by Dr. Bredt in his letter of September 12, 1973, to Dr. Johnston, resistivity measurements on undercooled PbTe will not be of much technical value. The real benefits that might be gained by undercooling this or other semiconductors such as SnTe require much more sophisticated measurements of items such as carrier concentration and mobility. Such involved determinations are beyond the scope of the current program, but may be of significant interest to consider for future work.

Therefore, with the concurrence of the COR, the resistivity studies proposed on PbTe were dropped from the program and efforts concentrated on the alloy studies deemed more important.

2.11 Theoretical and Experimental Considerations

2.111 Undercooling and the Nucleation Process. The ability to undercool a material to a significant degree depends on the elimination of effective heterogeneous nucleating agents from the molten bath so that homogeneous nucleation, formation of nuclei from the homogeneous melt, is not superseded by the energetically easier heterogeneous nucleation. Thus, to understand the undercooling process it is mandatory that the

factors that affect both homogeneous and heterogeneous nucleation be well understood. These include both the basic material properties and the contribution of external fields such as gravity.

2.112 Homogeneous Nucleation. The classical theory of homogeneous nucleation has as its basis the theoretical development of Volmer and Weber[5] and Becker and Doring[6]. The change in free energy, ΔG, associated with a first-order transformation can be represented by

$$\Delta G = \Delta H - T\Delta S \quad , \tag{1}$$

where

ΔH = change in enthalpy

T = absolute temperature

ΔS = change in entropy.

At equilibrium, $\Delta G = 0$; and if the liquid-solid transformation is of interest, ΔH becomes the heat of fusion, ΔH_f, and T is the melting temperature, T_m. Therefore, at T_m the free-energy change associated with fusion becomes

$$\Delta G_f = \Delta H_f - T_m \Delta S_f = 0 \quad , \tag{2}$$

and ΔS_f, the change in entropy on fusion, becomes

$$\Delta S_f = \frac{\Delta H_f}{T_m} \quad . \tag{3}$$

At a temperature different from the equilibrium transformation temperature, and assuming that ΔH_f and ΔS_f are little affected by the temperature change, we find by combining Equations (1), (2), and (3)

$$\Delta G_f = \Delta H_f - \frac{T\Delta H_f}{T_m} \quad , \tag{4}$$

or

$$\Delta G_f = \frac{\Delta H_f \Delta T}{T_m} \quad , \tag{5}$$

where $\Delta T = T_m - T$, or the interval between the equilibrium solidification temperature and that temperature at which the transformation occurs, and thus represents the degree of undercooling.

Considering classical nucleation theory, assuming the formation of a spherical embryo of radius, r, the overal change in free energy, ΔG, is given by

$$\Delta G = 4\pi r^2\sigma + 4/3\ \pi r^3 \Delta G_f \quad , \tag{6}$$

where σ is the surface free energy (always positive and thus a barrier to nucleation) and ΔG_f is the volume free energy as discussed above and is always negative below the equilibrium melting point. At temperatures below T_m, the first term of Equation (6) increases with r, whereas the second term decreases. Thus, a maximum in the $\Delta G(r)$ relation, ΔG^*, exists at the critical radius, r^*. To form a nucleus of critical size (one that will continue to grow), a random fluctuation of atoms producing a localized energy change, ΔG^*, is required. The critical radius, r^*, can be found by taking the first derivative of Equation (6) with respect to r and setting it equal to zero.

$$r^* = \frac{2\sigma}{\Delta G_f} \quad . \tag{7}$$

Substituting the relation for ΔG_f from Equation (5),

$$r^* = \frac{2\sigma T_m}{\Delta H_f \Delta T} \quad , \tag{8}$$

and by combining Equations (6) and (8), we find

$$\Delta G^* = \frac{16}{3}\left(\frac{\pi\sigma^3 T_m^{\ 2}}{\Delta H_f^{\ 2}\Delta T^2}\right) \quad . \tag{9}$$

ΔG^* can be considered as the thermodynamic barrier to the formation of a critical nucleus. It can be seen that ΔG^* decreases rapidly with increasing undercooling, ΔT.

By using Equation (9) and introduction of the barrier free energy, ΔG_A, for transfer of material across an interface,[7] a rate law for homogeneous nucleation can be derived. For liquid metals this rate can be represented by

$$I = C \exp\left[-\Delta G_A/kT\right] \exp\left[-\frac{16\pi\sigma^3 T_m^2}{3\Delta H_f^2 \Delta T^2 kT}\right] , \qquad (10)$$

where C is constant for most metal systems. The form of Equation (10) is such that I, the nucleation rate, remains very small until ΔT reaches a critical value and then increases very rapidly. The temperature at which this occurs is, therefore, defined as the homogeneous nucleation temperature.

The most fruitful experimental approach employed to confirm the theory is that performed by Turnbull and co-workers on finely divided metal droplets. Quantitatively, these studies have shown that for metals the maximum undercooling achieved is about 0.2-0.3 of the absolute melting temperature and agrees well with values calculated on the basis of Equation (10). For more complex structures where $\Delta G_A > 0$, larger undercoolings would be possible.

Using measurements of ΔT conducted on fine droplets, Holloman and Turnbull[8] used Equation (10) to calculate the interfacial energies for the metals experimentally undercooled as droplets. These energies are of the right order of magnitude and are self-consistent in that they plot linearly against the respective heats of fusion. A few interfacial energies have been measured and agree well with the calculated values, thereby lending support to the theory of homogeneous nucleation which suggests maximum undercooling of $\sim$ 0.2-0.3 times the absolute melting temperature.

More recent treatments of nucleation theory, based on statistical mechanical approaches,[9,10] have raised some other important questions regarding the classical theory. For example, considerations of translational and rotational contributions have led Lothe and Pound[7] to conclude that nucleation rates predicted by the classical theory may be about 10^{15} times smaller than actual experimental rates.

Very recent work on nucleation theory has involved atomistic studies of small atomic clusters using appropriate interatomic potentials to describe atom-atom interactions within the clusters (see, for example, the work of Burton[11,12] and of Abraham and Dave[13]). It has been with this type of study that quantitative evaluations of the capillarity approximation used in the classical theory have been made feasible. For example, "exact" calculations of nucleation rates have been carried out by Burton[12] based on atoms situated on face-centered-cubic lattice sites interacting only via nearest-neighbor harmonic forces. He found that with statistical mechanical factors included the ratio of the "exact" nucleation rate to that predicted using the classical theory can vary from 10^{-2} to 10^{7} and is a strong function of temperature and supersaturation.

Thus, much progress has been made in recent years in the perfection of the theory of homogeneous nucleation and in closing the gap between theoretical predictions and experimental results. One major area that requires significant work deals with the effect of external fields, especially gravitational, on the nucleation process.

2.113 Heterogeneous Nucleation. The theory of heterogeneous nucleation is largely based on classical thermodynamic principles.[5,6,14,15] The treatment generally introduces a planar surface of a foreign material (catalyst) into the liquid bath and a spherical cap-shaped embryo of solid is assumed to form on the catalyst and take up a configuration which depends on the interfacial energies between liquid and solid, σ_{LS}; between liquid and catalyst, σ_{LC}; and between solid and catalyst, σ_{SC}. The equilibrium between the interfacial energies depends on the contact angle, θ, between the solid and the catalyst in the presence of the liquid, and is given by

$$\sigma_{LC} = \sigma_{SC} + \sigma_{SL} \cos \theta \quad .$$

The Gibbs free-energy barrier for the heterogeneous nucleation process, ΔG^{*}_{het}, is then given by the relation

$$\Delta G^{*}_{het} = \Delta G^{*}_{hom} f(\theta) \quad ,$$

where ΔG^*_{hom} is the barrier Gibbs free energy for homogeneous nucleation and $f(\theta)$ in the case of the spherically shaped cap on the planar catalyst is given by

$$f(\theta) = 1/4\ (2 + \cos\theta)\ (1 - \cos\theta)^2 \quad .$$

$f(\theta)$ thus varies between 0 and 1 as θ ranges between 0 and 180 degrees, respectively. Thus, in the case of complete wetting between the solid embryo and the catalyst ($\theta = 0$), the barrier free energy is zero and little undercooling is necessary to produce nucleation of the solid. On the other hand, if $\theta = 180$, the catalyst is completely ineffective as a nucleating agent and the energy barrier is the same as that for homogeneous nucleation.

Since one important factor determining $f(\theta)$ is the interfacial energy between the solid embryo and the catalyst, a good deal of effort has been applied to examining σ_{SC}, especially in terms of the lattice mismatch, and its effect on the degree of undercooling, ΔT.[8,16-18] Some success has been achieved in applying the concept, but it is not always successful.

The theory has been moderately successful in interpreting the behavior of heterogeneous nucleating agents in application to grain refinement. It has also been used as a guide for interpretation of undercooling experiments in which the degree of undercooling, ΔT, has been measured in samples divided into small isolated droplets as a function of droplet volume.[8] The undercooling behavior of liquids from which heterogeneous nucleating agents have been removed by separation processes such as centrifuging or slag reactions[1,3,4,19] has also been generally interpreted in terms of this theoretical framework.

There are some large barriers, however, to the application of heterogeneous nucleation theory to the understanding of undercooling phenomena. One of these is the lack of information about interfacial energies; and the second, the absence of a well-developed theory considering the effect of concentration, geometry, and size distribution of catalysts on heterogeneous nucleation and undercooling.

2.2 Task 2. Experimental Studies

One of the objectives of this task was to determine the terrestrial-based limits of undercooling of selected materials. This was accomplished by levitation melting of small samples so that nucleation by container surfaces was eliminated.

Materials for property evaluation were undercooled by solidification in glass-slag envelopes.

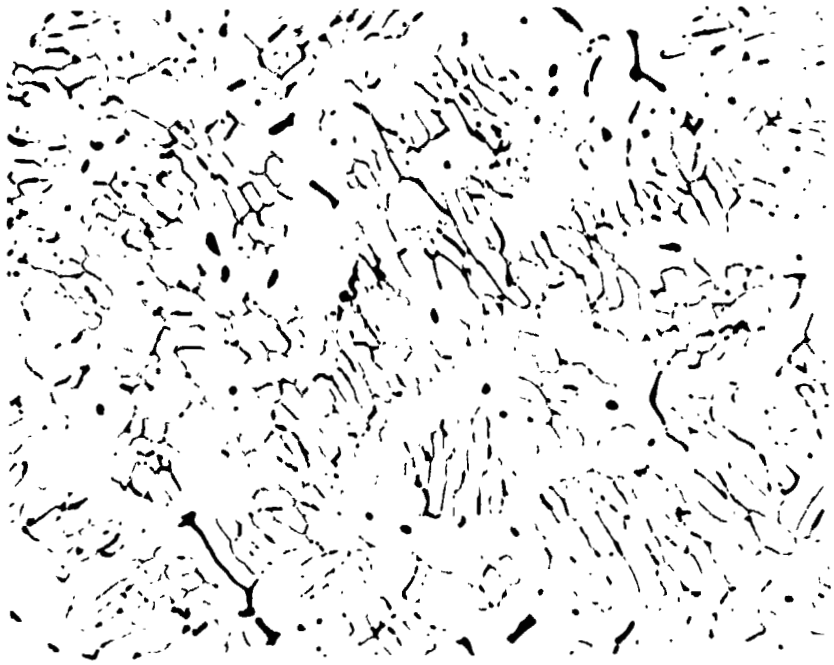
2.21 Levitation-Melting Experiments

Samples approximately 3/16-in. cube were cycled through the melting range several times in an atmosphere of hydrogen and helium in a ratio of about 4:1, respectively. Samples were heated to about 50 C above the liquidus, and the temperature was measured by means of a two-color pyrometer. Cooling of the sample during levitation was achieved by increasing the flow rate of the gas mixture past the sample.

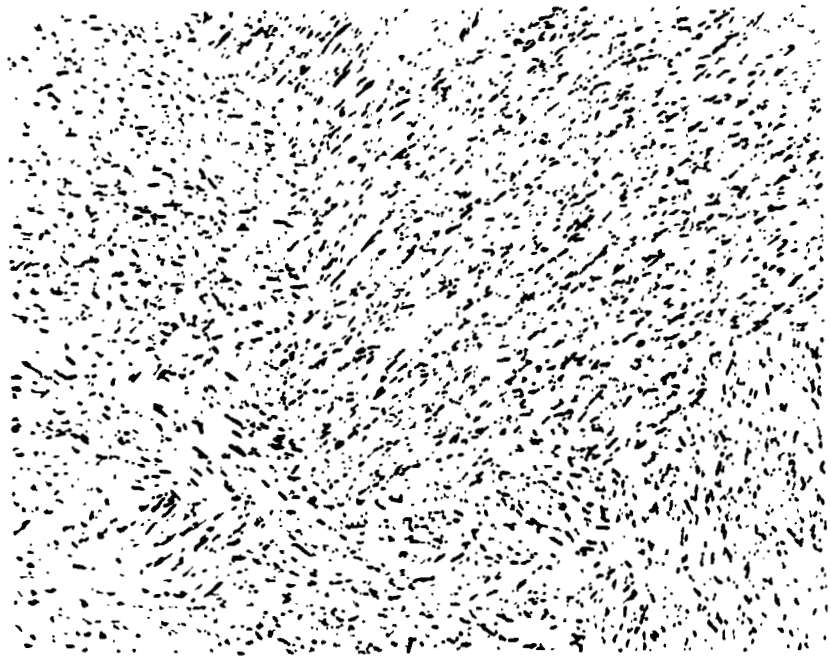
Pure nickel was undercooled under levitation to a maximum of 245 C, while the Co - 1 wt % Sn achieved an undercooling of 250 C.

Earlier program studies indicated that complex alloys such as In-100 and Inconel 718 could not be undercooled in slag-envelope experiments. It was postulated that the high-temperature phases, such as carbides and oxides, associated with the titanium and aluminum additions to the alloys are stable in the melt, provide sites for heterogeneous nucleation, and thus prevent undercooling. Several levitation experiments to undercool these alloys were made to check this thesis without the possibility of a container providing sites for heterogeneous nucleation. Essentially no undercooling was attained with either alloy under levitation; therefore, these results tend to support the thesis previously presented.

Experiments on Type 304 stainless steel under levitation resulted in undercoolings of 0 and 195 C. Figures 1a and 1b show the metallographic



250X a. No undercooling 7G683



250X b. Undercooled 195 C 7G684

FIGURE 1. TYPE 304 STAINLESS STEEL STRUCTURES FROM LEVITATION EXPERIMENTS

structures of these levitated samples. A considerable refinement effect is noted by the 195 C undercooling. Measurements of secondary dendrite-arm spacings (DAS) showed the following.

Degree of Undercooling, C	DAS, μ
0	10
195	5

These spacings are much smaller than those measured on samples from slag-envelope experiments with comparable undercoolings (76 μ for 0 C and 46 μ for 170 C). The levitation specimens were very small compared to those in slag and thus the measured differences are attributed to differences in "local solidification time".

2.22 Glass-Slag Envelope Experiments

Two types of alloys were studied in an attempt to obtain properties on undercooled materials. These are hardenable steels and nickel-copper alloys. In addition, several experiments were performed with Type 304 stainless steel to complete the series for structural evaluation that was initiated in the last fiscal year.

2.221 Type 304 Stainless Steel. Two bulk specimens of Type 304 stainless steel were undercooled in slag-envelope experiments to 55 and 105 C and were examined metallographically. The dendrite arm spacings (DAS) between the secondary branches were measured and are compared below with those previously measured at undercoolings of 0 and 170 C.

Degree of Undercooling, C	DAS, μ
0	76
55	63
105	53
170	46

The results are plotted in Figure 2, where they are compared with the two data points obtained when undercooling very small specimens of Type 304 stainless steel under levitation conditions. The marked decrease in DAS attributed to size effects (faster cooling rate) is prominent.

In accord with the suggestion made by Dr. Bredt (September 12, 1973, letter to Dr. M. H. Johnston), a slag-envelope experiment was performed on a ≈ 1-g sample of Type 304 stainless steel for structural comparison with the small, levitated samples. This was accomplished by using a double-quartz, thermocouple protection tube system currently being employed for temperature monitoring in the undercooling experiments. The sample was placed in the larger tube while the smaller tube, containing the thermocouple, was allowed to fall into the sample when it became molten. Examination after the experiment showed the head of the thermocouple to be surrounded by metal on the bottom and sides; thus, the recorded temperatures may be questionable. After undercooling, the thermocouple reading on the recorder never indicated recalescense to the melting point, but this response problem may be due to the very small sample mass. An encouraging note was that on heating, a reproducible indication of the melting point, consistent with that observed on bulk samples, was observed. A maximum undercooling of ≈ 275 C was achieved, but the final condition chosen was an undercooling of 170 C for comparison with levitation and bulk slag experimental results.

The specimen was examined metallographically, and the structure is shown in Figure 3. The normal cored or dendritic solidification structure is not observed in this photomicrograph. Many different etching

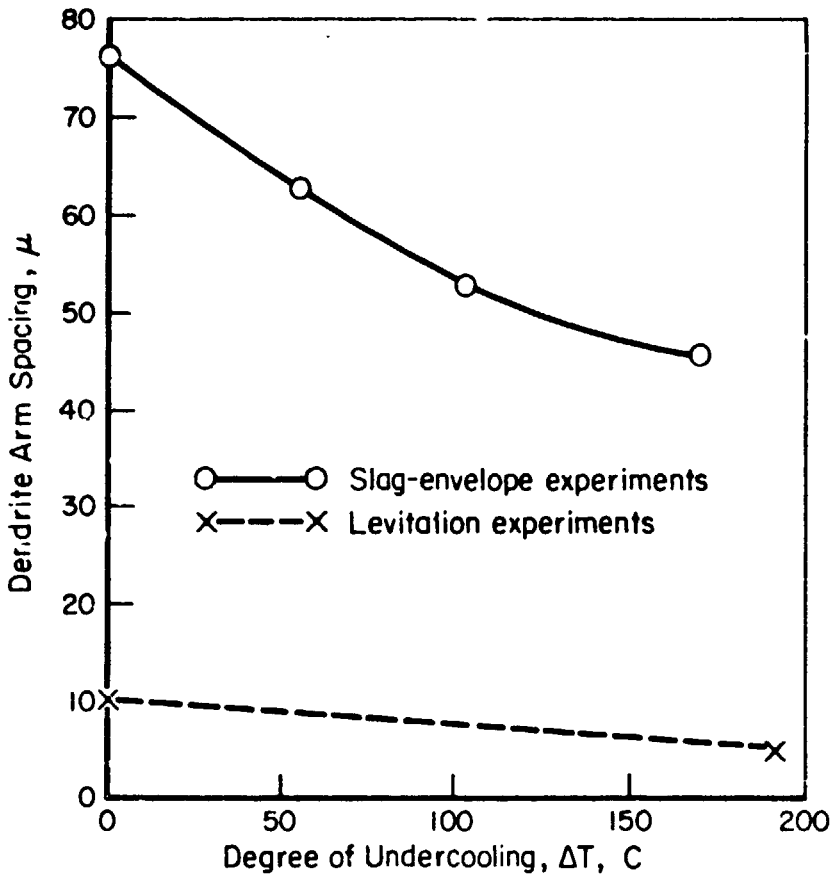


FIGURE 2. TYPE 304 STAINLESS STEEL DENDRITE ARM SPACING VERSUS DEGREE OF UNDERCOOLING

250X 9G268

FIGURE 3. TYPE 304 STAINLESS STEEL

Undercooled 170 C in a glass envelope. A very small ≈ 1.2-g specimen.

techniques and solutions were tried, but the only structure brought out is that shown in Figure 2. This structure suggests a degeneration of the normal dendrites to a spherical morphology as observed by Kattamis for iron- and nickel-base alloys at high degrees of undercooling.[20] Measurement of DAS is, therefore, difficult if not impossible, but the structure is definitely finer than that observed in bulk specimens undercooled to a comparable degree and approaches the fineness previously reported for levitated samples undercooled 195 C. Kattamis further suggests that cooling rate does not affect the Δi undercooling at which this morphology transformation occurs. The results here, however, suggest that increased cooling rate does influence the ΔT at which the transformation is observed.

2.222 Hardenable Steels. The alloy initially chosen for undercooling and subsequent mechanical property evaluation was Type 440C steel. This alloy is a general-purpose, hardenable stainless steel, which upon quenching develops maximum hardness together with high-strength and corrosion resistance.

A total of about ten slag-envelope experiments with Type 440C steel were performed. The charge in all experiments was about 1-1/2 lb, sufficient to obtain at least three tensile specimens from each resultant ingot. Some modifications of the furnace set-up were required to handle this larger charge compared to that used in the past for slag-envelope experiments. None of the experiments resulted in a significant degree of undercooling, and in many cases violent bubbling, suggesting a gaseous reaction product, was observed. In several experiments a portion of the charge was actually pushed up in the glass liner so that a two- or three-layered ingot resulted. A further description of a number of the experiments made is given below so as to detail some of the problems encountered and the variables investigated.

During the first run, a thin layer of sand was introduced between the ceramic liner and the graphite susceptor to fill a slight annulus to support the ceramic liner. The charge could not be heated sufficiently under these conditions and so was removed from the furnace.

The second experiment was performed in normal fashion, but was terminated after five cycles through the melting temperature since no undercooling was achieved. A failure of the ceramic liner was determined to be responsible.

A third experimental run was performed but the heating rate was still poor. An undercooling of 110 C was achieved on the first cycle, but subsequent cycles resulted in negligible undercooling. Examination of the ingot after the experiment indicated that the quartz protection tube for the thermocouple had failed, allowing the metal charge to contact the rough, crystalline Al_2O_3 inner protection tube around the thermocouple. This contact apparently nucleated the melt at the normal freezing temperature and prevented undercooling.

For the fourth experiment, the graphite susceptor was eliminated and the thermocouple was protected with two quartz protection tubes. The heating rate was greatly improved but no undercooling was realized after seven cycles. Subsequent examination showed the thermocouple to be intact, so this problem had apparently been eliminated. Two items remain to be investigated regarding the lack of undercooling. In the fourth experiment, a new crushed glass of Corning Type 7052 was used to cover the top of the melt. This glass contains more Al_2O_3 and other minor oxides than the Pyrex powder previously employed. This glass may have devitrified and caused heterogeneous nucleation.

Since the powdered-glass covering over the melt was suspect as preventing undercooling during previous experiments, it was eliminated completely for the next experiment. Without the glass on top, the metal itself could be observed during melting and a bubbling action was found to continue during each of the four cycles made through the melting point. No undercooling was achieved, and the observed behavior suggests a gaseous product from the melt or a reaction with the crucible.

Another melt was made with a different commercial 440C steel alloy. Crushed Pyrex, as used successfully in the past, was used to complete the slag envelope. After seven cycles, a maximum undercooling of only 45 C was attained. During this experiment the Pyrex, after fusing together, rose in the crucible and formed a dome at the crucible surface.

This again suggests a gaseous reaction in the melt. A similar experiment with Pyrex glass but using the original 440C resulted in the same behavior.

At this point the purity of the commercially obtained 440C steel became suspect in preventing undercooling. Therefore, two 1-1/2-in.-diam by ≈ 5-in.-long castings were prepared from high-purity elemental charge materials (Fe_3C used to introduce carbon). The alloy was prepared by induction melting in an Al_2O_3 crucible under 1/2-atm argon and poured into copper molds. These castings required annealing at 760 C to permit machining, since the alloy hardens (martensitic transformation) when cooling from temperatures as low as 815 C.

A sample from the synthesized 440C steel was prepared for undercooling using the Pyrex glass on top. Again the glass rose in the crucible. However, after five cycles an undercooling of 90 C was obtained and the experiment was terminated. Subsequent examination of the specimen revealed that not only the Pyrex glass was pushed up but also about one-half of the charge which was not even melted at the top surface. The thermocouple was in the lower portion of the charge in which 90 C undercooling was finally achieved. Unfortunately, this charge was not large enough to obtain meaningful tensile specimens.

To insure that, as now suspected, the 440C steel itself was posing undercooling problems, a charge of the synthesized alloy was machined to fit the smaller scale set-up that was successfully used to undercool cobalt, Ni_3Sn_2, and Type 304 stainless steel. After nine cycles through the melting point, an undercooling of only 50 C was reached. Subsequent examination also showed the charge to have separated into approximately two equal parts. Here, however, the top section was at one time completely molten.

One additional experiment was made using the synthesized alloy with no glass covering so that the melt surface could be observed. Violent stirring and bubbling was noted and the experiment terminated.

We now postulate two different but related causes for lack of undercooling of 440C steel. Both relate to the high carbon content of the alloy. First, if the alloy is not fully deoxidized, the oxygen in

the alloy will react with the carbon to effect a carbon boil which generates CO. This would account for the bubbling noted experimentally, and such agitation would certainly limit the degree of undercooling obtainable. A vacuum melt prior to experimental undercooling to allow complete deoxidation appears to be a requirement. It is of interest to note that Kattamis and Flemings[20] report one experimental undercooling of 440C steel to a level of 150 C. The melt was, however, very small (100 g versus ≈ 600 g in our current work).

The second source of CO may come from reaction with the quartz crucible in accordance with the following reaction:

$$SiO_2(s) + C_{(Fe)} \rightarrow SiO(g) + CO(g) \quad .$$

The equilibrium constant for this reaction is ≈ 2×10^{-3} atm at 1700 K, and as the carbon content increases the reaction proceeds to a greater degree and the gaseous pressure increases. Thus, both SiO and CO could be bubbling through the melt and reduce undercooling possibilities.

A charge of the synthesized 440C steel was vacuum melted in a magnesia crucible to effect deoxidation. No bubbling or other evidence of outgassing was noted. This is in direct contrast to the observations made when melting 440C steel in fused silica. Rather than attempt to undercool this material, the approach was somewhat changed since the carbon-silica reaction appeared to be causing the problem. It was reasoned that since the 440C steel contains ≈ 1 wt % carbon, a steel with a lower level of carbon may exhibit improved behavior. Type 4340 steel having a nominal carbon content of 0.4 wt % was melted in a fused silica crucible with no powdered glass on top of the charge. The two experiments conducted produced extensive gas evolution in both cases and a portion of the charge rose in the crucible and, on subsequent cycles through the melting point, was separated from the remainder of the charge. Undercoolings of up to 65 C were observed after a few cycles, but the form of the resultant ingot prevented its use for tensile property measurement.

During this period of time, Type 304 stainless steel containing only 0.08 wt % C was successfully undercooled. As a result of this and the previous observations, the following conclusions may be made.

First, there is nothing wrong with the experimental setup since Type 304 stainless steel was successfully undercooled with no gas evolution problem causing metal separation and poor ingot integrity. Second, the thesis that the carbon-silica reaction has been causing the problem is confirmed by these results. In fact, the very reaction discussed previously is currently employed to prepare foamed glass.[21]

On the basis of these findings, it was suggested that a lower carbon-content steel be employed to determine the effect of undercooling on mechanical properties. Type 8615 steel was chosen. This low-alloy, heat-treatable steel is used in both the cast and wrought conditions. The alloy is comparable to Type 4340 steel (Cr, Ni, and Mo addition) which exhibits a well-defined dendritic solidification structure. However, the carbon content is only 0.15 percent as compared to 0.40 percent in the 4340. Based upon results to date, this lower carbon content is desirable to realize good-quality specimens of sufficient size for tensile evaluation.

A 6-kg heat of the steel alloy, Type 8615, was synthesized by vacuum-induction melting. The resultant cast ingots were hot forged to reduce the diameter to a size convenient for charging the quartz crucibles for slag-envelope experimentation. An undercooling experiment was performed, but because of the previous problems encountered when attempting to undercool steels in glass-envelope experiments, a double-quartz crucible was employed. No undercooling was observed after seven cycles through the melting range. Subsequent examination revealed that the inner quartz crucible had failed and allowed some of the alloy to run out of the crucible. Examination of the ingot suggested that this may have happened while the alloy was cooling through the liquid-plus-solid-equilibrium region, since the liquid appears to have decanted leaving vivid dendrites on all visible surfaces.

Two more slag-envelope experiments were performed with the Type 8615 steel. A single-wall, thicker quartz crucible was employed to give a more rigid support for the experiment. A maximum undercooling of

only 20 C was attained, and examination after both experiments revealed that the quartz crucibles had failed and the metal was in contact with the ceramic support liner.

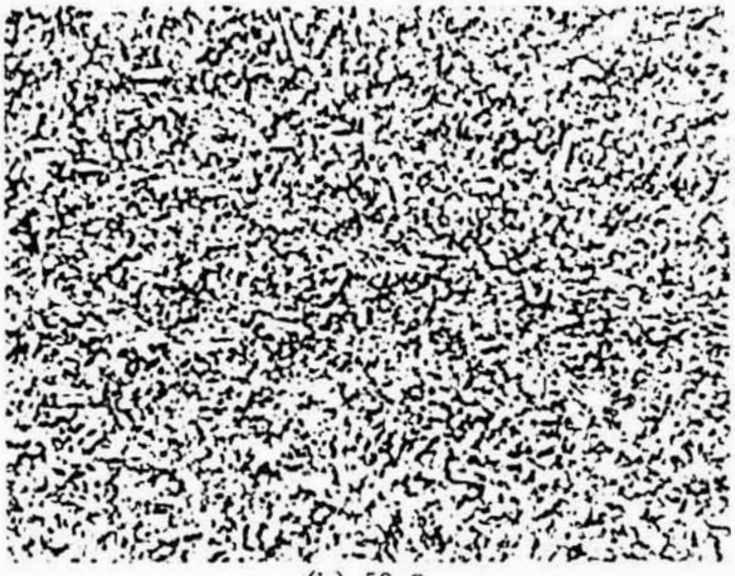
With the continued experimental difficulties in undercooling the steels, the emphasis was changed to the nickel-copper alloy system. Since mechanical property data are of paramount importance to the program, the resulting undercooled nickel-copper specimens would be used for this evaluation.

2.223 Nickel-Copper Alloys. Initial efforts were made using commercial-grade Monel 400, which contains 32 wt % Cu and 2 wt % Fe. Six slag-envelope experiments were performed, and three usable data points obtained: 0, 50, and 110 C. During these studies another interesting finding was made. When Corning 7052 powdered glass was used, the problem of charge separation, as noted with the high-carbon steels, once again occurred and the resultant ingots had high-gas contents. Investigation revealed that this glass is used as a Kovar (Ni-Fe-Co alloy) sealing glass.[22] This implies some reaction between the glass and the metal which may contribute to the problems encountered during undercooling studies. When Corning 7740 (Pyrex) was employed, no problems were encountered. However, it was found that the glass powder on top of the charge is not required to achieve undercooling.

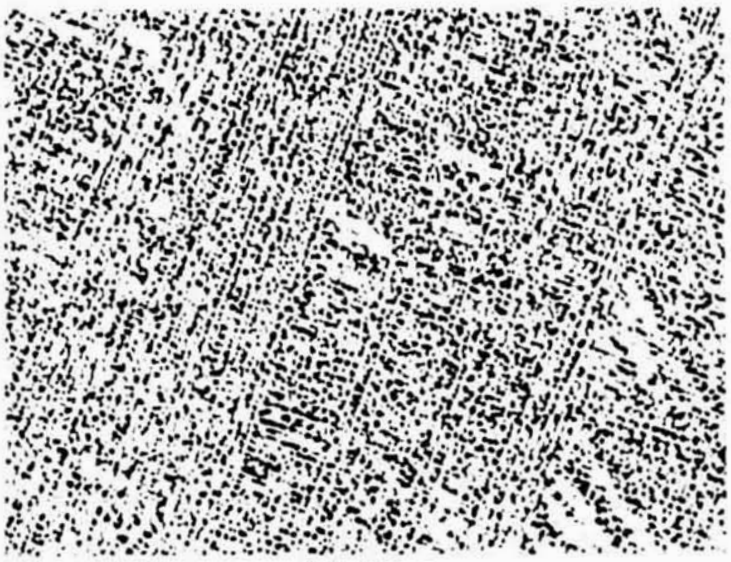
During the previous experiments, an undercooling of up to 190 C was recorded. Therefore, an additional sample of Monel 400 which had achieved at least this level of undercooling was sought. However, after four more attempts undercoolings of only 120 C were realized. Since this ΔT is not significantly greater than those already available, these samples were not further evaluated.

The three Monel 400 specimens undercooled in slag-envelope experiments at 0, 50, and 110 C were examined metallographically, and the resultant structures are shown in Figures 4a-c, respectively. Figure 4a, 0 C undercooling, shows a very well-defined dendritic structure as one might expect as a normal solidification pattern. Figure 4c, ΔT = 110 C, also has a dendritic appearance, but there does seem to be evidence of a

(a) 0 C



(b) 50 C



(c) 110 C

FIGURE 4. MONEL 400 UNDERCOOLED VARIOUS AMOUNTS

spheridization of the dendrite elements. The spacings are obviously much reduced with the 110 C undercooling. The structure shown in Figure 4b is from the specimen undercooled 50 C. It does not appear to "fit" with the other two structures. There are no well-defined dendrites, and the structure is cellular in nature. It is interesting to note that Tarshis, et al,[23] also observed some anamolous behavior in the microstructural variation of undercooled nickel-copper alloys. At moderate degrees of undercooling, they observed equiaxed structural elements of fine-grain size. The temperature range of this occurrence is not in exact agreement, but the alloy compositions employed were slightly different.

At this point efforts were shifted to undercooling a pure Ni-30Cu alloy, synthesized from elemental materials, in the hopes of achieving greater degrees of undercooling. A 6.3-kg heat of the alloy was synthesized by vacuum-induction melting. The resultant cast ingots were hot forged to reduce the diameter to a size convenient for charging the quartz crucibles for slag-envelope experimentation.

A total of 11 glass-envelope experiments were made in attempting to undercool the nickel-30 percent copper alloy. One experimental problem encountered was containment of the alloy in the quartz crucible. Many experiments were unsuccessful because the quartz failed, allowing the molten metal to contact the ceramic supporting crucible. This, of course, caused heterogeneous nucleation and severely limited any undercooling. It was finally concluded that the larger samples being employed (≈ 500 g) to obtain reasonably sized tensile specimens place too much stress on the quartz which was only loosely supported by the ceramic crucible. The last three experiments were made using a modified design to ensure adequate support of the quartz crucible. This was accomplished by eliminating the ceramic crucible and supporting the quartz with moderately packed chipped alumina particles. With this modification consistent containment has been achieved, although undercooling results have been erratic. With the prealloyed material being used, an undercooling of 65 C was attained. When using very high-purity elemental material

(99.999 pure), 120 C undercooling was realized. Because of material cost, this latter specimen was only 250 g and was not large enough to obtain the designed tensile specimen.

Two charges that were undercooled 15 and 80 C were retained for evaluation. The resultant ingots, about 1-3/8-in. diameter by 2 in. long, were sectioned to form 1/4-in.-thick plates which were radiographed to aid in selecting sound sections for the preparation of tensile specimens. Two tensile bars having a gauge diameter of 3.18 mm, a gauge length of 2.03 cm, and 1/4-20 threaded ends were machined from each ingot and tested at room temperature to determine the influence of undercooling (15 and 80 C) on mechanical properties.

Metallographic specimens from each experiment were prepared, and the resultant structures are shown in Figure 5. The specimen undercooled only 15 C (Figure 5a) shows a very coarse dendritic structure. At 80 C undercooling (Figure 5b), the dendritic pattern is difficult to observe, and the segregated phase has assumed more of a spherical morphology. However, the spacing is apparently reduced at the higher undercooling.

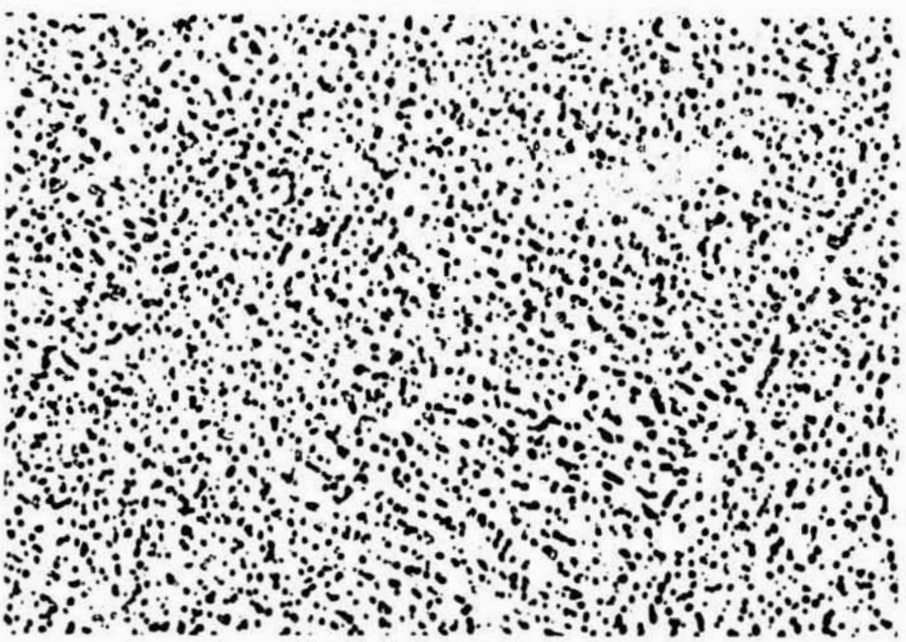
Hardness determinations were made on each metallographic section as a preliminary prediction of strength levels. At ΔT = 15 C the Rockwell B hardness is 24 while at ΔT = 80 C the hardness is 30 (average of six measurements in each case). Duplicate specimens were tensile tested at room temperature. The results are tabulated below.

Undercooling, ΔT, C	0.2% Offset Yield, psi	UTS, psi	Elongation, percent
14	23,600	41,600	7
14	16,300	38,100	12
78	17,900	38,400	21
78	(a)	42,800	19

(a) Specimen bent during machining. Could not attach extensometer to obtain yield strength.

20X 1H135

a. Undercooled 15 C



20X 1H136

b. Undercooled 80 C

FIGURE 5. STRUCTURES OF NICKEL - 30 WEIGHT PERCENT COPPER

It is evident that the greater degree of undercooling, even though significant microstructural refinement was noted, had little effect on the yield or ultimate tensile strengths. However, a significant improvement in ductility is evidenced by an increase in elongation of about 100 percent.

Since Ni - 30 wt % Cu can be strengthened by thermomechanical processing, it is suggested that future efforts with the alloy be directed toward homogenization and working subsequent to undercooling in an attempt to derive additional mechanical benefits from undercooled alloys.

2.3 Task 3. Materials Most Benefitted by Solidification in 0 g

Based upon the analysis performed during the program efforts, the classes of materials most probably benefitted from 0-g melting processes would be that of multicomponent alloys. Microsegregation in commercially important alloys can be described in terms of segregation ratio and segregate spacing. We have documented cases where increasing the amount of undercooling in an alloy leads to substantial reductions in both the segregation ratio of alloying elements and of dendrite-arm spacings. As a consequence, the rate of homogenization of an alloy increases with increasing undercooling. The increased homogeneity should improve such physical properties as corrosion resistance. Other structural changes derived from undercooling are reduction in grain size, refinement of endogenous inclusions such as silicates and sulfides, and homogeneous distribution of porosity. All these factors are beneficial to mechanical properties of the resulting castings.

The materials most easily undercooled are those that do not contain effective heterogeneous nucleating agents. Effective nucleating agents are those that have a proper surface energy relation and a close match in lattice properties with the nucleating solid. Since information concerning the interfacial energy relations is almost completely lacking, it is possible to predict, in but only a few cases, the effectiveness

as a nucleating agent of a solid phase in a molten bath. The solid phases may originate from dust in the atmosphere or container. They may be the container walls themselves or may be due to reaction of the molten bath with the atmosphere or container. Lastly, the second-phase particles need not be from foreign material but can be due to alloy phases which initially precipitate in the molten bath and then act as effective nuclei. An example of this is the formation of $TiAl_3$, which acts as a nucleating agent in Al-rich Al-Ti alloys.[24]

As previously discussed in Section 2.11, it is difficult to predict the effect of gravity on undercooling beyond the obvious removal of sources of heterogeneous nucleation by crucibless processing. It is not clear what effect gravity has on the heterogeneous nucleation process. Homogeneous nucleation may be hindered and larger undercoolings promoted by 0 g. This could occur if embryo growth is promoted by collisions between the embryos. The collision frequency can be increased by gravity-driven processes.[25]

2.4 Task 4. CVT: Low-Temperature Alloy

A low-temperature CVT experiment was carried out by MSFC personnel using the Pb-Sn eutectic alloy. After temperature cycling through the melting range in a graphite crucible, an undercooling of 24 C was obtained. Metallographic examination of the resultant specimen revealed gross segregation due to gravity. As expected, BCL participation in this task was minimal, consisting only of several discussions about the experiment with the COR.

2.5 Task 5. CVT: High-Temperature Alloy

It was proposed that CVT experiments be performed on a superalloy of significant commercial interest. One such alloy is Inconel 718 with which we have had some experience, even though it has not been of a positive nature regarding undercooling. This alloy has been used at

intermediate temperatures (700 C) in the hot parts of liquid-fueled rocket engines and in aircraft turbine engines. There are also considerable data available on cast microstructure and microconstituents of the alloy which provide good baseline data for comparing the effects of undercooling. Both micro- and macrosegregation resulting during normal solidification are major problems, even after the alloy has been wrought. The potential benefits of undercooling on minimizing segregacion have been documented by BCL on this program as well as by others.

After a review meeting with the COR, Dr. Mary Helen Johnston, it was decided that the melting temperature of Inconel 718 is beyond the current capability of the GPL for current CVT experimentation. This alloy, since it has practical applications and problems which may be solved by undercooling, might be considered for future experiments.

The copper-base alloy Narloy Z (Cu - 3 wt % Ag - 0.4 wt % Zr) is one which has a melting temperature in the range of current GPL capabilities. This alloy has many of the aforementioned attributes of Inconel 718 and is of current interest as a liner material for the Space Shuttle. The alloy is age hardenable and relies on precipitation of silver for strengthening. The zirconium addition promotes favorable distribution of the silver precipitate and also deoxidizes the alloy and removes Cu_2O from the grain boundaries. The zirconium may, however, form an oxide which may inhibit undercooling. Furthermore, the zirconium is known to form a high-temperature compound with the copper and silver.

Several preliminary experiments concerning Narloy Z were performed. The small-scale setup using two quartz thermocouple protection tubes and a sample size of ≈ 1.5 g was employed. A Narloy Z sample obtained from the COR at MSFC was cycled 15 times through the melting temperature, but a maximum of only 10 C undercooling was attained. It was noted that the alloy appeared dirty. Suspecting the zirconium to be limiting undercooling, a copper-3 percent silver alloy sample was prepared from 99.999 percent pure elemental stock. After nine cycles this alloy only undercooled 8 C. A further experiment with pure copper resulted in a maximum undercooling of only 15 C.

It may be recalled that some question arose regarding the accuracy of the temperature measurements when using this small-scale technique in the past for undercooling Type 304 stainless steel, since the bead of the thermocouple housed in the inner quartz tube was not inserted deeply into the sample. For the current studies, the inner tube was allowed to drop nearly to the bottom of the outer tube in an attempt to obtain accurate temperature readings. This resulted in a nearly annular specimen, which provided a very high glass-contacted surface-area-to-sample-volume ratio. This was postulated as the cause for lack of undercooling.

Therefore, the sample size was increased to one comparable to that used in obtaining consistent behavior with other alloys undercooled successfully. Two glass-envelope experiments were made in an attempt to undercool the Narloy Z alloy. The charge weight was ≈ 250 g, and a Vycor crucible was employed. The alloy was synthesized in situ using OFHC copper, 99.95-purity silver, and crystal-bar zirconium. The first experiment was made with no powdered glass on top of the charge while in the second experiment the charge surface was covered with -120 mesh-powdered Pyrex. In both experiments no undercooling was observed after six cycles through the melting temperature range. Examination of both specimens after the experiment revealed a very dark scale on all surfaces of the specimen. This is believed to be ZrO_2, which is a very high melting phase and might prohibit any undercooling by causing heterogeneous nucleation. One of the roles of the zirconium addition to Narloy Z is to deoxidize the copper, and in addition, it forms a more stable oxide than SiO_2. Thus, it may have reduced both Cu_2O and SiO_2 to form the ZrO_2.

Two experiments were made with a modified composition containing only Cu-3Ag. One had a crushed Pyrex cover while the other did not. In both cases no undercooling was observed, although the resultant specimens appeared very clean, i.e., no black scale as with the zirconium-containing alloy.

In the next experiment the silver was eliminated, the charge being 250 g of OFHC copper (the same grade used in the previous alloy

experiments). Once again, no undercooling was achieved after four cycles through the melting temperature. For the next experiment copper of 99.999 percent purity was employed. This material is significantly more pure than OFHC copper which is nominally 99.9 percent pure. The maximum undercooling achieved was 35 C.

As a result of the difficulty in obtaining consistent undercooling behavior in the silver-base alloys and in the copper, the goal of the CVT experiments in the General Purpose Laboratories was changed to investigate the effect of processing variables on the degree and consistency of the undercooling effect in a Ag - 5 wt % Cu alloy. Task 7 was also formulated to provide backup support for the CVT experiments in the form of working out the techniques, making independent consistency measurements on both Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys, and providing Ag - 5 wt % Cu samples for the CVT experiments.

2.6 Task 6. CVT Participation

Our participation in the 5-day CVT experiment conducted in December of 1974 consisted of a planning session, aid in equipment design, development of experimental techniques, and preparation of experimental encapsulated samples.

The planning session was held at MSFC with M. H. Johnston, COR; C. S. Griner; R. Snyder; S. H. Gelles; and R. Mehrabian, who is a consultant to the program, in attendance. It was decided at that point that the variables to be investigated would be

(1) Method of alloy preparation
(2) Number of heating-cooling cycles
(3) Effect of elevated temperature treatment above the liquidus
(4) The effect of stirring.

Our support role in the other areas is described in the following section of the report (Task 7).

The CVT experiments were successfully carried out in December, 1974.

2.7 Task 7. Investigation of the Inconsistency of Undercooling

2.71 Introduction

One of the major problems interfering with the performance of the originally planned CVT experiments and with future 0-g experiments is the lack of consistency in the undercooling behavior found in many of the materials that we and other investigators have examined. This stems from a lack of understanding of the particular sources of heterogeneous nucleation in these systems. It should be noted that there have been some past efforts expended in attempting to rectify this situation. For example, Powell[3] and Powell and Hogan[4] in working with unalloyed silver and silver-copper alloys determined that undercooling was most readily achieved if the silver or silver-copper was somewhat oxidized by first melting in the presence of air or treated with sodium carbonate. The second prerequisite was the presence of a suitable glass envelope. If either of these conditions was missing, large degrees of undercooling could not be achieved. It was reasoned by these investigators that heterogeneous nucleating agents were being removed from the molten metal by first being converted through oxidation to suitable forms for reaction or dissolution in the glass slag. Although some initial attempts were made to identify the species involved, little progress has been made in this direction.

More recently, Marcantonio and Mondolfo[19] have shown that removal of heterogeneous nucleating agents from 99.999^{+} pure aluminum by centrifuging the molten bath produced increased undercooling and grain refinement. Similar results were obtained in 3003 aluminum by using a flux to remove the nucleants.

In the light of the above discussion, our efforts during the final few months of the program were directed at

(1) Selecting systems in which the greatest consistency in undercoolings can be achieved

(2) Investigating the sources of any inconsistencies

(3) Establishing the statistical nature of undercooling in the systems of our choice at BCL and in CVT experiments

(4) Designing low-g experiments aimed at determining the effect of convection currents, etc., on the undercooling process.

One of the constraints placed on the systems selected for the above work was that they have liquidus temperatures of $\sim$ 1000 C or lower so that supporting experiments could be conducted in the General Purpose Laboratory and be easily adaptable to existing space facilities.

The studies were conducted on

- Ag - 5 wt % Cu, Liquidus $\sim$ 930 C
- Cu - 5 wt % Ag, Liquidus $\sim$ 1050 C.

These have been selected on the basis of their liquidus temperatures and on the basis that the pure components have demonstrated large undercoolings.

In order to study the effect of preparation technique, the alloys were prepared by two different methods:

(1) The soda-glass-slag technique[4]

(2) Vacuum melting and casting.

Techniques and equipment were developed for automatic cycling of multiple samples through the melting and solidification temperature range and for measurement of the degree of undercooling by thermal analysis.

A series of Ag - 5 wt % Cu alloys were cycled as many as 146 times, and a maximum undercooling of $\sim$ 58 C was achieved. The specimens had to be cycled many times (> 30) before undercoolings of this order were achieved and, more often than not, holding the sample at a temperature of $\sim$ 1000 C for several hours produced the most dramatic increases in the degree of undercooling.

One of the more troublesome problems that was encountered during the development of the cycling method concerned the fused silica capsule containing the alloy specimen embedded in a soda-lime glass slag. First of all, it was found that both the original design and final capsule designs could not survive the cool-down to room temperature without severe cracking. This made it impossible to precycle a specimen to achieve a consistently high degree of undercooling without reencapsulation, an operation which largely destroys the beneficial effects of conditioning. This effect is apparently caused by the reintroduction of heterogeneous nucleating agents. This problem needs to be overcome before material having consistent undercooling behavior can be supplied to a 0-g experiment. It is believed that the capsule problem can be solved with some additional effort.

Another capsule problem was encountered during the study when large undercoolings were first achieved. It was at this point that the capsules failed making it impossible to carry on further cycles. Failure was presumably a result of the sudden shock produced by the solidification process. This problem was satisfactorily solved by providing an outer alumina tubular container around the capsule and filling the annular space between the outer and inner tubes with soda-lime glass.

In the light of our successful development of the cycling techniques and demonstration that the Ag - 5 wt % Cu alloys could be undercooled appreciably, a series of 15 encapsulated Ag - 5 wt % Copper alloys having variations in the method of preparation were supplied to Dr. M. H. Johnston, COR for conduct of the CVT experiments dealing with the consistency of the undercooling effect in this system.

Some work was also initiated on Cu - 5 wt % Ag. Four alloys were prepared by the glass slag technique and cycled 35 times showed sizeable undercoolings ($\sim$ 50 C) after only a few cycles. A maximum undercooling close to 100 C was obtained with one of the samples. Two of the samples had been prepared from a large number of small copper pieces and two from a few larger copper pieces. Although the results need further checking, the behavior of the alloys prepared with the

larger copper pieces appear to oscillate over a wide range of undercoolings. The undercoolings obtained with the alloys made from the smaller copper pieces appear to follow a series of plateaus, oscillate much less wildly, but are not as reproduceable as those made with the larger copper piece.

The results obtained thus far on the Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys are consistant with the assumption that the soda-lime glass slag is removing heterogeneous nucleating materials from the molten alloy bath. The understanding of what these nucleating agents are and how they are removed should permit more consistant and larger degrees of undercooling to be achieved. In addition, identifying the nucleating species, their concentration, morphology, and relation to the degree of undercooling should provide a significant contribution to our understanding of heterogeneous nucleation.

2.72 Experimental

2.721 Sample Preparation and Capsule Design. Alloy specimens weighing approximately 80 gm of the compositions, Ag - 5 wt % Cu and Cu - 5 wt % Ag were prepared by the glass slag technique.[4] In the preparation of the alloys the required weight of 99.95 pure, fine silver shot contained in a fused silica tube, was initially melted in air at ∿ 1000 C, soda lime glass powder was then added, and the mixture heated to 1100 C. Small pieces of the required weight of copper, either OFHC or high purity (99.999 pct pure), were then pushed through the glass slag into the molten silver by means of a fused silica rod. As anticipated and desired, some oxidation of the copper occurred during the loading operation. Except for our initial attempt, the technique was applied successfully. In the first experiment, too much pressure was exerted in pushing the copper through the viscous glass slag and resulted in failure of the fused silica tube. In subsequent runs, the copper was successfully inserted by using less pressure.

Two types of soda-lime glass were used in these experiments. The material used for the initial experiments (soda lime glass - 1) was

replaced by a better controlled higher purity soda lime glass (Corning 0080) after only small amounts of undercooling were achieved in samples which used the more impure grade. Analyses of these glasses and some of the metallic starting materials are shown in Table 1. The higher iron content of the soda-lime glass-1 may be important, as will be discussed in a later section dealing with specimen characterization.

Specimens of the Ag - 5 wt % Cu alloy were also fabricated from a vacuum induction melted alloy prepared from 99.999% Ag and 99.999% Cu by pouring into a copper mold having 12.7-mm-diameter cylindrical channels. Specimens cut from this rod were also ∿ 80 g.

The initial samples of Ag - 5 wt % Cu were prepared directly in capsules designed for the conduct of thermal analysis experiments (see Figure 6). These are flat-bottomed tubes 18-mm-ID x 1.5-mm wall thickness, containing a central fused silica tube 3-mm ID x 5-mm OD, which are designed to contain a Pt-10 percent Rh thermocouple fabricated from 0.25-mm-diameter wire and sheathed in two-hole alumina protection tubes ∿ 1.5-mm OD. (∿ 2-mm-OD porcelain insulating tubing was used to sheath the thermocouples used in the preliminary experiments.)

The central fused silica thermocouple tube is held in place by fused silica bands fused to the outside tube. The central fused silica thermocouple tube interfered with the production of alloys in these capsules. In preparing later alloys somewhat smaller inside diameter tubes (13 mm) were employed without the central thermocouple tube. After preparation, they were removed from the tube, and a central hold drilled in the alloy to accommodate the thermocouple tube for thermal analysis. Specimens prepared in this way by the glass-slag technique and also those prepared by vacuum melting were encapsulated in containers of the same design as before (Figure 6).

The capsules were filled before fusing the central thermocouple tube in place. A layer of soda-lime glass was poured into the bottom of the outer fused silica tube, the alloy cylinder inserted and the encapsulation completed by inserting the thermocouple tube into the alloy and fusing it in place to the outer tube. More glass powder was then added to fill the annular space between metal and tube and to provide a glass layer on top of the alloy.

TABLE 1. OPTICAL EMISSION SPECTROGRAPHIC ANALYSES OF STARTING MATERIALS(a)

Element	Soda-Lime Glass-1	Corning 0080 Soda-Lime Glass	99.95Ag	OFHC Cu
Si	20-40(b)	20-40(b)		
Na	5-10(b)	5-10(b)		
Mg	2-3(b)	2-3(b)		<0.0001
Fe	0.3	0.02	<0.0005	0.0005
Al	0.2(b)	0.7(b)		
K	0.3	1.0		
Ca	7-12(b)	4-7(b)		<0.0001
Pb	0.03	0.01		<0.0001
Mn	0.002	0.001		<0.0005
Ba	0.005	<0.005		
B	0.005	<0.005		
Sb	<0.005	0.07		
Ti	0.01	0.3		
Zr	0.005	0.01		0.001
Sr	0.01	0.02		
Cu			0.02	
Ag				0.0007

(a) Analyses given in wt %. Other elements were sought and not found.

(b) Usual components of soda-lime glass.

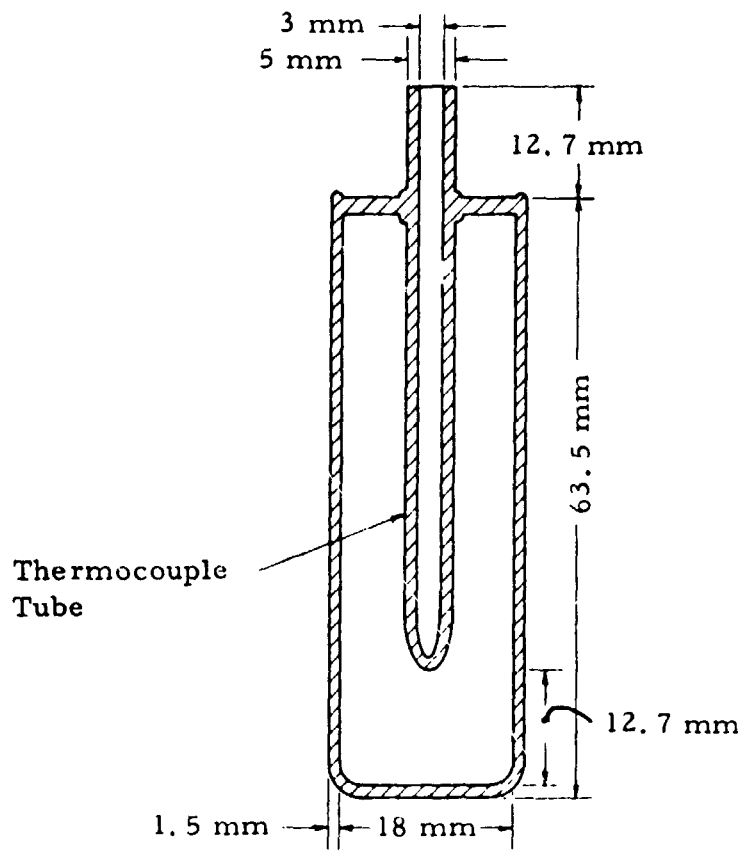


FIGURE 6. FUSED SILICA CAPSULE USED IN PRELIMINARY EXPERIMENTS

As will be discussed subsequently, these capsules failed during thermal analysis cycling when the degree of undercooling approached several tens of degrees. To counteract this problem, the inner capsule was contained in an alumina crucible ∿ 32 mm in diameter. The annular space between the alumina outer crucible and the fused silica capsule was filled with soda-lime glass. This design was successful in preventing these failures presumably caused by the shock from rapid solidification.

Both of the capsule designs suffered from a serious defect; namely, capsule failure during cool-down. This precluded the use of a sample which was "conditioned" by high-temperature thermal treatment or cycling through melting and solidification to produce a large and consistant undercooling unless the sample was first reencapsulated. Cooling to room temperature and/or reencapsulation of a "conditioned" sample, however, appears to destroy the "conditioning" process. This is probably due to the introduction of heterogeneous nucleating agents during the reencapsulation process. Further experimentation into capsule design to eliminate breakage on cool down is warranted. A possible design may substitute a metallic outer container of somewhat smaller diameter for the alumina crucible presently used. This would tend to support the inner-fused silica tube in a more effective way, especially since the higher thermal contraction of the metallic container should tend to produce compressive stresses around the inner capsule.

The ability to condition a sample in order to achieve a consistant degree of undercooling and then to cool it down without loosing the beneficial effects of the "conditioning" treatment, is very important to the success of studies on the effect of the space environment on the undercooling process. What is needed in this case is a specimen which exhibits consistant and large degrees of undercooling terrestically and which, then, can be subjected to a 0 - g experiment for direct comparison of the undercooling behavior.

2.722 Thermal Analysis. The undercooling behavior of the Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys was measured from the temperature-time records obtained during cooling. In order to acquire a large amount

of data concerning the consistancy of undercooling in the different alloys, it was necessary to design and assemble equipment for automatic cycling of multiple samples through melting and solidification and to continuously record specimen temperature.

The equipment assembled for carrying out the automatic cycling experiments consists of a unit for support of the encapsulated samples and thermocouples and a control and recording system.

The sample support system shown in Figure 7 consists of a K-30 brick containing recesses for four samples and four thermocouples which enter the system through holes in an Al_2O_3 top plate and are placed in the fused silica thermocouple tubes centrally mounted in each capsule. A central stainless steel rod ties the K-30 brick support and the Al_2O_3 top plate together as a unit. The design allows the easy removal of the entire unit when desired.

The thermocouple readings from the four samples are recorded on a pair of two-pen Honeywell Recorders having adjustable ranges and adjustable zeros. The cycling behavior is controlled by two microswitches mounted on one of the recorders at the desired high- and low-temperature positions of the cycle. When the switches are activated by one of the pens, the furnace power is either applied or shut off.

2.73 Results

2.731 Undercooling of Ag - 5 wt % Cu Alloys. A summary of the undercooling experiments conducted on the Ag - 5 wt % copper alloys is presented in Tables 2 and 3 and Figures 8-11. These were conducted to determine the degree of undercooling attainable in this system and the consistancy of the effect. Another purpose of the experiment was to test the capsule design, specimen preparation procedures, and performance of the automatic cycling equipment in support of the CVT experiments.

Table 2 summarizes the sample histories including the method of preparation and the cycling history.

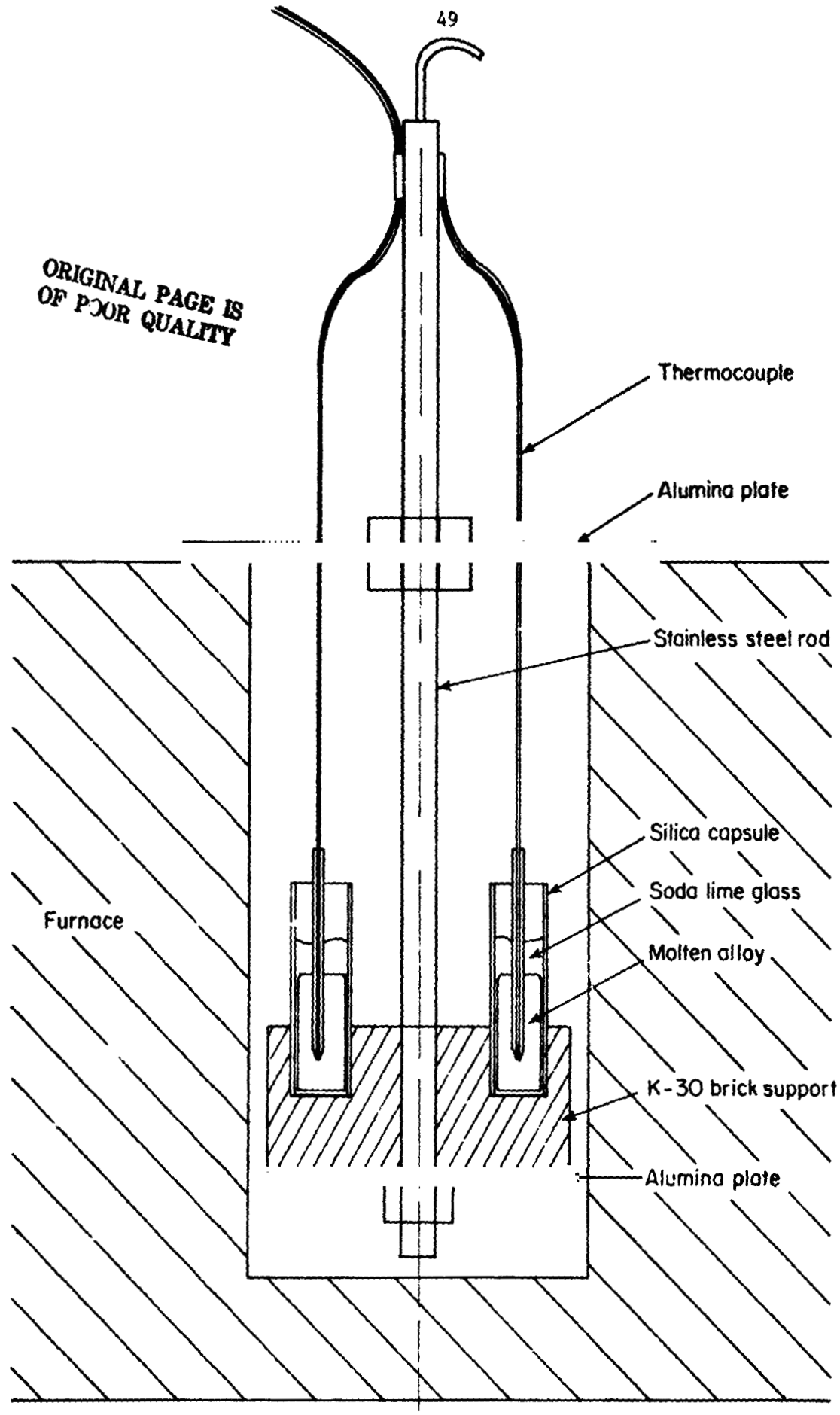


FIGURE 7. SCHEMATIC DRAWING OF AUTOMATIC CYCLING EQUIPMENT

TABLE 2. THERMAL ANALYSIS SAMPLE SUMMARY, Ag-5 Wt % Cu ALLOYS

Sample No.	Fabrication Method(a)	Remarks
1	1	Sample failed during fabrication.
2	1	Ran 4 cycles. See Table 3. Capsule failed during cool-down to room temperature. Reencapsulated as Sample 3.
3	1	Sample failed during heat up.
4	1	Ran 10 cycles. Reencapsulated with Corning 0080 soda-lime glass. Ran an additional 68 cycles. Reencapsulated in capsule with surrounding alumina thimble. Ran an additional 68 cycles. See Figure 8.
5	1	Ran 10 cycles. Reencapsulated with Corning 0080 soda-lime glass. Ran an additional 32 cycles before capsule failure. See Figure 9 and Table 3.
6	1	Ran 15 cycles. See Table 3. Some characterization performed on this sample.
7	2	Ran 67 cycles. Capsule failure after large undercooling effect. See Figure 10.
8	2	Ran 64 cycles. Capsule failure after large undercooling effect. See Figure 11.

(a) Fabrication Method Code

1. Made from 99.95 % Ag and OFHC copper by the Glass Slag Technique with soda-lime glass-1.
2. Made from 99.999 % Ag and Cu by vacuum induction melting. Corning 0080 soda-lime glass used in capsule.

TABLE 3. THERMAL ANALYSIS OF PRELIMINARY Ag-5 Wt % Cu ALLOYS PREPARED BY SODA LIME GLASS SLAG METHOD

Specimen	Cycle	$T_{max.}$, C	$T_{trans.}$, C	$T_{equil.}$, C	ΔT, C	Cooling Rate, C/min
2	1	998	940	948	8	6.7
	2	1042	936	948	12	6.9
	3	1049	935	947	12	6.8
	4	1049	937	946	9	6.4
5[b]	1	~1072	(a)	(a)	(a)	(a)
	2	~1049	(a)	(a)	(a)	(a)
	3	1050[c]	902[c]	902[c]	0	--
	4	1048[c]	899[c]	901[c]	2	--
	5	1058[c]	898[c]	898[c]	0	--
	6	1045	919	920	1	6.6
	7	1045	917	920	3	--
6[b]	1	1072	(a)	(a)	(a)	(a)
	2	1049	(a)	(a)	(a)	(a)
	3	1092	918	920	2	6.3
	4	1088	919	920	1	--
	5	1095	919	919	0	6.2
	6	1058	917	918	1	--
	7	1062	913	917	4	6.6
	8	1061	906	911	5	5.6
	9	1059	902	910	8	6.2
	10	1058	904	910	7	6.2
	11	1060	917	920	3	5.8
	12	1053	905	909	4	5.9
	13	1052	905	908	3	6.0
	14	>1050	912	913	1	6.1
	15	>1051	910	913	3	6.3

(a) No indication of thermal effect.

(b) Specimens 4, 5, and 6 cycled together for first ten cycles. Temperature monitored only on Samples 5 and 6. Samples 4 and 5 removed from furnace after 10th cycle. Sample 6 cycled an additional five times. Recording pen failure on sample 5 during cycles 8-10.

(c) Short in thermocouple suspected. Temperatures are probably low.

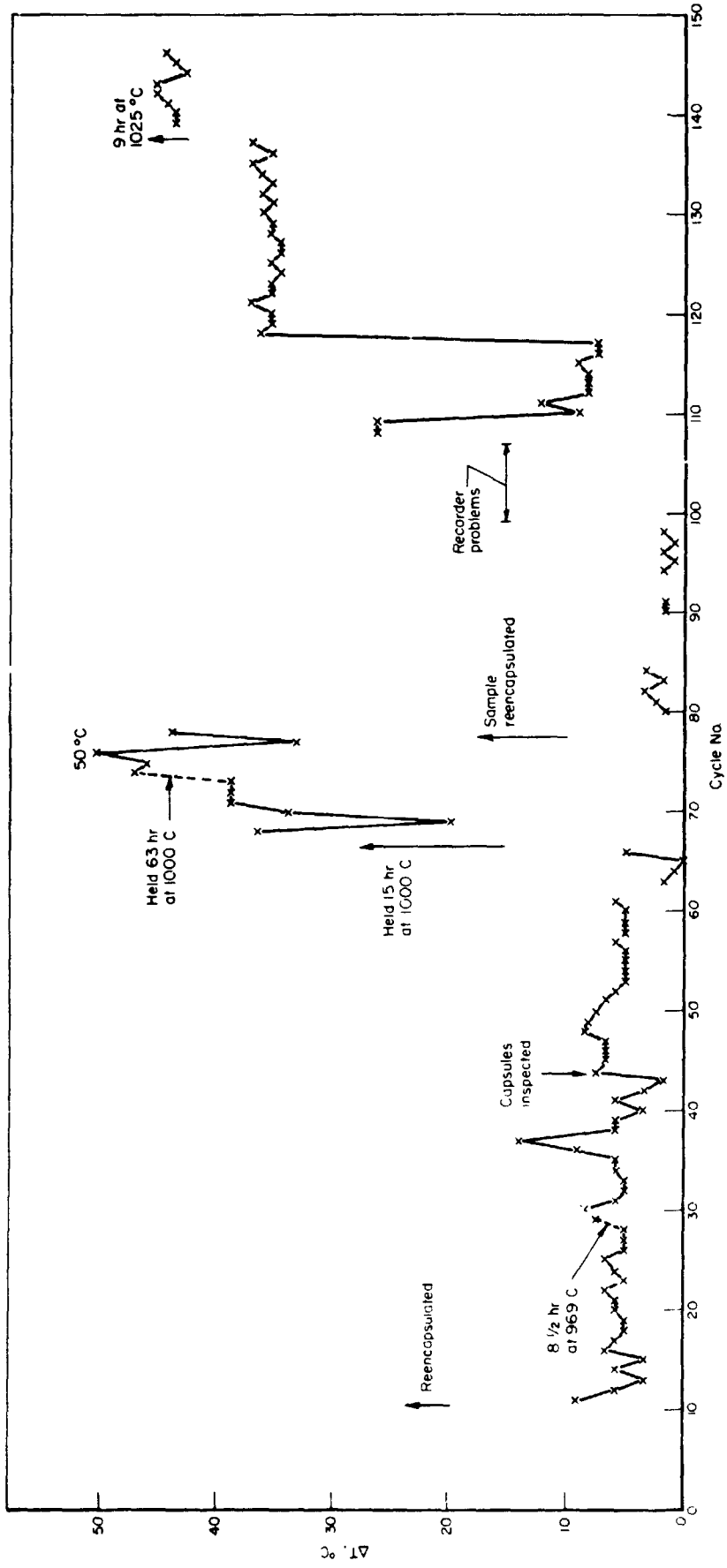


FIGURE 8. DEGREE OF UNDERCOOLING OBTAINED AS A FUNCTION OF THE NUMBER OF CYCLES. SPECIMEN 4 PREPARED BY GLASS-SLAG TECHNIQUE

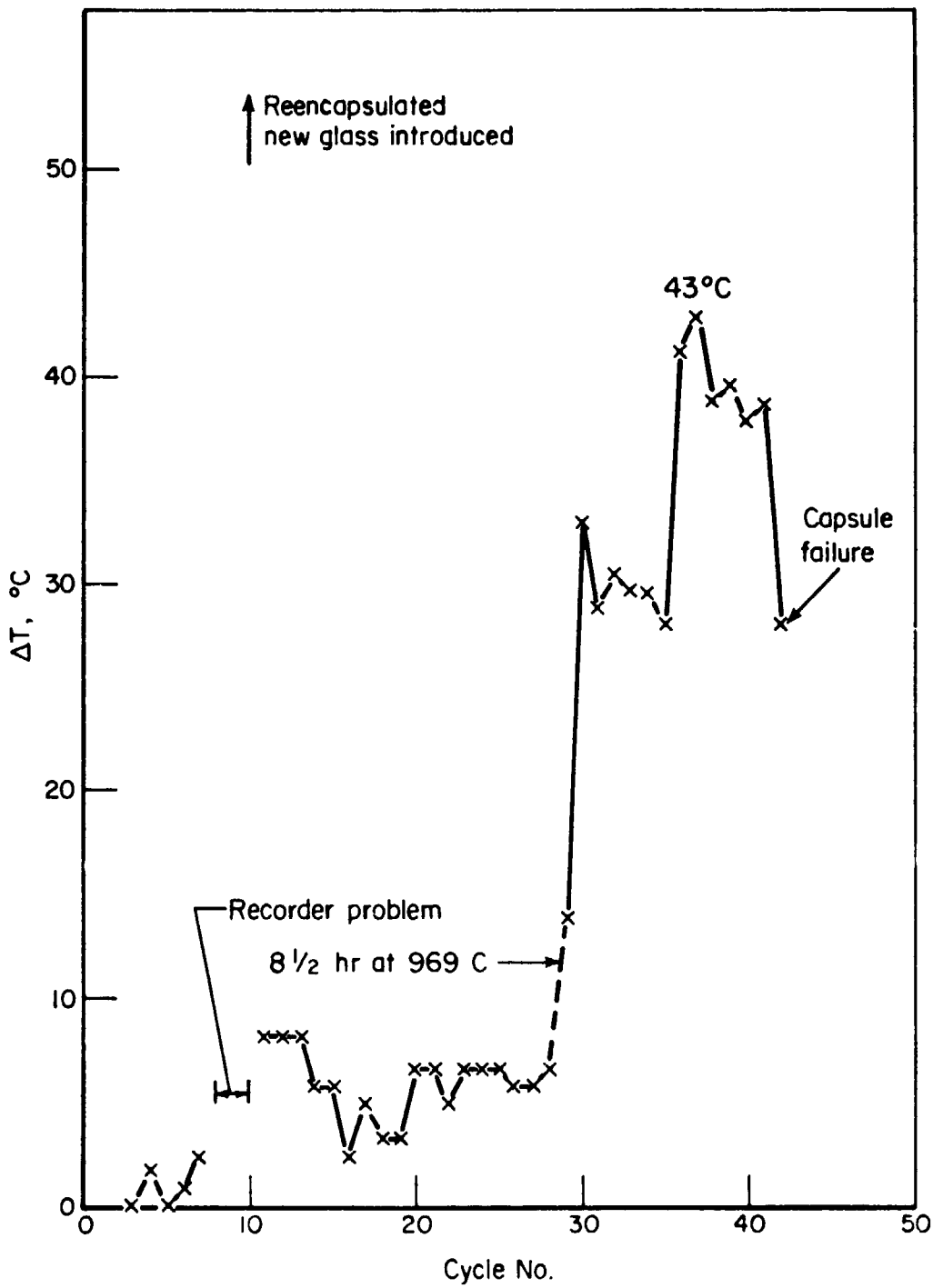


FIGURE 9. DEGREE OF UNDERCOOLING OBTAINED AS A FUNCTION OF THE NUMBER OF CYCLES SPECIMEN 5 PREPARED BY GLASS-SLAG TECHNIQUE

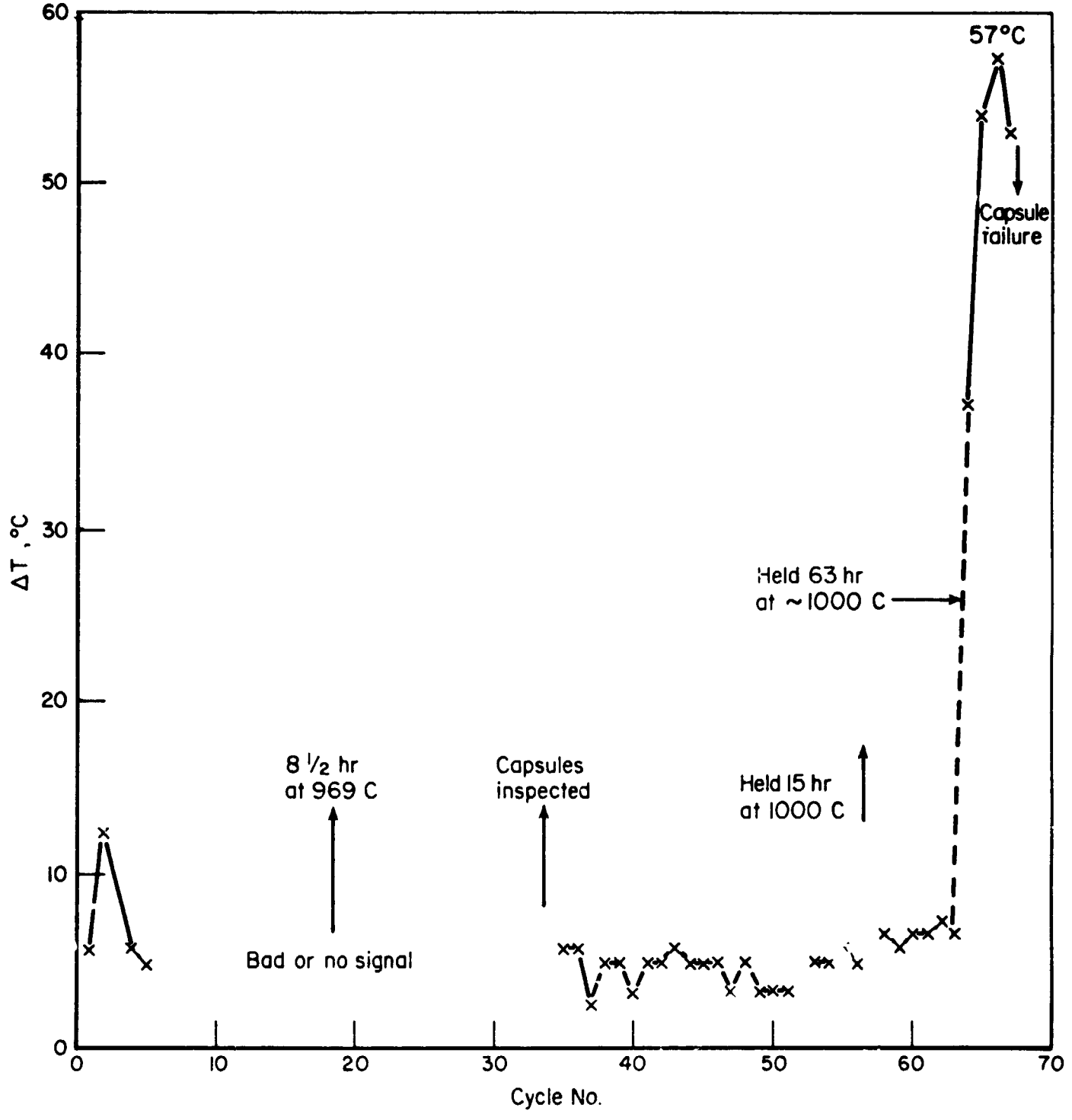


FIGURE 10. DEGREE OF UNDERCOOLING OBTAINED AS A FUNCTION OF THE NUMBER OF CYCLES SPECIMEN 7 PREPARED BY VACUUM INDUCTION MELTING

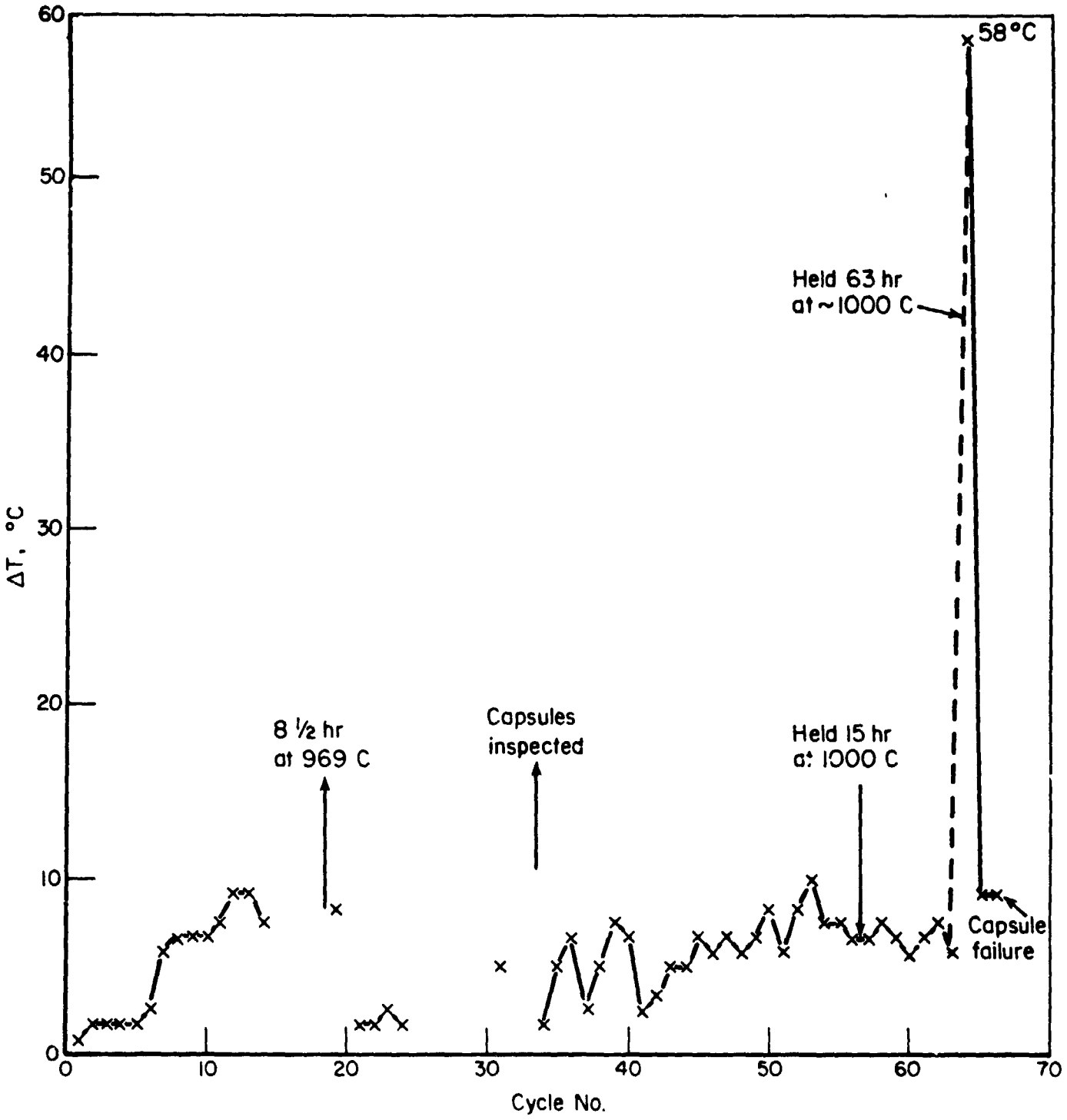


FIGURE 11. DEGREE OF UNDERCOOLING OBTAINED AS A FUNCTION OF THE NUMBER OF CYCLES SPECIMEN 8 PREPARED BY VACUUM INDUCTION MELTING

The first measurements were taken from the initial cooling curves of Samples 2, 5, and 6, and provided the data summarized in Table 3, wherein the temperature at the start of the cooling curve, $T_{max.}$, the temperature at which solidification begins, $T_{trans.}$, the temperature at the end of recalescence, $T_{equil.}$, and the degree of undercooling, ΔT, are recorded. The cooling rate, where measured, is also listed and has been found to be $\sim$ 6 C/min. in these cases.

Specimen 2 was cycled four times after being held at $\sim$ 1000 C for 2-3/4 hr. $T_{equil.}$, which should correspond to the liquidus temperature, is appreciably higher than the equilibrium temperature for the Ag - 5 wt % Cu alloy, 910-922 C[26,27]. Also, a thermal arrest at 771 C corresponding to the eutectic temperature was observed. Because of the high indicated liquidus temperature, it was concluded that the alloy had not been sufficiently homogenized and that the copper was segregated in the sample. The fairly steady decrease of $T_{equil.}$ with the number of cycles tends to support this conclusion. Specimens 4, 5, and 6 were subjected to ten thermal cycles at the same time (only specimens 5 and 6 were monitored), after which Specimens 4 and 5 were removed. Specimen 6 was subjected to an additional five cycles.

The cooling curves obtained from Specimens 5 and 6 indicate that these alloys were much better equilibrated than Specimen 2. In most cases, $T_{equil.}$ is close to the range 910 to 922 C given as the equilibrium liquidus for this alloy composition [26,27].

Some problems were encountered in carrying out the initial thermal analyses. Thermocouple shorting was felt to account for the low results found in Cycles 3, 4, and 5 of Specimen 5. After adjusting the thermocouples, Cycles 6 and 7 of Specimen 5 agreed with Cycles 6 and 7 of Specimen 6 within 2 C. It was also found that after several cycles, the central fused silica thermocouple tubes had broken away from the outside central tubes to which they were initially fused. This allowed the tube to float in the denser liquid or to become positioned in a noncentral location and, thus, has lent some uncertainty to the temperature measurements. This deficiency has been corrected through better alignment of the thermocouples and a stronger support for the central fused silica tube.

The thermal analysis measurements on Specimens 5 and 6 were conducted over a period of a few days. The first cycle in which usable measurements were made on these samples (Cycle 3) was carried out after the samples had been at ∿ 1050 C for 15 hours. This thermal treatment appears sufficient to produce a homogeneous alloy.

The amount of undercooling obtained in the initial experiments was disappointingly low (< 12 C). It was reasoned that this behavior could be due to an insufficent opportunity to eliminate heterogeneous nuclei from the bath, i.e., an insufficient time at temperature or insufficient number of cycles or could be due to impurities in the alloy components or pick-up from the soda-lime glass slag. Investigation of possible impurity pick-up (see Table 1) led us to substitute Corning 0080 soda-lime glass for the soda-lime-glass-1 previously used. It also prompted us to examine one of the samples (Specimen 6) to characterize any second-phase particles which might offer heterogeneous nucleation sites and, thus, interfere with the undercooling process.

A longitudinal section of Specimen 6 has been examined by means of optical and scanning electron microscopy (SEM) and by energy dispersive X-ray analysis (EDXA). Optical microscopy revealed that the microstructure generally consisted of coarse silver-rich dendrites containing copper-rich interdendritic regions. Two types of second-phase particles were often found in the center of the interdendritic region. The more common of these is probably copper containing dissolved silver. The identity of the second type is unknown. The EDXA work, in general, confirmed the interpretation of the metallographic observation. Some particulate regions very high in copper content were found. It is also of great interest that some particulate regions were found to be rich in Fe and Al and also to contain some Ag and a little Cu. Other silver-rich regions were extremely high in iron and aluminum and relatively high in copper.

The presence of second phases of the type found could lead to heterogeneous nucleation and a lack of undercooling. However, there is great need for additional work in this area to check this possible conclusion.

Specimens 4 and 5, which had been previously cycled ten times, were reencapsulated. Two additional samples (nos. 7 and 8) from a vacuum-induction melted Ag - 5 wt % copper alloy made from high-purity components, were also encapsulated using the same procedure. The four samples (two made by the glass-slag technique and two by vacuum induction melting) were assembled into the automatic cycling unit and up to 68 additional cycles were run. Time-temperature curves were recorded for most of these experiments. However, some problems were encountered in pen operation which caused some loss of data.

The results of the undercooling experiments are included in Figures 8 through 11. In these charts the degree of undercooling, ΔT, is plotted as a function of cycle number. Intermediate treatments are also noted on the graphs. In all four cases small degrees of undercooling generally occurred in the earlier cycles and remained about constant for many cycles. Discontinuous increases in ΔT were found in later cycles after thermal treatment at temperatures between $\sim$ 969 and 1000 C. It is encouraging to note that undercooling in the 43-58 C range have been achieved by these treatments. This fact, plus the observation of a range in ΔT, which might be related to changes in chemistry or second-phase content, makes the Ag - 5 wt % Cu alloy a suitable material for the CVT experiments.

It should be noted that capsule failure occurred in three out of the four samples after 1-5 cycles in which the degree of undercooling was significant ($\geq$ 43 C). As previously discussed, the failure was probably caused by the shock of sudden solidification. Incorporation of a modification to the capsule design in the form of an alumina thimble surrounding the fused silica capsule was found to be successful. This new variation in design was tested on Sample 4, which once again was reencapsulated. An additional 68 cycles were successfully run on this sample without failure for a total of 146 cycles. These additional results are also incorporated in Figure 8.

It should also be noted from Figure 8 that the beneficial effects of cycling and annealing are lost during the reencapsulation process.

Little difference is noted between the undercooling behavior of the samples prepared by the glass-slag technique and those prepared by vacuum-induction melting. (Compare Figures 8 and 9 with Figures 10 and 11.) The undercooling behavior of the vacuum-induction melted samples was much more reproducible.

As a result of determining that Ag - 5 wt % Cu alloys would respond to cycling and thermal treatment, and that the modified capsule design would perform well, a series of 15 Ag - 5 wt pct Cu alloys were prepared for the CVT experiments. These are listed in Table 4 and represent variations in method of production, in purity of starting components, and in thermal treatment after preparation, but before reencapsulation.

2.732 Undercooling of Cu - 5 wt % Ag. Four samples of Cu - 5 wt % Ag alloy were produced by the glass-slag technique with the variation that the copper pieces which were added to the silver were many and small for Samples 10 and 11 and were few and large for Samples 17 and 18. All four samples were successfully cycled together in the automatic cycling equipment, each for 35 cycles. The undercooling results shown in Figure 12 reveal some differences between the samples processed in the two ways. The fluctuations in the degree of undercooling for the samples with copper added as small pieces are much smaller than for those in which the copper was added as a few larger pieces. The sample-to-sample reproducibility, however, appeared much better in the latter case.

2.74 Discussion

The variation in undercooling behavior of the Ag - 5 wt % Cu and Cu - 5 wt % Ag alloys has demonstrated that both these systems are good candidate materials for study of the heterogeneous nucleation process and its relation to undercooling. The results thus far can be generally interpreted in terms of removal of effective nucleating agents from the melts during cycling and thermal treatment, probably due to

TABLE 4. LISTING OF BATTELLE-SUPPLIED SILVER - 5 WT % COPPER ALLOYS FOR CVT EXPERIMENTS[a]

Specimen Number	Material		Treatment Time at 1100 C, hr
Glass-Slag Melted Specimens			
A-1	4N Ag	5N Cu	89.5
A-2	4N Ag	5N Cu	89.5
A-3	4N Ag	5N Cu	89.5
A-4	4N Ag	5N Cu	89.5
A-5	4N Ag	5N Cu	7.5
A-6	4N Ag	5N Cu	7
A-7	5N Ag	5N Cu	6.5
A-12	5N Ag	5N Cu	7
A-13	4N Ag	Oxidized OFHC	6
A-14	4N Ag	5N Cu	7
A-15	4N Ag	5N Cu	7
A-16	4N Ag	5N Cu	7
Vacuum-Melted Specimens			
	Material		History
VM-3	5N Ag	5N Cu	Cast into ~ 1-cm-diam mold
VM-4	5N Ag	5N Cu	Remelt
VM-5	5N Ag	5N Cu	Remelt

(a) After initial fabrication, all samples were cleaned and encapsulated.

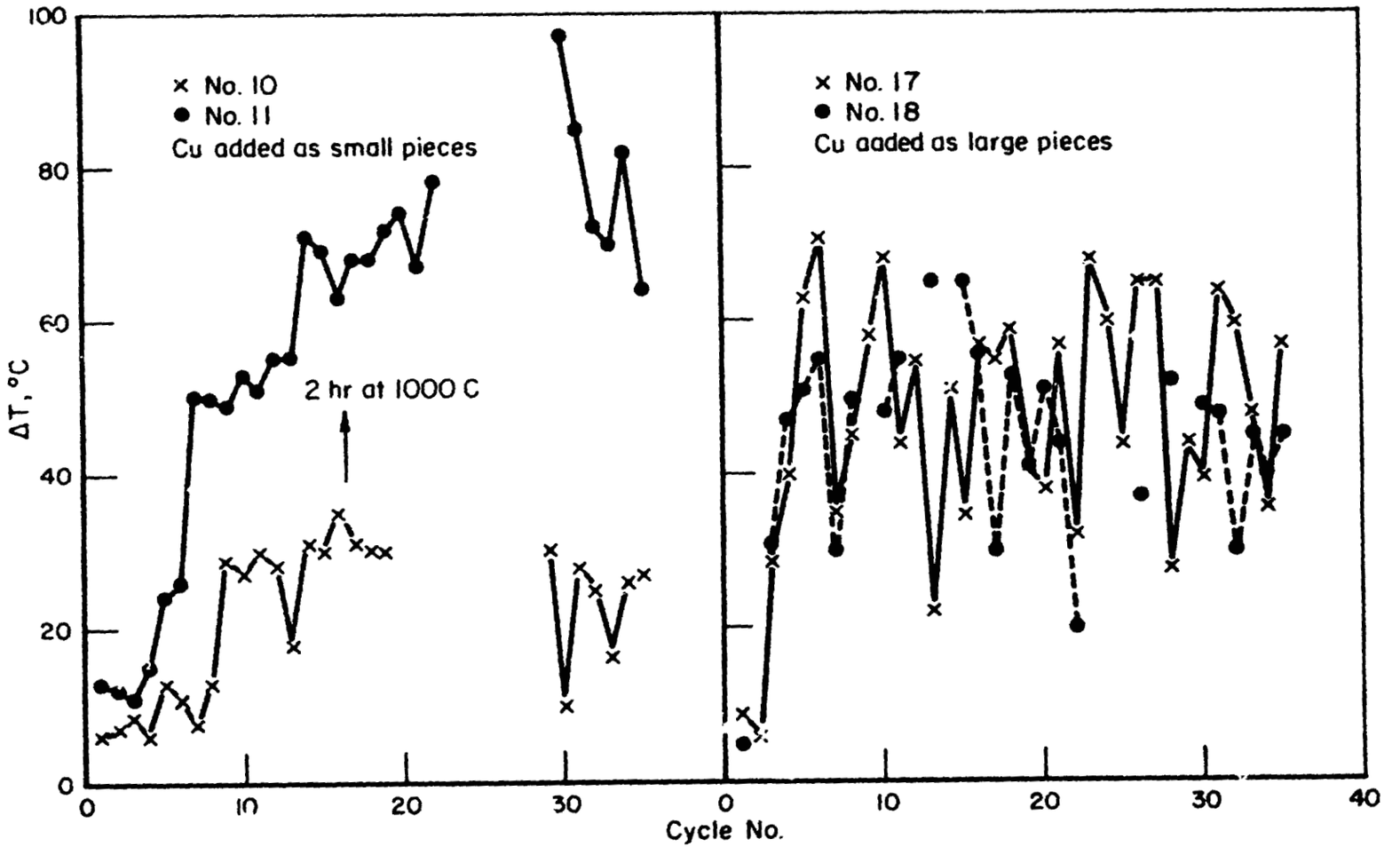


FIGURE 12. UNDERCOOLING BEHAVIOR OF Cu - 5 wt % Ag ALLOYS PRODUCED BY THE GLASS-SLAG TECHNIQUE

reaction with the glass slag. The role of oxygen in the removal process is not clear. For the Ag - 5 wt % Cu alloy, there appears to be little difference between the undercooling behavior of the slag melted (presumably higher in oxygen content) and the vacuum induction melted material. In contrast, the behavior of the Cu - 5 wt % Ag alloys showed a significant difference in behavior when the alloys were made from many small pieces versus a few large pieces of copper. The former would presumably have a higher oxide content than the latter.

There is much experimental work that has yet to be done in order to be able to interpret the measured undercooling behavior. Measurement of changes in chemistry as the undercooling behavior changes with cycling and thermal treatments is one obvious way to proceed. Following the changes in amount and kind of second-phase particles especially near nucleation sites by optical microscopy SEM, TEM, SAD, and EDXA is another.

Lastly, it should be mentioned that understanding undercooling and its relation to nucleation will help improve the consistancy of the phenomenon so that the effect of gravity on nucleation and undercooling may be determined in space experiments.

In regard to this latter point, it should be noted that a small development effort is needed to produce an encapsulated sample that can survive terrestrial "conditioning" designed to achieve a reliable degree of undercooling. Samples so conditioned could be the subject of a 0-g experiment to experimentally determine the effect, if any, of net gravitational fields on nucleation and undercooling.

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