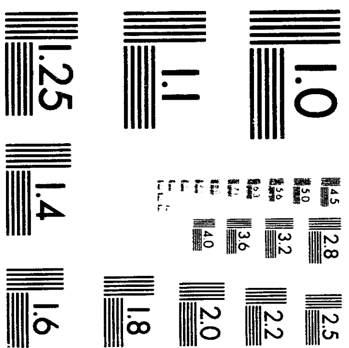

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EXPERIMENTAL DETERMINATION OF THE CU-IN-PB TERNARY PHASE DIAGRAM

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Abstract

The use of lead-indium solders in microelectronics packaging has increased over the last decade. Increased usage is due to improved properties, such as greater thermo-mechanical fatigue resistance, lower intermetallic formation rates with base metallizations, such as copper, and lower reflow temperatures. However, a search of the literature reveals that no comprehensive studies have been performed on the phase equilibrium relationships between copper metal and lead-indium solder. Our effort involves a combination of experimental data acquisition and computer modeling to obtain the Cu-In-Pb ternary phase diagram. Isotherms and isopleths of interest at low temperatures are achieved by means of differential scanning calorimetry and electron probe microanalysis. Thermodynamic models of these sections served as a guide for efficient experimentation.

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1.0 Introduction

Lead-rich alloys, especially 95 wt.% Pb - 5 wt.% Sn (Pb-5Sn) have been traditionally used as the standard industrial solders for chip-to-carrier interconnections in microelectronics packaging. A common connection scheme at this level is referred to as C-4, which means Controlled Collapse Chip Connection. Figure 1 is schematic of this technology. Attributes of C-4 joints include high strength, self-alignment, easier processing automation, and the large number of I/O's (input/output interconnections) attainable [1].

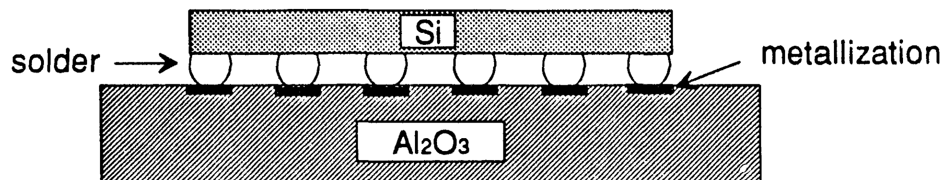

Figure 1: Schematic illustration of C-4 joining technology

During normal service, the joints in C-4 interconnections experience a shearing strain each time the device is addressed and when the machine is turned on and off. The strain is due to the thermal expansion mismatch between silicon ($2.8 \times 10^{-6}/°C$) and alumina ($6.0 \times 10^{-6}/°C$) [1-2]. The number of I/O's on a chip can reach several hundred, yet the break-down of any one joint by thermo-mechanical fatigue can cause failure of the whole device. This problem becomes more serious with the advent of increasing chip sizes and device miniaturization, along with the simultaneous demands on thermal management. Therefore, the need arises for alternative solders which exhibit improved thermo-mechanical fatigue resistance, thus providing greater device reliability.

Goldmann, et al. reported that Pb-In solders exhibit significantly greater thermo-mechanical fatigue resistance than Pb-5Sn solders [1,3]. Controlled thermal cycle tests showed that joint lifetime is parabolically dependent on indium concentration, as indicated in Figure 2. Along with this improvement, other advantages to using Pb-In solder have been demonstrated. Low amounts of indium, replacing an equivalent amount of tin, scavenge lesser amounts of metallization upon wetting through reduced intermetallic formation at the interface [3-4]. Finally, the low liquidus temperatures of Pb-In alloys make these solders useful for packaging components which are extremely heat sensitive, such as opto-electronic devices [5].

In light of the increasing popularity of Pb-In solders, a literature search reveals that no experimental investigation of the phase equilibria between Pb-In solder and copper metal has been reported, even though copper is used widely as a metallization for joint pads and circuit tracks. Knowledge of the phase equilibria between these metals is essential for studies of the kinetics of intermetallic formation at the interface, which directly affect joint strength and overall reliability. This lack of information provides the driving force for studying the phase equilibria relationships in the Cu-In-Pb ternary system, i.e., the determination of the ternary phase diagram.

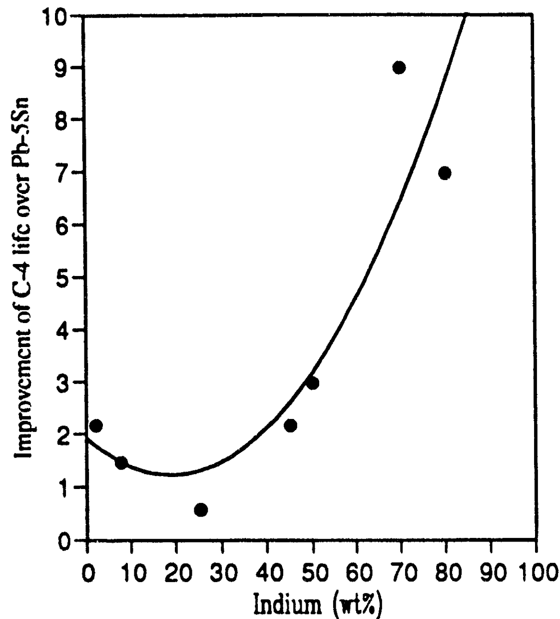

Figure 2: C-4 joint lifetime improvement when Pb-In solder replaces Pb-5Sn solder (from Goldmann, et al., [1,3])

2.0 First Order Model

An important strategy in this study is to model the Cu-In-Pb ternary diagram thermodynamically. Initially, a first-order diagram is calculated by extrapolating the thermodynamic parameters, which describe the constituent binary solution phases, into the ternary region. Here, an extrapolation method suggested by Muggianu is utilized [6], and the computer program written by Lukas [7] is used for calculation. The prediction may not be fully accurate, but it is a sufficient guide to direct subsequent experimental investigations. The calculated ternary diagram can also aid interpretation of experimental data, such as onset temperature or phase composition measurements. Next, the experimentally determined phase diagram is compared to the first-order calculation. If the two differ significantly, the experimental data is then used to calculate ternary interaction parameters for the model, thus accounting for the solution behavior in the ternary region. In this way, a phase diagram is attained which is not only physically realistic, but also thermodynamically accurate. The final model can also be utilized to observe phase equilibria in regions of the diagram where experimental data are not available.

For the purposes of this study, the most important information gained from the first order model calculations are predictions of isothermal and isoplethal sections. The regions of most interest are those below the melting point of lead (327°C), since it is below this temperature that soldering and device storage takes place. The calculated isothermal and isoplethal sections in this region aid in the selection of ternary compositions to analyze and the temperatures at which the various analyses take place. Figures 3 and 4, respectively, are a representative isothermal section at 200°C and an isoplethal section at 75 at.% In. Using these sections as a guide, their experimentally determined counterparts are determined using two analytical techniques: thermal, i.e. differential scanning calorimetry and differential thermal analysis (DSC/DTA), and quantitative, i.e. electron probe microanalysis (EPMA).

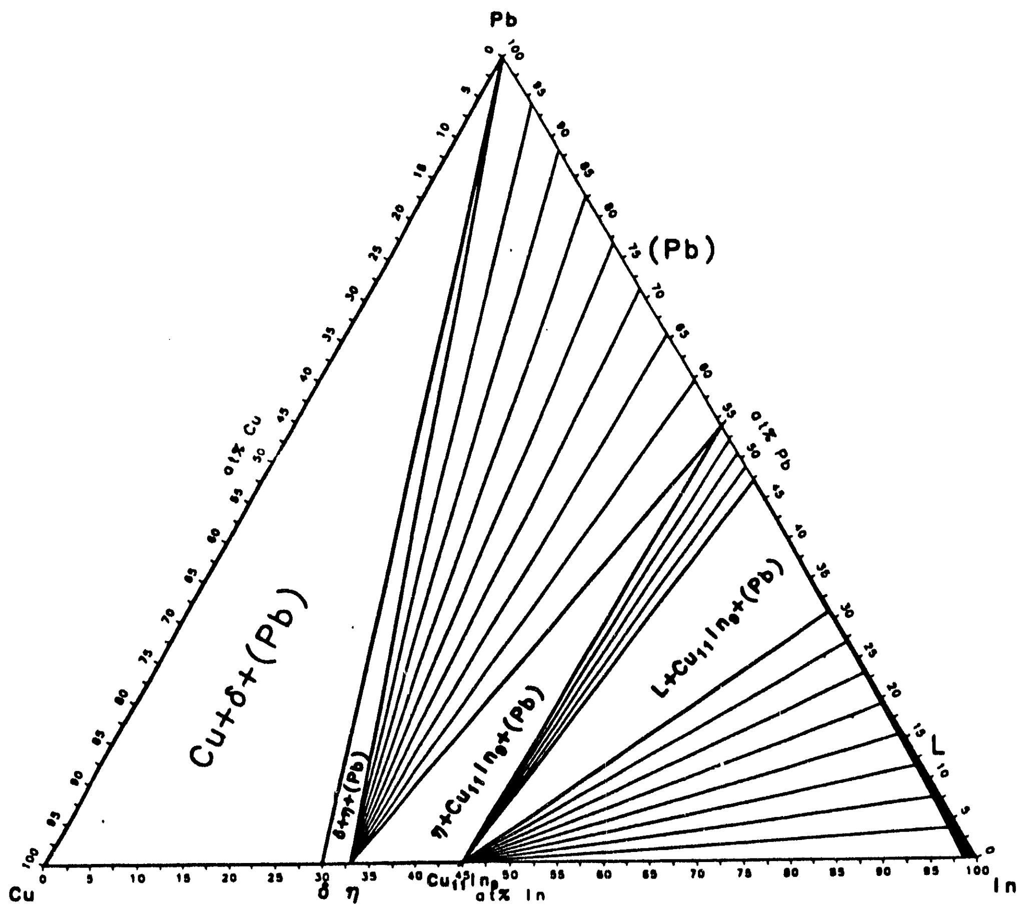

Figure 3: The calculated Cu-In-Pb isothermal section at 200°C, using the Muggianu extrapolation method [10]

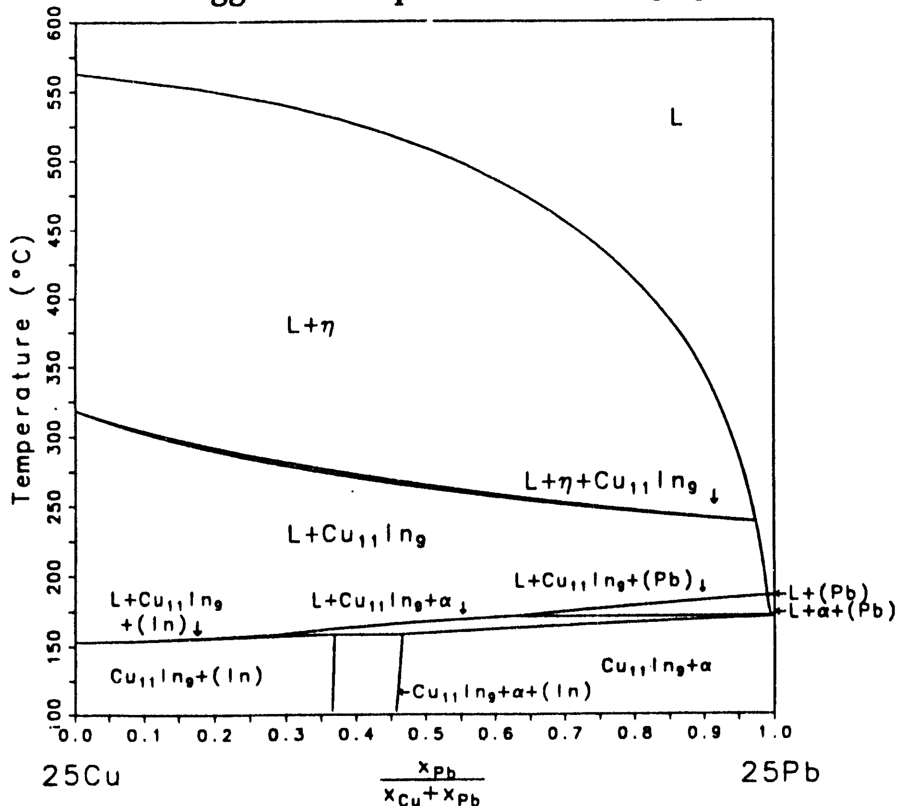

Figure 4: The calculated Cu-In-Pb isoplethal section at 75 at.% In, using the Muggianu extrapolation method [10].

3.0 Experimental Analysis

3.1 Differential Scanning Calorimetry

DSC was used primarily to detect phase boundaries and invariant equilibria of bulk sample alloys at low temperatures (< 400°C). At these temperatures, it is a much more sensitive technique than DTA. The DSC apparatus used was a Perkin-Elmer DSC7. The sample and reference cell was purged with high-purity nitrogen in order to prevent sample oxidation. The cell unit was also placed in a chamber of de-ionized ice water so as to maintain thermal stability of the system and to reduce baseline noise. The standards used for calibration were pure indium and pure zinc, with aluminum sample pans employed for all standards and alloys. Heating and cooling rates were 10°C/min. and 2°C/min., respectively. All reaction temperatures were obtained from the heating curves, so as to avoid undercooling effects. The value of the onset temperature is determined by a computer program contained with the DSC7 software package.

Figure 5a is a representative DSC heating curve for an alloy of composition 15 at.% Cu - 75 at% In - 10 at% Pb (15Cu-75In-10Pb). For this particular alloy, there are two onsets, indicated by the presence of two endothermic peaks: one at 160°C, and another at 287°C. This would seem to indicate that there are only two reactions or phase boundaries at this ternary composition as a function of temperature up to 300°C. Yet, upon analysis of the associated cooling curve, shown in Figure 5b, an additional peak emerges from the exothermic peak denoting the lower temperature onset.

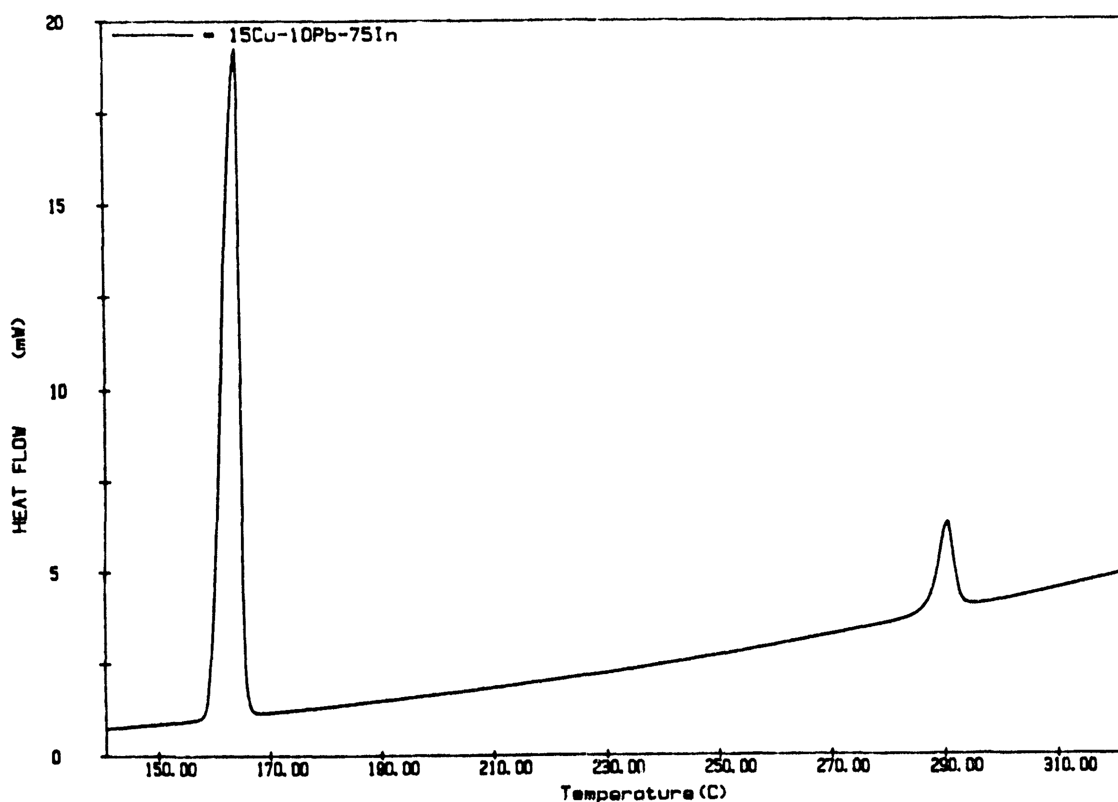

Figure 5a: DSC heating curve for alloy at 15Cu-75In-10Pb

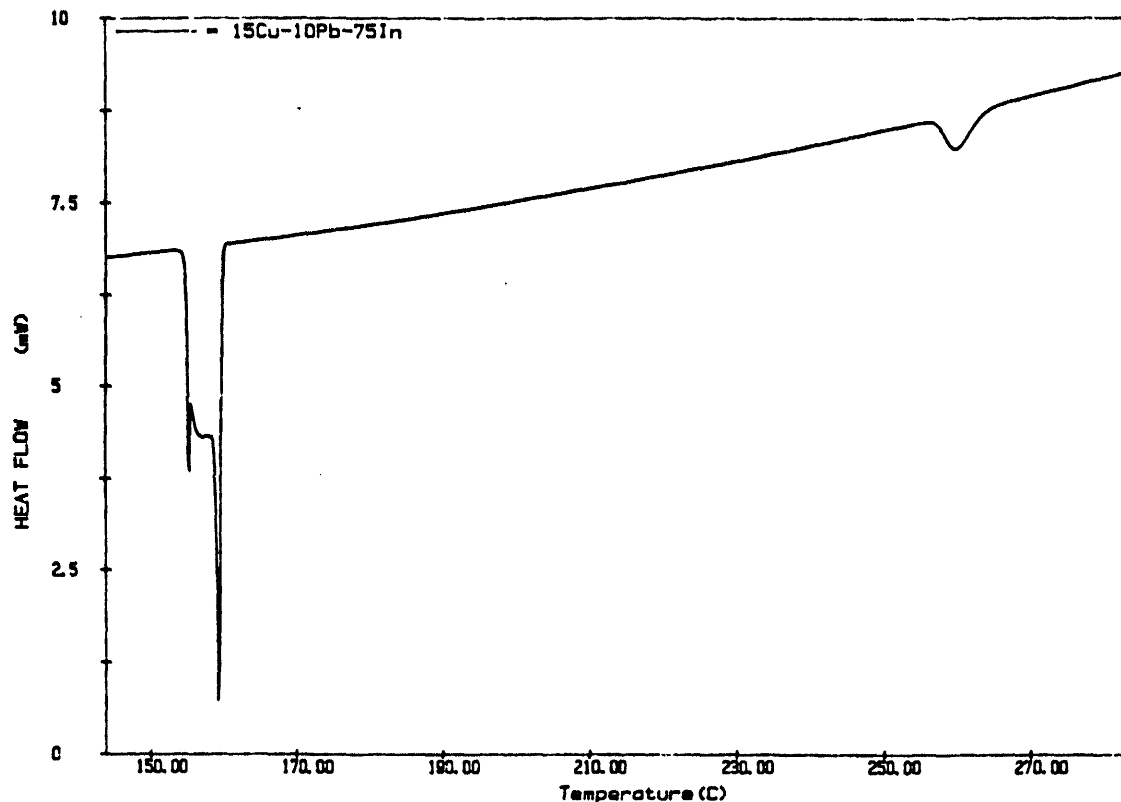

Figure 5b: DSC cooling curve for alloy at 15Cu-75In-10Pb

In this instance, the slow cooling rate increases the resolution for detecting embedded peaks. The large, sharp exotherm which appears below 170°C is likely due to the solidification of most of the liquid. To determine the onset temperature of the embedded peak, the DSC is programmed to remain at a temperature just slightly above the onset of the observed endotherm, allowing the reaction to take place. After the unit has stabilized, the temperature is increased again at the constant heating rate, so that the onset of the adjoining embedded peak can be determined. For this alloy, the embedded peak has an onset temperature of 163°C.

3.2 Differential Thermal Analysis

DTA analysis was employed to measure onset temperatures higher than 400°C. The apparatus used was a Perkin-Elmer DTA 1700 system. The samples and reference, Al_2O_3, were encapsulated under 0.33 atm. argon in 3 mm ID and 4 mm OD fused silica tubes. Pure indium, lead, antimony, silver, and copper are used to establish the calibration curve. Results were obtained from heating scans so as to avoid the effects of undercooling, with the actual onsets determined by comparison to the calibration curve. Heating and cooling rates were 20°C/min. and 5°C/min., respectively.

Figure 6a is a heating curve for an alloy with the same composition as that shown in the DSC curves. The same endotherms as those seen in the DSC heating curve can be observed, as well as the melting point, indicated by an "s-curve" on the far right. Upon comparison with the calibration curve, the actual onsets can be determined. The liquidus in this alloy is measured to be 543°C.

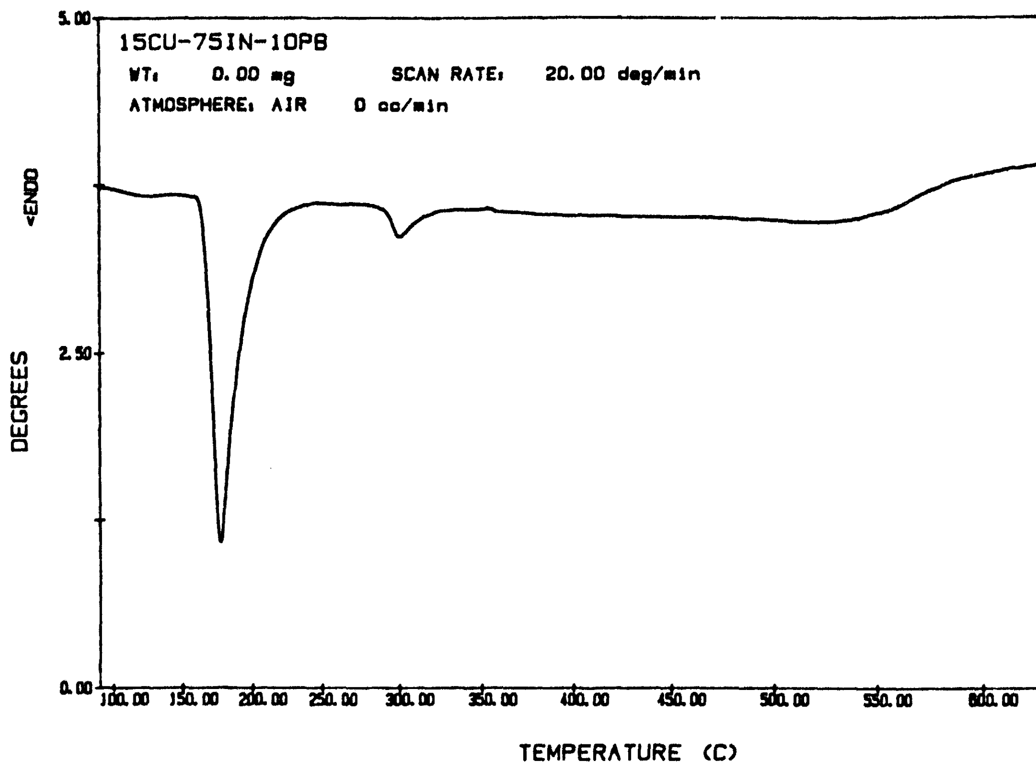

Figure 6a: DTA heating curve for alloy at 15Cu-75In-10Pb

The cooling curve, given in Figure 6b, reveals no hidden peaks within the liquidus. It is noted that the exothermic peak corresponding to the reaction at 283°C is barely visible above the baseline. Also, only one peak is indicated on the far left, whereas in the DSC cooling curve, two were present, indicative of the better sensitivity of DSC at lower temperatures.

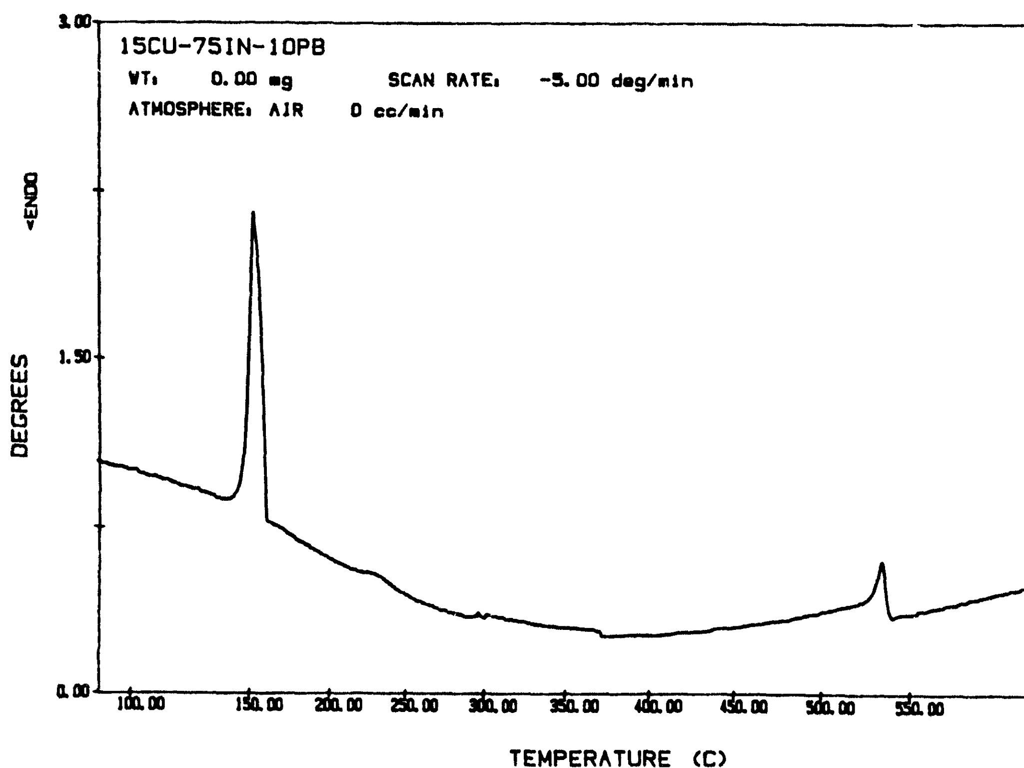

Figure 6b: DTA cooling curve for alloy at 15Cu-75In-10Pb

After all thermal analyses had been completed on compositions throughout the ternary phase fields, the onset data can be compared to that proposed by the computer model. Figure 7 is an isopleth located at 75 at% In, the same composition as the calculated isopleth presented in Figure 4. The location of the alloy 15Cu-75In-10Pb is indicated on the compositional axis, with the data points corresponding to the measured DSC/DTA onsets placed within the diagram.

Comparison with the calculated isoplethal section indicates that in this region of the ternary diagram, there is very good agreement between the two sections with respect to the phase regions and the invariant reactions. There are slight differences in the shape of the liquidus and the location of some of the two and three phase regions, but these can be reconciled in the model through the optimization process.

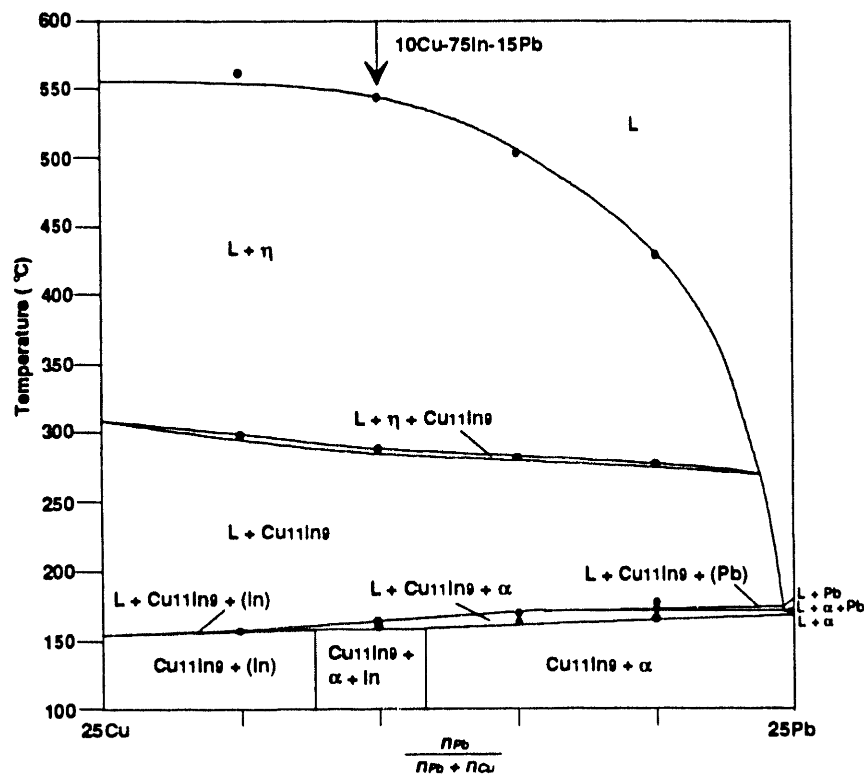

Figure 7: Cu-In-Pb experimental isoplethal section at 75 at% In

3.3 Electron Probe Microanalysis

EPMA was used to determine quantitatively the stable phase equilibria in selected isothermal sections of interest. Compositional analysis of quenched alloys was done by wavelength dispersive spectrometry (WDS) of characteristic x-rays using a JEOL 8600. Pure copper, indium phosphide, and lead sulfide were used as standards. CuK_{α} and PbM_{α} x-rays were diffracted with a LiF crystal, and InL_{α} x-rays were diffracted with a PET crystal. Corrections were employed [$\phi(\rho z)$] to compensate for atomic number differences, absorption, and fluorescence. The operating voltage of the microprobe was 15 KV, and the current is selected to be between 20 -25 nA. The spectral resolution for microanalysis was approximately 1 μm.

Quantitative data for phase composition at each point of the analysis were accepted only if the total weight percent is 100.0 ± 1.0. At high concentrations of lead, the allowable error becomes more difficult to maintain because of the high absorption of indium x-rays by lead. For alloys which exhibit this effect, the indium concentration is measured by difference, (i.e. it is determined by summing the concentration of copper and lead, and subtracting this number from 100 wt%).

Using EPMA, the phase diagram at a given temperature can be determined. Figure 8 is the 200°C isotherm determined by this method at , the same temperature as the calculated isotherm given in Figure 3. In this section, the single and three phase regions are labeled according to the phases present. The two phase regions are denoted by the measured tie lines. As can been seen upon comparison with Figure 3, the model differs in several ways to this experimentally determined isotherm. For example, the three phase field δ+η+(Pb) has a (Pb) phase composition that is much different than initially predicted.

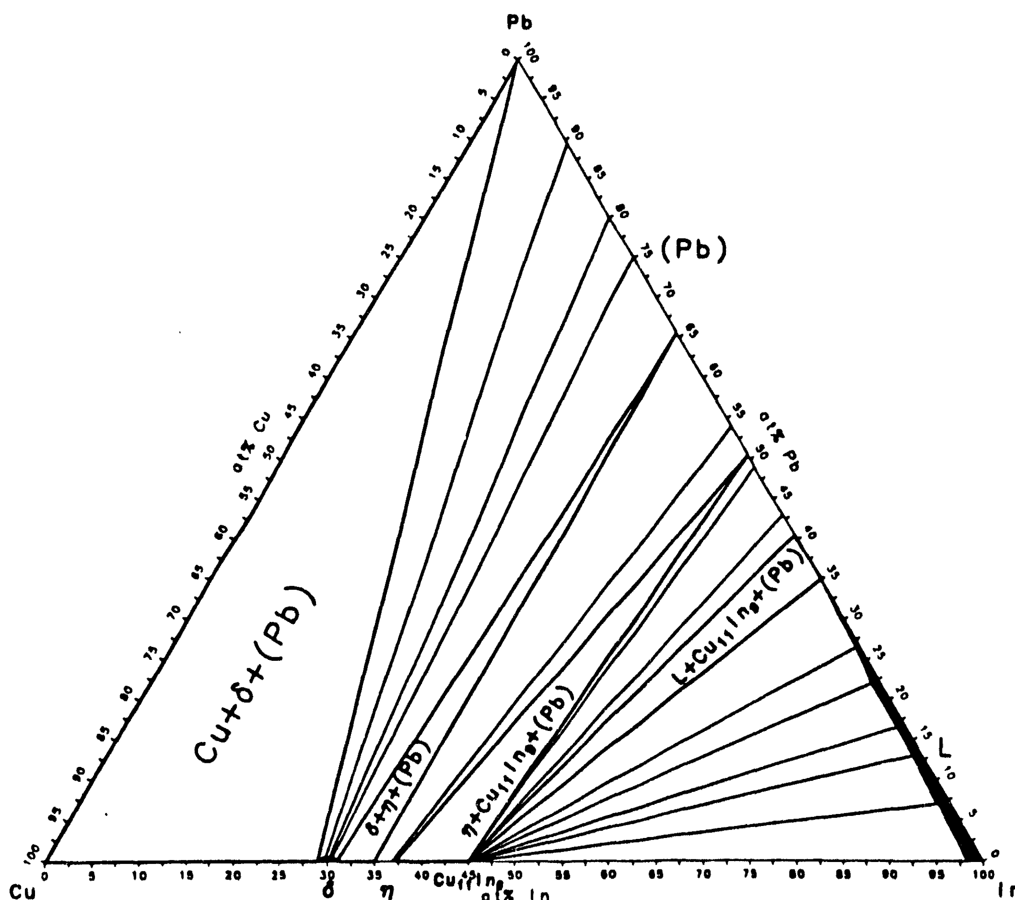

Figure 8: Cu-In-Pb experimental isothermal section at 200°C

4.0 Discussion

The isothermal and isoplethal sections presented here are a small portion of the areas of the Cu-In-Pb phase diagram being investigated. Comprehensive study of other isothermal and isoplethal sections is in progress. It should be noted that the isoplethal sections are not constructed independent of EPMA data, and the isothermal sections are not constructed independent of DSC/DTA information. All data are necessary for the accurate determination of each of the sections of interest.

In fact, each different analysis serves to verify the accuracy of information provided by other analyses.

The experimental and thermodynamic assessment data show that a Cu substrate is not in equilibrium with Pb-In solder. A line drawn from Cu to any Pb-In composition indicates that a series of intermetallics will form. Through the course of this study, it has been found that this is the case at all temperatures where Pb-In is in equilibrium with solid Cu. Whereas the isotherm suggests which intermetallics may form, it cannot predict what the diffusion path will be or at what rate the intermetallics will form at the interface. For this information, a complete and thorough diffusion study is required.

The experimental results also substantiate other attributes of the thermodynamic model. No evidence of ternary phases in this alloy system appears. This is actually to be expected, since there are no intermetallics in the Cu-Pb binary phase diagram. Furthermore, little solubility of copper exists in Pb-In solutions at low temperatures, as demonstrated by the tie lines in the isothermal section at 200°C. As there is virtually no solubility of copper in both lead and indium, this too is to be expected.

After completing all experimental evaluations, the first order calculation will be optimized so that it more realistically reflects the assessed diagram. In essence, the data provided by DSC/DTA and EPMA will be inserted into the model, and the parameters which describe the ternary solution behavior will be calculated. When this is accomplished, it will be possible to extrapolate to all areas of the Cu-In-Pb phase diagram, even those that are not investigated experimentally, especially at lower temperatures where kinetic limitations to timely equilibrium exist. A section of interest at any temperature can be calculated that in all probability will closely resemble true equilibrium. This Cu-In-Pb phase diagram will therefore be unique in that it will be comprised of a careful combination of experimental data and calculated thermodynamic parameters, thus exhibiting internal consistency.

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