Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

EUTECTIC EXPERIMENT DEVELOPMENT FOR SPACE PROCESSING
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R.H. Hopkins

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Prepared for

George C. Marshall Space Flight Center
Marshall Space Flight Center
Alabama   35812

Westinghouse Research Laboratories
PITTSBURGH,   PENNSYLVANIA   15235

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

APOLLO 16 Pb-Sn EUTECTIC SOLIDIFICATION EXPERIMENT

R. H. Hopkins

ABSTRACT

A ground base test plan and a specimen evaluation scheme have been developed for the aluminum-copper eutectic solidification experiment to be run in the M518 Multipurpose Electric Furnace during the NASA Skylab mission. Besides thermal and solidification studies a detailed description is given of the quantitative metallographic technique which is appropriate for characterizing eutectic structures. This method should prove a key tool for evaluating specimen microstructure which is the most sensitive indicator of changes produced during solidification.

It has been recommended that single grain pre-frozen eutectic specimens be used to simplify microstructural evaluation and to eliminate any porosity in the as-cast eutectic specimens. High purity (99.999%) materials from one supplier should be employed for all experiments.

Laboratory studies performed in support of this program indicate that porosity occurs in the MRC as-cast eutectic ingots but that this porosity can be eliminated by directional freezing. Chemical analysis shows that the MRC ingots are slightly Al rich and contain about .03% impurity. Because of the impurity content the lower cooldown rate (1.2°C/min) should be used for eutectic freezing if MRC material is used in the M518 furnace.

1

I. INTRODUCTION

Composite materials produced by the rather elegant technique of unidirectional solidification from a liquid of eutectic composition have evoked widespread interest because their inherent structural anisotropy leads to enhanced structural, electrical, optical and magnetic properties [1,2]. While success in the development of high strength eutectic composites seems to have brought such materials close to commercial usage[3], the application of eutectic composites to non-structural areas has been limited[4]. This restriction stems in part from structural irregularities introduced during growth which tend to degrade composite properties relative to theoretically expected values. The most prevalent defects in lamellar eutectics are extra phase platelets (faults) and their associated structural mismatch (fault lines)[5] branched fibers and fiber packing errors are common in rod-like composites[6].

While the origins of lamellar faulting and rod-branching (as well as more complicated structural phenomena such as lamellar rotation[7]) still remain obscured, some attempts have been made to study and explain their occurance. Jackson and Hunt[8] in carefully controlled experiments on organic eutectics concluded that faulting was the most likely mechanism for interphase spacing changes. That is, when growth

2

fluctuations occur a fault forms to increase or decrease the local lamellar spacing. From their point of view, fault formation is an inherent feature of eutectic growth. Bertou and Gruzleski[9], however, were able to grow Cd-Sn eutectic ingots containing grains in which no faults existed. They claimed that crystallographic factors rather than freezing conditions were the controlling influence on fault production. However, the ambient conditions in these experiments were carefully controlled and convection effects were minimized by vertical growth. Growth variables, therefore, may have played a greater role in preventing fault formation than realized by the authors.

The expected use of eutectic composites in optical, electrical and magnetic applications that would follow the development of more perfect composite microstructures is an impetus to further studies of the way in which freezing conditions influence defect formation. One experiment suggested of this kind is the controlled freezing of a eutectic liquid under the unique zero-gravity conditions present in the NASA Skylab facility. This experiment (NASA-M554 and its successor, designated M566) utilize the Al-CuAl$_2$ binary eutectic, a model system which offers the advantages of previous extensive investigation, low melting point and easy metallographic preparation[1,5,11].

II. PROGRAM OBJECTIVES

The overall objectives of this program were to devise plans
and conduct studies aimed at a) enhancing the feasibility and scientific
value of the NASA composite casting experiments, b) identifying acceptable
sample or flight hardware refinements for the experiment, and c) con-
tributing to an understanding of gravity effects in materials processing.

The program was divided into two phases:

Phase A -- the development of a ground based study plan to aid in
optimizing the experiment and provide comparative data for the space
flight experiment.

Phase B -- the conduction of laboratory tests to support and improve
the studies outlined in Phase A.

III.   PHASE A -- GROUND BASE TEST PLAN

Thorough ground base testing is a prerequisite for maximizing the information to be gleaned from the eutectic samples returned from the Skylab flight. This is because data acquisition during zero-g solidification is limited primarily to the time-temperature histories of the hot and cold ends of the furnace. The most important objectives of ground base testing can be summarized as follows:

1. Characterization of the thermal environment and ingot freezing conditions prevailing in flight hardware during simulation of a space solidification run. This includes correlation of the monitored temperatures with those measured on the eutectic samples.

2. Development and testing of a standard specimen evaluation plan for the analysis of flight and ground base samples, as well as the identification of the analytical techniques to expedite such a plan.

3. Solidification of eutectic samples in flight hardware and their analysis according to the specimen evaluation plan to provide specimen characteristics for comparison with flight data. Prior to these tests any ingot preprocessing as well as the ingot composition must be identified.

A.   Thermal Analysis of Flight Hardware

A knowledge of sample thermal environment and thermal history is critical to understanding microstructural evolution during solidification.

5

This is because the shape and motion of the solid-liquid interface is controlled by heat flow and the eutectic microstructure in turn is dependent on the configuration and motion of the interface.

For this reason the heat flow through the specimen should be evaluated both theoretically and experimentally (in part, some of this work is being carried out by Westinghouse under NASA Contract NAS8-28271). One set of experiments should be conducted under conditions designed to simulate as closely as possible a flight run (minimum convection). Such an experiment can be conducted in the M518 multipurpose electric furnace by means of an instrumented cartridge. This cartridge contains thermocouples positioned in intimate thermal contact with the hot and cold ends of an eutectic ingot. During freezing the ingot temperatures as well as the furnace temperatures can be monitored. From the data a correlation can be obtained so that by monitoring the furnace temperatures only, the sample temperature history can be obtained. The shape of the solid-liquid interface at various points during solidification can be obtained by abruptly perturbing the furnace temperature. Temperature fluctuations produce structural discontinuities (bands) which delineate the shape of the solid-liquid interface and can be examined after freezing terminates.

It would also be useful for comparative purposes to run experiments in which convection is maximized (see Section IIIC). For the proper interpretation of these experiments thermal data again would be necessary and could be obtained as described above.

From the measured ingot temperatures the temperature gradient in the liquid (and solid) during freezing as well as the ingot freezing velocity can be calculated. These are two important parameters necessary for understanding eutectic freezing behavior[5]. Since these parameters are expected to vary along the ingot length as the relative volumes of solid and liquid change during freezing, the importance of thermal-history data is evident.

A third set of thermal experiments, while not mandatory, are potentially valuable. These consist in measurements of the time-temperature history for samples freezing with passive control, i.e., free cooling. In the event that power were lost during a run, a knowledge of the free cooling behavior of the sample would provide a means to interpret the solidification data in what might otherwise be a useless experiment.

B. Sample Evaluation

1. General

Structural, chemical, physical and mechanical evaluation techniques provide the main means by which eutectic samples can be characterized and compared. The sequence of testing as well as the type of test is also important. For example, sample characterization must usually proceed from non-destructive to increasingly destructive test methods in order to maximize the amount of information which can be obtained from any given sample. In Table I are listed those properties which will probably be most useful for characterizing directionally

TABLE I

Possible Properties and Parameters to be Measured in a Eutectic Freezing
   Experiment (or Collected from the Literature where Appropriate)

A. <u>System Parameters</u>

1. Freezing rate – should be known as a function of distance along sample (if it varies).
2. Temperature gradient in liquid and solid as a function of distance along sample (if variable).
3. Temperature fluctuations – magnitude of deviation in sample temperature from average temperature (if any).

B. <u>Sample Characteristics</u>

1. Macrostructure--

   a. sample surface – porosity, shrinkage, reaction with crucible, inclusions, sample shape,
   b. sample interior – porosity, inclusions banding, grain competition, colony structure.

2. Microstructure--

   a. lamellar spacing, degree of orientation, and length of interphase boundary,
   b. fault density (and type of faults),
   c. rotation of lamellar interface about growth axis,
   d. volume percent of phases present,
   e. arrangement of phases–at nucleation, in aligned portion, in colony structure (if present),
   f. subgrain structure.

3. Fine Structure--

   a. crystallographic relations between primary phases,
   b. interfacial crystallography ($CuAl_2/Al$)
   c. dislocation structure at interface and in primary phases,
   d. precipitation in primary phases.

8

4. Chemistry--

    a. bulk sample density,
    b. bulk sample composition,
    c. variation in composition along sample (if any),
    d. variation in composition across sample (if any),
    e. local composition fluctuations-banding (if any),
    f. impurity element content.

5. Physical Properties--

    a. thermal conductivity (solid and liquid)
    b. resistivity.

6. Mechanical Properties--

    a. strength (bend or tensile),
    b. elastic moduli.

frozen Al-Cu eutectic ingots. Table II is a compilation of test
techniques suitable for measuring the properties listed in Table I.
While the lists are not exhaustive each should be representative of the
analyses required to evaluate the success of the eutectic composite
casting experiment.

On the assumption of the data requirements and methods of
Tables I and II, a specimen evaluation plan has been derived. The
plan itself is intended as a guide; the final evaluation plan cannot
be fixed until the proposed plan has been assessed during ground base
testing.

2. Possible Test Sequence

The graphite crucibles encapsulating the ingots are carefully
removed from their stainless steel cartridges after cutting off the
steel end caps. The graphite crucible is examined for leaks then slit
longitudinally to expose the Al-Cu ingot.

The two crucible halves and ingot are positioned as they
were during growth and macrophotographed (1-10X range). Any significant
features relating crucible and ingot are documented (for example, reaction
between ingot and crucible). The ingot surface is then examined with
the optical and/or scanning electron microscope (SEM) to reveal any
features of interest (surface reaction products, ingot shrinkage, gas
holes, etc.). Photographs to characterize the sample are taken up to
50X with the light microscope and at higher magnification with the SEM
where required. The sample is then examined for internal features by

10

TABLE II

Useful Techniques for Analysis of Eutectic Composites

	Technique	Feature to be Analyzed
1.	Radiography	Internal structure: porosity, shrinkage, inclusions, gross chemical variations.
2.	Macrophotography	External surface structure. Gross features of internal structure--banding, grain competition, colony structure evolution.
3.	Microphotography	Phase arrangements, volume percent phases, lamellar spacing, fault density, lamellar rotation, evolution of aligned structure, eutectic grain and subgrain features.
4.	Scanning Electron Microscopy	Spatial distribution of phases (by selectively etching one phase), crystallographic orientation from electron channeling patterns, inclusions (or void) examination.
5.	Transmission Electron Microscopy	Crystallographic orientation relations, interface crystallography, fine structure including precipitation and dislocation arrangements lamellar spacing. Analysis of fractures (if any) by replication techniques.
6.	Electron-Microprobe	Chemical analysis on local scale (few microns), variation of composition across and along sample, chemical analysis of specific features, e.g., inclusions, bands.
7.	Wet Chemistry X-Ray Fluorescence	Bulk chemical analysis, Cu and Al.
8.	Mass and Emission Spectroscopy	Trace, impurity element analysis at points within a sample.

9.	X-Ray Diffractometry	Lattice parameters of primary phases, residual stress in composite--this requires calibration studies.
10.	X-Ray Topography	Berg Barrett, Lang techniques, etc. can be used to analyze subgrain structure and crystal perfection.
11.	Resistivity	In principle would give information about degree of continuity of phases in sample. In practice the necessary calibration and sensitivity might be difficult to obtain.
12.	Sound Velocity Measurement	Can be used to obtain elastic constants as a function of specimen orientation.
13.	Tensile or Bend Testing	Young's modulus, composite yield and ultimate strength. The scatter in these tests is usually large and can be strongly affected by specimen preparation. The value of data from one or two samples is questionable. If other analyses show the samples to be significantly different from those obtained in earth experiments, strength measurements might be considered worthwhile.

point source radiography. Electron probe microanalysis is employed to measure the composition of any extraordinary surface features of the ingot or crucible revealed by optical or scanning microscopy. The steps outlined above are portrayed schematically in Fig. 1.

Using the surface analysis as a guide, a longitudinal section is made on the sample for optical metallography. This section (A_1, Fig. 1) is simply ground a few mils deep on one surface giving a strip 1-2 mm wide along the sample. This flat section is polished using standard metallographic techniques then etched (e.g., 20% Nitric acid in H_2O, or Keller's reagent) to reveal the microstructure near the ingot surface. Both macro (1-10X) and microphotographs (20-1000X, selected areas) are made. Here SEM and electron probe measurements may be used if significantly interesting features must be analyzed in more detail. Based upon analysis of the first section, A_1, and radiographic evidence, a second longitudinal section (A_2, Fig. 1) is fabricated by slicing parallel to the ingot growth axis. This section will probably pass through the center of the specimen to reveal the structure characteristic of the bulk material. After polishing and etching the sample is again macro and microphotographed. Bulk non-destructive chemical analysis by x-ray fluorescence (Cu,Al content) at selected points along the sample can be performed at this point if desired. The local variation of Cu and Al across and along the ingot can be ascertained by electron microprobe (especially at areas such as bands or colony structure, if present). The variation of trace elements at

1. Eutectic Ingot Removed from Crucible:

                    ← Surface Examination   1-5X Whole Sample
                      Macrophotograph   20-50X Selected Areas

                    ← Radiography
                    ← SEM   ⎫
                    ← Microprobe   ⎬ Selected Areas
                    ← Bulk Density   ⎭
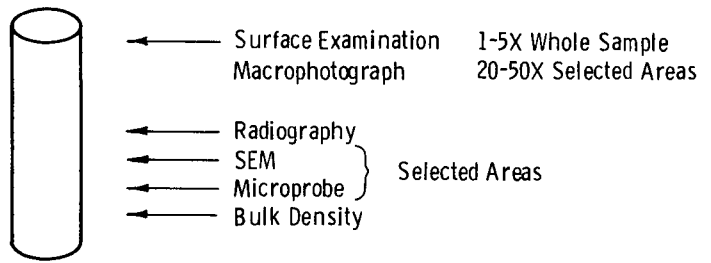
2. Ingot Sectioned Longitudinally

        Section B   Section A₁   Section A

    Verify Results of A →   ← Macrophotograph 1-10X
    Wet Chemical Analysis →   ← Microphotograph 20-1000X Selected Areas
    X-ray Lattice Parameter →   Sect.   Sect.   ← Microprobe − Local Composition Variation
    Elastic Constant, etc. ----→   B   A₂   ← Emission Spectrograph—Trace Element Analysis
                                                                     ← X-Ray Fluorescence−Cu, Al Content
                                                                     ← Microhardness − Selected Features
                                                                     ◄----- Resistivity, etc.
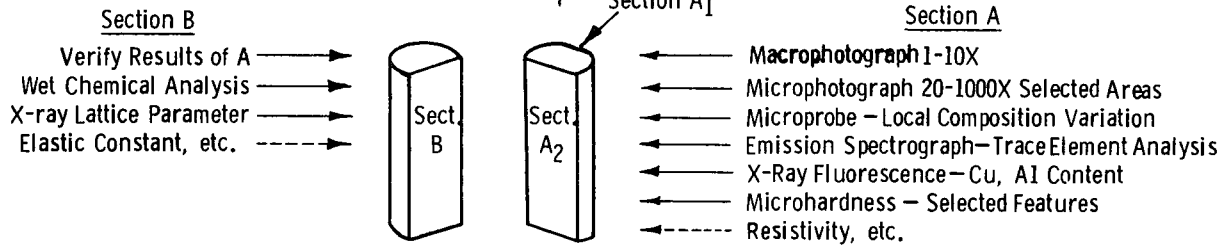
3. Ingot Sectioned Transversely

    Thin Slice for Electronmicroscope   Macrophotograph   1-10X
         X-Ray Topography   →   [TA₁]   Microphotograph   20-1000X
                                                              Measure: Lamellar Spacing
    Deep Etch for SEM ————   Fault Density
                                                                       Phase Volumes
                                                                       Lamellar Rotation
                                                         Microprobe
                                           [TA₂]   Emission Spectrograph
                                                         Reflection X-Ray Topography

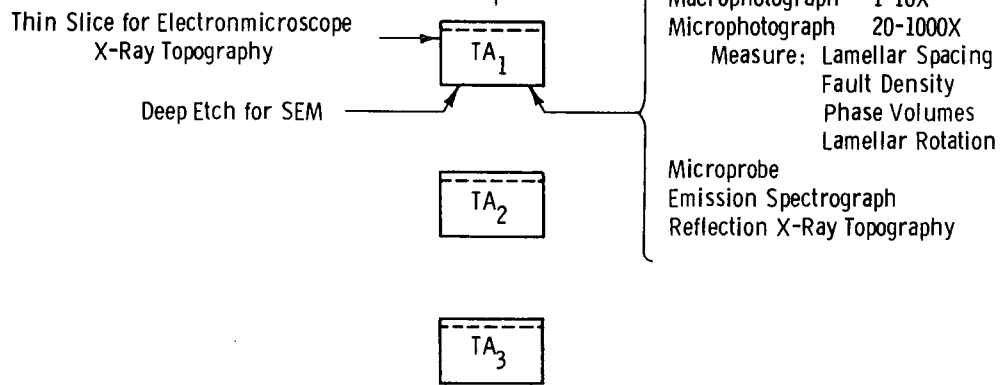   [TA₃]

Fig. 1 -- Schematic Diagram of Specimen Characterization Plan

points along the sample length can be obtained by mass spectroscopy or emission spectroscopy for correlation with the ingot structure. Physical property measurements such as sample resistivity or thermal conductivity, may also be carried out on the same half of the sample just analyzed unless a larger cross-section is required.

Following the above analyses the sample half (A_1, Fig. 1) is then sectioned sequentially, normal to the growth axis, at convenient intervals (say 0.5 cm) to produce a series of transverse sections (TA_1, TA_2, etc., Fig. 1) which are polished and etched in the same manner as section A_1 and A_2. Macro and microphotographs are again made. On each transverse section a measurement of the lamellar spacing, fault density, lamellar rotation, or any other structural feature than can be determined by quantitative metallography are made. Thus, the variation in structural perfection as growth proceeds can be documented. The use of quantitative metallographic techniques is discussed in more detail in Section V.

Particular attention should also be given to the structure present at the beginning and end of growth. Cu and Al compositional variation across each slice can be obtained if necessary by microprobe, and trace element segregation by the methods given above. If possible the crystallographic fine structure of the eutectic should be evaluated by rocking curves and reflection x-ray topography. The transverse sections may then be deep etched on one surface to preferentially remove one phase thus revealing the spatial distribution of phases in

15

the SEM. Following this examination thin slices are cut from each transverse section and chemically thinned. The initially thinned samples can be examined by transmission x-ray topography for further fine structure analysis then jet thinned for transmission electron microscopy. Here the orientation relations between phases, the $Al-CuAl_2$ interface plane and the crystallography of any other pertinent features can be established.

Section B of the sample may be used to verify the results from A. It may also be used for such destructive tests as bulk wet chemical analysis and x-ray lattice parameter determinations along the sample length.

It may also be desired to measure mechanical properties. Such measurements usually require a good statistical sampling to insure reproducibility. In ground based testing this may not present a problem since many samples can be run and tested. It is expected that flight samples will be limited to three in number, therefore it is not clear that mechanical properties if measured would be statistically significant. A possible exception would be acoustic measurements of elastic constants, though again it isn't clear how this would relate to freezing conditions and ingot structure.

Two other points should be kept in mind with regard to the characterization scheme and methods presented above. First, it may not be necessary to perform all the testing suggested while some other tests not discussed may be desirable. An important segment of ground

based testing and analysis should be devoted to assessing which methods are likely to give pertinent information relating to ingot structure and freezing conditions. For example, the correlation between lamellar spacing and growth rate is important and obvious. However, if high purity materials are used it is not obvious that measurement of trace impurities along the sample length would provide any useful information. Thus, ground based testing must be used to some extent to screen evaluation methods.

Second, no matter what evaluation techniques are used, steps should be taken to document the reproducibility of the results and the expected measurement error. This may involve statistical studies to establish confidence limits for a given analysis (e.g., quantitative metallography) or it may require the duplicate analysis of one sample by several investigators using the same technique. In this way confidence can be established for any given set of results. This will be especially important if the affects of zero-g gravity on eutectic solidification turn out to be subtle in nature.

C. Solidification Studies

1. Ingot Preprocessing and Composition

Several variations of the eutectic composite casting experiment are possible by making changes only in the ingot freezing history or Al/Cu ratio. Microstructural pre-alignment (single or multi-grain)[12], growth from a liquid off-eutectic composition, and seeding eutectic

ingots with a single crystal of one primary phase, either Al solid solution or $CuAl_2$, are some of the primary candidates for implementation.

2. Pre-Alignment of Specimen Microstructure

As originally envisaged the samples for the composite casting experiment contained as-cast microstructure, i.e., Cu-Al eutectic grains having essentially random lamellar orientation with respect to the ingot axis. By freezing these ingots under unidirectional heat flow (prior to the space experiment) it is possible to produce: (a) multi-grained ingots with axially aligned lamellae or (b) single eutectic grains with axially aligned lamellae.

At present there seems no apparent advantage in producing pre-aligned structures containing many grains, since upon resolidification a multi-grained structure would again develop. Multi-grained structures would also develop from initially as-cast material frozen under directional heat flow.

However, if a single grain, pre-aligned ingot were used, a great simplification in the interpretation of the microstructural data obtained during the space experiment could be achieved. This is because the presence of eutectic grain boundaries introduces some ambiguity in the measurement of such microstructural features as lamellar terminations, fault lines, and growth induced boundaries which are of special interest.

Production of single grain ingots of the Cu-Al system is not overly difficult (see, for example, G.A. Chadwick, Progress in Materials

Science[11]). If eutectic ingots several centimeters long are directionally
solidified, competitive grain growth continuously reduces the number of
eutectic grains as growth proceeds. This process is aided if the
solid-liquid interface is slightly convex to the liquid. By using ingots
of suitable length or by reversing a given ingot between growth runs
single grain ingots are produced.

Single grain ingots appear both _feasible_ and _scientifically_
valuable, and were recommended for use in the composite casting experi-
ment. This recommendation has been implemented by NASA-MSFC through a
contract with United Aircraft Research Laboratories.

3. Seeded Ingots

Seeding of the Pb-Sn eutectic with single crystals of Sn
primary phase resulted in a fault density reduction compared to unseeded
ingots.[13] No such microstructural improvement was obtained, however,
seeded LiF-NaF eutectic specimens[14]. It has been
suggested that seeding the Al-Cu eutectic ingots with either Al or
$CuAl_2$ single crystals might have a beneficial effect in the case of the
Al-Cu eutectic.[12]

There is much potential merit to the suggestion of seeding.
To justify such a suggestion, however, a series of experiments must be
first performed to (1) develop methods to grow $CuAl_2$ crystals, if these
are used, (2) develop procedures to assure epitaxial nucleation of the
eutectic on the seeds, (3) determine which seed orientations actually
improve the structure (in the Pb-Sn experiments only two orientations

of seven studied improved the structure; other orientations led to structural deterioration[13]), and (4) determine what structural changes are produced by seeding and how they correlate to the growth conditions. None of these experiments is trivial by itself; each is time-consuming and must be carried out with diligence if the results are to be interpreted unambiguously.

In the short time left for the preparation of samples and ground based testing it does not seem likely that experiments such as those described above could be efficiently performed so it is recommended that no seeded specimens be used in the M554 or M566 experiment. Experiments employing seeding might be feasible for future flights, however.

4. Ingot Composition

Aligned composite microstructures can be produced from samples whose composition deviates from the eutectic if: (a) the growth rate is fairly slow, (b) the temperature gradient in the liquid is high and, (c) liquid convection is minimal.[15] The particular growth rate and temperature gradient for which aligned growth of off-eutectic alloys is possible depends upon the system chosen. For the Al-Cu system some data are available which can be used to judge the ranges over which aligned structures would be expected.[16] In general the farther the melt composition deviates from the eutectic composition the larger is the value of G/V (G is the temperature gradient in the liquid during freezing and V is the freezing rate) required to obtain structural

alignment (see table). If G is assumed to be 60°C/cm, a value typical

of that found by B.R. Aldrich in measurements conducted with the M554

experiment hardware, we can use Jordan and Hunt's data to calculate

the maximum growth rate, V_{max}, above which an aligned structure cannot

be produced at several alloy compositions. If G = 40°C/cm, a value more

characteristic of the M566 experiment, V_{max} would be lowered by the factor

$\frac{40}{60}$, as indicated in parentheses. (For reference the eutectic composition

in the Al-Cu system is 67 wt % Cu-33 wt % Al.) The alloy compositions,

minimum G/V for stability, and V_{max} are tabulated below:

Approx. Alloy Composition (wt % Al)		$\frac{G}{V}$ (°C sec cm^{-2})[16]	V_{max} (cm/hr)
Cu-rich	Al-rich		
67	70	0.05×10^6	3.9 (2.6)
63.5	74	1×10^6	0.22 (.14)
61.4	77.5	2×10^6	0.10 (.07)
60	79	3×10^6	0.07 (.05)

Typical growth rates obtained in the M554 and M566 experiments

are about 2.5 cm/hr, so that dendrites would be expected for all alloy

compositions in the table except those involving small deviations from

the eutectic composition. In fact, Jordan and Hunt's data[16] indicate

that no excess in Cu can be tolerated without dendrite formation occurring

under the conditions present in the M554 and M566 experiments. Some small

excess in Al, perhaps up to 2% could be tolerated without dendrite forma-

tion with 60°C/cm gradient (less tolerance is possible with the 40°C/cm

gradients and 2.5 cm/hr average growth rate. Actually our calculations indicate that for the M554 experiment the gradient will slowly drop by a factor of about 0.6 and the freezing rate slowly increase by about 2.7 times as more solid material is formed by solidification. Conditions favoring dendrite formation would be enhanced as growth proceeds. The order of magnitude for these changes in the M566 experiment is about the same.

An important question is what increased scientific knowledge can be expected by off-eutectic growth under the above assumptions? It would seem that very little new information would be obtained relative to the present experiment if only a 2-3% deviation from the eutectic composition were allowed. Furthermore, the chance of dendrite formation due to the changing gradient and growth rate during freezing would seem to negate any small benefit that could be obtained by growing off the eutectic composition. Finally, off-eutectic ingots are more susceptible to structural instability in the presence of slight temperature changes during growth,[8] so that unless extremely good temperature control is available in the system, banding of the ingot microstructure would be promoted. For all these reasons it is recommended that no off-eutectic composition ingots be grown in the M554 or M566 experiments as presently conceived. In fact, great care should be exercised to obtain ingots which contain no excess in Cu over the eutectic composition, and are as close to the eutectic composition, Al 67 w/o-Cu 33 w/o, as possible. This recommendation has been implemented in the NASA purchase specifications submitted to MRC Corporation and United Aircraft Corp. for eutectic ingots.

Besides fixing the ratio of Al/Cu in the alloys purchased, careful consideration should also be given to minimizing the presence of any dissolved elements or gases in the raw materials, Al and Cu, used to cast the eutectic ingots. The highest purity Al and Cu (at least 99.999% pure) available should be specified in order to prevent the formation of "colony" microstructure[5] during unidirectional freezing under the conditions expected to prevail in the M554 or M566 experiments. All test and flight specimens should be manufactured from the same lot of raw materials to minimize the variation in composition and impurity content from ingot to ingot. The material purity and composition should be verified independently of the manufacturers analysis (see Section IV).

5. Freezing Conditions

The purpose of the ground base solidification tests is four-fold: to verify proper hardware functioning, to correlate freezing conditions with specimen properties, to assess the scope and methods embodied in the specimen evaluation plan, and to provide well-characterized samples suitable for comparison with space grown material. With proper planning the solidification studies can be carried out concomitantly with the thermal studies outlined in Section IIIA.

All solidification experiments should be carried out in flight hardware, with high purity single eutectic grain material. (Preprocessing the eutectic material serves two purposes: data from single grain material should be easier to interpret and the MRC eutectic

23

ingots purchased are known to contain porosity which can be removed by a melting-freezing cycle, see Section IV.) The programmed freezing cycle in ground based testing should be the same as used in the flight.

Fluid flow during freezing is expected to be a primary influence upon the perfection of eutectic microstructures. For this reason it is suggested that ground base solidification experiments be conducted in such a way that convective flow is either maximized or minimized. This can be achieved in the following way. In one experiment the specimens are frozen vertically with the heat source at the ingot top. This configuration is known to minimize convective flow[9,15] and should provide some simulation of the zero-g environment. In a second set of experiments the solidification direction would again be vertical, however, the heat source would be positioned at the ingot bottom. This maximizes density variation along the samples and promotes convection. It is expected that the high oxide surface tension on the Al-Cu liquid would support the weight of liquid in this configuration. Should this arrangement prove experimentally unmanageable horizontal solidification of the eutectic ingots might be substituted. With the temperature gradient horizontal some convection will occur in the liquid, although not as much as would be expected with the vertical arrangement. The properties of samples frozen with convection present should represent the worse case as far as structural perfection is concerned and will provide direct comparison data for the space grown and minimum convection ground-grown material.

In each solidification experiment one of the three cartridges should be instrumented to provide a thermal history of the run. Following freezing each sample should be completely characterized by following a standard specimen evaluation scheme like that outlined in Section IIIB. Again, it should be stressed that the properties of all samples from a given experiment be compared with one another as a check for internal consistency. Duplicate runs under the same conditions should be made where possible and run to run data reproducibility verified.

D. Ground Base Test Scheme (Summary)

There are many possible alternatives for directing test sequences, material flow, specimen analyses and related ground base testing. One possible test scheme, outlined below, is based upon the items discussed in detail above.

1. Eutectic Material

   a. Obtain hi-purity Al-Cu eutectic ingots cast from the same lot of raw materials by one vendor.

   b. Perform independent analysis of Al,Cu and trace element composition of the ingots to verify specifications.

   c. Grow single grain eutectic specimens and have them chemically analyzed subsequent to solidification.

2. Hardware

   a. Obtain flight hardware and control system.

b. Set up furnace hardware to simulate the thermal and ambient conditions expected to prevail the flight experiment.

c. Verify hardware function and furnace programming.

3. Solidification-Thermal Tests

a. Run simultaneous solidification and thermal testing using two standard and one instrumented cartridge per run (instrumented cartridge can be eliminated if sufficient time-temperature correlations are available for any given set of experimental conditions).

   (1) growth rate and gradient chosen to simulate space experiment.

   (2) duplicate runs in following sequence:

   vertical freeze - hot end in top

   vertical freeze - hot end in bottom

   horizontal freeze as alternate to #2

b. Analyze specimens (see below).

c. Correlate specimen properties and thermal data.

4. Specimen Evaluation

a. Organize in-house and contract personnel into groups performing the same type of specimen analysis.

b. Identify the desired and minimum samples requirement for each group.

c.   Standardize the type of sample for each type of analysis.

d.   Standardize the sampling sequence and sample evaluation

plan to maximize the information available from the

eutectic ingots.

e.   Analyze all ground base and flight samples according to

the sample evaluation plan.

f.   Compare and contrast data from various investigators and

define error limits on all experiment analyses.

5. Data Correlation

Analyze and correlate all ground base test data and revise

test sequence or evaluation plan where necessary.

IV. PHASE B -- SUPPLEMENTARY LABORATORY STUDIES

During Phase B of this program laboratory experiments and studies were carried out to supplement the concepts developed during Phase A.

A. M518 Prototype Run-Shop Grade Eutectic Material

Two types of solidification experiments were carried out using "shop grade" eutectic ingots supplied by B. Aldrich, NASA-MSFC. The experiments, designed to gather thermal development data for the M566 cartridge-crucible system, were carried out in the M518 simulation and prototype furnaces. The metallographic and chemical analyses of one instrumented cartridge which was first frozen by passive cooldown in the simulation furnace, then resolidified in a controlled manner in the prototype furnace are described below.

The Al-Cu ingot was contained in a graphite crucible under a slight pressure of He. The experiments were conducted in the following order. The graphite crucible, encapsulated in a stainless steel cartridge, was heated at several temperatures in the simulation furnace to obtain thermal data. (This data is reported by R. G. Seidensticker under NASA Contract NAS8-28271.) Following equilibration at the highest furnace temperature employed, about 850°C, power to the furnace was cut off and the sample froze at a rate fixed by the heat loss of the

system. The cartridge was removed from the simulation furnace then
placed in one well of the prototype furnace (the other wells contained
a second eutectic specimen and a "low loss" cartridge). The furnace was
heated to about 800°C equilibrated for two hours and cooled at 1.2°C/min
(this corresponds to a freezing rate on the order of 2 cm/hr). Following
this run the cartridge was opened; the ingot was removed from the
graphite, sectioned lengthwise, polished then etched with Keller's
reagent for optical metallography.

The general features exhibited by the ingot following the
freezing runs can be described with reference to Fig. 2, a longitudinal
macrograph of the specimen (magnification $\sim$ 1.3X). Four distinctly
different kinds of microstructure can be distinguished within the
sample. The regions indicated in Fig. 2 can be classified as follows:
1 - as received (unaligned) structure present in the threaded (cold)
end of the specimen which remained unmelted during our experiments,
2 - partially aligned cell structure formed during passive cooldown in
the simulation furnace, 3 - aligned lamellar structure formed by
controlled freezing in the prototype furnace and 4 - mixed dendrite and
colony structure formed in the hot end during final transient freezing
in the prototype furnace. Note that regions 1 and 2, as well as 2 and
3, are separated by dark lines (remelt regions) in the photograph.
These regions are composed mainly of aluminum primary phase formed
during melt back prior to freezing in the simulation furnace and
prototype furnace, respectively.

Region 1, shown at 50X in Fig. 3, consists of a cell structure with random freezing direction, i.e., no alignment. The presence of the cell structure strongly suggested that the material was contaminated with elements other than Al and Cu. This is perhaps to be expected since only "shop grade" Al and Cu were available for the master ingot.

Region 2 (again at 50X) in Fig. 4 is composed of a cell structure like that in region 1 except that the cell alignment shows that freezing for the most part occurred in a direction parallel to the ingot axis. Since the cooling rate was no doubt fairly rapid during free cooling a cell structure would be expected in this impure material. More important, however, is the fact that partial alignment was obtained. This indicates that heat flow was axial in the gradient region of the specimen even though the cooling rate was not controlled.

An aligned lamellar structure, free from cells and dendrites was obtained in region 3, Fig. 5, during controlled freezing in the M518 prototype furnace. No banding was evident to the naked eye or during examination in the optical microscope. There are variations in lamellar thickness within region 3 but these do not appear to cross the sample width at any one point. The lamellar thickness variations may be due to the changing of the angle of intersection of the lamellae with the plane of polish. The dark circular spot in region three is due to porosity in the sample.

The remelt region between regions 2 and 3 is shown at 100X in Fig. 6. It is mostly single phase and remains light when etched with
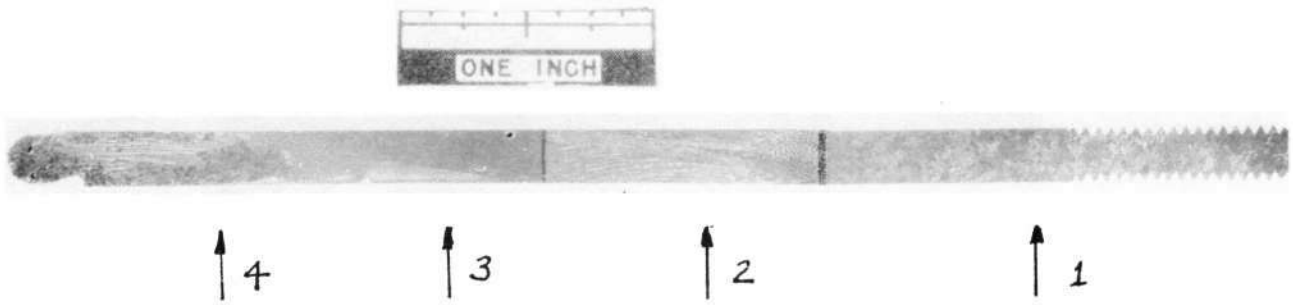
Figure 2.

Figure 3.

Figure 4.

Figure 5.

32

an 80% H_2O-20% HNO_3 mixture signifying that it is Al rather than $CuAl_2$. The remelt region between regions 1 and 2 is similar to that shown in Fig. 6. The excess of Al in the remelt regions suggests that the sample is not of eutectic composition.

The last portion of the sample to freeze, region 4 – Fig. 7, contained aluminum dendrites mixed with a cell structure (magnification 50X). Normally the last portion of an eutectic sample to freeze will contain some cell structure due to the partitioning of impurities during freezing and the rather uncontrolled freezing conditions which exist during the final transient. The presence of Al dendrites supports the hypothesis that the ingot is off eutectic composition.

To verify the results of the metallographic examination the eutectic ingot was analyzed chemically for Al and Cu content, as well as for the presence of any trace impurities. Briefly, the method of analysis was the following. Portions were cut from the head (cold end) and tail (hot end) of the ingot, dissolved and the Cu plated out on a platinum cathode. The weight percent Cu was determined from the known sample weight and the weight of the plated material. The Al, after conditioning to remove any Fe interference, was precipitated from ammonia solution. The expected error in the Cu determination is $\pm$ 0.05 w/o while that for Al is $\pm$ 0.3 w/o. The larger error in the case of the Al is due to the cumulative weighing errors involved in the several-step Al determination. Trace impurity elements were determined by emission spectroscopy with error limits of 1/3 to 3X the amount detected.
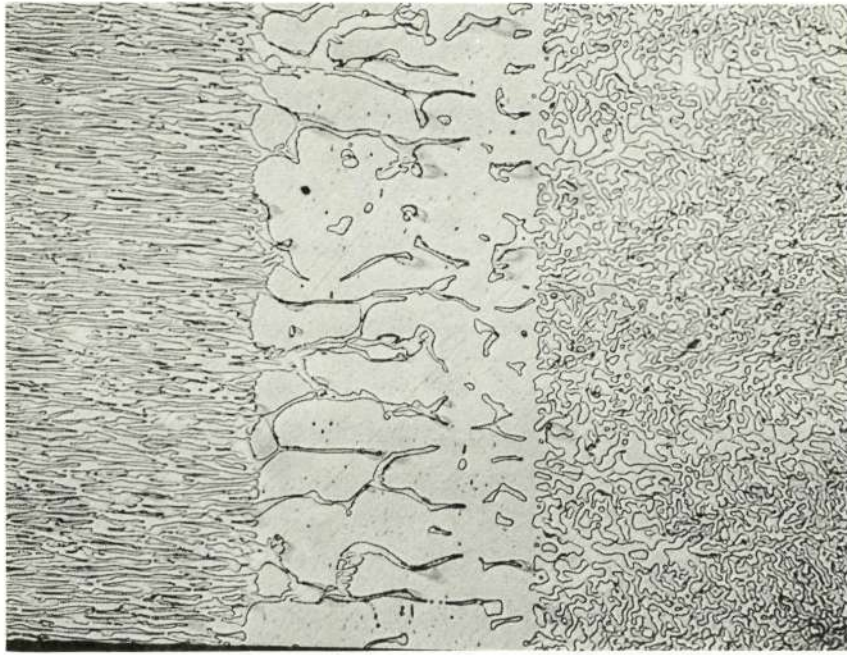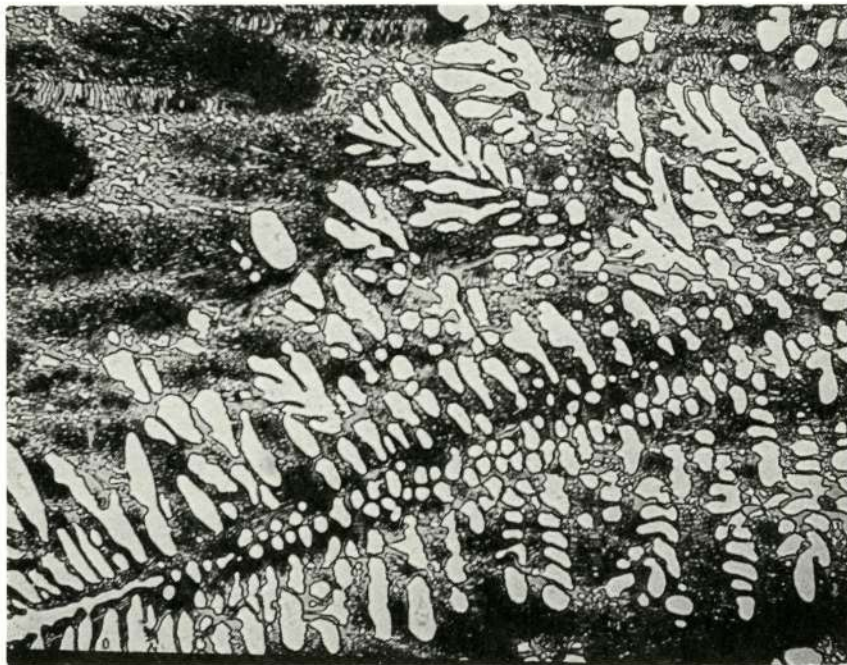
Figure 6.

Figure 7.

34

The analytical results indicated that the ingot contained 64.5 w/o Al-35.2 w/o Cu at the head end and 69.7 w/o Al-30.2 w/o Cu at the tail end. Since the eutectic composition is 67 w/o Al-33 w/o Cu it is evident that considerable segregation exists along the ingot in agreement with the metallographic findings. The fact that the unmelted portion of the ingot is Al-poor and the solidified portion Al-rich suggests that most of the segregation was present prior to freezing.

Trace impurity analysis showed no significant partitioning of impurities from the head to the tail of the ingot. The average values for the two determinations showed that the prominent impurities are 0.003 w/o Ag, 0.002 Fe, 0.001 K, 0.003 Si, 0.001 Ti and < .03 Na. All other metallic impurities are < .001 w/o. As expected from the microstructural evidence, considerable amounts of impurities are present.

Several conclusions were drawn from these experiments.

1. The solid-liquid interface, Fig. 2, is slightly covex to the liquid at equilibrium which tends to promote well aligned microstructures in pure eutectics.

2. Heat flow in the gradient section of the M566 cartridge is axial, a prerequisite for structural alignment.

3. Microstructural control can be developed, Fig. 5, even in impure, off-eutectic ingots, albeit only over short distances.

4. It is obvious that the diverse microstructures that form during the freezing of impure material can render ambiguous the interpretation of a test run. For this reason the use of high purity

eutectic material is recommended in all ground based tests, except those designed only for the acquisition of thermal data.

B. Analysis of Cast MRC Al-Cu Eutectic

A lot of high purity (99.999%) Al-Cu eutectic was prepared by Materials Research Corporation (MRC) to specifications submitted by NASA-MSFC. This material is intended for use in the M566 ground base tests and flight experiments. One ingot in the as-cast condition was metallographically and chemically analyzed at the Westinghouse Research Laboratories.

The ingot structure shown in longitudinal section, Fig. 8, is composed of columnar eutectic grains which grew from the cold mold wall with somewhat more equiaxed grains toward the ingot centerline. The lamellar eutectic structure is extremely fine and in most grains is resolvable only at high magnification, e.g., Fig. 9. Portions of the ingot contain a grey second phase (denoted by the arrow in Fig. 9) which appears quite brittle and tends to pull out during polishing. This is likely Al_2O_3 from the crucible. This phase would be detrimental if present in all ingots. The ingot also contains porosity distributed apparently at random along its length.

Specimens were removed from each end of the ingot and analyzed by wet chemistry (see Section IVA) for bulk Al and Cu content. The results were

> Specimen 1   67.1 w/o Al-32.7 w/o Cu
> Specimen 2   67.1 w/o Al-32.6 w/o Cu

indicating that the as-cast ingots are somewhat Al-rich relative to the eutectic composition.

Figure 8.

Figure 9.

37

The presence of porosity is detrimental to solidification studies for two reasons. First, if porosity is present in the unmelted portion of an ingot the heat flow to the heat extraction section of the crucible can be lowered thus affecting the gradient in the specimen. Second, porosity can perturb the growth of aligned lamellae. For both reasons it was recommended that MRC eutectic specimens be prefrozen prior to ground base and flight experiments.

C. Analysis of MRC Al-Cu Eutectic Solidified at UARL

Following the recommendation for sample prefreezing one MRC cast ingot was refrozen unidirectionally at United Aircraft Research Laboratories (UARL). The growth rate was about 30 cm/hr. The ingot, examined after freezing at Westinghouse Research Laboratories, contains a fanned lamellar or "colony" microstructure, Fig. 10, typical of Al-Cu eutectic ingots which are solidified rapidly[5]. No porosity or second phase particles were observed metallographically in this sample. The removal of the porosity by solidification was also confirmed by radiographic analysis at NASA-MSFC.

Bulk chemical analysis of the above ingot was carried out on specimens removed from the head and tail ends of the ingot:

Specimen 1 (head end)   67.1 w/o Al-32.6 w/o Cu

Specimen 2 (tail end)   66.6 w/o Al-33.1 w/o Cu

Redistribution of Al and Cu during freezing is evident. The last portion of the ingot to solidify is closer to the eutectic
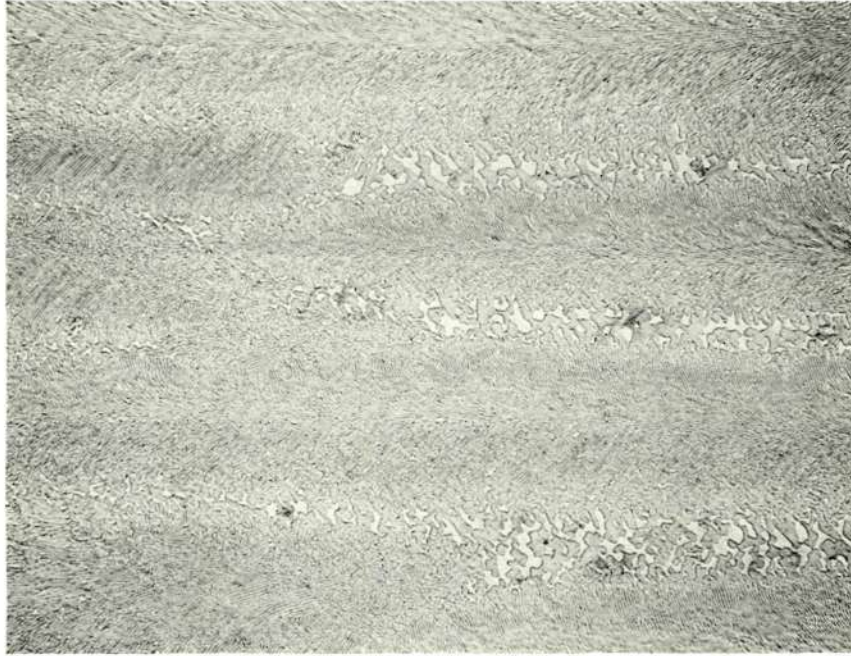
Figure 10.

composition than the initially frozen material. Solute redistribution would be expected if the original ingot were slightly off-eutectic composition[8] as indicated by the analysis of the cast material, Section IVB.

D. Analysis of M518 Prototype Run M566-3

Three as-cast MRC eutectic ingots were supplied to Westinghous Astronuclear Division by NASA-MSFC for prototype experiments in the M518 Multi-Experiment Furnace. These specimens, one of which was instrumented with thermocouples, were frozen in run M566-3. Following freezing the ingot from the instrumented cartridge was sectioned longitudinally and subjected to metallographic analysis.

A macrograph (1.5X) of the longitudinal section, Fig. 11, illustrates that five regions of distinctly different microstructural morphology are present in the ingot:

(1) equiaxed eutectic grains in the unmelted, threaded section (cold end)

(2) a rim of coarser equiaxed material that appears to have been extruded out of the crucible around the ingot

(3) partially aligned lamellar material

(4) relatively well-controlled lamellar growth

(5) fanned lamellae (colony structure)

The arrow in Fig. 11 denotes a large rounded pore about 1 mm in diameter which was intersected by the plane of polish. Several smaller pores varying from 0.1 to 0.3 the size of the large pore are
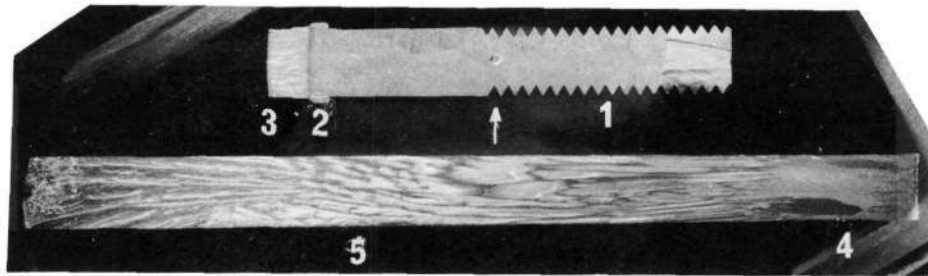
Figure 11.

41

also present on the section. The ingot in the instrumented cartridge melted back significantly farther than the ingots in the other two cartridges utilized in run M566-3. The ingot porosity observed may be directly related to this anomalous behavior. In any case the facts that (a) porosity can conceivably affect freezing behavior adversely in the eutectic ingots and (b) porosity is easily removed by prefreezing indicate that a prefreezing step should be a requirement for all ingots utilized for ground base testing and flight experiments.

V. QUANTITATIVE METALLOGRAPHY OF EUTECTIC SPECIMENS

Metallographic examination is one of the simplest yet most versatile techniques for the analysis of eutectic microstructures. In most cases investigators rely upon visual (microscopic) examination of two-dimensional sections through a specimen to build up a qualitative picture of the shape and distribution of the phases present in the bulk. However, it is possible by means of the technique of quantitative stereology[17] to characterize numerically those features of the micro-structure which are of particular interest. This section describes the application of quantitative techniques for the characterization of lamellar eutectic composites.

Briefly, a lamellar eutectic consists of alternating platelets of two phases which are nearly parallel to each other and to the solidi-fication direction. This perfectly parallel arrangement of phases is interrupted on sections transverse to the growth axis by boundaries across which lamellae are tilted slightly from the average lamellar direction, Fig. 12. Across the boundary, termed a fault line or trace line[21], an extra lamella is often inserted into the structure. The locus of points delineating the edge of an extra lamella in three dimensions is designated a fault (termination).[18] The fault line represents the two-dimensional trace of "mismatch surfaces" which lie
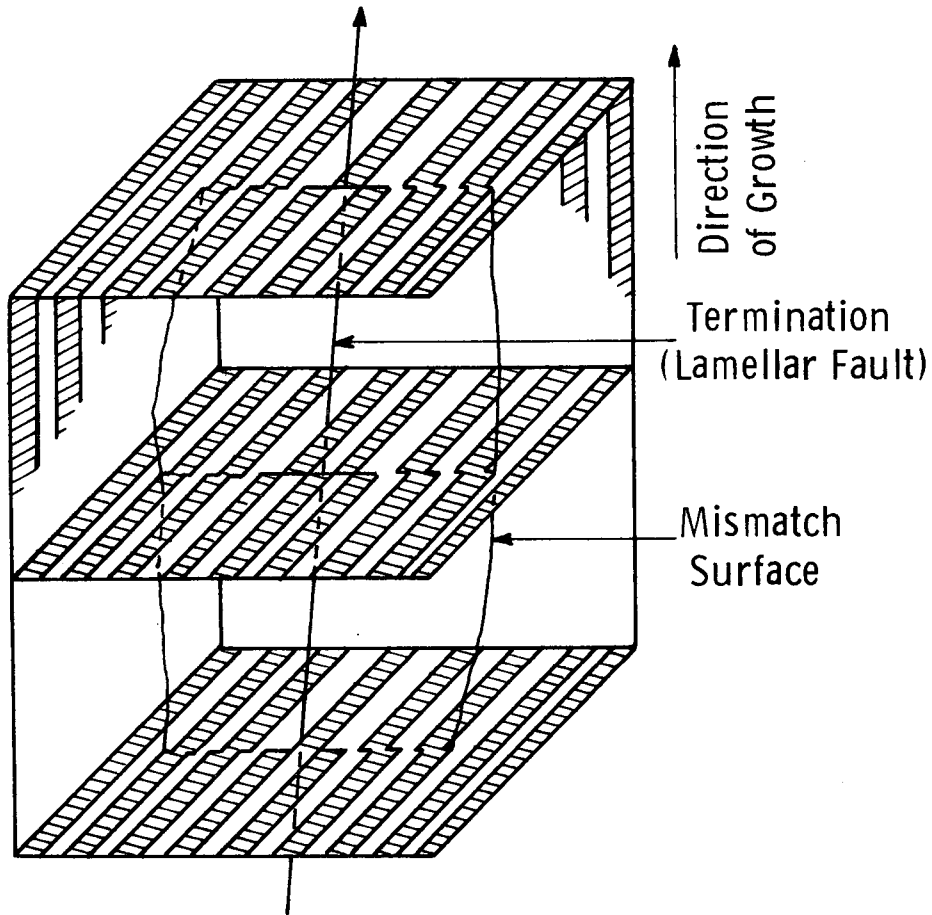
Fig. 12—Schematic of unit defect and associated mismatch surface in a lamellar eutectic (after Hogan, et al[21])

roughly parallel to the growth direction and enclose volumes of
eutectic material having substantially the same crystallographic
orientation. In the Al-Cu system the volumes enclosed between mismatch
surfaces are about 20 x 50 μm and often extend several hundred μm in
the growth direction.[21]

A. Lamellar Spacing

The most characteristic feature of a lamellar structure is
the uniform periodicity of the constituent phases. The center to
center distance between platelets of the same phase on a transverse
section is termed λ, the lamellar spacing, Fig. 13. The inverse
relation between lamellar spacing and eutectic freezing velocity (R),
$\lambda = AR^{-1/2}$ has been verified for many systems including Al-Cu.[11]

Computation of the average lamellar spacing is a relatively
simple matter. A test line of known length is applied perpendicular to
lamellae on a transverse eutectic section (either a photomicrograph or
ground glass screen can be used). The number of intersections of Al-CuAl$_2$
interphase boundaries per unit length of test line, $(P_L)_\perp$ in cm^{-1},
is counted. The interlamellar spacing in microns is given by

$$\lambda\,(\mu m) = \frac{2 \times 10^4}{(P_L)_\perp}$$

B. Interphase Boundary Length

From Fig. 12 it is evident that the presence of faults in
the lamellar structure increases the length of Al-CuAl$_2$ interphase
boundary per unit area of microstructure relative to that which would
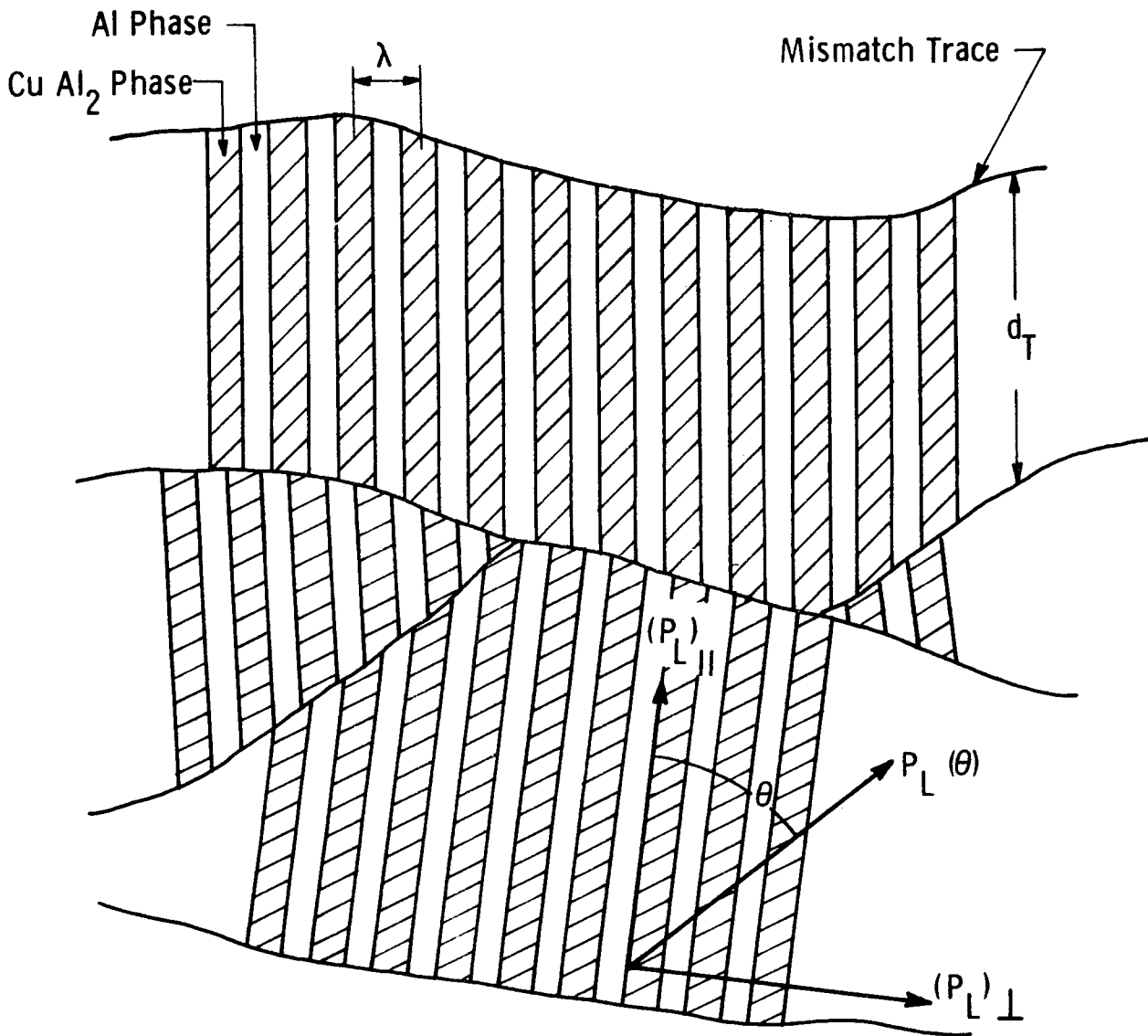
45

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Fig. 13—Schematic of a portion from a transverse AL-Cu eutectic microsection

be observed if no faults were present. Hence L_A, the interphase

boundary length per unit area[17], provides in principal a measure of

structural perfection. $L_A = \frac{\pi}{2} \bar{P}_L$ where $\bar{P}_L$ is the average value of P_L

obtained by counting interphase boundary intersections for various

orientations (θ) of the test line with the lamellar structure, Fig. 13.

(Note: lamellar tilting is exaggerated in the figure.) Since the scale

of the lamellar structure is a function of growth rate[12], values of L_A

must be compared for structures having the same spacing or else all data

must be normalized to account for variations in λ.

In Cd-Sn, the one eutectic system for which it has proved

possible to obtain fault-free lamellar grains, Gruzleski and Winegard[10]

have shown that the interphase boundary was indeed decreased for grains

in which faults were eliminated.

C. Structural Anisotropy

The transverse section of a fault-free eutectic would be

composed of grains whose lamellae were perfectly parallel to one another.

For a completely oriented structure of this sort the parameter

$\Omega_{12} = 1.0$. Ω_{12} is termed the degree of orientation[17] and is computed

from the relationship

$$\Omega_{12} = \frac{(P_L)_{\perp} - (P_L)_{11}}{(P_L)_{\perp} + 0.571\ (P_L)_{11}}$$

where $(P_L)_{\perp}$ and $(P_L)_{11}$ are the number of phase boundary intersections

per unit length of test line normal and parallel to lamellae, Fig. 13.

As the lamellar structure deviates from perfect alignment, the value

of Ω_{12} decreases. For a perfectly unoriented structure the value of Ω_{12} is zero. The presence of faults in a lamellar structure induces tilting of lamellae from the average direction so that $\Omega_{12} \neq 1$. Measurements performed on a specimen of Al-Cu eutectic frozen at about 1 cm/hr in fact gave a value of $\Omega_{12} \approx 0.8$.[20] It follows then that the variation of Ω_{12} can be used to classify the amount of alignment and hence perfection of a lamellar structure.

A more pictorial representation of anisotropy can be obtained by plotting the variation of P_L as a function of θ, Fig. 13, on polar coordinate paper. The curve of obtained in the way, termed a rose figure[17]) has a shape dependent upon the anisotropy of the structure and an area proportional to L_A.[20]

D. Mismatch Surfaces

Mismatch surfaces are usually associated with faults, Fig. 12. On transverse sections the surfaces are manifested as lines across which irregularities in the packing of lamellae are evident. Since lamellae are tilted across these trace lines, the greater the concentration of trace lines the more imperfect is the lamellar structure. The length of trace lines per unit area, T_A, can be computed in the same fashion as the length of interphase boundary per unit area, i.e., $T_A = \frac{\pi}{2} \bar{P}_L^T$ where $\bar{P}_L^T$ designates the average number of intersections per unit length of a test line with the trace lines on a plane section of eutectic structure. The larger is T_A, the more imperfect the

48

structure. As in the case of L_A measurements, values of T_A must be normalized against the variations in λ from sample to sample.

The average distance between mismatch traces (d_T) can also be estimated from the number of intersections with a test line parallel to lamella.

E. Fault Density

The most direct measure of the defect content of a lamellar structure is of course measurement of the fault density $(\bar{F}_A)$ itself. Kraft and Albright[5] described the detailed procedure by which the intersections of faults, Fig. 12, with the sectioning plane are marked and counted. The number of faults divided by the area sampled in principle gives $\bar{F}_A$.

The measurement which appears at first simple is, however, subject to ambiguity for the following reasons. It is impossible to precisely fix the number of faults on a section because the extra lamella producing the fault shifts depending upon the plane of section as shown in Fig. 12 (see also Ref. 18). It is not obvious whether to count the defect as one fault, three negative and two positive faults, etc. Thus, a certain amount of subjectivity and definition enters into the counting. It has been suggested that errors in fault density data can be minimized by careful observation of both phases on photographs plus the knowledge that one extra lamella usually distorts three to five adjacent lamellae[18]. As the section plane deviates from the transverse photographic interpretation becomes increasingly difficult.[18]

From this discussion it seems clear that obtaining statistically meaningful fault density measurements depends upon (1) the agreement

49

between investigators has to how they define a fault, (2) collection of sufficient data to establish statistical confidence, and (3) precise sectioning normal to the growth axis to minimize errors in micro-structural interpretation.

As in the case of L_A and L_A^T measurements, care must be taken to normalize all fault density data to the lamellar spacing in order to eliminate fault density variations due to lamellar spacing changes.[9]

F. Volume Percentage of Phases

The simplest and least time-consuming technique for estimating the relative volume fraction of two phases present in a sample by the method of point counting.[17] The volume fraction of a phase is simply given by the fraction of the total number of points from a test array which fall upon the phase. In practice an array of points, e.g., a square grid, is overlaid on a micrograph or projected on a ground glass screen bearing the image of the microstructure under study. The number of points falling upon a given phase divided by the total number of points in the grid gives the volume fraction of the phase. The total number of points that must be counted to achieve statistical confidence can be calculated.[17]

VI. SUMMARY

A ground base test plan and specimen evaluation scheme have been developed for the aluminum-copper eutectic experiment now scheduled to be run in the M518 Multi-Experiment Furnace during the NASA Skylab mission. This plan includes a description of the thermal and solidification studies needed to characterize the furnace and specimens for comparison with the flight experiments. The characteristics of the specimens most likely to be affected by solidification in zero-g are identified as are the analytical techniques for evalauting these characteristics. Particular attention has been given to the application of quantitative methods for characterizing specimen microstructure. This is because microstructural changes are highly sensitive indications of changes occurring during solidification.

Variations of the Al-Cu experiment were evaluated including (1) pre-freezing, (2) off-eutectic growth, and (3) seeding. It was concluded that only prefreezing was both feasible and scientifically significant at this time. It was recommended that high purity (five-nines) eutectic ingots be purchased from one supplier and that these ingots be prefrozen to obtain specimens in which only one eutectic grain was present. The presence of a single grain should greatly enhance the ability to interpret the specimen microstructure formed during zero-g solidification.

51

Laboratory experiments were performed in support of the above studies. Porosity was found in high purity eutectic ingots purchased from MRC Company and it was demonstrated that resolidification eliminated porosity from the as-cast bars. Hence, porosity can be eliminated during the formation of the single-grain ingots.

Chemical analysis shows that the MRC material is 0.1-0.2 w/o rich in aluminum. This should not be detrimental for the thermal gradients expected in the Al-Cu experiment. The trace impurity level of the MRC ingots exceeds the specified 99.999% purity. For this reason the cooldown rate in the M518 furnace should be 1.2°C/min to minimize possible colony formation during ingot freezing.

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