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THE FORMATION OF Cu_3Sn INTERMETALLIC ON THE REACTION OF Cu WITH 95Pb - 5Sn SOLDER

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ABSTRACT

This study characterizes the interfacial reactions that occur when Cu is soldered with 95Pb- 5Sn solder. A continuous layer of Cu_3Sn ε phase forms during the soldering process. Previous studies suggest that the intermetallic layer spalls off during soldering. However, the present work shows that the intermetallic layer is intact after soldering and that any spalling observed is due to improper polishing. A new polishing technique was developed to preserve the intermetallic layer. The Cu_3Sn has a fine columnar grain structure that is very brittle. Both intergranular and transgranular fracture modes are observed. The size of the intermetallic layer is dependent upon the length of time the solder is molten. The rate of formation of ε phase was measured and used to determine an activation energy for diffusion of Sn in 95Pb - 5Sn of 13 kcal/mol.

INTRODUCTION

The electronic packaging of integrated circuit chips has been cited as the limiting factor in the performance and reliability of high speed data processing units [1]. A method of packaging these integrated circuit chips is to use 95Pb-5Sn solder to bond the devices on the chip directly to the package. The solder joint is critical in that a failure in one joint could render the entire chip inoperable. The same 95Pb-5Sn solder is also used as a mechanical bonding material in automobile radiators where, again, a coherent joint is essential.

In view of these applications, this study focusses on the interfacial microstructure that forms when 95Pb-5Sn solder reacts with Cu. A Cu substrate was chosen because Cu is the metal that is joined in both packaging and automobile radiator applications.

Previous studies have looked at the reaction of Pb-Sn solder on copper [2-10]. Most of the work has been performed on eutectic Pb-Sn [2-8]. When eutectic solder is used two layers of intermetallic phases form, ε phase (Cu_3Sn) adjacent to the copper and η phase (Cu_6Sn_5) next to the solder. These layers were found to form instantaneously when copper came in contact with molten solder [3,7]. However, research on 95Pb-5Sn shows that only ε forms on reaction with Cu [10]. Apparently the smaller amount of Sn present in the 95Pb-5Sn solder precludes the formation of the Sn-rich η phase. Some researchers claim that the intermetallics spall off into the molten solder on formation [3,10]. The work presented here suggests that this spallation occurs during polishing; the brittle intermetallic fractures even under small polishing loads. Cu has also been observed to dissolve into the molten solder bath [2] when Cu wires are submerged in a eutectic solder bath. The dissolution is attributed to the large source of Sn that absorbs Cu into solution. Dissolution of Cu is not observed for 95Pb-5Sn solder.

This paper presents observations of the intermetallic phase Cu_3Sn that forms when 95Pb-5Sn is used to solder Cu. The chemical state and

morphology of the intermetallic layer and its growth kinetics are discussed in the context of these observations.

EXPERIMENTAL PROCEDURE

Three oxygen-free Cu plates were cut to dimensions of 101.6 mm x 31.75 mm, with two plates 0.32 mm thick and one plate 0.64 mm in thickness. These plates were polished down to 1 μm Al_2O_3 powder and were etched with 25% HNO_3 + 75% H_2O to clean off the oxide. A light coat of Johnsons Stainless Steel Soft Soldering flux was dried on the interior surface and the plates were assembled as shown in Fig. 1. A 0.13 mm gap for the solder was created using a thin strip of stainless steel.

The assembled sample was then placed in a vacuum furnace, Fig. 2. The specimen was held above the molten solder bath for 1/2 hour to burn off the flux and create an oxide free Cu surface for soldering. A pull rod was used to submerge the Cu plates briefly in a molten bath of 95Pb-5Sn solder at 400^oC. Capillary action pulls the molten solder between the Cu plates. The furnace was then turned off, the specimen allowed to cool and the excess solder removed from the specimen.

Samples for optical analysis were cut from the soldered specimen. For reflow experiments the samples were placed horizontally in the furnace so that the solder would not flow out. In this orientation the surface tension of the solder was sufficient to keep the molten solder between the Cu plates. Samples were reflowed at 400^oC for microstructural observations. Additional reflows were performed at 350^oC and 450^oC for determination of diffusion constants.

For optical observations the sample was first mounted in Klarmount. Before polishing a small amount of the solder was etched away using 30% H_2O_2 + 70% glacial acetic acid. A layer of epoxy was then dried into the gap formed. The specimens were then polished to 600 grit on silicon carbide paper. Polishing was performed using 6 μm diamond paste followed by a 0.6 μm silica suspension. The specimens were etched in 5 parts NH_4OH, 5 parts H_2O, and 2 parts H_2O_2 (30%). The samples were then viewed in a Carl Ziess optical microscope.

A sample was etched with 20% H_2O_2 + 80% glacial acetic acid until the Cu interface was free of solder to reveal the intermetallic for examination in the scanning electron microscope (SEM).

RESULTS AND DISCUSSION

A. Chemical State of Joint

The as-soldered solder/Cu joint is shown in Fig. 3. As-soldered signifies that the solder flowed between the Cu plates and then was cooled to room temperature over a total time of approximately four minutes. The joint consists of solder, a thin layer of intermetallic, and the Cu base plate. Energy dispersive x-ray analysis of the joint determined the intermetallic to be ε phase Cu_3Sn. The solder in the

joint was found to be depleted to 3-4% Sn. Thus the formation and growth of the intermetallic also weakens the solder joint by depleting the solder of Sn. The Sn acts as a solid solution and precipitation hardening element in Pb. As the solder is drained of Sn the strength of the solder decreases. No evidence of the Sn rich η phase was found in the as-soldred or reflowed specimens. As has been observed previously [10] for η to form a higher content of Sn must be present in the solder.

B. Physical State of Joint

Figure 4 is a micrograph taken with polarized light of the intermetallic layer after 5 hours at 400°C. This specimen was selected for observation since the morphologies of specimens reflowed for various times were all similar, but the intermetallics are more clearly observable after longer reflow times. As can be seen in the figure, the ε grains are columnar. The Cu/intermetallic and solder/intermetallic interface profiles match closely. The similar contours suggest that Sn diffuses from the molten solder into the Cu allowing the ε to form at the Cu interface. This hypothesis is in accord with results in the literature that Sn is the faster diffusing species in the ε phase and that Sn diffuses into the Cu [9,11-13]. However, the direction of interface motion was not determined.

The interface between the intermetallic and Cu is continuous and intact. No spalling of the intermetallic was observed. Previous observations of the intermetallic breaking off during soldering are apparently a polishing artifact. The Cu_3Sn intermetallic is brittle so during polishing it may fracture and imbed itself in the soft solder. However, if during polishing the soft solder is reinforced with a layer of epoxy the intermetallic layer remains intact.

Figure 5 is a micrograph of ε grains after 5 hours of reflow. The joint was sectioned through the intermetallic almost parallel to the Cu surface. Figure 6 is an SEM micrograph of a similar sample. Here the solder has been completely etched off and the top intermetallic grains are revealed at the solder/Cu_3Sn interface. The number of cracks present in the intermetallic gives evidence of the brittleness of this layer. There is no evidence to suggest that these cracks formed during soldering. However, if the interface was not reinforced with epoxy during mechanical polishing there was a large increase in the number of cracks present in the intermetallic. This observation suggests that the intermetallic cracks formed under the relatively small stresses applied in cutting and polishing. The crack in the center of Fig. 5 runs both transgranularly and intergranularly showing that both the grain boundaries and the grains themselves are susceptible to cracking. This result contrasts with previous work [14] that found cracking in the ε phase occurs via a cleavage mechanism along particular crystal planes.

C. Layer Growth

Reflow experiments were performed to observe changes in the intermetallic that occur while the solder is molten. Reflow was performed at 400°C in an air ambient. Oxidation during heat treatment was not a problem because the oxide formed only on the surface of the specimens. To avoid the surface oxide the specimens were cut in half after reflow

and observations were confined to the central portions of the specimen. Samples were allowed to air cool after the heat treatment. Figure 7 is a plot of ε phase layer thickness versus time at molten temperature, 400°C here. In the as-soldered condition the intermetallic is 4 μm thick. A typical micrograph of this joint is shown in Fig. 3. After three hours at 400°C the intermetallic layer is 11 μm thick. The saturation at 11 μm occurs because at this thickness the solder in the joint is almost totally depleted of Sn after which the layer no longer coarsens. An example of the intermetallic after 5 hours of reflow is shown in Fig. 4.

The determination of diffusion constants was performed using three reflow temperatures 350°C, 400°C, and 450°C. No diffusion markers were used so the layer thickness was taken to be the distance between the Cu/Cu_3Sn and $Pb\text{-}Sn/Cu_3Sn$ interfaces. A plot of the square of the layer thickness versus time is shown in Fig. 8. The slope of these lines gives the diffusivity, D. An Arrhenius plot of the natural logarithm of D vs. 1/T, shown in Fig. 9, gives the activation energy for diffusion, -Q/R. From this plot Q was found to be 13 kcal/mol and the pre-exponential constant D_o to be 2.1×10^{-6} cm^2/sec.

The activation energy of 13 kcal/mol is consistent with values reported in the literature. Reported values are 11 kcal/mol [9], 14.6 kcal/mol [11], and 21± 4.8 kcal/mol[15] for pure Sn reacting with Cu to form Cu_3Sn. One study [6] found the activation energy to be 20.5 kcal/mol for the formation of ε phase on the reaction of 95Pb - 5Sn with Cu. The pre-exponential constant $D_o = 2.1 \times 10^{-6}$ cm^2/sec calculated in this study is also in accord with published values [9,11].

CONCLUSIONS

The reaction of 95Pb-5Sn solder with Cu results in the formation of ε phase Cu_3Sn intermetallic. The size of the intermetallic layer increases with the length of time the solder is molten. The formation of the intermetallic causes a decrease in the Sn concentration of the solder. The Cu_3Sn phase that forms has a fine columnar grain structure and is brittle. Both intergranular and transgranular cracks were found to form in the intermetallic during polishing. The intermetallic did not spall off, as some previous studies have stated. The spalling tendency appears to be a polishing artifact. The activation energy for diffusion was found to be 13 kcal/mol and the pre-exponential diffusion coefficient D_o to be 2.1×10^{-6} cm^2/sec, both of which are consistent with previously published values.

ACKNOWLEDGMENTS

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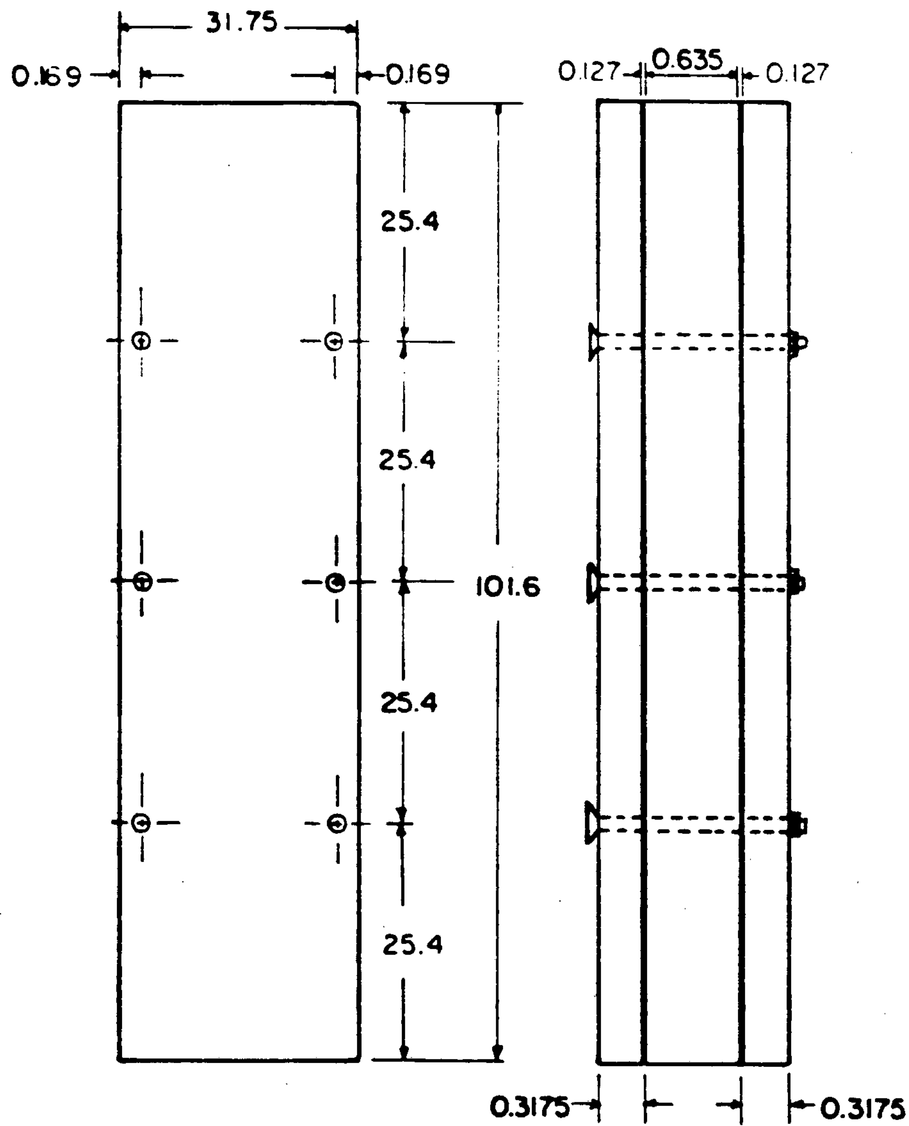
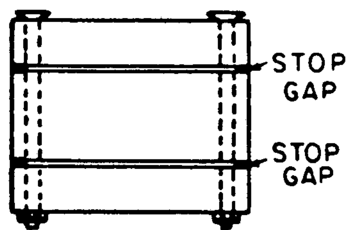




DIMENSIONS IN mm

XBL847-7214

Fig. 1. Assembly diagram of Cu plates. The solder flows into the gaps by capillary action thus forming the bond.

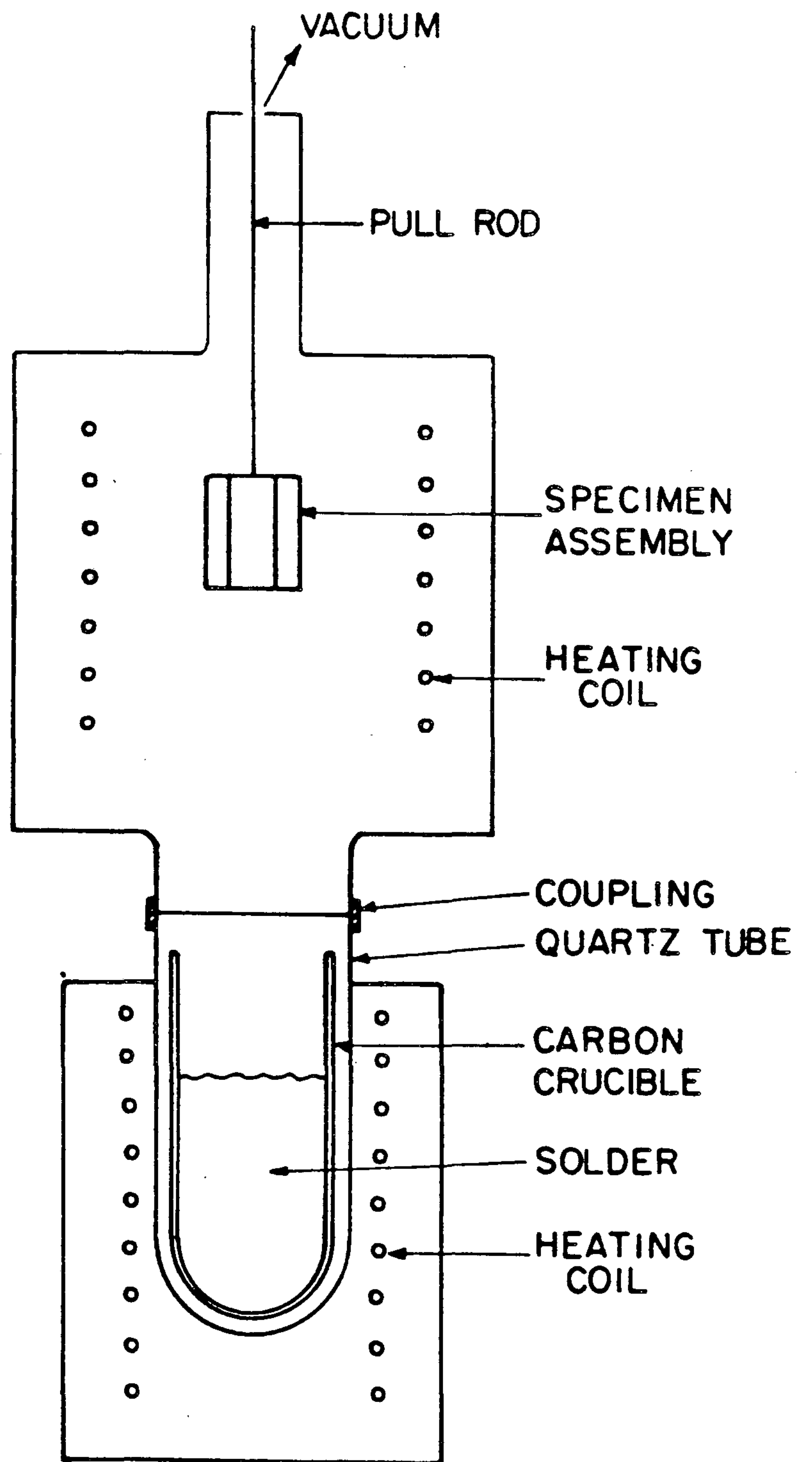
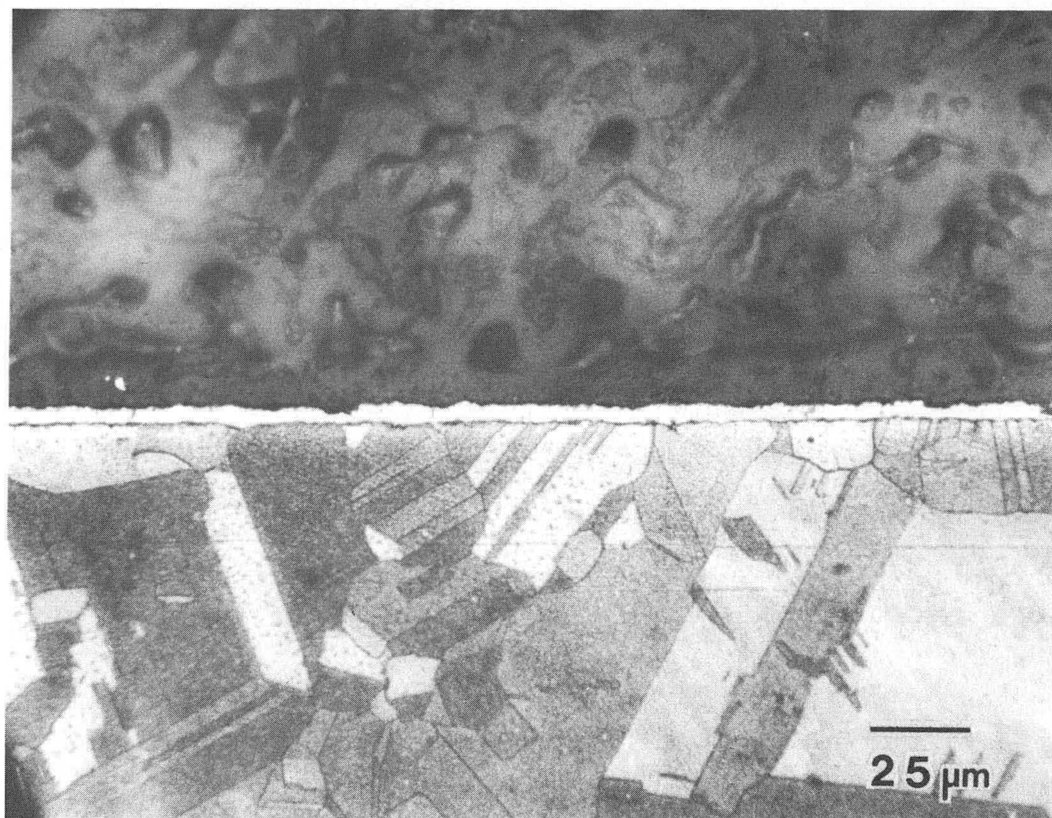
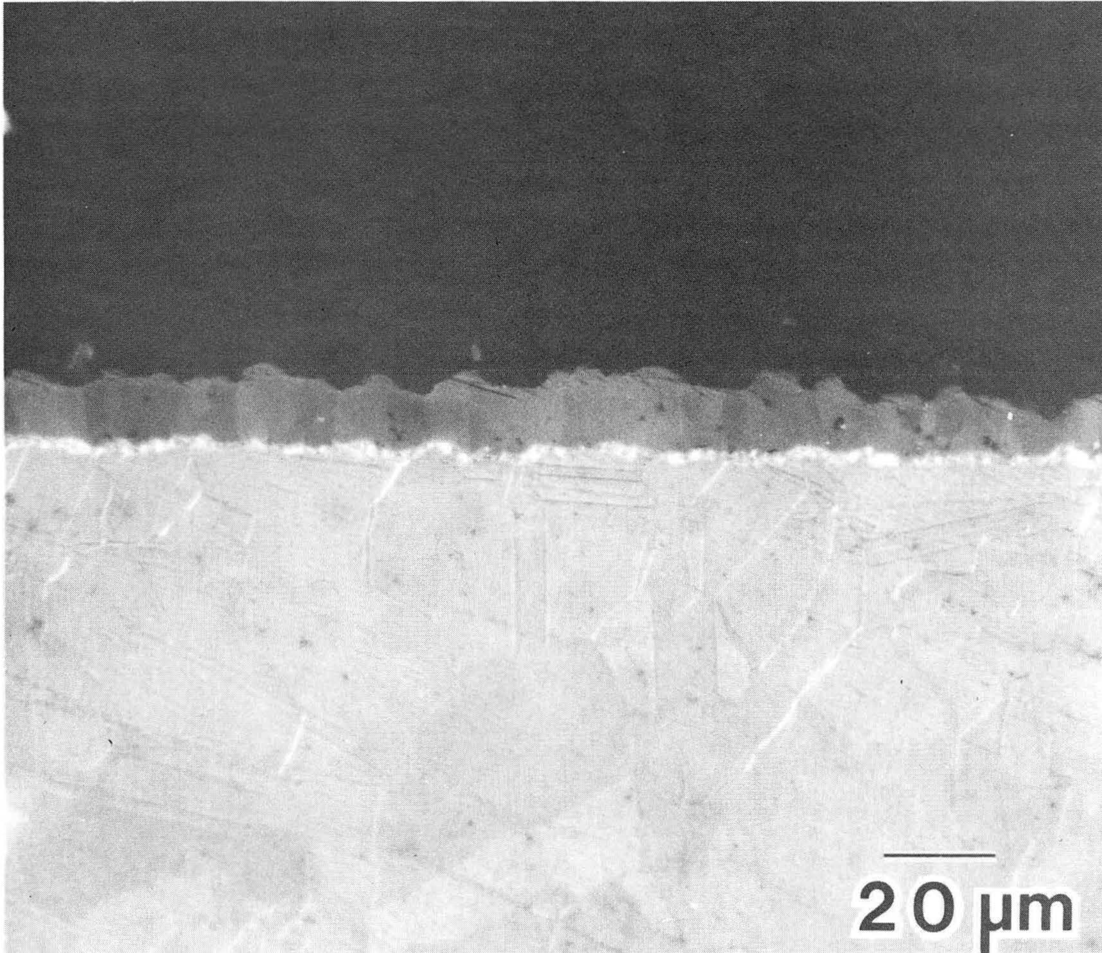


Fig. 2. Vacuum furnace configuration used in specimen preparation.



XBB 854-2592

Fig. 3. Cu_3Sn layer that forms in the as solidified condition.



XBB-857-2519

Fig. 4. Planar interface after 5 one hour reflows revealing columnar grains are revealed by polarized light.

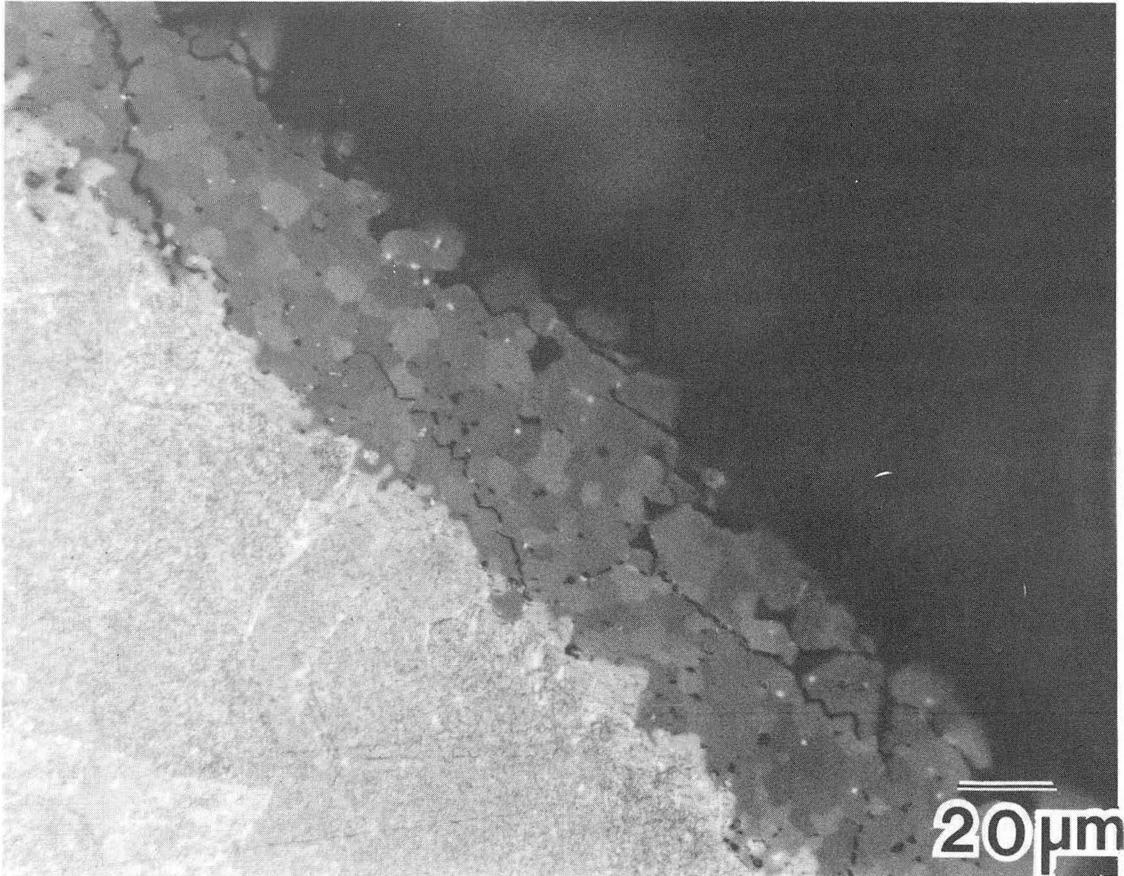


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Fig. 5. Intermetallic layer after 5 one hour reflows at an angle of 10° off parallel, taken using polaraized light.

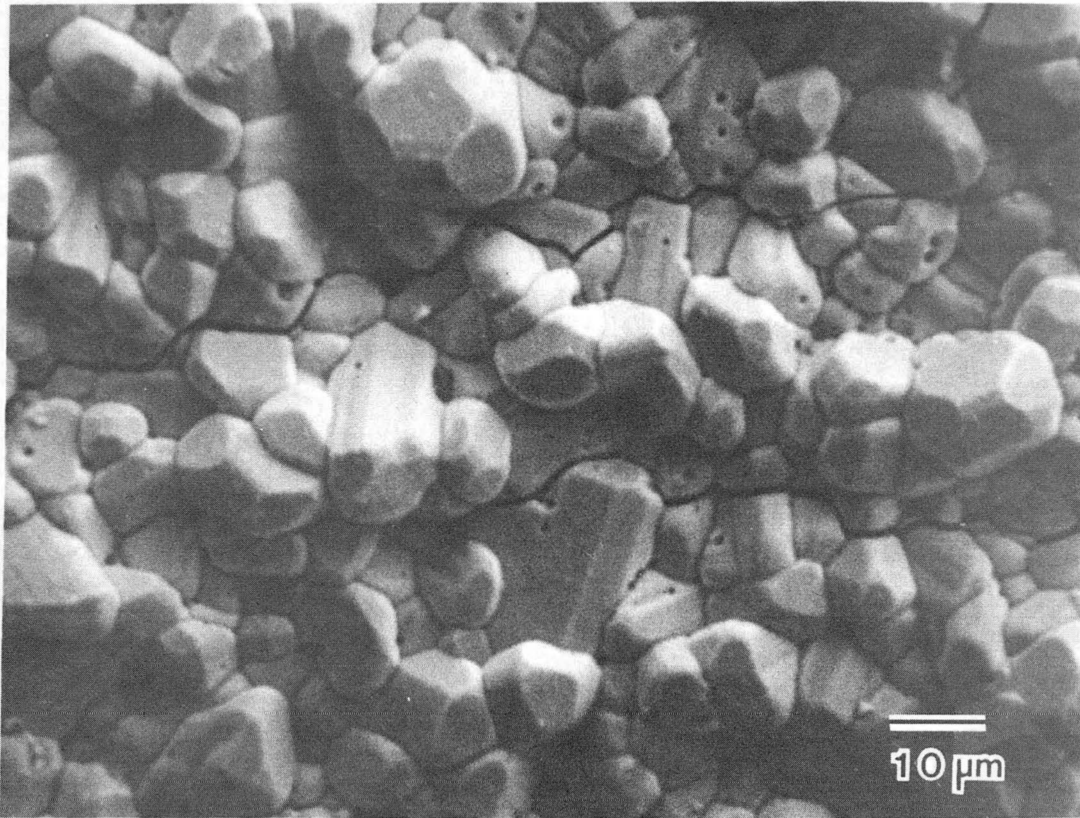

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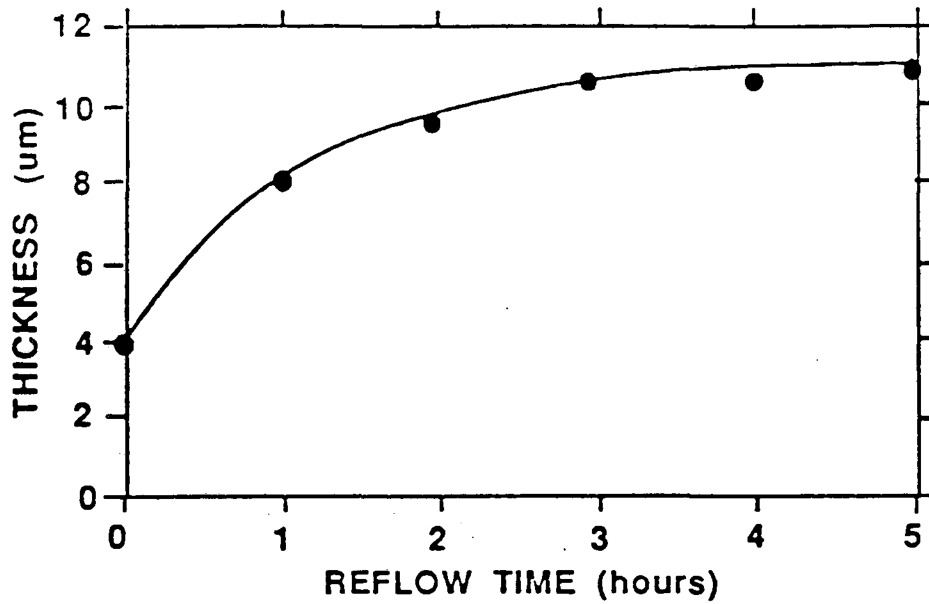
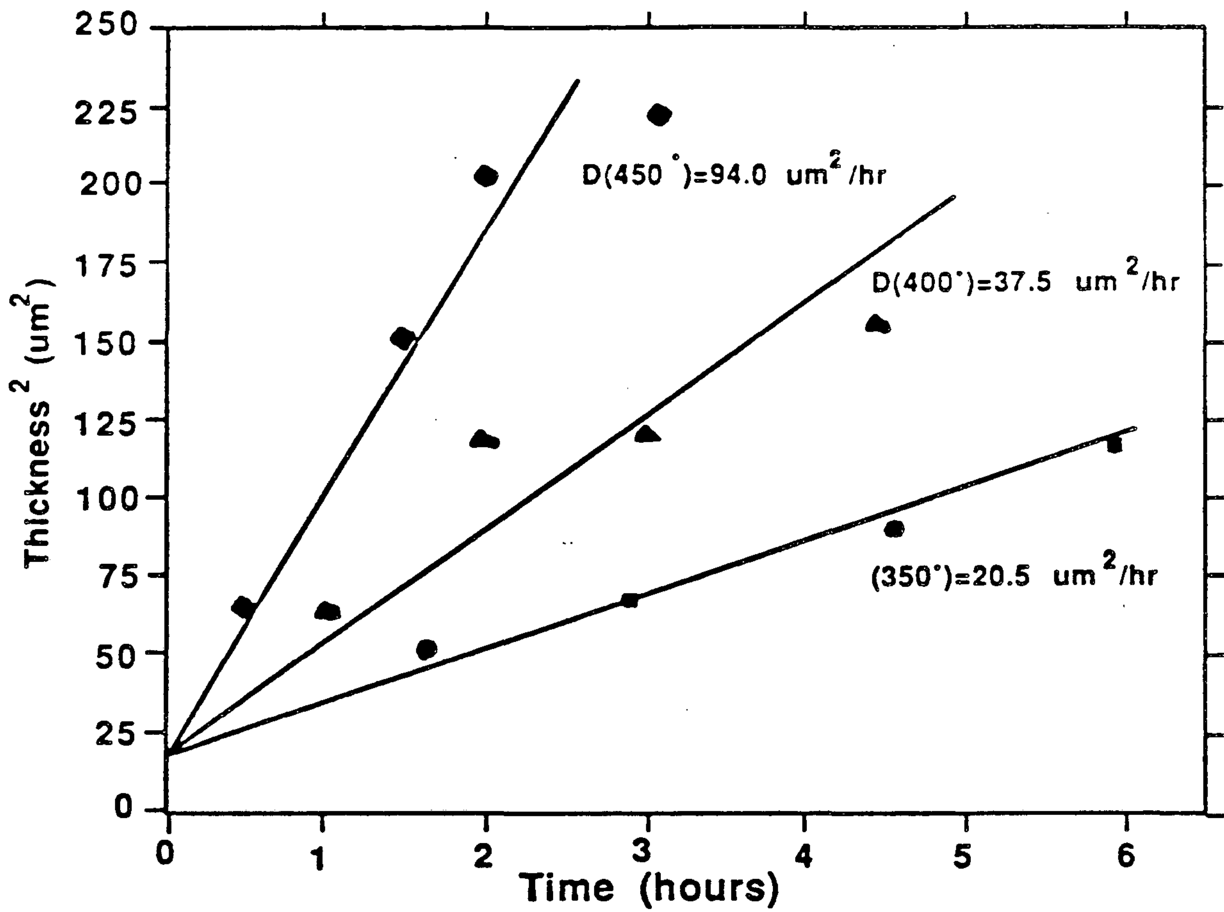
Fig. 6. SEM micrograph of a top view of the intermetallic at the Pb-Sn/Cu_3Sn interface.



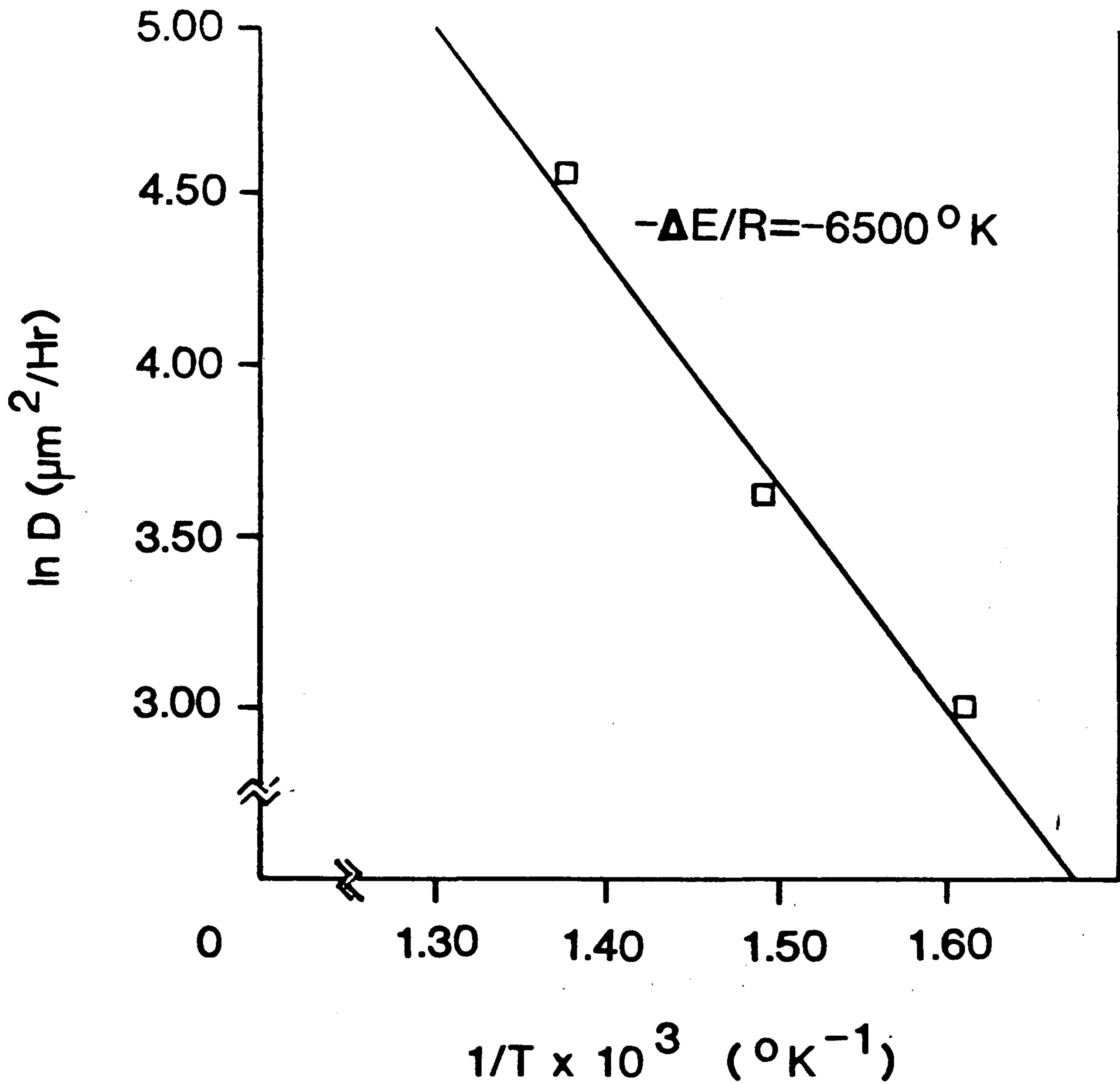
XBL 867-2571

Fig. 7. Intermetallic thickness versus time at 400 ^{o}C.



XBL 867-2572

Fig. 8. Cu_3Sn layer thickness squared versus time at temperature.



XBL 857-2957

Fig. 9. Arrhenius plot of diffusivity versus 1/T. The slope determines the activation energy for diffusion.

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