Pb-Zn Liquid Metal Diffusion

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The Lead-Zinc binary equilibrium system has indicated for a long time the limitations placed on Pb-Zn alloys due to the extended solubility gap in the liquid state. The two separate melts existing above the monotectic temperature have such greatly different densities that they quickly segregate into two layers by gravitational forces. Such a phenomenon has denied us alloys of Pb-Zn lying between the limits of 0.9% and 99.5% Pb.

With the capabilities afforded by micro-gravity processing it should be possible to generate the entire spectrum of Pb-Zn alloys. Since virtually no gravity driven segregation is expected in space processing any alloy composition could be generated by putting the desired ratio of Zn and of Pb into a container, heating above the consolute temperature for that alloy (under micro-gravity conditions), holding at temperature for a sufficient period of time to allow homogenization by diffusion and then solidifying the alloy by lowering the temperature. The question is "how long will the homogenization effort take?" or "what are the diffusion constants for liquid Pb and liquid Zinc?"

There are three generally accepted methods for determining the extent of diffusion in liquid metals. They are incoherent scattering of slow neutrons, NMR relaxation spectroscopy, and radioactive tracer methods. The most direct method is found in the use of radioactive tracers.(1) This is the method used by Ukanwa in a Skylab experiment.(2)

The current investigation concerns the Lead-Zinc system. Ground based studies of this system were carried out under a previous contract (NAS8-33046) to examine the possibility of obtaining a couple which, after diffusion, could be examined continuously along the diffusion axis by quantitative metallography to determine the extent of diffusion.

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In this ground based study, a method was developed to generate the Pb-Zn diffusion couple. This "liquid shear cell" design was utilized in manufacturing the specimens for the current study. Wire type specimens of high purity zinc and high purity lead were inserted in the graphite shear cell (see Fig. 1). The graphite part A was rotated relative to part B after the cell with its load was elevated in temperature to just above the melting point of Zn (and therefore above the melting point of Pb). This developed a diffusion couple in which diffusion began immediately. However, the couple was solidified from the Zn end immediately after the shear operation so that an almost planar liquid solid interface will be maintained. The resulting solid diffusion couple from cavity 1 has a small L_1 and L_2 region as illustrated in Fig. 2. The couple from cavity 2 was discarded since gravity convection upset the phase configuration after the shearing operation. The specimens were manufactured in the multi-cavity liquid shear cell illustrated in Fig. 3. Flight specimen No. 10 in Fig. 3-A illustrates the characteristic shape of the couple interface in specimens produced in this shear cell.

The specimens were analyzed by x-ray florescence in the scanning electron microscope along their length to provide exact information on the chemical composition gradient (see Fig. 2).

The dimensions of the specimens are 0.185 inches diameter by .600 inches long. The couple interface was situated at the midposition of the length. Each specimen was contained within a metallurgical grade graphite crucible having a pressed fit graphite cap and a wall thickness of 0.102 inches. This graphite assembly is 0.468 inches diameter by 0.660 inches long and will fit into the GPRF-Cartridge (Drawing 95M19100-2, June 1975) supplied by Marshall Space Flight Center. The graphite assembly was baked out before the specimen was loaded into it.

After the specimen in its graphite holder was inserted into the stainless steel cartridge, it was TIG welded under vacuum to provide a flight worthy sample. A sheathed Type K thermocouple was welded to the cartridge to provide a means of monitoring the temperature of the assembly during flight. This assembly is illustrated in Fig. 4.

Two diffusion experiments were run simultaneously in the multipurpose furnace each in its own isothermal cavity. Two flight samples, two flight backup samples, and two flight space samples were generated for this study. One couple was required to be held at a temperature of 440°C (minus 10°C, plus 1°C) which is just above the eutectic temperature (and also above the melting point of zinc) for 40 minutes and then quenched to at least 315°C within three minutes. The other couple was required to be held at a temperature of $820^{o}C$ (± $10^{o}C$) for 40 minutes and then quenched to at least $315^{o}C$ within 8 minutes.

Since the success of the investigation depended on the temperature, it is appropriate to examine the origins of the values. In the previous ground based studies, diffusion couples having the diffusion direction parallel with gravity direction and zinc (the lighter material) on top were maintained at temperature for specific times after which they were rotated 90 degrees and solidified. Second phase material was precipitated from the melt; its volume depending upon the position along the axis and the diffusion time. The gravity segregation was presumed to be primarily radial, and identification of the micro-constituents and measurement of the segregated volume by quantative metallography allowed an approximation of the extent of diffusion. A summary of some of this data is presented in Fig. 5. This approximation limited the diffusion time to 40 minutes due to the short length of the couple. After this time period, the specimen would begin to level in composition.

Two soaktemperatures were selected to allow examination of diffusion rates in the case where only a single liquid phase was involved at all times during the diffusion as well as in the case where four phases and three interfaces result from the diffusion and during the diffusion cycle. If the specimen was uniformly cooled, then in the solid state at least five interfaces should be present as can be ssen from Fig. 6.

In order to discuss the solidification process, the following symbols are used:

L_1 = zinc rich Pb-Zn liquid
L_2 = lead rich Pb-Zn liquid
T_M = temperature of monotectic reaction
L_{1M} = liquid of the montectic composition
L_{2M} = liquid L_2 at the monotectic temperature (98% Pb)
T_E = temperature of eutectic reaction
L_{2E} = liquid of the eutectic composition

We can now trace the following steps in the solidification process:

(a) As T_2 decreases to T_M, L_2 precipitates L_1 and L_1 precipitates L_2.

(b) Just above T_M exists primary L_{1M} and primary L_{2M}.

(c) Just below T_M exists a layer containing in monotectic form solid (monotectic) Zn and L_{2M}

derived from L_{1M}, and a layer of primary L_{2M} containing small islands of monotectic Zn.

(d) Between T_M and T_E, post monotectic zinc crystallizes from L_2.

(e) Just above T_E exists a layer of montectic Zn containing droplets of L_{2E} with post monotectic primary zinc and a layer of L_{2E} containing crystals of post monotectic primary zinc.

(f) Below T_E exists a layer of monotectic zinc containing islands of eutectic with post monotectic Zn and a layer of eutectic of Pb and Zn containing crystals of post monotectic Zn.

X-ray florescence can be used to identify the microconstituents at various positions along the diffusion path and then quantitative metallography used to establish the chemical gradient. This allows a Fick type of analysis to produce the diffusion constants.

Specimens 9 and 10 were run in a MEA capsule on a shuttle flight the first week in November, 1985. It is our understanding that due to a frozen exit valve on the gas cooling system, Specimen 9, which had diffused at 820°C for forty minutes, was not quench cooled and therefore stayed at the elevated temperature for over 60 minutes resulting in a degree of leveling as can be seen in Fig. 7. X-ray florescence analysis and quantative metallography analysis show the composition at the tip of the couple to be 46% lead.

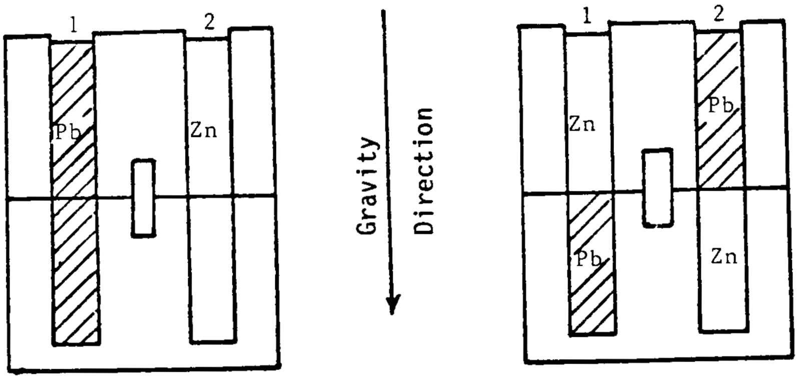
For some unknown reason, Specimen 10 did not achieve the melting temperature of zinc much less the specified 440°C, and therefore a liquid metal diffusion system never developed. This can be seen in Fig. 8 wherein the zinc can be observed to have never melted. X-ray florescence analysis of this speciment has justified the fact that the zinc never melted as the Zn contains far less than 1% Pb.

This experiment is expected to be rescheduled utilizing the backup specimens already prepared and submitted.

REFERENCES

1. N.H. Nachtrieb, "Diffusion in Liquid Metals," Chapt. 12, Liquid Metals: Chemistry and Physics, Ed. by Sylvan Z. Beer, Marcell Deckker, Inc. New York, 1972.

2. A.O. Ukanwa, "Radioactive Tracer Diffusion," Proceedings of Third Space Processing Symposium - Skylab Results 1974 - NASA.



Before Rotation

After Rotation

Figure 1 Liquid Shear Cell

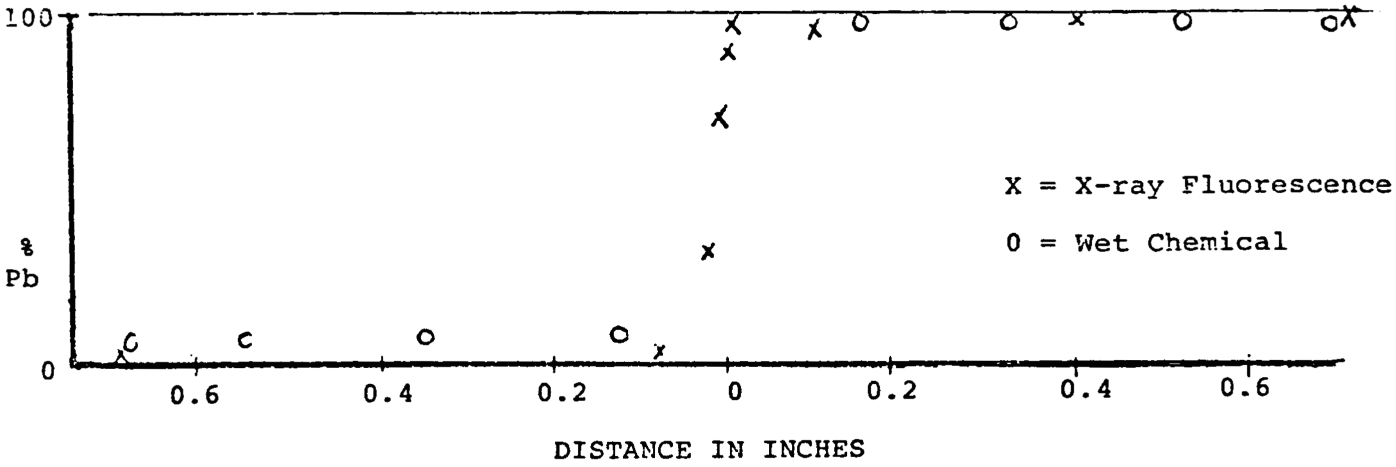


FIGURE 2

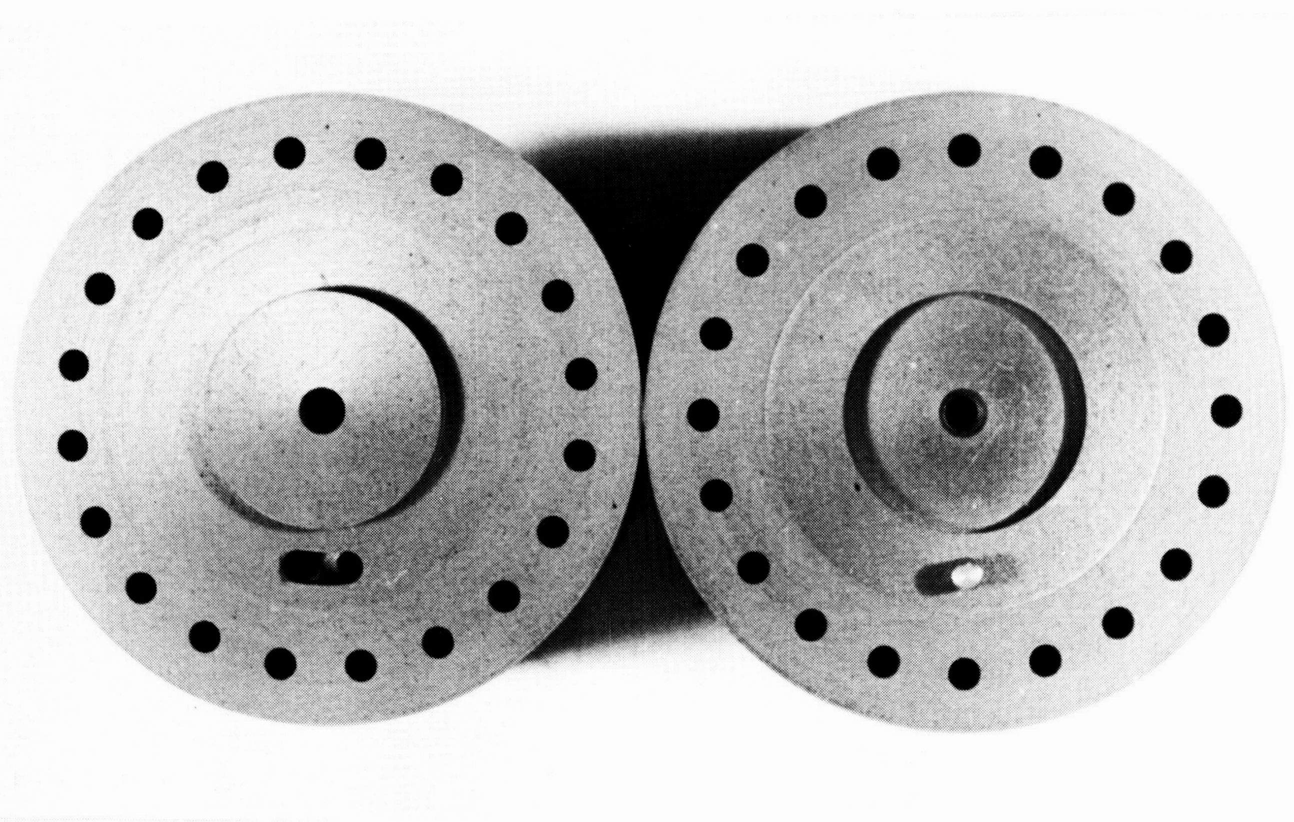


Figure 3 Graphite Shear Cell

Figure 3- A Pb-Zn Interface
Flight Specimen No. 10 15X

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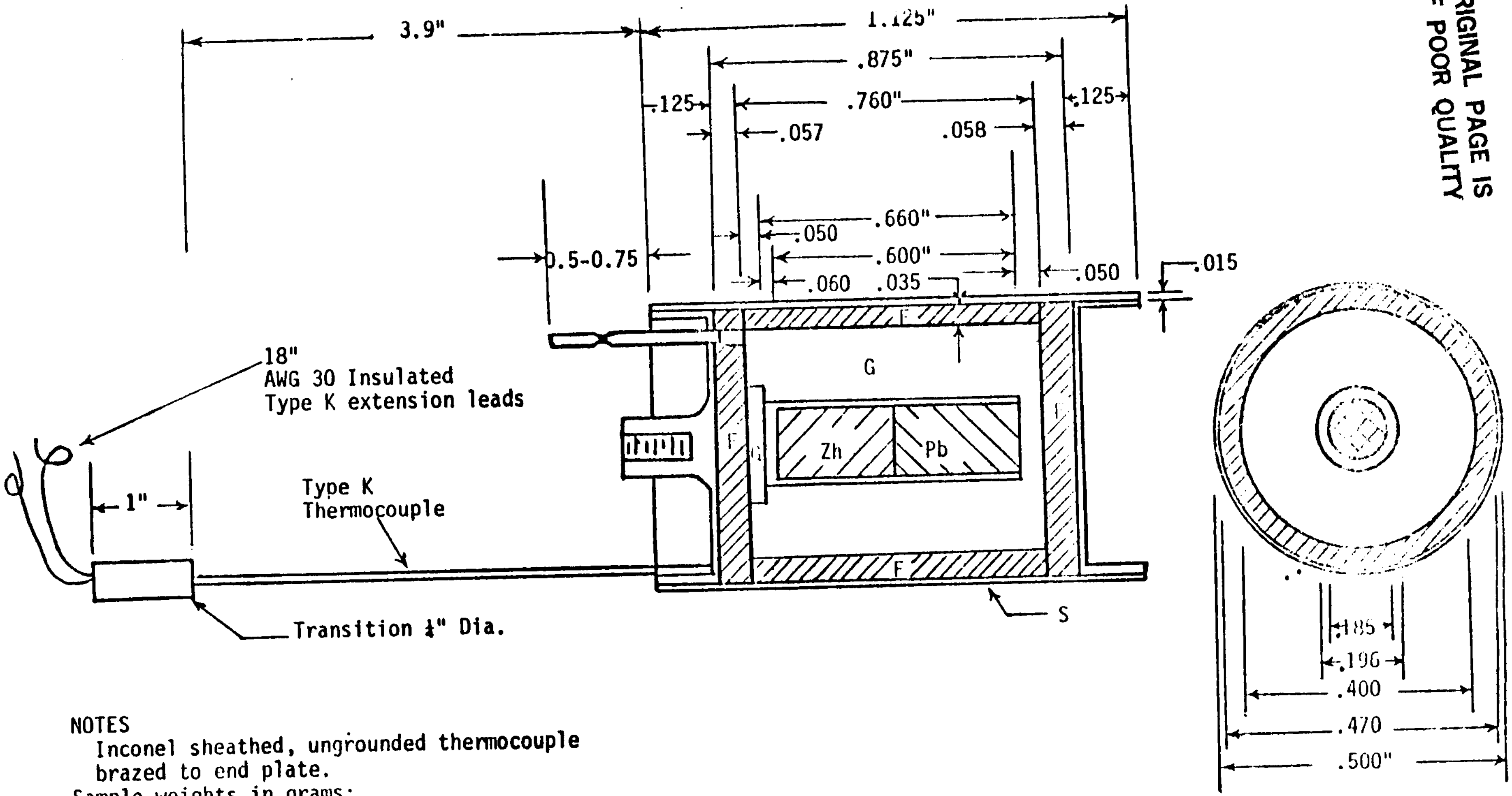


NOTES
Inconel sheathed, ungrounded thermocouple
brazed to end plate.
Sample weights in grams:
No. 9 -- 2.495 -- Flight
10 -- 2.530 -- Flight
11 -- 2.514 -- Flight Back-up
12 -- 2.498 -- Flight Back-up
13 -- 2.496 -- Flight Spare
14 -- 2.507 -- Flight Spare

Materials
F - Fiberfrax
G - Graphite
S - Stainless steel cartridge
(Drawing 95M19100-MSFC)

Marvalaud, Inc.
Specimen-Crucible-Cartridge-Assembly
MEA - A - 2 - Exp. 83-01
Module 1 and 2 4-1-84

Figure 4. Sketch of Specimen-Crucible-Cartridge Assembly.

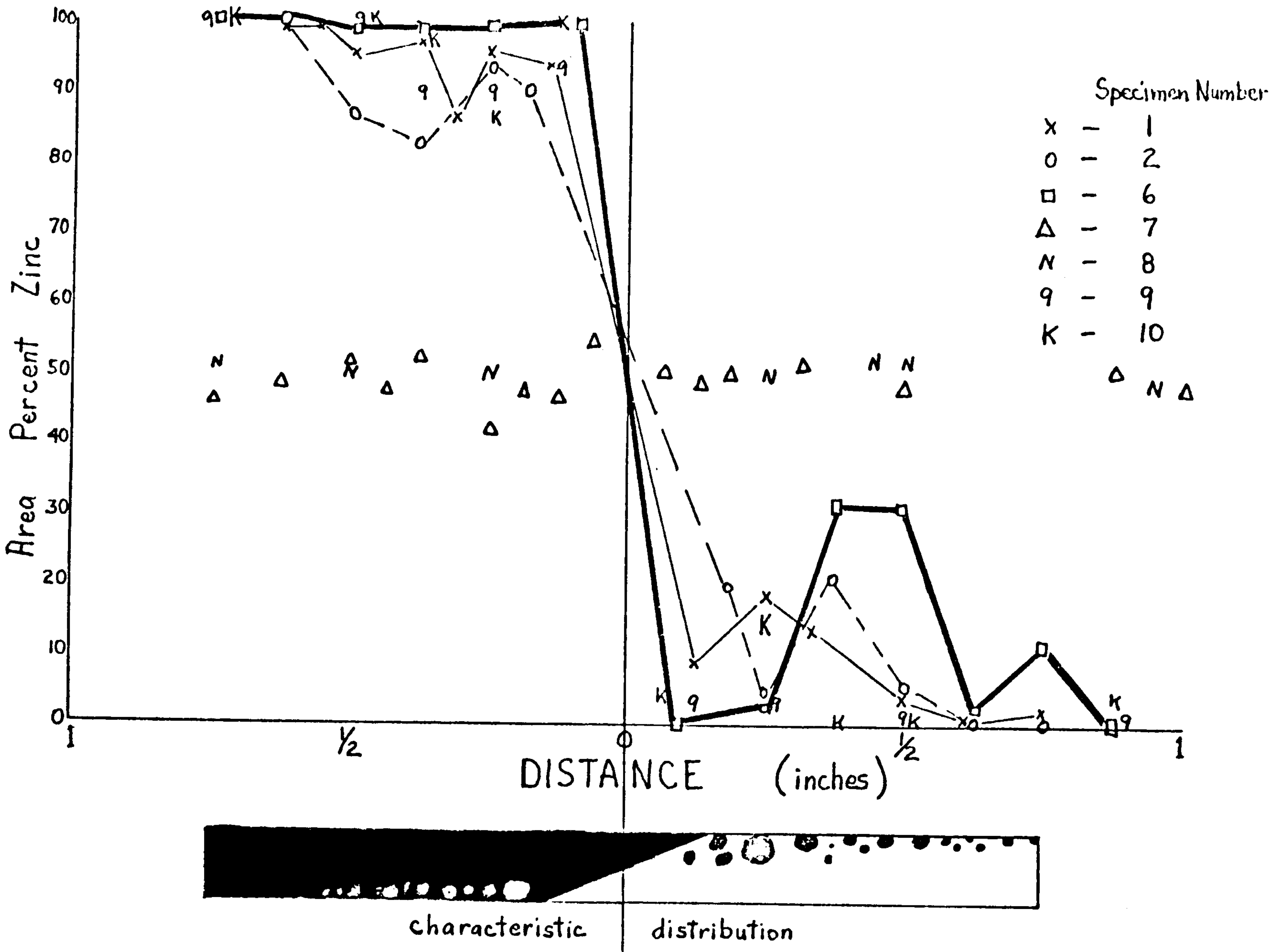
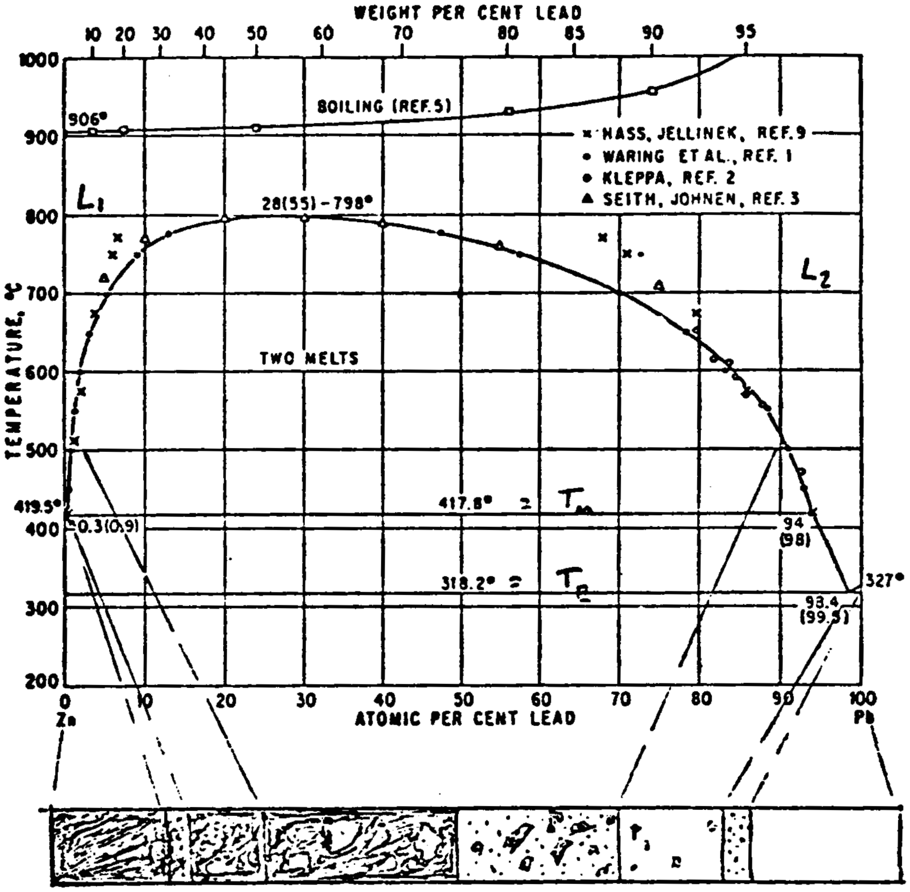


Figure 5 Measured Data



ROOM TEMPERATURE PROFILE

FIGURE 6

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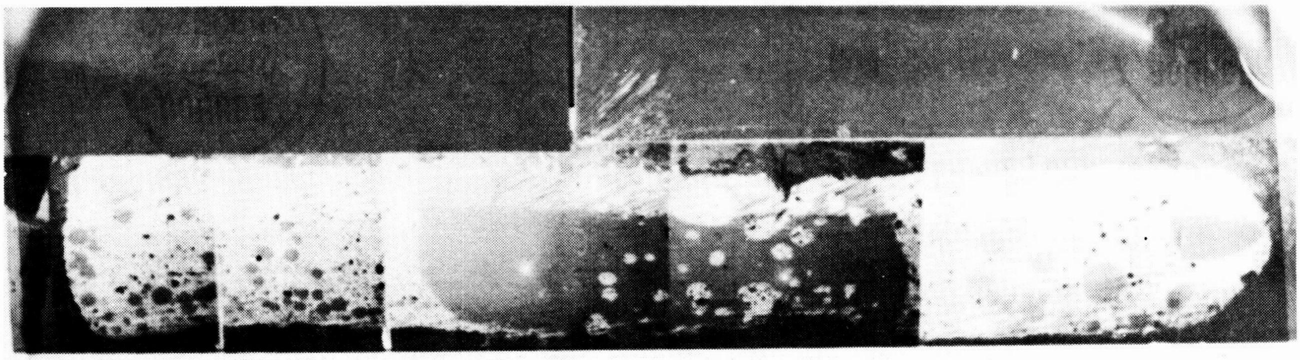

Figure 7 Micrographs of Flight Specimen No. 9

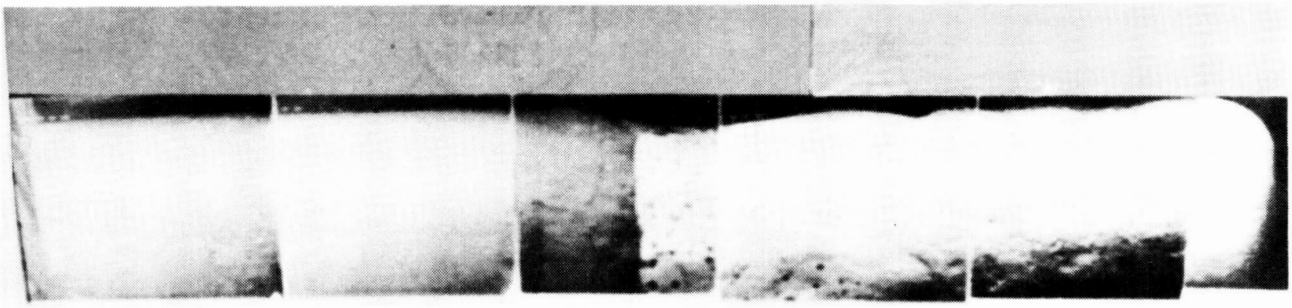

Figure 8 Micrographs of Flight Specimen No. 10