

## **DETERMINATION OF THE LIQUIDUS TEMPERATURE AND COMPOSITION OF TIN/LEAD SOLDERS USING DIFFERENTIAL THERMAL ANALYSIS \***

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### **ABSTRACT**

Thermal analysis was used to measure the liquidus temperature,  $T_L$ , and determine the composition of tin/lead solders electrodeposited on an electronic component and plain metal substrates. To calibrate the thermal analysis equipment, a phase diagram of the tin/lead system was developed. A procedure was developed to distinguish hyper- from hypoeutectic alloys. Analysis of the electroplated solder on small mounting pins of an electronic component found that the solder's  $T_L$  was in excess of the temperature attained in soldering thus explaining the formation of a rough solder surface on the pins. The composition of solder electrodeposited onto stainless-steel panels was found to be a function of the current density used during the electroplating process. Analysis of a known standard confirmed the accuracy of this method of alloy analysis.

### **INTRODUCTION**

In the electronics industry, the rapid and accurate determination of the lowest temperature at which an electroplated tin/lead solder will completely melt, the liquidus temperature ( $T_L$ ), is of great importance. To achieve a solder joint exhibiting a smooth shiny surface, the solder must totally melt during the soldering procedure thus the soldering temperature must be in excess of the alloy's  $T_L$ .

Currently, the  $T_L$  of an electrodeposited tin/lead solder is indirectly determined by analyzing the composition of the alloy and then ascertaining the  $T_L$  of the alloy from a tin/lead phase diagram. However, accurate compositional analysis of these solders is usually difficult because of small sample size. For instance, solder coatings on printed circuit boards only have a thickness of 0.2 mm. Wet chemical analysis of these solders is not practical so atomic absorption and X-ray fluorescence are commonly used for analysis. Unfortunately both of these methods have inherent problems.

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To determine the composition of the alloy by atomic absorption, the sample must be completely dissolved in a solvent. However, this is difficult to achieve with solders because tin has a propensity to slowly precipitate in solvents commonly used for lead [1]. Accurate analysis using X-ray fluorescence is difficult to achieve because of continual alloy segregation and preferential oxidation of tin near the surface; both effects will enrich the surface in tin [2] and alter the area that is analyzed. In addition, because of alloy segregation, the standard used for calibration must be routinely recast to remove inhomogeneities [3] or the outer surface should be milled away until constant values for alloy composition are obtained [2]. Because of the problems with those methods, it was decided to develop a thermal procedure that would directly measure an alloy's  $T_L$  and indirectly determine alloy composition.

This effort was initiated in response to a request to determine the tin/lead composition of an alloy that had been deposited on some cobalt–nickel–iron pins at a thickness of 1.5 mm and a weight of less than 0.5 mg per pin. In a subsequent step, the solder on the pins would be reflowed using the condensation soldering technique to form a smooth solder joint between the pin and a ceramic disc. In this soldering technique, the relatively cool parts to be joined are placed in a saturated vapor environment of an inert, refluxing organic material with a high boiling temperature. The parts to be united are heated by the condensation of the organic fluid's vapors. To insure that the reflowed solder will form a satisfactory smooth solder joint, it is advisable that the reflux temperature of the fluid be 30°C above the alloy's  $T_L$ . Initial analysis of the solder on the pins was done using an X-ray fluorescence instrument primarily designed to measure the thickness of electrodeposited coatings but with modifications to permit compositional analysis. The solder was determined to be a 59/41 alloy which would have a  $T_L$  of 189°C. This 59/41 alloy almost meets the requirements for the condensation soldering procedure, since the condensation fluid used in the soldering step had a boiling point of 215°C. However, it was noticed that occasionally after the soldering procedure the joints had an unacceptable rough, sandy surface whose integrity was questionable. Confirmation of the X-ray fluorescence analysis was needed.

To use thermal analysis for alloy analysis, a correlation curve relating  $T_L$  to alloy composition initially had to be constructed. Previously, other workers [4] have determined the tin/lead phase diagram using different procedures. Tin and lead are known to form a eutectic material melting at 183°C which has a 62/38 wt.% tin/lead composition. Because tin and lead have limited solid solubilities, they form two terminal solid solutions; the  $\alpha$  solid solution which has a maximum solubility of 19% tin in lead and a  $\beta$  solid solution which has a maximum of 2% lead in tin. In their book, Pope and Judd [5] briefly outlined a procedure for generating the phase diagram of a hypothetical binary eutectic material using DTA thermograms. By

measuring the  $T_L$  of an alloy of known composition, the liquidus of an equilibrium diagram can be determined. However, subsequent measurement of the  $T_L$  of a tin/lead alloy of unknown composition does not always lead to the correct alloy analysis. Because tin and lead form a eutectic material, the relationship between  $T_L$  and alloy composition is not unique in the range 185–232°C, the melting point of the lower melting metal, tin. Therefore, an alloy having a  $T_L$  between 185 and 232°C could either have a hypereutectic composition (higher in tin than the eutectic) or a hypoeutectic composition (higher in lead than the eutectic). To use thermal analysis for alloy determination an additional observation was needed to relate  $T_L$  to the correct composition.

To determine the composition of tin/lead alloys, Fyans [6] proposed a method that involved determination of the alloy's mass,  $T_L$  and the heat evolved during the melting of the eutectic component. However, that technique is not applicable to electrodeposited alloys which are often scraped from a substrate or analyzed while still adhering to the substrate because the mass of the alloy cannot be determined. In both cases the sample would contain an unknown amount of substrate; thus the value for the heat of fusion of the eutectic component would be erroneous.

The present paper describes the procedure used to measure the  $T_L$  of an alloy, the method used to construct the tin/lead phase diagram, a means of distinguishing hyper- from hypoeutectic alloys and the results of the analyses of several electroplated alloys and of National Bureau of Standards 40/60 alloy.

## EXPERIMENTAL

### *Instrumentation*

A DuPont 1090 thermal analyzer equipped with a 912 dual scanning calorimeter was used to record the melting and solidification thermograms. The sample weight was varied between 2 and 15 mg. Uncrimped aluminum pans were used since crimping resulted in poorer resolution of the important weak, secondary peaks. To retard oxidation the cell was swept with nitrogen which was operated at a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.

### *Determination of $T_L$*

To ensure good thermal contact with the pan and to remove inhomogeneities present in the electrodeposited alloys, a sample was initially melted by heating from 170°C to 30°C above the sample's estimated  $T_L$  or to 350°C, at a rate of 10°C min<sup>-1</sup>. This heating was followed by a rapid cooling to 150°C and a subsequent heating at 5°C min<sup>-1</sup> from 170°C to 30°C above the estimated  $T_L$ , or 350°C. During this second melting, the trace was recorded and the temperature of total melting,  $T_M$ , determined by noting the return to

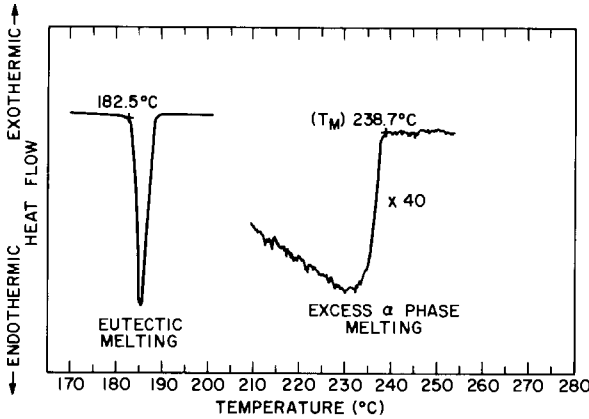


Fig. 1. DTA trace recorded during melting of a 40/60 Sn/Pb alloy.

baseline after the secondary component had melted (Fig. 1). The sample was then slowly cooled to  $150^{\circ}\text{C}$  at a rate of  $5^{\circ}\text{C min}^{-1}$  and from that recorded trace, the temperature of the onset of crystallization of the secondary component,  $T_C$ , noted (Fig. 2). To compensate for superheating and supercooling the values obtained for  $T_M$  and  $T_C$  were averaged to give  $T_L$ ; except when the difference between  $T_M$  and  $T_C$  was greater than  $10^{\circ}\text{C}$ , as observed with the hypereutectic alloys, in which case the value of  $T_M$  was used for  $T_L$ .

#### *Construction of the Sn/Pb phase diagram*

The tin/lead phase diagram (Fig. 3) was constructed by melting and cooling samples of known composition. Standards (100 g) were prepared by melting together known amounts of tin (purity, 99.99%) and lead (purity, 99.7%) in an iron crucible, stirring the slurry, adding  $\sim 1$  g of stearic acid

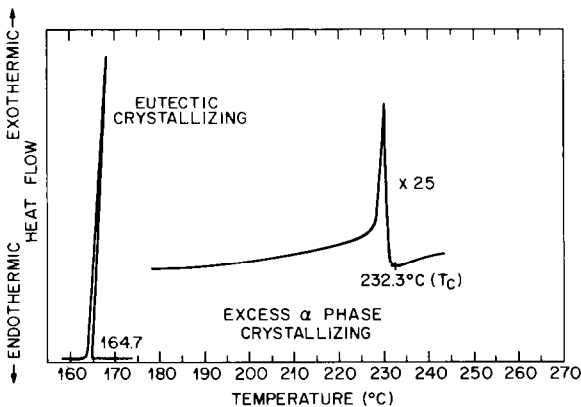


Fig. 2. DTA trace recorded during solidification of a 40/60 Sn/Pb alloy.

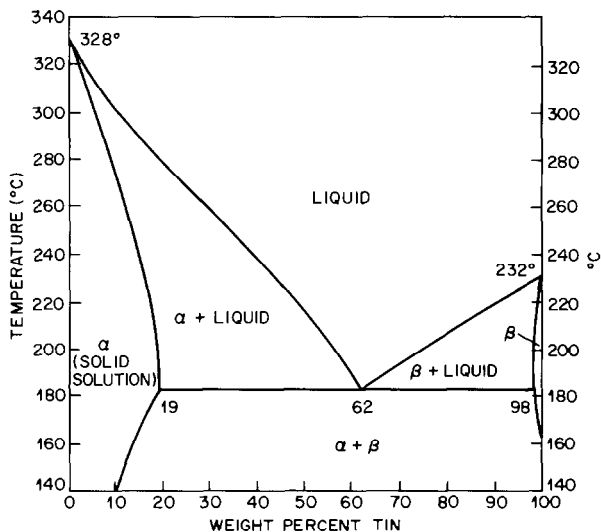


Fig. 3. Sn/Pb phase diagram constructed from the DTA measurements.

and skimming the surface with a spatula to remove any oxides that had formed, and then pouring the molten solution into a narrow iron trough. Standards in 10 wt.% increments over the range 0–100% tin were prepared. In addition, standards having the following tin/lead composition were prepared: 13/87, 16/84, 19/81, 62/38 and 98/2.

The liquidus in the phase diagram was obtained by plotting the values obtained for  $T_L$  as a function of alloy composition. The solidus, the boundary separating a liquid plus solid region from a solid solution region, was determined by noting the temperature  $T_0$ , when melting commenced, with standards exhibiting a very weak eutectic endotherm and no component melting immediately thereafter (Fig. 4). Efforts to define the solvus, the

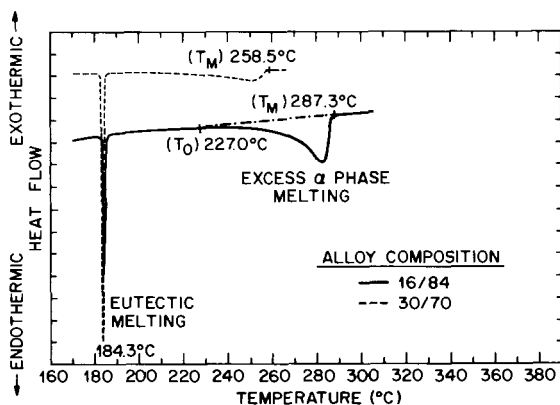


Fig. 4. Comparison of the melting trace of a 16/84 Sn/Pb alloy with that of a 30/70 alloy.

boundary between a solid solution and the region of the mixture of the solid solutions, were largely unsuccessful.

#### *Reproducibility of measuring the $T_M$ and $T_C$ of an alloy*

The reproducibility of determining  $T_M$  and  $T_C$  was measured by melting and crystallizing four samples of the prepared 40/60 alloy. The values obtained for  $T_M$  and  $T_C$  were  $239.5 \pm 0.4^\circ\text{C}$  and  $232.3 \pm 0.4^\circ\text{C}$ , respectively.

#### *Alloy analysis*

The composition of an unknown alloy was determined by measuring the  $T_L$  of the solder and, when  $T_L > 232^\circ\text{C}$ , reading from the phase diagram the corresponding tin/lead composition. When  $T_L < 232^\circ\text{C}$ , visual inspection of the thermogram recorded during heating usually was sufficient to differentiate between an alloy having a hyper- or hypoeutectic composition (Fig. 5). To confirm the visual observation, the ratio of the amount of heat absorbed during the melting of the secondary component to that of the eutectic component can be determined for the unknown. A comparison can then be made with the ratios obtained with hyper- and hypoeutectic alloys having the same  $T_L$  as the unknown (Fig. 6). After determining if the unknown had a hyper- or hypoeutectic composition, the phase diagram was used to determine the specific composition.

It should be noted that determination of the  $T_C$  of an alloy was found to be helpful in defining the temperature range where the alloy's  $T_M$  could be found. Crystallization cannot occur until there are a sufficient number of nucleation sites present. Then the solidification commences spontaneously and there is a sudden release of heat. With non-eutectic alloys the metal

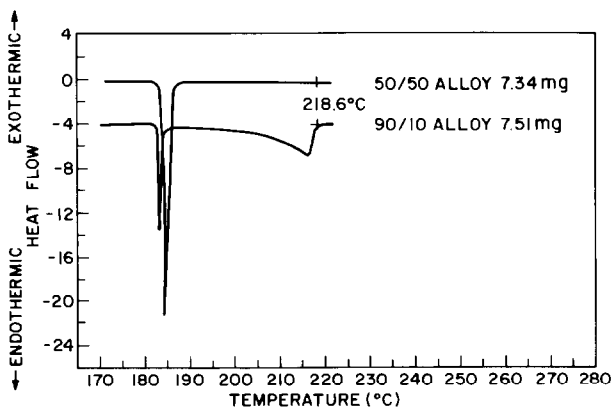


Fig. 5. Comparison of the melting traces obtained from a hypoeutectic alloy and a hyper-eutectic alloy using about the same weight of sample.

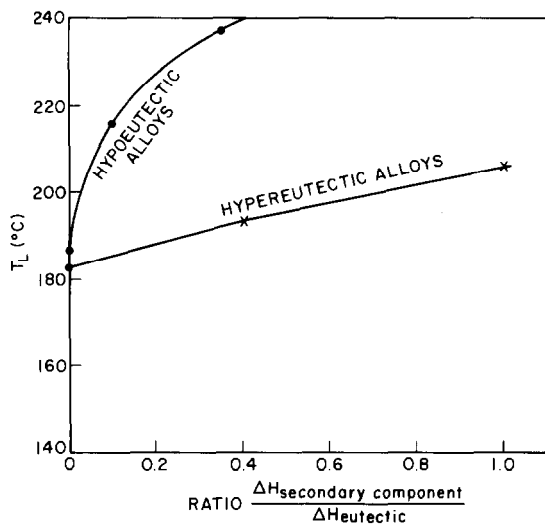


Fig. 6. A plot used to differentiate hyper- from hypoeutectic alloys.

which is present in excess of the eutectic composition will start crystallizing. This transition can be more readily detected by thermal analysis than the transition corresponding to the cessation of melting. In the latter case there is no threshold as individual metal atoms existing in the solid state just slowly drift into the surrounding liquid. To determine the accuracy of this technique, the composition of the National Bureau of Standards 40/60 tin/lead alloy was measured.

### Materials

The  $T_L$  and composition of the electrodeposited solder on the pins were determined by cutting the pins so that only that portion of the pin plated with solder was used for analysis. This minimized the heat sink effect of the substrate.

To define more precisely the electroplating conditions which would result in a solder having a  $T_M$  near the optimum eutectic temperature, six foils ( $1.4 \times 0.064 \times 0.001$  in.) were prepared by electrodepositing solder onto stainless-steel panels from a 60/40 solder bath using cathode current densities of 10, 20 and 30 amps/sq.ft. Prior to testing, the foils were peeled from the panels, and each foil was cut into approximately 36 pieces (four vertical cuts followed by eight horizontal cuts) and the location of the specimens on the foil noted.

## RESULTS AND DISCUSSION

The solder electrodeposited on the pins was found by means of thermal analysis to have  $T_M$  and  $T_C$  values of 232 and 227°C, respectively. The  $T_L$  for this alloy is 230°C which is 15°C higher than the reflux temperature of the condensation soldering fluid. Therefore, complete melting of the alloy could not occur during the soldering procedure. This would result in the solder joint having a rough sandy surface, similar to that actually observed.

Melting of the tin/lead samples of known composition yielded four distinct types of DTA traces (Fig. 7). The first type, a trace consisting of a single sharp endotherm (a) corresponded to the melting of a sample having the eutectic composition (62/38 tin/lead). The onset of melting for the eutectic was observed at 183°C. The second type, a trace with a broad unsymmetrical endotherm and no component melting immediately after the eutectic temperature (b) resulted when a sample having the composition of one of the terminal solid solutions was melted. The maximum solid solubility of tin in lead was found to be 19 wt.% by plotting the heat of fusion of the eutectic component versus alloy composition and extrapolating to zero heat of fusion for the eutectic. The maximum solid solubility of lead in tin was determined to be 2 wt.%. It should be noted that hypoeutectic alloys with tin concentrations less than 19% did evidence a eutectic component on melting. This anomaly was attributed to non-equilibrium solidification during the initial quick cool down which resulted in the formation of a cored tin-poor  $\alpha$

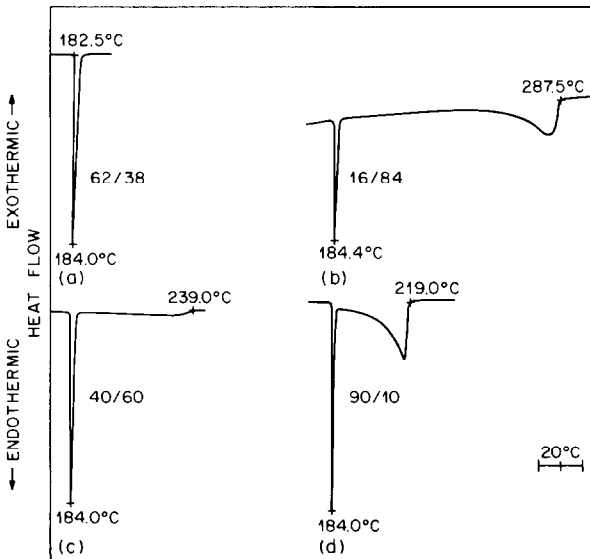


Fig. 7. Representative DTA traces of (a) eutectic, (b)  $\alpha$ -solid solution alloy, (c) hypoeutectic alloy and (d) hypereutectic alloy.



solid solution and liquid phase that solidified at the eutectic temperature [7]. Cooling the melt of these alloys at a slower rate resulted in decreasing the eutectic component but even at a  $1^{\circ}\text{C min}^{-1}$  cooling rate a small amount of eutectic was still produced.

The two remaining types of traces were generated when the tin concentration was between 19 and 98%. The melting of hypoeutectic alloys yielded traces similar to (c) while hypereutectic alloys gave endotherms similar to (d). The sharp peak at the lower temperature corresponds to the melting of the eutectic component and the broad peak to the melting of the secondary component. This broad endotherm which commenced immediately after the eutectic had melted, originates from the gradual melting of the solid solution present in excess of the eutectic composition. That is, for hypoeutectic alloys, the broad peak corresponds to the melting of the  $\alpha$  solid solution and to the  $\beta$  solution with hypereutectic alloys. The obvious disparity between traces (c) and (d) originates from heat of fusion of the  $\beta$  solid solution being almost three times greater than that of the  $\alpha$  solid solution.

With this knowledge of the relationship of melting trace patterns and alloy composition, the composition of the solder deposited on the pins was determined by using the tin/lead phase diagram and the  $T_L$  measured for the alloy. The composition of the solder on the pins was found to be 43/57. This analysis substantially differs from the 59/41 composition obtained by X-ray fluorescence.

Analysis of the six foils showed the direct relationship between cathode current density and the tin concentration of electrodeposited alloy (Fig. 7). During electroplating the current density is greater on the two vertical edges than in the middle of the substrate. In addition the current density will increase with the depth of penetration of the substrate into the electroplating

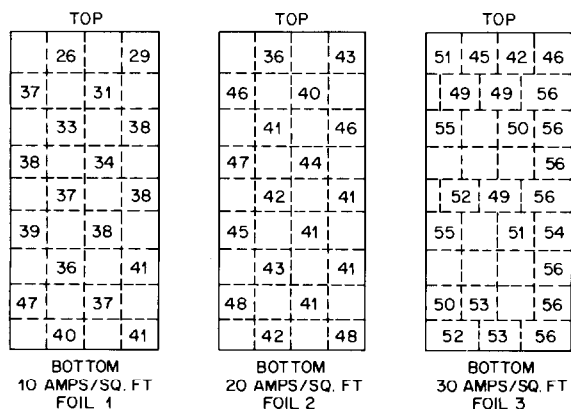


Fig. 8. The percentage of tin found in electrodeposited foils prepared at various cathode current densities.

both due to positioning of the anode on the bottom of the bath. As the current density was increased from 10 to 20 to 30 amps/sq.ft., the average tin composition of the foils increased from 37 to 43 to 51%.

Analysis of the tin/lead NBS standards gave a composition of 40/60 tin/lead with a  $T_L$  of  $237 \pm 0.9^\circ\text{C}$ . The latter value agrees quite well with  $236^\circ\text{C}$   $T_L$  previously measured with the prepared 40/60 alloy.

## SUMMARY

Thermal analysis was used to determine the  $T_L$  and composition of several tin/lead solders. An electroplated alloy which yielded an unsatisfactory rough solder joint after reflow was found to have a  $T_L$  in excess of the temperature attained during soldering. This composition was found to be different than that previously determined by X-ray fluorescence. Analysis of several foils confirmed the direct relationship between cathode current density and the tin concentration of the deposited alloy. Using DTA, the composition of a known standard alloy was correctly determined.

## ACKNOWLEDGEMENTS

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