Improved Solder Alloy for Printed Circuit Board Application

Compared to conventional Sn-Pb solders, a 90Pb-9Cd-1Zn solder that was developed for polyimide and other higher temperature circuit board materials is more reliable and costs less

BY M. C. DENLINGER AND D. W. BECKER

ABSTRACT. A more reliable, lower cost solder alloy compatible with electronic component leads has been developed for use with polyimide or other higher temperature circuit board materials. The solder shows no evidence of cracking after exposure to 500 temperature cycles between 200 C (392 F) and −55 C (−67 F). A comparative test with Sn63 between 125 C (257 F) and −55 C (−67 F) resulted in cracking after 200 cycles.

The alloy (90Pb-9Cd-1Zn) was the result of selecting, testing and modifying all possible alloy systems that would be suitable for printed wiring board application. The resulting alloy, in addition to providing increased reliability, offers a significant cost reduction over the conventional tin-lead system.

Introduction

A new solder alloy capable of passing hundreds of temperature cycles has been developed for use with polyimide printed wiring boards. The new alloy offers improved reliability and lower cost over conventional tin-lead solder. Because of its relatively high melting range, i.e., over 238 C (460 F), its usage is limited to polyimide or other higher temperature circuit board materials.

Conventional tin-lead solder has been used exclusively in the electronics industry for many years. Despite its many advantages and universal usage, it has some significant disadvantages. In addition to its high cost which has been increasing rapidly in the past few years, it has limited resistance to thermal fatigue. Many instances of solder joint cracking have been observed. While some of these instances may be attributed to design deficiencies, it would be advantageous to have a solder that is more resistant to thermal fatigue.

Recent developments in polyimide materials have made it possible to extend the upper temperature limit of printed wiring boards beyond the range of eutectic tin-lead solder. Presently, polyimides are used for their manufacturing advantages, i.e., less tendency to smear during drilling and less tendency to craze during rework. An additional advantage is that a higher temperature solder offering greater economy and reliability can now be used.

During the course of this study an alloy was found that possesses both of these characteristics. The alloy not only has phenomenal resistance to thermal fatigue cracking but would be approximately one-fourth the cost of eutectic tin-lead solder. This development could be the first step in a significant advance for electronic assembly. However, the manufacturing methods for printed wiring board fabrication and assembly processes need to be established before the system can be considered feasible for production.

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Program Plan

The primary objective of the program was to develop or modify a higher temperature solder alloy suitable for polyimide printed wiring board assembly. Thirty-two specific solder alloys representing eight different binary systems (tin-antimony, lead-silver, lead-cadmium, lead-indium, lead-antimony, lead-tin, cadmium-antimony and cadmium-zinc) and four separate ternary systems (lead-tin-copper, lead-tin-zinc, lead-cadmium-zinc, lead-cadmium-copper) were prepared and evaluated. During the preliminary characterization study, each solder alloy was tested to determine solidus and liquidus temperatures, solderability, microstructure, electrical resistivity, and room temperature and elevated temperature mechanical bond strength properties.

A final characterization study was conducted on the two alloy systems that were determined to have the most desirable overall properties (90% lead-10% tin and 90% lead-9% cadmium-1% zinc) of the original thirty-two alloys tested. In addition to these two optimum high temperature alloys, control samples soldered with the standard eutectic tin-lead alloy (Sn63) were also subjected to the final characterization study of metallurgical stability, thermal fatigue and shock loading tests. In this manner, a common ground for comparison was established with the most commonly used solder alloy in the electronics industry.

The body of this paper concerns itself mainly with the final characterization study of metallurgical stability, thermal fatigue and shock load testing of the 90Pb-10Sn, 90Pb-9Cd-1Zn and Sn63 solder alloys. If additional information is desired concerning test results of the other 30 candidate solder alloys, refer to the cited reference.

Preliminary Characterization Tests and Testing Procedures

Preliminary characterization tests and procedures consisted of determining melting range, solderability and mechanical bond strength as described below.

Solidus and Liquidus Temperature Determination

While each candidate solder alloy was prepared, the master melt was thoroughly mixed and held approximately 150 C (270 F) above the freezing point of the alloy and subsequently allowed to cool. The cooling rate was monitored with a standard chart driven temperature recording device. The solidus and liquidus temperatures were read from corresponding slope change points on the recorded time-temperature cooling curves.

Solderability Determination

The solderability properties of each candidate solder alloy were determined on copper, Kovar (glass sealing alloy: 55Fe-28Ni-17Co) and gold plated Kovar surfaces. Circular disks, 12.7 mm (0.50 in.) in diameter and 0.39 mm (0.015 in.) thick, were used as the standard preform configuration.

The test samples were placed inside a glove box continuously purged with specially dried argon gas. The base sheet metal pieces were preheated on a contained hot plate that was maintained at 25 to 35 C (45 to 81 F) above the liquidus temperature of the particular solder alloy being tested. The individual preforms were immersed in liquid flux (Type RMA per MIL-F-14256) and immediately placed on the preheated base sheet metal samples. The preforms were allowed to melt and remain molten for a 1 min period. The solderability properties of each candidate alloy were measured by visually comparing the degree of spread over the base material test surfaces with the spread factor produced by the standard Sn63 alloy.

Electrical Resistivity Determination

Electrical resistivity measurements were made on specimens 0.476 cm (0.188 in.) wide, 20 cm (8.0 in.) long and 0.038 cm (0.015 in.) thick using a four terminal Kelvin Bridge. Since electrical resistivity is also directly proportional to the amount of induced cold work (strain hardening imparted into the strip material during the cold rolling process), the reported values are slightly greater than would normally be expected for samples fabricated from fully annealed strip material.

Mechanical Bond Strength Determination

Samples for the bond strength test were soldered, using solder coated, gold-plated Kovar leads. A capacitor discharge welding machine was used in conjunction with a dc power supply and a peg type resistance heater tip. The joint was made by reflow soldering a previously solder coated lead (0.43 mm wide and 0.10 mm thick (0.017 in. wide × 0.004 in.)) to a previously solder coated, copper clad, polyimide circuit board using Type RMA flux per MIL-F-14256. This fluxing operation reduces any oxides that may exist on or form during the soldering process thereby optimizing the bond strength of the joint.

Since the purpose of the bond test is to determine the relative strength of a solder joint produced with certain solder alloy and base material combinations, the samples were pulled in a 45 deg peel mode. In this manner, the mechanical failure during the peel test always occurred in the solder joint rather than in the base material. Samples for the 45 deg peel test were prepared and tested at room temperature and 200 C (392 F). The reported strength values shown in Table 1 are an average of 10 individual peel tests for each solder alloy and testing temperature combination.

Table 1—Test Results Summary

	90Pb-9Cd-1Zn	90Pb-10Sn	Sn63
Liquidus, °C (°F)	260 (500)	305 (581)	182 (360)
Solidus, °C (°F)	238 (460)	278 (532)	182 (360)
Solderability:			
Copper	Average	Average	Good
Gold-plated Kovar	Good	Good	Excellent
Kovar	Fair	Poor	Good
Electrical resistivity, Microhm-cm	17.69	20.30	14.73
Bond strength (45 deg)[a]—grams (lb):			
Room temperature	291 (0.64)	536 (1.18)	250 (0.55)
200 C (or 392 F)	268 (0.59)	272 (0.60)	109 (0.24[b])
Thermal fatigue	Passed 500 cycles	Failed (10 cycles)	Failed (200 cycles)[b]

[a] Peel strength values are based upon a 0.43 mm (0.017 in.) lead width.
[b] All high temperature testing for the Sn63 alloy was at a maximum of 125 C (257 F).

Final Characterization Tests and Testing Procedures

Final characterization tests and procedures consisted of determining metallurgical stability, thermal fatigue, shock loading and mechanical bond strength properties as described below.

Metallurgical Stability Determination

Each base material and solder alloy combination was tested to determine the intermetallic compound growth rate experienced during soldering and high temperature exposure (200 C (392 F) for 500 h). Scanning electron microscope (SEM) line scans were recorded across sectioned soldered interfaces for the "as soldered" and "as exposed" conditions. In this manner, the amount of intermetallic compound that formed during high temperature exposure through solid state reactions was monitored. The line scan recordings were also used for purposes of identifying the intermetallic compound products by determining their approximate chemical composition. In addition to the SEM analysis, the samples were examined optically to establish the structural integrity of the joints.

Thermal Fatigue Test

Bond test and plated-through-hole type samples (Fig. 1) soldered with the 90Pb-10Sn and 90Pb-9Cd-1Zn alloys were subjected to temperature cycling between the operational limits of 200 C (392 F) and −55 C (−67 F). Five hundred cycles were run allowing 10 min at the cold station, 22 min at the hot station and 4 min at ambient conditions prior to and following hot and cold exposure. One cycle is

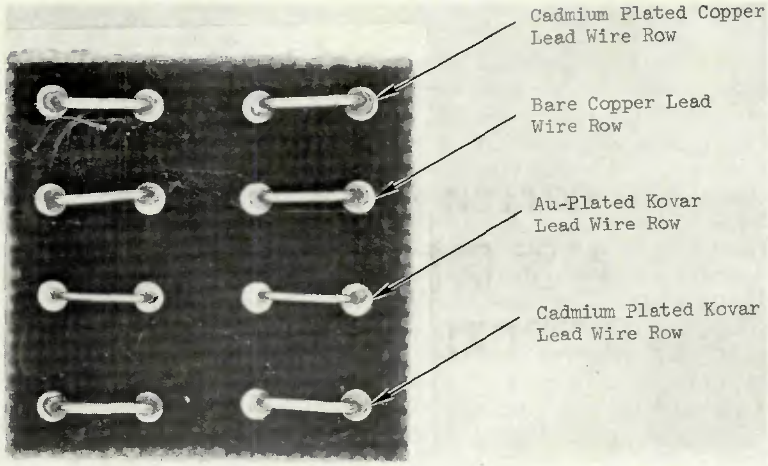

Fig. 1—Thermal fatigue and metallurgical stability test sample configuration (component side). ×4 (reduced 30% on reproduction)

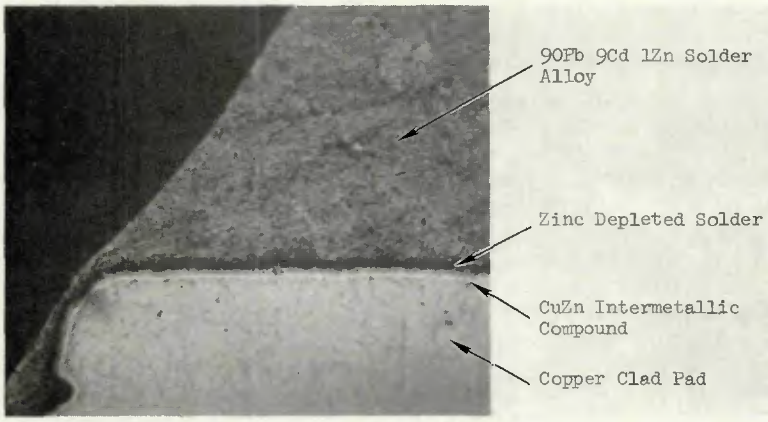

Fig. 2—90Pb-9Cd-1Zn solder joint cross-section in the "as soldered" condition (unetched). ×500 (reduced 30% on reproduction)

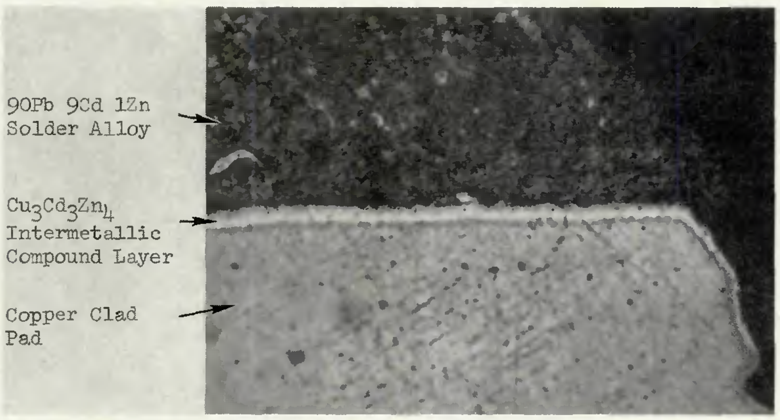

Fig. 3—90Pb-9Cd-1Zn solder joint cross-section following exposure to 200C for 500 hours (unetched). ×500 (reduced 26% on reproduction)

defined as follows:

200 C (392 F) for 22 min ⟶ 20 C (68 F) for 4 min ⟶ −55 C (−67 F) for 10 min ⟶ 20 C (68 F) for 4 min ⟶ 200 C (392 F)

Periodic in-process samples were withdrawn from the automatic thermal fatigue chamber and examined under the scanning electron microscope. In addition to the SEM surface examination, these plated-through-hole samples were sectioned so that the internal quality of the plated-through-hole to lead solder interfaces could be established.

Samples were withdrawn after completion of 10, 35, 100, 200, 300, 400 and 500 cycles and subsequently evaluated. Bond tests were performed after 10, 35, 100, 300 and 500 cycles to determine any change in bond strength properties. The Sn63 tin-lead thermal fatigue control samples were subjected to the same thermal cycle test and evaluation schedule as were the 90Pb-10Sn and 90Pb-9Cd-1Zn high temperature alloys except the Sn63 control sample hot station was maintained at 125 C (257 F).

Two-sided 1.57 mm (0.062 in.) thick polyimide circuit board material was utilized for the 90Pb-10Sn, 90Pb-9Cd-1Zn and Sn63 tin-lead control samples. Figure 1 illustrates the component side of the plated-through-hole specimens. Bare copper, cadmium plated copper, gold plated Kovar and cadmium plated Kovar lead materials were used.

In every case the lead wire diameter was 0.51 mm (0.020 in.), the drilled hole diameter was 0.81 mm (0.032 in.) and the plated-through-hole diameter was 0.74 mm (0.029 in.). The lead wire material was soldered to the plated-through-hole and copper clad pads by floating the specimen in molten solder for a period of 10 s. Type RMA flux per MIL-F-14256 was used, and the soldering operation was performed in an inert argon atmosphere.

Shock Loading Test

Sample configuration for the mechanical shock loading test consisted of a gold plated Kovar flatpack component reflow soldered to a previously solder coated polyimide circuit board. The body of the flatpack was bonded to the circuit card with Nomex tape. These soldered samples were subsequently bonded to each face of an aluminum alloy fixturing block with an epoxy adhesive and mounted in the shock testing apparatus.

The shock loading procedure was conducted in accordance with MIL-STD-883, Method 2002.1. Each face of the aluminum testing block was impacted to 5 tension, 5 compression, 10 shearing and 10 peeling type impacts at 1550, 1650, 1800, 1900, 2000, 2150, 2300, 2450 and 2600 acceleration G levels. A visual inspection at 10 times magnification was performed following each acceleration level shock series so that any change in the structural quality of the solder joint could be detected.

Test Results

The preliminary characterization test results are listed in Table 1. Complete results for the other 30 alloys that were examined during the course of the preliminary characterization study are given in the cited reference.

The high temperature metallurgical stability test (200 C (392 F) for 500 h) for the 90Pb-10Sn and 90Pb-9Cd-1Zn solder alloys and the low temperature

Fig. 4—SEM photomicrograph of a typical 90Pb-10Sn solder joint in the "as soldered" condition. ×50

Fig. 5—SEM photomicrograph of a typical 90Pb-9Cd-1Zn solder joint in the "as soldered" condition. ×50

metallurgical stability test (125 C (257 F) for 500 h) for the Sn63 control alloy were performed on lead to plated-through-hole test samples (Fig. 1). The samples were subsequently sectioned and examined to determine the intermetallic compound formation rate on copper base material.

The 90Pb-10Sn solder alloy was found to produce 76×10^{-4} mm (3×10^{-4} in.) of Cu_6Sn_5 intermetallic compound during high temperature exposure. The 90Pb-9Cd-1Zn solder alloy formed 12.7×10^{-4} mm (5×10^{-5} in.) of cadmium rich CuZn intermetallic compound during soldering (Fig. 2) which was eventually converted to 25×10^{-4} mm (1×10^{-4} in.) of $Cu_3Cd_3Zn_4$ ternary intermetallic compound during high temperature exposure (Fig. 3). The ternary intermetallic compound phase forms through a solid state diffusion reaction between the CuZn phase produced during soldering and the excess cadmium present in the solder alloy adjacent to the copper interface.

The plated-through-hole to lead sample configuration shown in Fig. 1 was also utilized for the thermal fatigue test. The SEM surface examination of typical 90Pb-10Sn and 90Pb-9Cd-1Zn plated-through-hole samples show the "as-soldered" conditions (Figs. 4 and 5, respectively) to be free of cracks and separations. Nominal amounts of interdendritic shrink cavity are evident but are within the normal limits expected for a solidified solder mass.

Pad-to-solder separation was first encountered in the 90Pb-10Sn samples after 10 high temperature thermal fatigue cycles. Subsequent cycling further enlarged and aggravated this

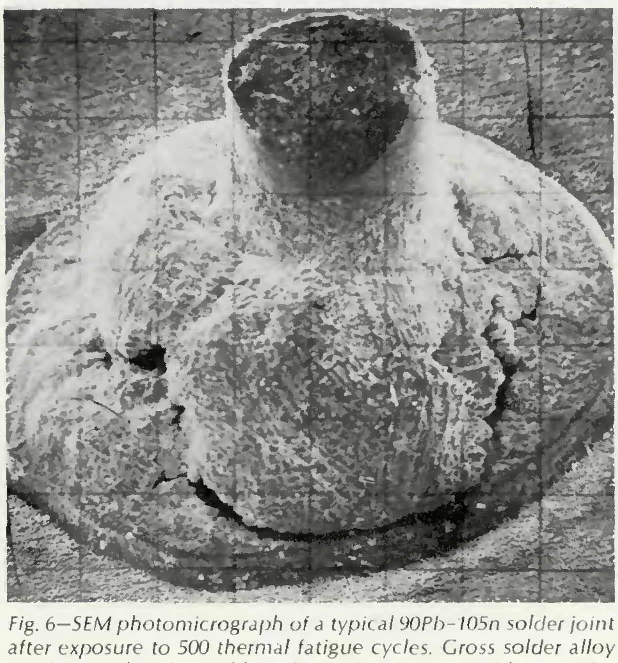

Fig. 6—SEM photomicrograph of a typical 90Pb-10Sn solder joint after exposure to 500 thermal fatigue cycles. Gross solder alloy cracking and pad-to-solder alloy separation are evident. ×50

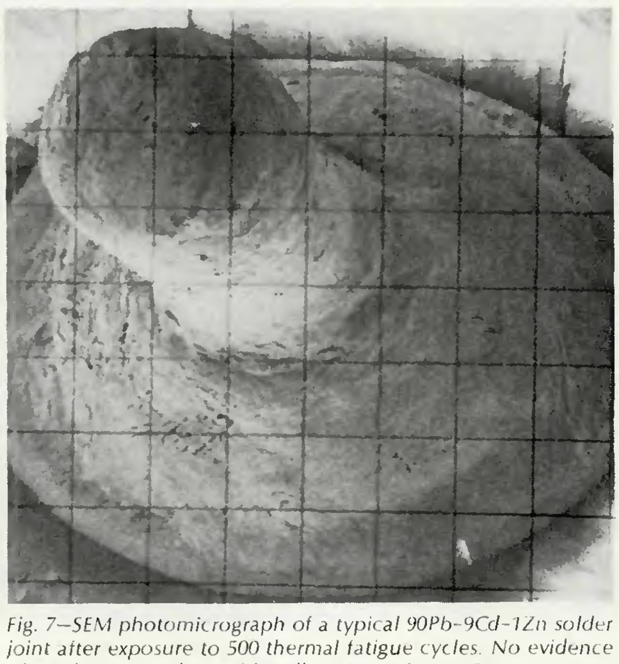

Fig. 7—SEM photomicrograph of a typical 90Pb-9Cd-1Zn solder joint after exposure to 500 thermal fatigue cycles. No evidence of cracking or pad-to-solder alloy separation. ×50

condition. Figure 6 illustrates a typical 90Pb-10Sn solder joint that was subjected to 500 high temperature thermal fatigue cycles. Solder alloy cracking and gross pad-to-solder separation are evident. No evidence of pad-to-solder separation or solder alloy fatigue cracking was found in joints soldered with the 90Pb-9Cd-1Zn alloy.

Figure 7 illustrates a typical 90Pb-9Cd-1Zn joint following 500 high temperature thermal fatigue cycles. The interdendritic shrink cavity is no more extensive than that found in samples representing the "as soldered" condition (Fig. 5). Therefore, the cavity shown in Fig. 7 was, in most probability, formed during the soldering operation.

The Sn63 solder samples failed the low temperature thermal fatigue test. Figure 8 illustrates a typical crack-free "as soldered" Sn63 joint. A normal amount of shrink cavity is present. Sn63 solder alloy fatigue cracking and solder-to-pad separation was first observed after 200 cycles of testing.

Figure 9 shows a typical Sn63 joint after 500 cycles of testing. The solder mass has separated from the copper clad pad, and thermal fatigue cracks are present in the lead wire fillet edge. Some Sn63 samples cracked more severely than others, but all the failures occurred independent of the lead wire and plating material combination.

Of the three alloys that were shock tested (Sn63, 90Pb-10Sn and 90Pb-9Cd-1Zn), none of the solder joints showed any evidence of failure when examined at ×10 magnification. These alloys, when tested per the requirements of MIL-STD-883, Method 2002.1, were found to be resistant to the cracking and delamination type defects that are commonly associated with shock loading failures.

Conclusions

The superior thermal fatigue properties exhibited by the 90Pb-9Cd-1Zn alloy are attributed to the ductile nature of the alloy itself and the ability to form and maintain a chemically inert solder interface with copper surfaces. Quantitative scanning electron microscope X-ray analysis revealed the wetting reaction on a copper surface to be the formation of CuZn intermetallic compound.

Since time at temperature during soldering is minimal and the zinc content of the alloy is relatively low, the resulting CuZn formation was found to be insignificant. During high temperature exposure (200 C (392 F) for 1 h minimum) the CuZn intermetallic compound is partially or totally converted to $Cu_3Cd_3Zn_4$ through a solid state reaction. This ternary interface reaction terminates when the solder alloy immediately adjacent to the copper surface is thoroughly depleted of the zinc constituent or until all the CuZn phase is converted to $Cu_3Cd_3Zn_4$.

Once the ternary reaction is complete, the resulting $Cu_3Cd_3Zn_4$ intermetallic compound layer serves as a barrier, thereby precluding the formation of any binary cadmium-copper intermetallic compounds. Therefore, the 90Pb-9Cd-1Zn solder alloy has its own built-in mechanism for terminating solid state intermetallic compound chemical reactions with copper base materials. By controlling the solid state formation of the $Cu_3Cd_3Zn_4$ phase, the solder-copper interface is ultimately rendered chemically inert and is therefore immune to failures associated with excessive formation of brittle intermetallic compounds. Since the 90Pb-9Cd-1Zn solder alloy is chemically inert at elevated temperatures, long term solder alloy degradation can be totally avoided.

The tin-lead solder system produces solder alloy fatigue cracks and pad-to-solder alloy separation during thermal fatigue testing. The Sn63 and 90Pb-10Sn solder alloys proved to be highly susceptible to cracking when subjected to thermal fatigue cycling. As the tin content of the solder alloy increases and as the hot station testing temperature increases, the higher the propensity for fatigue cracking type failures. The tin-lead solder system is therefore not recommended for high temperature applications where resistance to thermal fatigue cycling is required.

Table 1 illustrates the established properties for the 90Pb-10Sn, 90Pb-9Cd-1Zn and Sn63 solder alloys. A direct comparison of the more critical properties can be made. In addition to the optimum properties shown in the table, the 90Pb-9Cd—1Zn alloy is the least expensive as related to raw material cost. Also, since tin is the most costly elemental constituent of the three alloys listed, the Sn63 eutec-

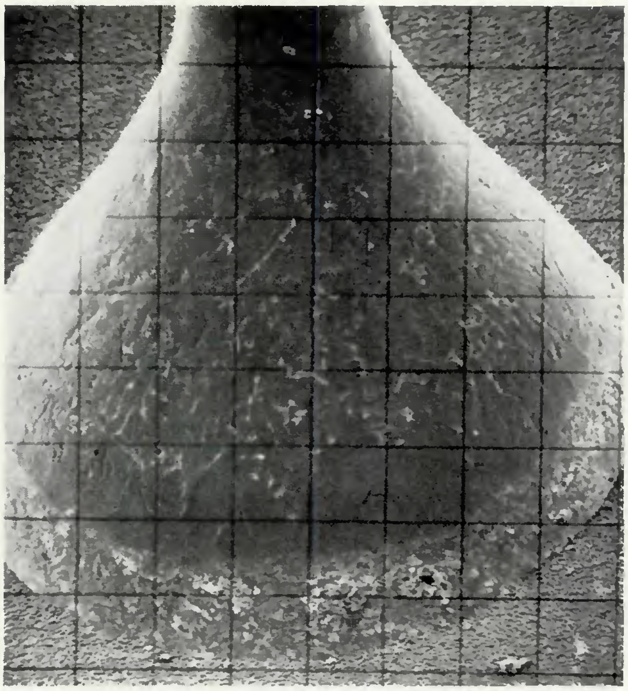

Fig. 8—SEM photomicrograph of a typical Sn63 solder joint in the "as soldered" condition. ×50

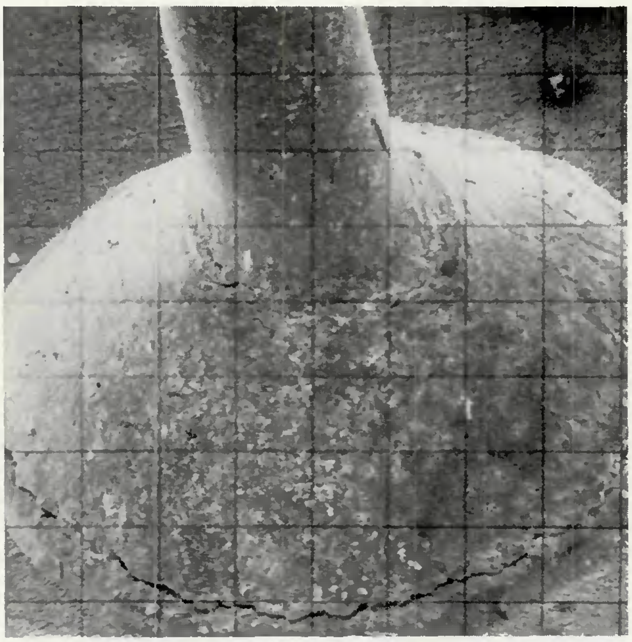

Fig. 9—SEM photomicrograph of a typical Sn63 solder joint after exposure to 500 thermal fatigue cycles. Note that lead wire fillet edge solder cracking and pad-to-solder alloy separation has occurred. ×50

tic alloy is by far the most expensive.

The recommended final solder alloy composition range for the 90Pb-9Cd-1Zn solder alloy is as follows: 8-12 wt-% cadmium; 0.5-1.0 wt-% zinc; 1.0-2.0 wt-% silver (optional); balance—lead.

If improved corrosion resistance properties are required, the addition of the optional silver constituent is recommended. The cadmium content may be increased to about 17 wt-% which would result in lowering the liquidus temperature of the alloy to about 238 C (460 F). This particular composition combination produces solder joints of good room temperature strength properties, excellent elevated temperature (200 C (392 F)) strength properties, and good electrical conductivity and solderability characteristics to copper and gold plated Kovar surfaces. The 90Pb-9Cd-1Zn solder alloy produces more reliable joints when compared with joints processed with eutectic tin-lead solder.

When processing the standard epoxy type circuit board material, it is necessary to use the low temperature tin-lead solder to preclude delamination of the copper clad epoxy bond during soldering. Since polyimide circuit board material will withstand significantly higher temperatures without incurring damage to the copper clad bond, higher temperature solder alloys may be used.

The new 90Pb-9Cd-1Zn improved solder alloy was developed for enhancing overall low temperature properties when compared with the presently used eutectic tin-lead alloy; it was also developed for lowering raw material cost and, as a by-product advancement, offering a capability for use in higher temperature applications. This particular development program could be the first step in a significant advance for electronic assembly. However, manufacturing methods for printed wiring board fabrication and assembly processes need to be addressed before the system can be considered feasible for production.

References

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