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Copper/Solder Intermetallic Growth Studies

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James Geis

ARL-TR-32

December 1992



93-02043



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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE December 1992		3. REPORT TYPE AND DATES COVERED Interim, from October 91 to May 92
4. TITLE AND SUBTITLE Copper/Solder Intermetallic Growth Studies			5. FUNDING NUMBERS PE: DE7	
6. AUTHOR(S) Kevin W. Kirchner, George K. Lucy (Army Research Laboratory), and James Geis (Tech International)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-32	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army MANTECH Soldering Technology Thrust Area 2800 Powder Mill Road Adelphi, MD 20783			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES AMS code: 768011.E77 HDL PR: 28E187				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This document is a summary of initial findings from a series of experiments involving copper/solder intermetallic compounds (IMC's). Particularly the study examines the IMC's contribution to the changing physical properties of a solder joint as a function of time and temperature. In these experiments Cu/Sn joint samples were placed in the hot stage of an environmental scanning electron microscope, heated to about 170°C, and monitored for about 3 hr. A visual documentation of events is included in this report. A real-time videotape record of the IMC growth was produced as part of the work. Additionally a working hypothesis is presented that involves the relationship between IMC's and the mechanical properties of joints.				
14. SUBJECT TERMS Solder, copper/solder, intermetallic compounds			15. NUMBER OF PAGES 15	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

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1. Introduction

Intermetallic compounds (IMC's) have been identified as important elements in soldering. Aside from the currently mounting evidence of their role in solderability, they are also being proposed as having a significant impact on the mechanical properties of soldered materials. In this document we discuss some initial findings from a series of experiments regarding this IMC contribution to the changing physical properties of a solder joint, all as functions of time and temperature. In addition to the discussion of the initial experimental findings, we also present a working hypothesis about the relationship between intermetallic compounds and mechanical property considerations.

2. Experiment

2.1 Sample Preparation

Oxygen-free high-conductivity copper (OFHC) substrates were cleaned in room temperature solutions made from equal parts of 30-percent ammonium hydroxide, 3-percent hydrogen peroxide, and deionized (DI) water. This immersion lasted for about 30 s. The samples were then rinsed in DI water followed by ethanol and finally blown dry. We then dipped the samples in a solder bath containing Kester ultra pure eutectic solder, held at 250°C, for about 30 s. The samples were then aged at 125°C for 59 days, providing reasonable thicknesses of both the Cu_6Sn_5 (eta phase) and Cu_3Sn (epsilon phase) intermetallics. After aging, the specimens were sectioned with a diamond saw and polished, finishing with 0.6- μm aggregate. Optical micrographs were produced and the IMC thicknesses were measured to be about 1 μm for the Cu_3Sn and 5 μm for the Cu_6Sn_5 (fig. 1). While no stains were used, polarizing filters helped distinguish the two IMC layers in the photomicrograph record made immediately following sample preparation.

2.2 Equipment

We performed the studies at ElectroScan Corporation of Wilmington, MA (Boston), using their recently introduced environmental scanning electron microscope (ESEM), which provides some unique features, including computer-controlled micro-positioning, 25 to 1000°C hot stage, and high pressure atmospheres (0 to 20 Torr) of nitrogen, H_2O , etc. These and other attributes allow emulation of real-world situations.

Figure 1. Optical micrograph—copper/solder interface immediately after aging and sample preparation and before ESEM.



2.3 Procedure

The sample was fixed in a 5-mm-diam ceramic crucible (part of the hot stage) using standard carbon paste and placed in the ESEM. We lowered the pressure of the specimen's chamber to about 4 Torr (the gas present was water vapor) and the temperature of the hot stage was ramped up, at a rate of about 10°C/min, to between 170°C and 180°C, and held there for about 2.5 hr. During this time a VCR film and a series of still images were recorded.

2.4 Images

In figures 2 through 7, the areas in the white boxes on the left side of the photographs are shown enlarged in the right half of the photographs, with the approximate temperature listed in the upper left corner.

The figures are listed in chronological order. Nearly 1.5 hr has elapsed between figures 2 and 7. All the images are of the cross-sectioned sample, reading from top to bottom in the figures: copper, intermetallic, and solder.

ESEM parameters listed along the bottom edge of the photograph are beam voltage, type of detector (secondary), magnification left image, magnification right image, working distance, and pressure (Torr). The next line down shows date and time. Figure 1 is a pho-

tomicrograph taken after sample preparation, with cross polarizers, making possible the differentiation of the two IMC's.

Figure 2. ESEM micrograph—copper/solder interface (time 0, arbitrarily chosen).

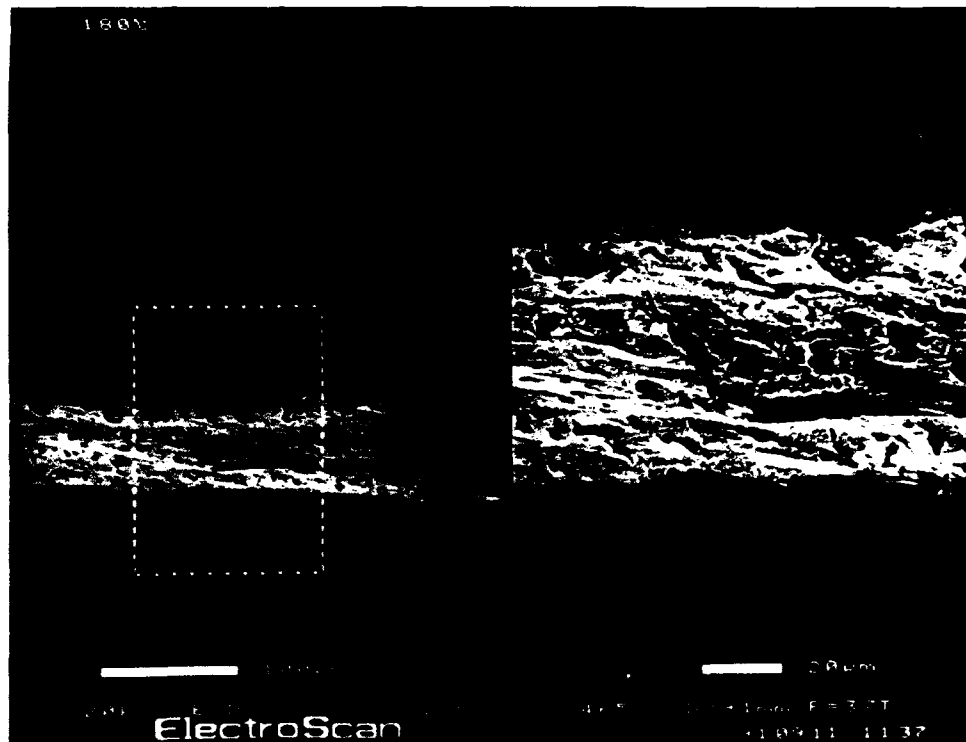


Figure 3. ESEM micrograph—copper/solder interface (Cu_3 clearly distinguishable from Cu_6Sn_5).

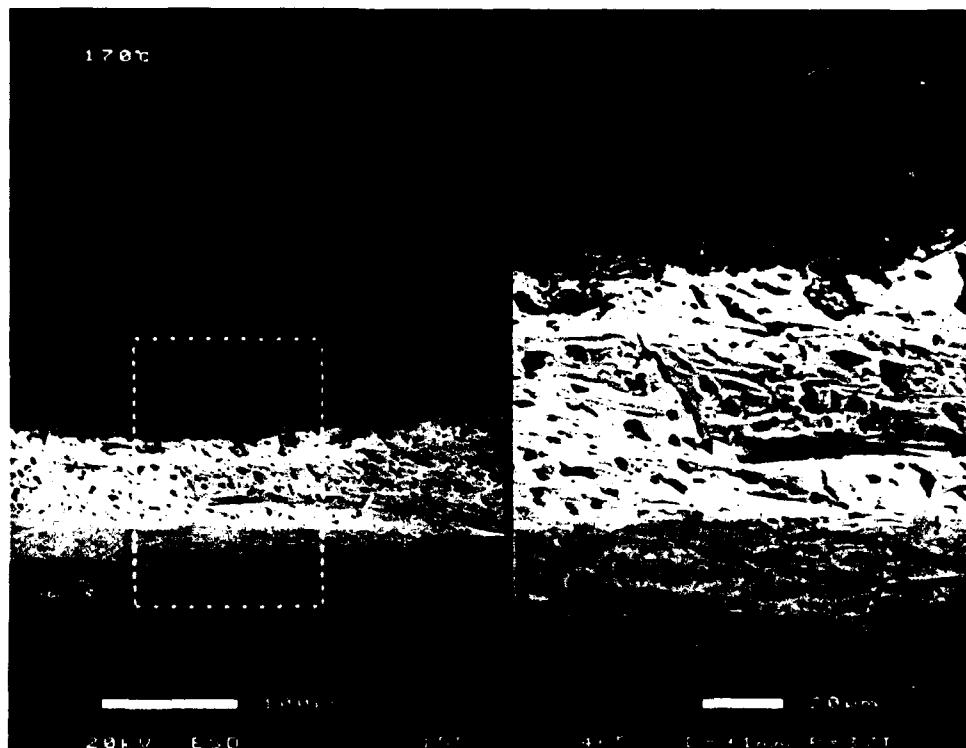


Figure 4. ESEM micrograph—copper/solder interface (time + 23 min).

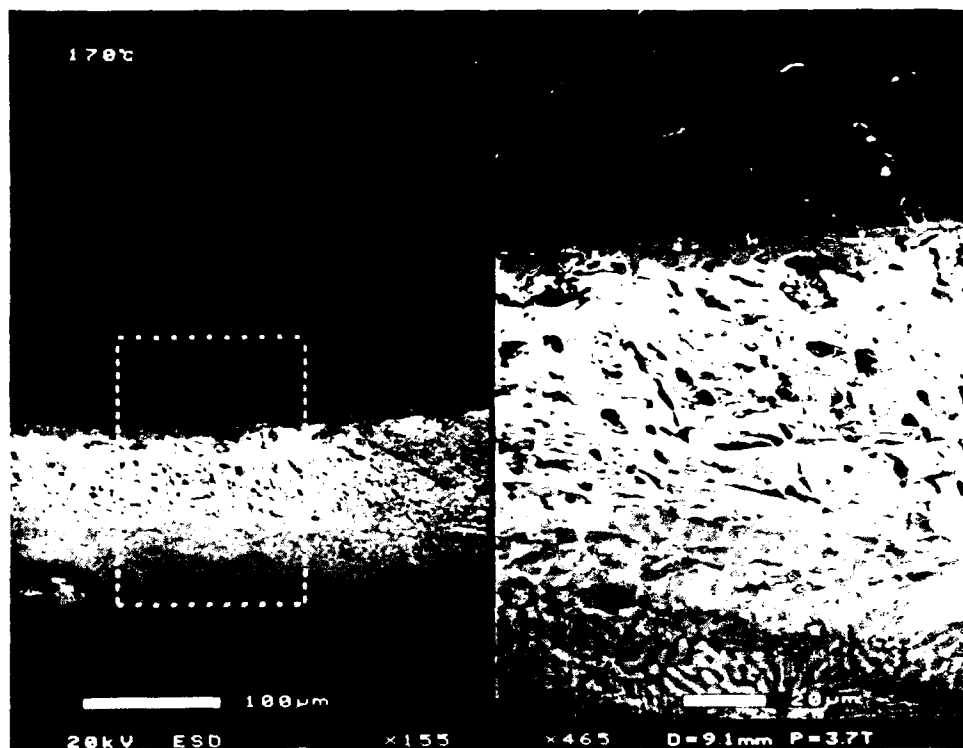


Figure 5. ESEM micrograph—copper/solder interface (time + 1 hr).

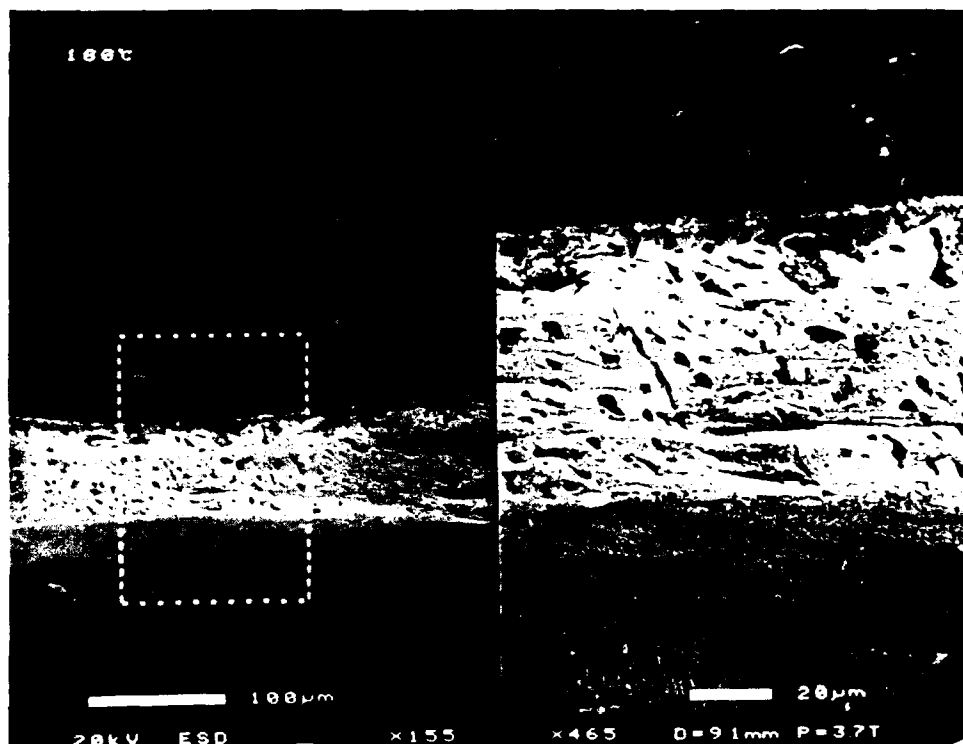


Figure 6. ESEM micrograph—copper/solder interface (time + 1 hr 15 min).

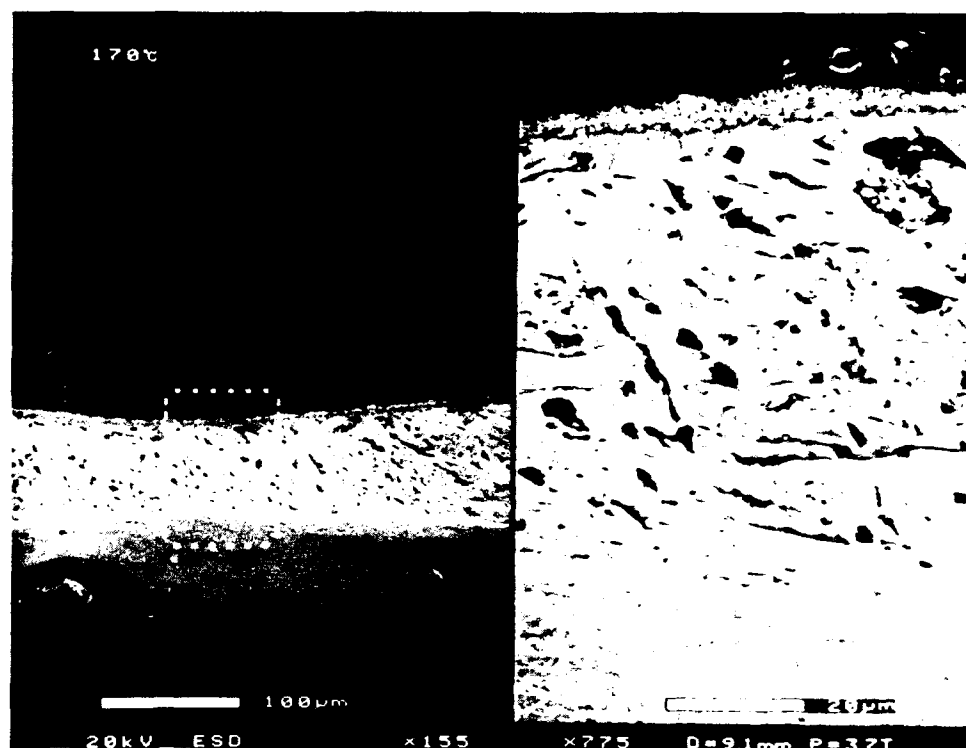
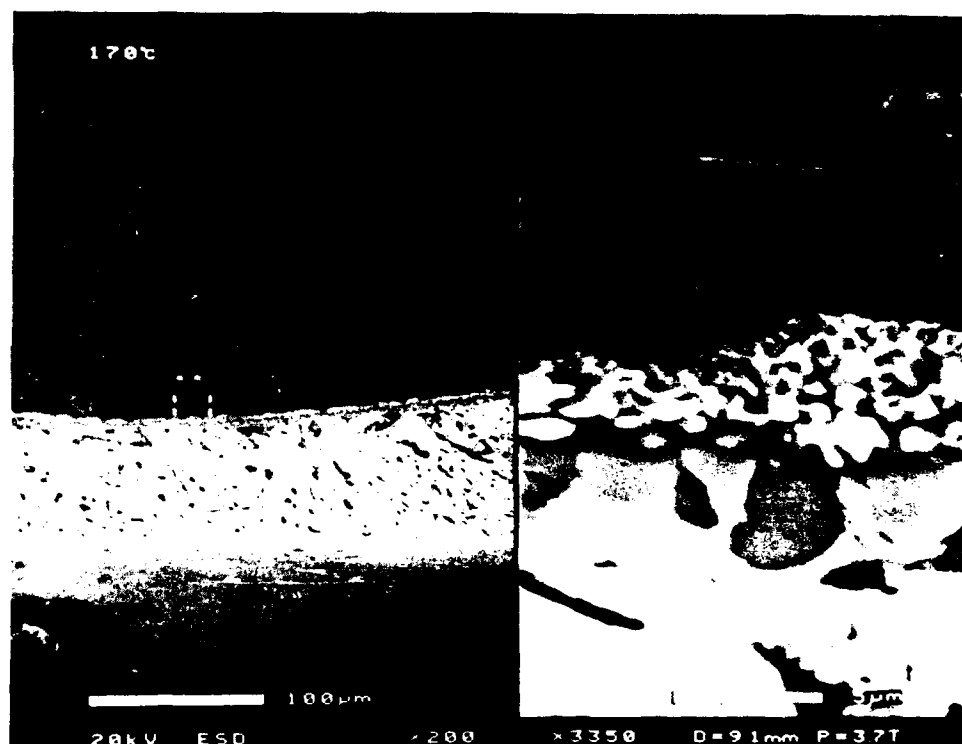


Figure 7. ESEM micrograph—copper/solder interface (extreme magnification—3350X—at time + 1 hr 27 min. Note out-of-plane growth of Cu_3Sn).



2.5 Observations and Remarks

Our most striking observation was that the Cu_3Sn showed the only signs of appreciable activity. The first signs of growth were small white flecks appearing at or near the $\text{Cu}/\text{Cu}_3\text{Sn}$ interface (fig. 2). About the same time these flecks appeared, a slight roughening of the Cu_3Sn became apparent, making the two intermetallics distinguishable. This was followed by additional roughening of the Cu_3Sn , which was caused by the out-of-plane component of the Cu_3Sn 's growth. It appeared that most of the grains grew at the same rate, making the field of them very regular in appearance (fig. 5 and 6). Over time the larger grains tended to be on the Cu_6Sn_5 rather than the Cu side of the Cu_3Sn (fig. 7). Also over time there was a difference in thickness (height out of plane) of the growing Cu_3Sn layer. The leading edge was thinner than the trailing edge (fig. 7). The question of whether all this activity might be just melting rather than growth behavior was answered by the fact that the melting points of all the constituents known to be present were above the sample temperature. Another concern was that the observed behavior might be the result of contamination. X-ray microanalysis showed potential contaminants to be below levels that could produce the results observed.

2.6 Followup Work

To assure that the results observed in the first set of experiments were not unique to that particular sample, we performed a second set of experiments, using a second specimen prepared and treated simultaneously with the first, but held aside and evaluated about a month later. Before working with the second sample, however, we verified calibration for the temperature of the ESEM hot stage by observing the controlled melting of pure elements. The accuracy of the stage was determined to be within 6°C across the range of interest (ambient to 175°C).

The second sample was treated in a similar fashion to the first as far as ramp rate, final temperature, gas pressure, gas species, and elapsed time. The same resulting changes and growth again appeared.

2.7. X-Ray Microanalysis

After ramp up, hold, and subsequent growth, we allowed the second sample to cool to near-ambient temperature, and while it was still within the chamber, we performed a series of energy-dispersive spectroscopy (EDS) analyses.

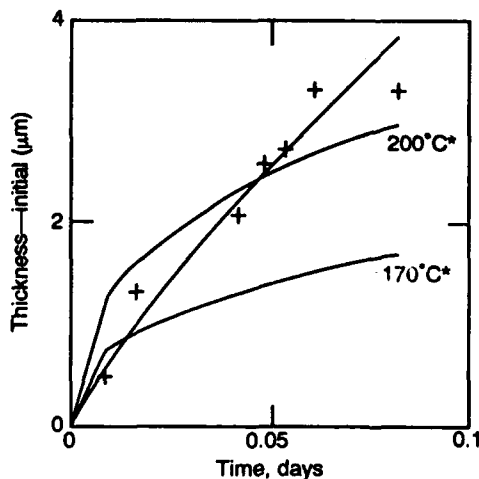
Spectra were first taken from the middle of the copper region and from a number of spots in the broad area of the solder. Next, successive spectra were taken stepping toward the IMC interfaces from the copper side and also from the solder side. These were designed to get a benchmark for the system and also to get a sense of the unwanted contributions to the spectra from neighbors. Finally, we chose a large but representative growth region and repeatedly probed areas of it; three spots were run two and three times each. The results showed that the analyses were reasonably well behaved. In particular, near-neighbor confounding of signals did not appear to be a problem.

Qualitative EDS showed the growth area to be composed of copper and tin. Quantitative standardless EDS produced atomic percent analyses that were within about 15 percent of those of Cu_3Sn .

3. IMC Growth

We evaluated the growth rates of the intermetallic layers by averaging the thicknesses of the layers over the cross section. This was done for the total IMC layer, the Cu_6Sn_5 (eta phase), and the Cu_3Sn (epsilon phase). For the total intermetallic layer, we compared the results to data published in *Solder Mechanics*.¹ This relationship is illustrated in figure 8, and shows a higher and more linear growth of our total IMC layer than is shown in previously published data. Figures 9 and 10 illustrate the growth of the eta and epsilon phase layers, respectively. It can be seen that the eta layer thickness decreases in time, being consumed by the epsilon layer, which grows into the eta as well as the copper. Figure 11 shows the ratio of epsilon to eta

Figure 8. Comparison of total IMC growth to published data [1].



*Plots of published data at 200°C and 170°C

¹D. R. Frear, W. B. Jones, and K. R. Kinsman, *Solder Mechanics: A State of the Art Assessment*, TMS-EMPMD Monograph Series, No. 1, Warrendale, PA (1991).

Figure 9. Cu_6Sn_5 growth with time.

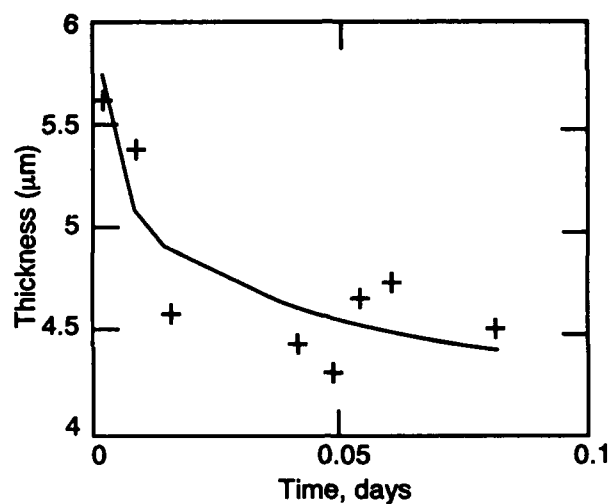


Figure 10. Cu_3Sn growth with time.

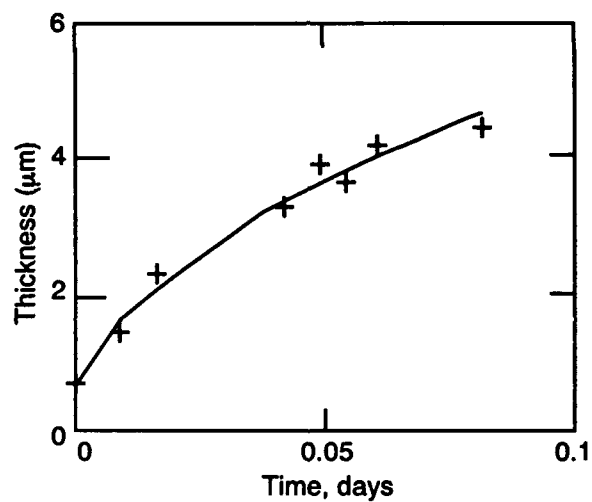
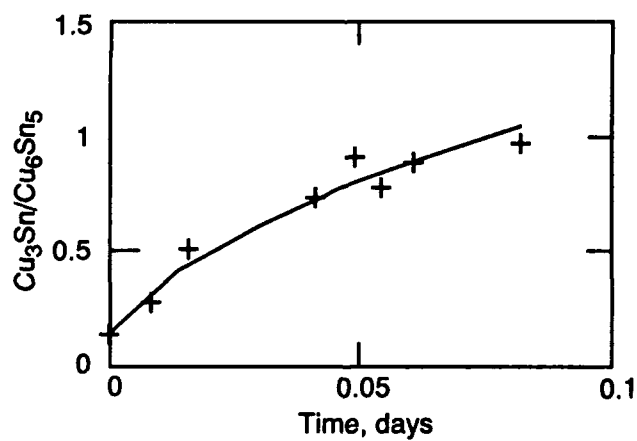


Figure 11. Ratio of Cu_3Sn thickness to Cu_6Sn_5 thickness as a function of time.



thickness in time and illustrates the increasing ratio of epsilon to eta. A percentage change in favor of the epsilon phase suggests a restriction of the tin supply to the interface region. Absolute movement of interfaces could not be determined since there were no markers placed in the cross section. All data gathering was performed at the surface of the sample. It is not known to what extent surface diffusion may have influenced the growth rates.

4. Hypothesis

The working hypothesis that is currently being examined proceeds as follows. The growth of the Cu_6Sn_5 nodule with long-term aging after reflow causes high strains in the solder bonded to the nodule's growth surface. The ductile Pb lamella deform with this growth and remain adhered, but the more brittle Sn lamella may actually debond. This debonding may be erratic because Sn properties vary widely in solder. With the reduced surface area caused by debonding, the diffusion of Sn from the bulk solder to the nodule is lowered. This serves as a self-limiting mechanism for the growth of the Cu_6Sn_5 nodule. With the reduction of the bulk Sn source, subsequent diffusion of Cu and the now limited Sn results in Cu_3Sn growth in two directions. First, Sn from the eta phase causes epsilon growth at the Cu interface. Second, Cu diffusing from the substrate causes additional epsilon to form at the eta/epsilon interface.

If the hypothesis is correct, the effect is a continual time degradation of electrical resistance, heat transfer, mechanical strength, and solderability at the IMC interface. Given that these parameters are critical to the reliability and maintenance of soldered components in the field, Cu_3Sn could be a critical parameter to detect and control in the manufacturing of electronic assemblies.

5. Future Research

The experiments should be repeated to establish a statistical basis for the results. Additional repetitions of our experiments should be conducted, in either an inert atmosphere or a vacuum, to eliminate corrosion or other environmental effects as potential contributors to the results. Relative bonding tendencies of Pb and Sn should be reviewed in the literature, by theory, or empirically. Higher magnification studies should be run primarily near areas of the more robust Cu_3Sn growth to look for the debonding phenomenon. Parametric monitoring should be included with future studies. For example, electrical resistance could be monitored as the Cu_3Sn growth pro-

ceeds. Finally, additional cross sectioning should be carried out to gather more bulk growth rate data to ascertain what relevant differences there are between the surface and bulk phenomena.

6. Conclusions

In our ESEM experiments, copper/tin intermetallic compounds were successfully observed to grow in copper/solder samples held at elevated temperatures. We made what we believe are the first movies of the growth of these intermetallics. A hypothesis was put forward suggesting that this growth could be detrimental to solder joint performance. Additional studies have been recommended to validate our preliminary results and test our hypothesis.

Acknowledgments

The authors are grateful to Ms. Janice Methe and Mr. Thomas Hardt of ElectroScan for their support with this project. Grateful acknowledgments are also due Dr. Richard Fields and Mr. Leonard Smith of the National Institute of Standards and Technology, Gaithersburg, MD, for providing the sample specimens used in this study.

This activity was initiated and supported by the U.S. Army MANTECH Program for Soldering Technology managed by the Army Research Laboratory.

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