

# Intermetallic Growth in Tin-Rich Solders

*Study affords better understanding of the performance of tin-base soldered joints exposed to temperatures of 100 to 200 C*

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**ABSTRACT.** For tin-rich solder alloys, 200 C (392 F) is an extreme temperature. Intermetallic growth in tin-copper systems is known to occur and is believed to bear a direct relationship to failure mechanisms. This study of morphological changes with time at elevated temperatures was made to determine growth rates of tin-copper intermetallics. Preferred growth directions, rates of thickening, and notable changes in morphology were observed.

Each of four tin-base alloys was flowed on copper and exposed to temperatures between 100 C and 200 C for time periods of up to 32 days. Metallographic sections were taken and the intermetallics were examined. Intermetallic layer thickening is characterized by several distinct stages. The initial growth of side plates is extremely rapid and exaggerated. This is followed by retrogression (spheroidization) of the elongated peaks and by general thick-

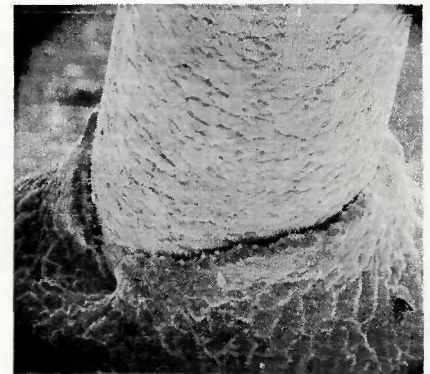
ening. The dual-composition intermetallic thickens from 1 to 70 microns with some tendency to grow through voids in the solder matrix. The possibility was noted that mechanical properties can be enhanced by the preferred growth of the copper-rich phase. The general theory for the diffusion-controlled growth of plates appears to be applicable to this metallic system.

## Introduction

The successful use of solder alloys requires (1) getting the right kind of solder joint made, and (2) assuring the soldered joint will withstand environmental stresses and strains. Each of these requirements is related to the materials being joined, to the filler metal alloy used, to the soldering procedure and to the environment encountered.

During the past ten years, much work has been done on improving soldering techniques. NASA's pioneering effort on contour soldering for highly reliable joints is probably the impetus behind most of the electronics industry's move in that direction.<sup>1</sup> As a result, a great deal of information regarding a supposedly

*Fig. 1 — Joint fracture that impairs conductivity of an electrical connection, as seen by scanning electron microscope (SEM) at X140 (reduced 50%)*



well-established process has just recently come to light. More people now have a better understanding of how the soldering operation should be done.

During the same time period, the need for this understanding was re-emphasized by the trend toward automation in soldering. When large numbers of connections are attempted simultaneously, it is imperative that conditions for soldering be closely controlled,<sup>2</sup> otherwise an intolerable proportion of joints will be found unacceptable. Much industry effort is still devoted to this aspect of the automated soldering process.<sup>3</sup>

On the other hand, investigations into the useful life of well-made soldered joints, have been given sporadic attention. Detailed analyses are often made only after the inadvertent misapplication of a soldered component results in failure. Now the demand is for more reliability and longer life under more severe service conditions, including higher allowable temperature limits.

As a result, the type of failure shown in Fig. 1 is found to occur more and more often. A seemingly well made, and an apparently high quality connection becomes electrically intermittent or open due to joint

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fracture. Metallurgical analysis of a number of such examples indicates that microstructural changes with time at temperature are, in large part, controlling factors in determining the useful lifetime of soldered connections.<sup>4</sup> Therefore, it seems advisable to learn more about the effect of the long-time exposure of common solder systems to high ambient temperatures.<sup>5</sup>

Despite the preponderance of technical information gathered on the subject of the elevated-temperature use of materials, much of the available data<sup>6</sup> pertains to the use of materials at temperatures in excess of 350 C. Few investigators, with some notable exceptions,<sup>7,8</sup> consider anything lower to fall within the realm of a "high temperature" application. Yet, those who deal with tin-rich solder alloys find that, for them, 200 C is an extreme temperature.

Some of the frequently encountered problems, even though manifested by an extreme operating environment originate in the soldering process.<sup>9</sup> Others are due to the effect of the environment itself. Some of the latter are considered in this paper.

### Experimental Procedure

On the intuitive assumption that problems of joint failure bear a direct relationship to the formation of intermetallic compounds, a series of experiments was designed for the evaluation of tin-rich solder alloys and copper wetting surfaces. An objective was to study microstructural changes after the prolonged exposure of soldered joints to temperatures as high as 200 C. As usual, the arbitrary limitation and selection of test parameters directs attention pointedly toward those desirable experiments which are left undone.

### Soldering and Sampling

There is a need, in work of this nature, to avoid becoming engrossed in the problems of soldering and solderability since these are arts and sciences within themselves. Of all the factors which combine to facilitate the making of a soldered connection, it seemed most important, for the purpose of this experiment, to control those related to intermetallic formation. Therefore, soldering temperatures were kept as low as possible, the volume of solder was kept nearly the same for each test, and the solder and terminal compositions were selected for high potential intermetallic content.

All samples were chemically prepared prior to the making of lap

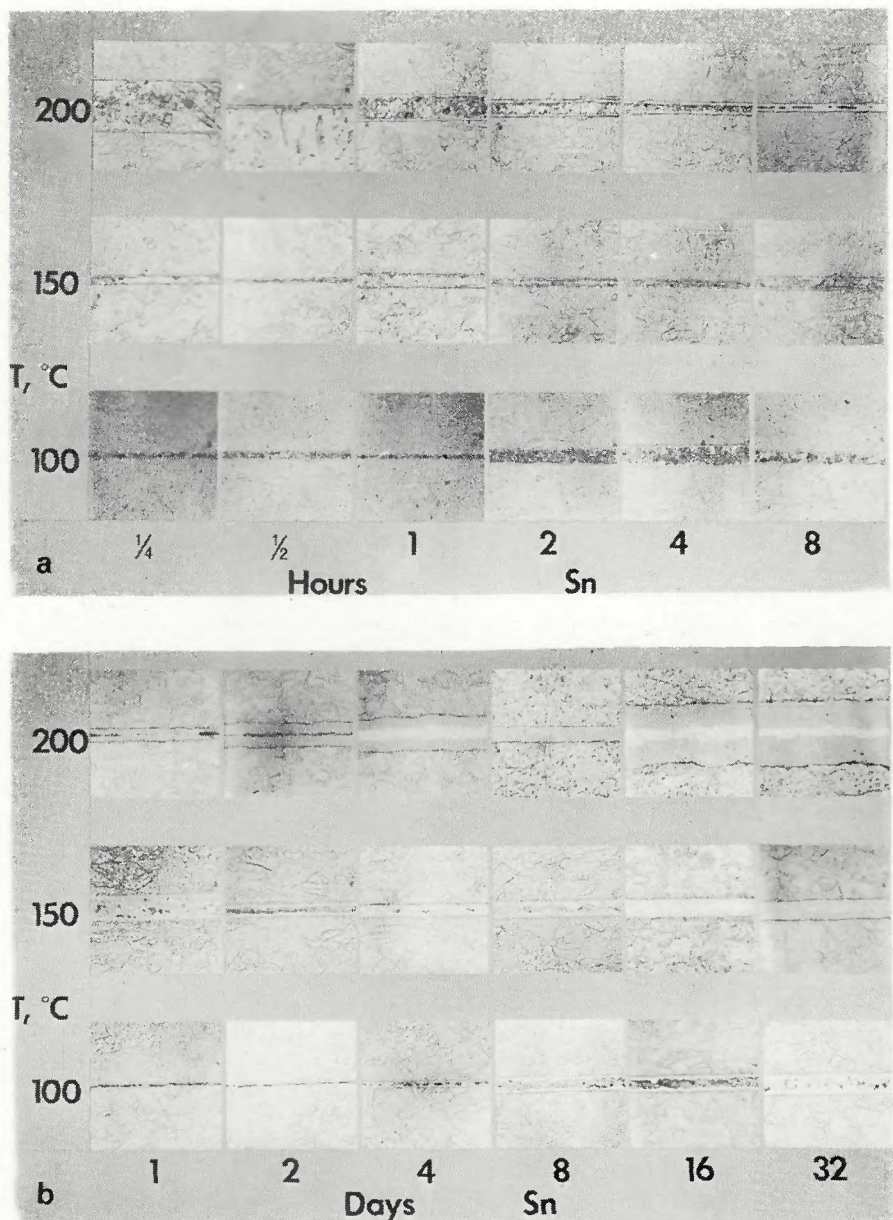


Fig. 2 — Tin solder morphology after exposure at temperatures shown for (a) ¼ to 8 hr, (b) 1 to 32 days. Joint cross section (X800, reduced 46%)

joints, and the faying surfaces were tough-pitch copper. A number of soldered samples were soaked at temperatures between 100 C and 200 C for periods of time as short as 15 minutes and as long as 32 days. A representative specimen for each solder composition and each set of time-temperature conditions was prepared for metallographic study, and another was used for an evaluation of mechanical properties.

### Morphology

Through the use of the metallographic sections, changes in the morphology of the CuSn intermetallic phases were observed. The extent of growth and growth rates were deter-

mined for intermetallic thickening. Other growth characteristics which indicate extreme complexity in these metallic systems were observed and studied. The bond interfaces and adjoining regions in the solder joints showed metallographic features characteristic of the CuSn metallic systems. The general morphology of the solder area was traced from that present in early (as-soldered) samples to that resulting from 32-day exposure. Selected samples were prepared for further analysis by scanning electron microscope (SEM) and x-ray probe methods.

### Composition

In order to evaluate the effect of

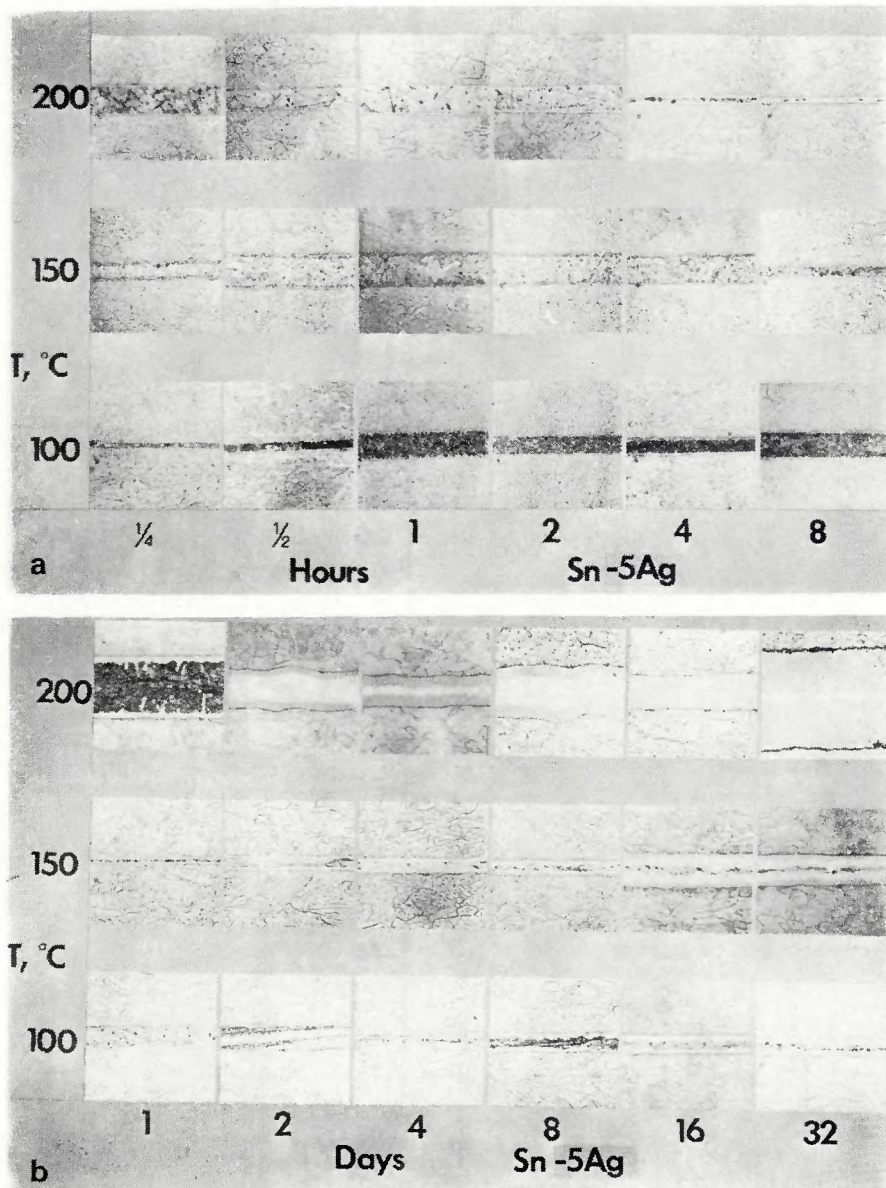


Fig. 3— Tin-silver solder morphology after exposure (a) and (b) to the same conditions shown in Fig. 2. Joint cross section (X800, reduced 46%)

composition on thermal response, four solders were selected for study. At the start of this project, it seemed important that differences in component solubilities and in melting temperatures, among other things, be monitored. For this reason Sn, Sn-2.5Sb, Sn-5Ag and Sn-40Pb solders were prepared for evaluation. Some of the data<sup>10</sup> pertinent to the objectives of the study are shown in Table 1. The major components (Cu and Sn) of each of these combinations are, for practical purposes, not soluble in one another. Tin is soluble in Sb, Ag and Pb to an appreciable extent, and in the SnPb alloy there is available a quantity of solvent sufficient to influence CuSn intermetallic growth rates if such an influence is to be of any importance.

### Experimental Results

Copper-tin intermetallic compound growth can be readily monitored in soldered joints. Actual growth modes are observed and measurements made by the use of metallographic techniques. Changes in the distribution of metallurgical phases as well as of chemical elements are plotted by combining metallography with scanning electron microscopy and x-ray fluorescence.

### Intermetallic Growth

Sections were prepared by the use of standard metallographic techniques. All samples were etched using a 10-sec swab with 60% H<sub>2</sub>O<sub>2</sub>-40% NH<sub>4</sub>OH followed by 10-sec swab with 2% HNO<sub>3</sub>-98% alcohol. These solutions were developed for the purpose of increasing the contrast of the intermetallics. In this way, morphological changes were monitored for all test conditions, and for each of the alloys selected for study.

Shown in Fig. 2 is a series of metallographic sections depicting the thermal response due to the Sn solder. A two-phase intermetallic layer can be seen to form, to grow progressively thicker and eventually to bridge the joint cross section. The same series at temperatures lower than or higher than 150 C show similar morphologies with expected differences that can be explained by changes in growth rates which exhibit the normal exponential dependence on temperature.

Table 1 — Physical Properties for Various Cu and Sn Alloy Systems

Solvent	Solute	Wt % in solution at		Intermetallic phases present at		Lowest liquid temp., C <sup>(b)</sup>
		200 C	RT <sup>(a)</sup>	200 C	RT <sup>(a)</sup>	
Cu	Sn	1.3	negl <sup>(c)</sup>	Cu <sub>3</sub> Sn	Cu <sub>3</sub> Sn	415
Cu	Sb	1.0	negl	Cu <sub>3</sub> Sb	Cu <sub>3</sub> Sb	526
Cu	Ag	negl <sup>(c)</sup>	negl	—	—	779
Cu	Pb	negl	negl	—	—	326
Sn	Cu	negl	negl	Cu <sub>6</sub> Sn <sub>5</sub>	Cu <sub>6</sub> Sn <sub>5</sub>	227
Sn	Sb	5.0	negl	SnSb	SnSb	232
Sn	Ag	negl	negl	Ag <sub>3</sub> Sn	Ag <sub>3</sub> Sn	221
Sn	Pb	1.0	negl	—	—	183
Sb	Cu	negl	negl	Cu <sub>2</sub> Sb	Cu <sub>2</sub> S	526
Sb	Sn	4.5	4.5	—	—	425
Ag	Cu	negl	negl	—	—	779
Ag	Sn	10.0	8.0	Ag <sub>3</sub> Sn	Ag <sub>3</sub> Sn	724
Pb	Cu	negl	negl	—	—	326
Pb	Sn	17.0	2.0	—	—	183

(a) RT = room temperature  
 (b) 50% or more solvent  
 (c) negl = negligible

Fig. 4— Tin-antimony solder morphology after exposure (a) and (b) to the same conditions shown in Fig. 2. Joint cross section (X800, reduced 46%)

Figure 3 is a metallographic series showing the thermal response in Sn-5Ag solder. As is true of each of these materials, after a day of elevated temperature exposure, the intermetallic layer is well-formed, continuous and generally free of angular side plates. The growth pattern is similar to that in Sn solder, except that complete bridging is delayed somewhat.

The metallographic series shown in Fig. 4 is that for Sn-2.5Sb solder. This system is characterized by slightly more irregularity in the intermetallic layer, otherwise the morphology for this alloy is not too different from that of the others. The two-phase intermetallic grows into the solder matrix with occasional bridging after long time at the lower temperatures and complete bridging at 200 C.

Shown in Fig. 5 is the series of metallographic sections for Sn-40Pb solder. The intermetallic layer is more rounded indicating that the spheroidization of side plates occurs rather early. Thickening also tends to proceed more rapidly, and the bridging which does not occur readily will probably never be continuous.

In attempting the determination of growth rates, the investigator is presented with the problem of deciding which of a variety of morphological features are significant as well as with some special measurement difficulties. There seems to be little doubt that the growth phenomena encountered here can be described by established diffusion theory. Purdy and Kirkaldy<sup>11</sup> show the mathematical procedures generally applicable to problems of this type. The work described here will, hopefully, define those parameters that deserve more rigorous experimental work and mathematical treatment.

The measurement of allotriomorphs or side-plates is probably not significant at exposures over 100 C because all traces of these morphological features are obliterated within several hours. Other possible measurements include an average layer thickness,  $Cu_3Sn$  thickness,  $Cu_6Sn_5$  thickness, change in joint gap, and decrease in solder matrix width.

Although the irregular surface at the intermetallic-matrix interface makes layer thickness rather difficult to measure, the results of such measurements are listed in Table 2.

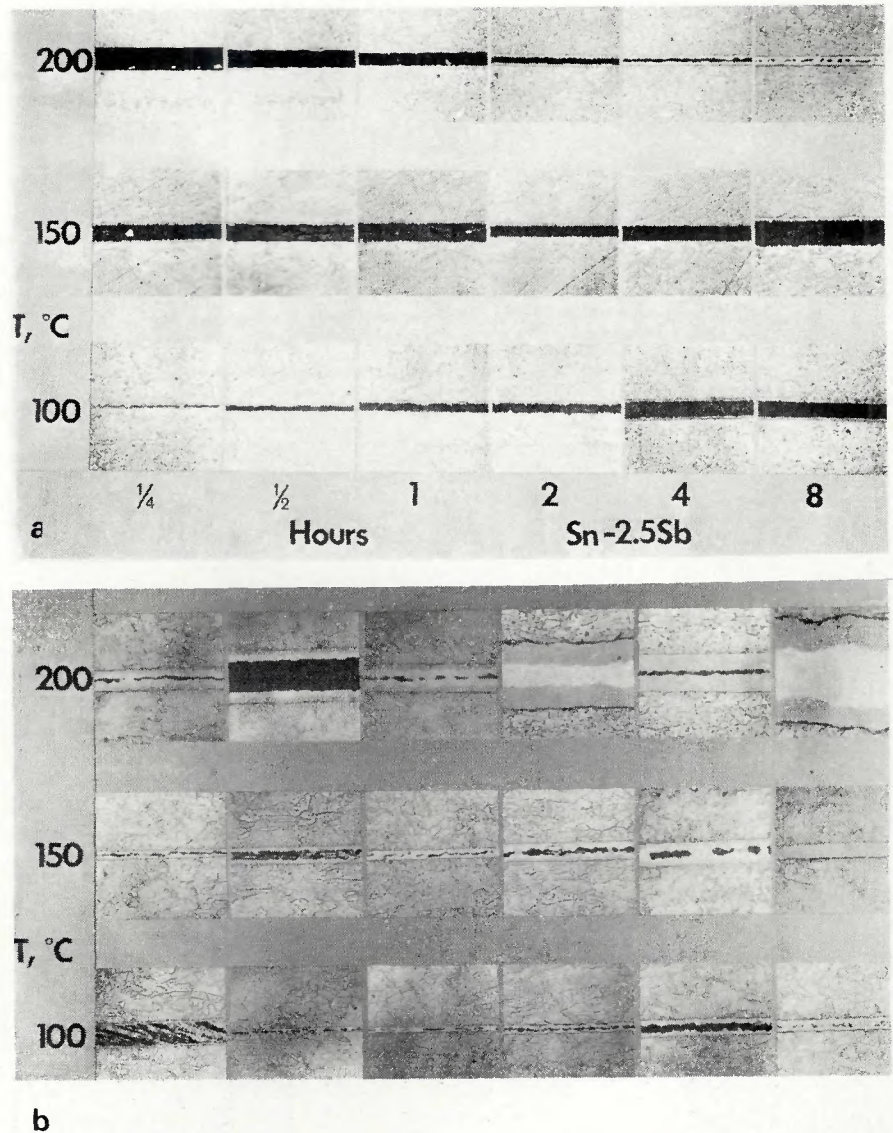


Table 2 — Observed Intermetallic Layer Thickness, Microns

Temperature, C	Composition	Time at temperature											
		Hours						Days					
		1/4	1/2	1	2	4	8	1	2	4	8	16	32
200	Sn-40Pb	3.8	4.5	5.3	5.3	3.1	7.6	7.8	12.5	14.4	15.6	18.1	17.5
200	Sn-2.5Sb	1.4	1.6	2.1	2.4	2.9	3.6	8.1	12.0	12.5	31.3	37.5	68.8
200	Sn-5Ag	1.5	1.7	2.4	2.6	3.1	4.1	5.2	18.7	18.1	28.8	14.1	50.0
200	Sn	1.7	1.4	2.4	2.7	3.6	4.3	6.2	8.5	14.8	6.2	31.3	34.4
175	Sn-40Pb	0.9	1.0	1.5	1.8	2.6	3.5						
175	Sn-2.5Sb	1.1	1.5	1.7	1.7	1.8	2.5						
175	Sn-5Ag	1.1	1.1	1.2	1.5	2.0	2.2						
175	Sn	2.1	1.4	1.3	1.9	1.7	2.8						
150	Sn-40Pb	1.0	1.1	1.4	1.2	1.2	1.9	9.7	9.9	10.1	15.0	16.7	16.6
150	Sn-2.5Sb	1.4	1.2	1.5	1.6	1.6	2.0	4.3	5.8	6.8	9.2	15.3	13.3
150	Sn-5Ag	2.1	2.4	1.5	0.5	0.8	1.8	3.9	4.6	5.6	8.0	18.2	13.7
150	Sn	1.0	2.7	2.1	1.6	1.6	2.4	6.8	7.0	7.3	9.7	9.9	10.0
125	Sn-40Pb	1.1	1.0	1.0	1.1	2.0	1.0						
125	Sn-2.5Sb	1.5	1.4	2.1	1.9	2.4	1.5						
125	Sn-5Ag	1.1	1.8	1.2	2.9	1.4	1.2						
125	Sn	1.9	1.9	2.2	2.4	2.0	2.1						
100	Sn-40Pb							1.5	1.9	2.3	4.1	4.1	6.5
100	Sn-2.5Sb							1.4	1.9	2.3	3.4	3.8	4.1
100	Sn-5Ag							1.3	1.6	2.4	4.5	4.8	5.0
100	Sn							1.0	1.5	2.0	3.0	3.6	4.3

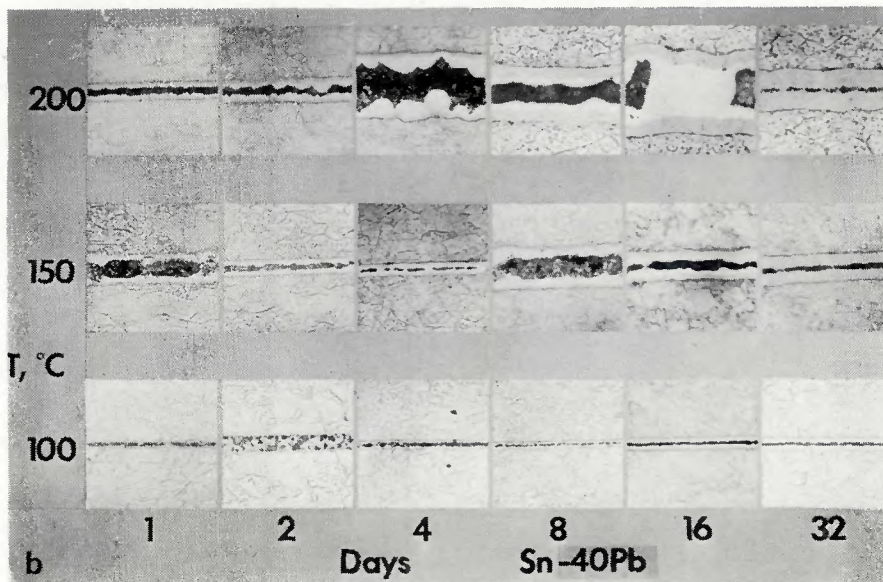
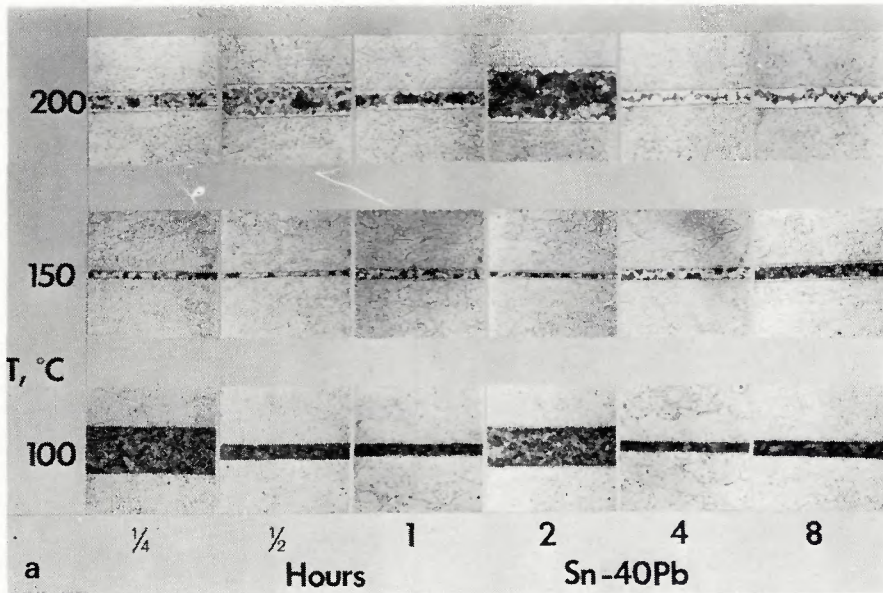


Fig. 5 — Tin-lead solder morphology after exposure (a) and (b) to the same conditions shown in Fig. 2. Joint cross section (X800, reduced 46%)

These data are shown graphically in Figs. 6, 7, 8 and 9.

There appears to be little dependence of growth rates on composition. The dominating factor is the maximum exposure temperature.

#### Morphology

During the initial stages of solder joint formation, the microstructure is characterized by the presence of allotriomorphs which are formed on solidification. There is no way to avoid the presence of this thin ( $\approx 1-2$  micron) layer of intermetallic due to nucleation from the melt. Immediately after solidification and upon elevated temperature exposure, side plate growth is extremely rapid. Next

the side plates tend to spheroidize while the intermetallic layer thickens. In later stages of growth, the thick layer becomes a continuum of massive intermetallic with a rounded leading edge. Finally, the intermetallic tends to bridge the entire joint gap, always without a parting line where the intermetallic layers eventually meet. Throughout the early stages of the growth process, the  $\text{Cu}_3\text{Sn}$  and the  $\text{Cu}_6\text{Sn}_5$  thicknesses are approximately equal. As tin is depleted from the solder matrix,  $\text{Cu}_6\text{Sn}_5$  growth slows while the  $\text{Cu}_3\text{Sn}$  continues to grow at the expense of the tin-rich intermetallic. Given sufficient time at temperature, the copper-rich phase consumes all of the available tin.

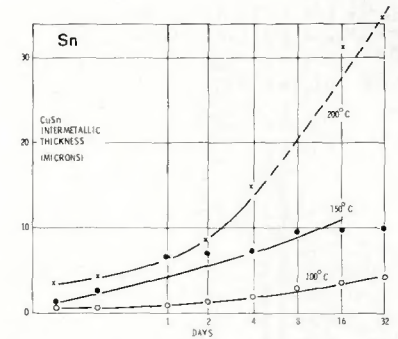


Fig. 6 — Growth in thickness of CuSn intermetallic layer with time at temperatures shown, using tin solder on copper

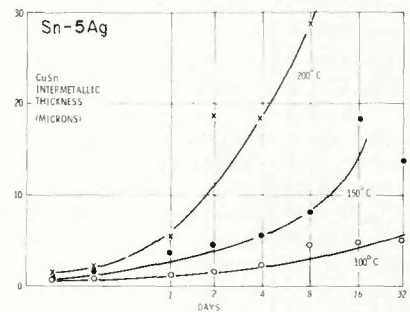


Fig. 7 — Growth in thickness of CuSn intermetallic layer with time at temperatures shown, using tin-silver solder on copper

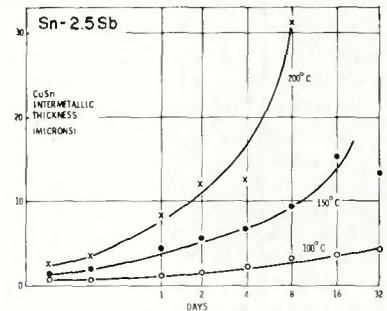


Fig. 8 — Growth in thickness of CuSn intermetallic layer with time at temperatures shown, using tin-antimony solder on copper

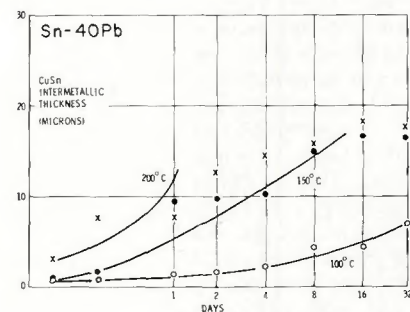


Fig. 9 — Growth in thickness of CuSn intermetallic layer with time at temperatures shown, using tin-lead solder on copper

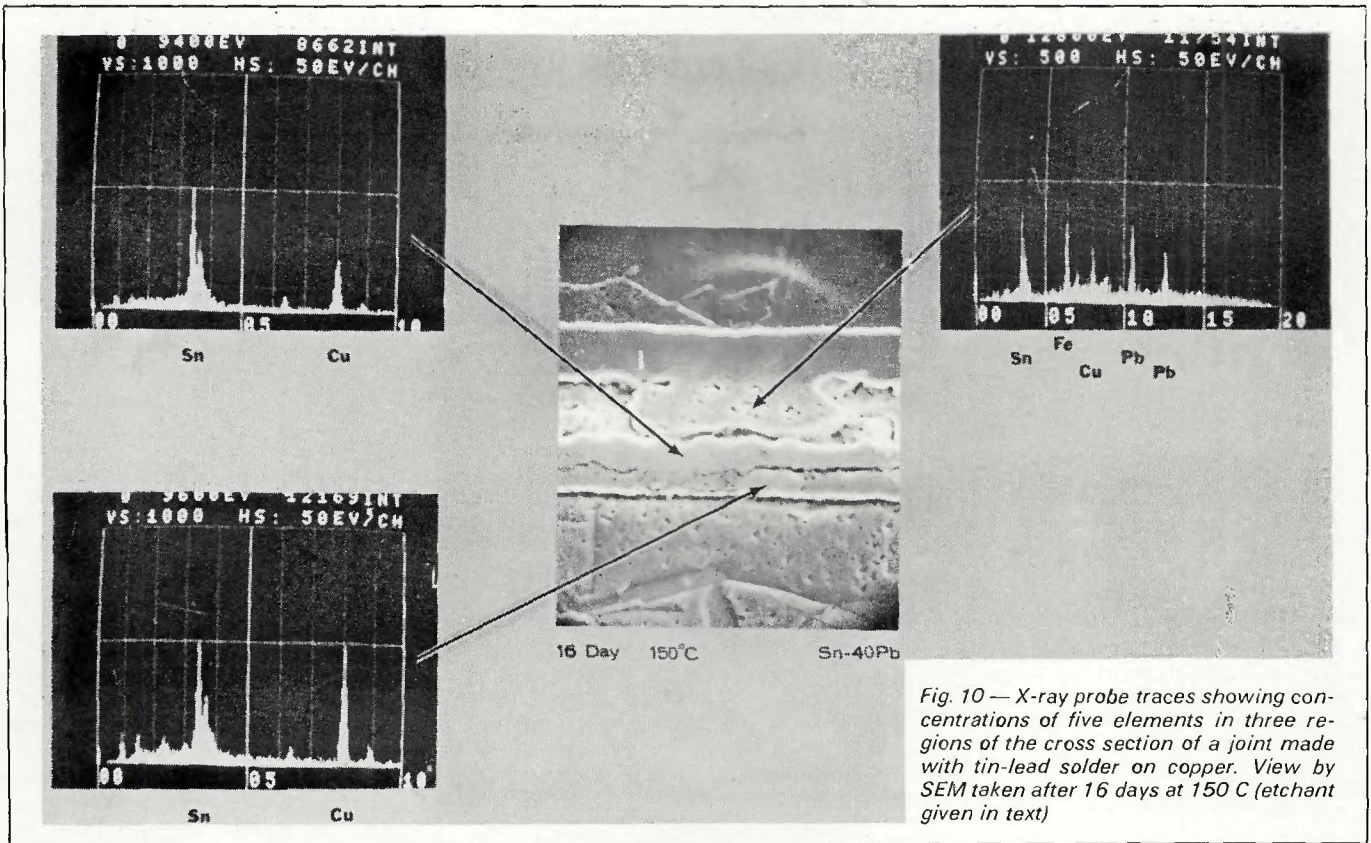


Fig. 10 — X-ray probe traces showing concentrations of five elements in three regions of the cross section of a joint made with tin-lead solder on copper. View by SEM taken after 16 days at 150 C (etchant given in text)

### Composition Gradients

In a newly formed solder joint, the cross section consists of a thin  $Cu_6Sn_5$  intermetallic layer at both copper interfaces and a solder matrix of fairly uniform composition between. SEM and x-ray probe analyses indicate that some segregation occurs in the solder matrix with primary tin as well as each intermetallic type dispersed throughout the joint area.

As intermetallic growth progresses, the x-ray probe reveals that the  $Cu_3Sn$  and  $Cu_6Sn_5$  intermetallics grow into the solder matrix and, at a slower rate, into the copper terminal. Insoluble and impurity elements are concentrated ahead of the leading edge of the  $Cu_6Sn_5$  layer until growth is completed by the depletion of the available Sn. Diffusion continues until the intermetallic conversion to  $Cu_3Sn$  is ended. In the Sn-Ag and Sn-Sb systems, a complex ternary intermetallic is the end result. In the Sn-Pb system, a Pb-rich zone remains between the intermetallic faces.

Figure 10 shows the SEM and x-ray probe trace taken from the Sn-40Pb sample after 16 days exposure. These results indicate both the tendency toward equilibrium in the intermetallic and the concentration of insolubles in the matrix.

### Conclusions

Copper-tin intermetallic compound growth occurs in soldered joints at low temperatures and in relatively short times. The growth that takes place can be significant in terms of joint characteristics.

The presence of insoluble alloying elements affects the intermetallic growth rate to a minor degree. The tin content and the maximum exposure temperature have the greatest influence on growth rates.

Intermetallic layer thickening is characterized by several distinct stages. The initial growth of side plates is extremely rapid and exaggerated. This is followed by retrogression (spheroidization) of the elongated peaks and by general thickening. The intermetallic thickens from 1 to 70 microns with some tendency to grow through voids in the solder matrix. In the high-tin alloys the  $Cu_6Sn_5$  readily bridges the joint section. In the final stages of growth, the dual intermetallic is transformed to  $Cu_3Sn$  by total consumption of the solder matrix and of the  $Cu_6Sn_5$  phase.

The possibility was noted that mechanical properties can be enhanced by the preferred growth of the copper-rich phase. The general theory for the diffusion-controlled growth of plates appears to be applicable to this metallic system.

### Acknowledgment

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