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Microstructure Investigation of Copper-Tin Intermetallics and the Influence of Layer Thickness on Shear Strength

Low-tin solders are recommended in applications where high temperatures encourage intermetallic buildup

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ABSTRACT. This study focuses on the behavior of the intermetallic layer forming at the interface between tin-bearing solders and a copper substrate. Scanning electron microscopy was used to reveal the morphology of this environment. Point analyses of energy dispersive x-rays identified the individual phases while elemental line scans yielded the tin and copper partition extent across the boundary zone, providing information about the diffusive interpenetration and phase growth. Transmission electron microscopy yielded electron diffraction patterns for the microstructures of the Cu_3Sn and Cu_6Sn_5 phases. The time-at-temperature dependence of the layer thickness was found to obey the expected $t^{1/2}$ dependence (Ref. 1). A series of plug-and-ring joints with known intermetallic layer thicknesses were produced by our previously developed method (Ref. 2), and their shear strengths were measured. Results show that both very thin and relatively thick layers are associated with weaker joints, indicating an optimum thickness in between.

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Introduction

The copper-tin intermetallic compounds, which normally form during soft soldering and afterwards, are imperative for the wetting process. They are notoriously harmful if overgrown, whether by too lengthy a soldering process, or whether during service at relatively high temperatures. Because of the brittleness of the intermetallic compounds, soldered joints become more sensitive to stresses the thicker the intermetallics. This is due to their tensile character developing even under predominantly shear loads, with the attendant proneness to failure in normal use, for example under thermal fatigue. The problem is especially acute in electronic assemblies, whose working temperatures nowadays reach 70°C (158°F) and even more, under normal, continuous operation conditions. At these temperatures the growth rate of the intermetallics is appreciable (Ref. 1), and they can easily attain a thickness of several microns in a few months.

KEY WORDS

Cu-Sn Intermetallics
Intermetallic Layers
Layer Thickness
Cu-Sn Microstructure
Cu_3Sn/Cu_6Sn_5 Phases
Phase Growth
Diffusive Penetration
Sn/Cu Interface
Electron Diffraction
Diffraction Patterns

The general objective of the present study was the formulation of solder compositions, improved through a reduction of the tin content. To this end, the formation, growth and morphology of the copper-tin intermetallic compounds were examined, and a substantial insight into these aspects was gained, as described below. The strength and thickness values are of the compositions stated and were obtained under the specific conditions. The solder compositions and other parame-

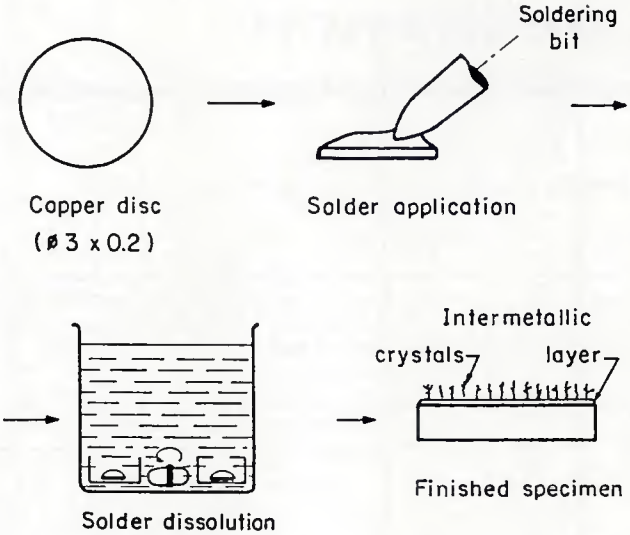

Fig 1 — Preparation of intermetallic layer for scanning electron microscopy.

ters were selected to suit the specific task, and are to be regarded as representing normal service conditions, simulated by laboratory practices.

Experimental

Because of their softness, soldered joints are preferably implemented as shear-loaded connections. Thus, the strength of specimen soldered joints is best assessed in shear, the background of which was described in a previous work (Ref. 2). Our present purpose is to correlate the soldering conditions affecting intermetallic thickness with the soldered joint strength. Shear strength measurements were made on plug-and-ring specimens in a custom-built apparatus. The preparation and testing procedures were described in detail in an earlier work (Ref. 2). The dimensions of the specimens being relatively small (3-mm-diameter ring, 1 mm high), their production closely simulates electric and electronic industrial soldering conditions. Typically, wetting is completed within 2 s after application of heat by a thermostatically regulated soldering iron, followed by rapid cooling afterwards.

Optical microscopy, and scanning and transmission electron microscopy were the methods used for the examination and characterization of the intermetallics formed as a result of different soldering conditions. In preparing the specimens for the various microscopical analyses, emphasis was placed on a selective chemical dissolution of the solder matrix, which left the intermetallic phases intact. The agent chosen for this purpose was a solution of 40 g o-nitro-phenol and 5 g sodium hydroxide per 100 mL water, at 50°C (122°F).

The procedure for preparing specimens is described schematically in Figs. 1, 4 and 7.

Results and Discussion

Scanning Electron Microscopy

Copper reacts with molten solders having an appreciable tin content, forming intermetallic compounds. Optical inspection of cross-sections of soldered joints, when polished, reveal these as shining, hard phases. A more detailed characterization is required in order to distinguish between Cu_6Sn_5 and Cu_3Sn, the two known copper-tin intermetallics. In order to grow crystals suitable for scanning electron microscopical (SEM) observation, a deliberately prolonged time (30 s) was allowed for interaction between a thin, molten layer of common Sn60 (60 wt-% tin, balance lead) and a copper substrate. The intact intermetallic phases, exposed by chemical removal of the matrix, as described above, are shown in Figs. 2 and 3. The first micrographs (Fig. 2) are a grazing-angle view of protruding intermetallic crystals of varying shape and dimensions. These are exclusively Cu_6Sn_5, as was proved by energy dispersive x-ray analysis (EDX); they form through growth into the liquid solder, which results in a dendritic morphology, and are quite distinct from their Cu_3Sn counterparts — Fig. 3. The latter, having a higher Cu concentration, are the first to form on the copper; they are small and form a relatively compact layer, even in these samples, which yielded the intermetallic phases by a solid-liquid reaction. Point EDX analyses yielded the expected relative Cu/Sn concentrations for the two intermetallic compounds.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) specimens have to be transparent to the electron beam, which for 100 kV electrons means a thickness less than 100 nm (0.1 μm). Thinning is conventionally achieved either by electrochemical dissolution or by ion milling, but we resorted to a simplified technique so as to avoid the difficulties due to the wide chemical dis-

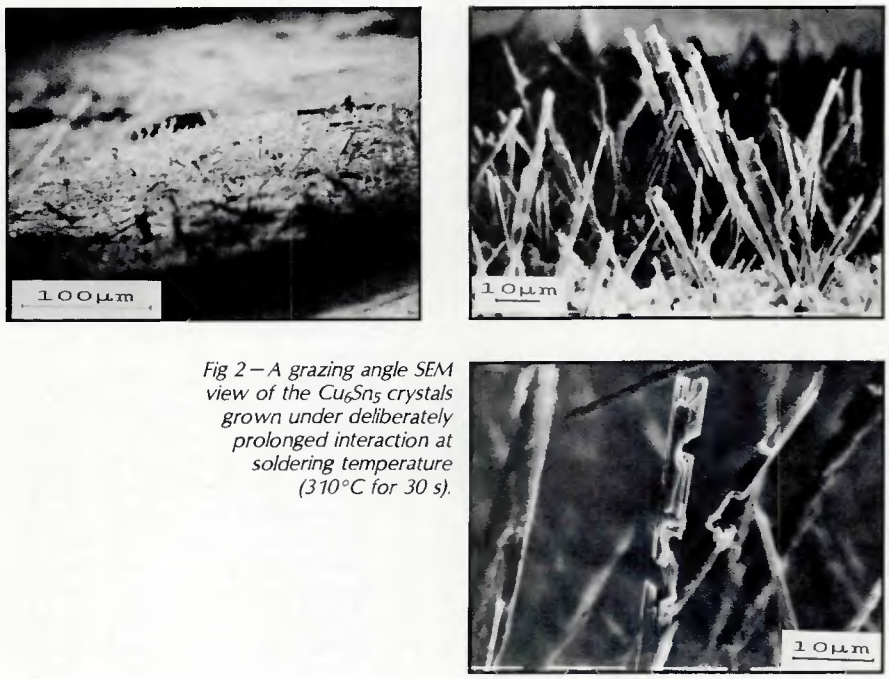

Fig 2 — A grazing angle SEM view of the Cu_6Sn_5 crystals grown under deliberately prolonged interaction at soldering temperature (310°C for 30 s).

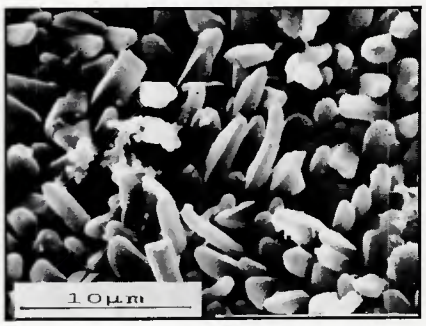

Fig 3 — Su_3Sn crystals in the specimen of Fig. 2.

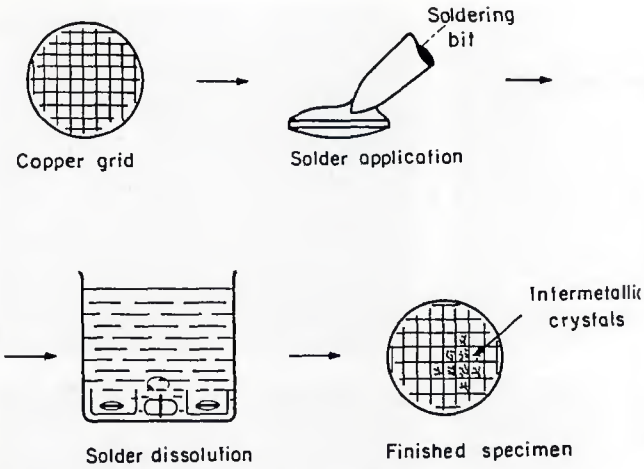

Fig 4 — Preparation of transmission electron microscopy specimens on standard 200-mesh copper grid.

Fig 5 — TEM micrograph of intermetallic crystals at low magnification, showing growth behavior and extent.

parity between the substrate and intermetallics.

The Cu_6Sn_5 specimens were prepared by applying liquid Sn60 solder to a standard 200-mesh copper grid used in TEM work, allowing the intermetallic crystals to grow for 30 s at 310°C (590°F), and finally exposing them by selective chemical dissolution — Fig. 4. Identification is provided by the electron diffraction pattern. The growth morphology is similar to that observed in SEM, or dendritic crystals growing into the melt, as shown in Figs. 5 and 6.

For the Cu_3Sn phase, which forms a thin and relatively continuous layer on the copper substrate, a solid copper disc was used instead of the grid — Fig. 7. The solder was selectively dissolved from the center of the upper face with the aid of a mask, after which the specimen was reversed and the copper on its bottom removed electrolytically in acid $CuSO_4$ solution at a regulated applied voltage of 1.2 V, again with masking. The crystals and their diffraction pattern are shown in Fig. 8.

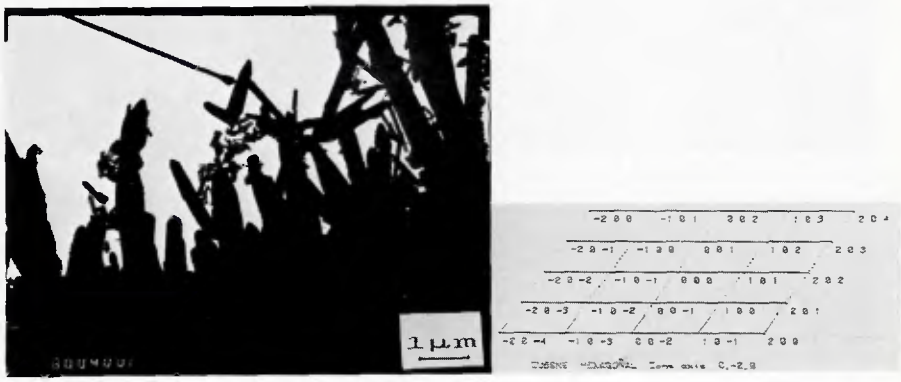

Fig 6 — TEM micrograph of Cu_6Sn_5 crystals at higher magnification and their electron diffraction pattern.

Effect of Intermetallic Layer Thickness on Shear Strength

Plug-and-ring shear strength specimens were prepared with Sn30 solder (30 wt-% tin) by prolonged residence at the soldering temperature (310°C), well above the minimal time in normal work. The mean thickness of the intermetallic layer obtained was measured under SEM by means of elemental line scans for tin concentration across the interface. Micrographs of the layer after successive interaction times are shown in Fig. 9, and thickness data in Table 1. The detailed procedures for the preparation of the specimens and their strength assessment were described in a previous work (Ref. 2). The layer thick-

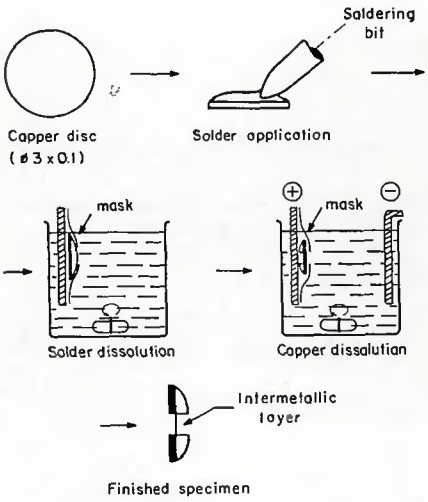

Fig 7 — Exposure of Cu_3Sn layer for TEM.

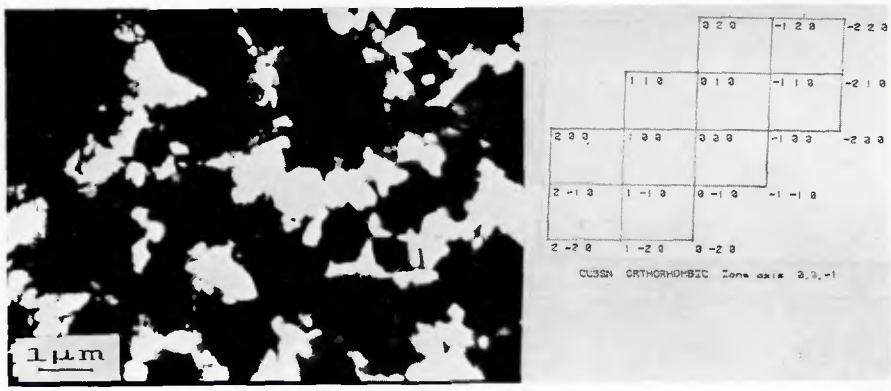

Fig 8 — TEM micrograph of Cu_3Sn crystals and their electron diffraction pattern.

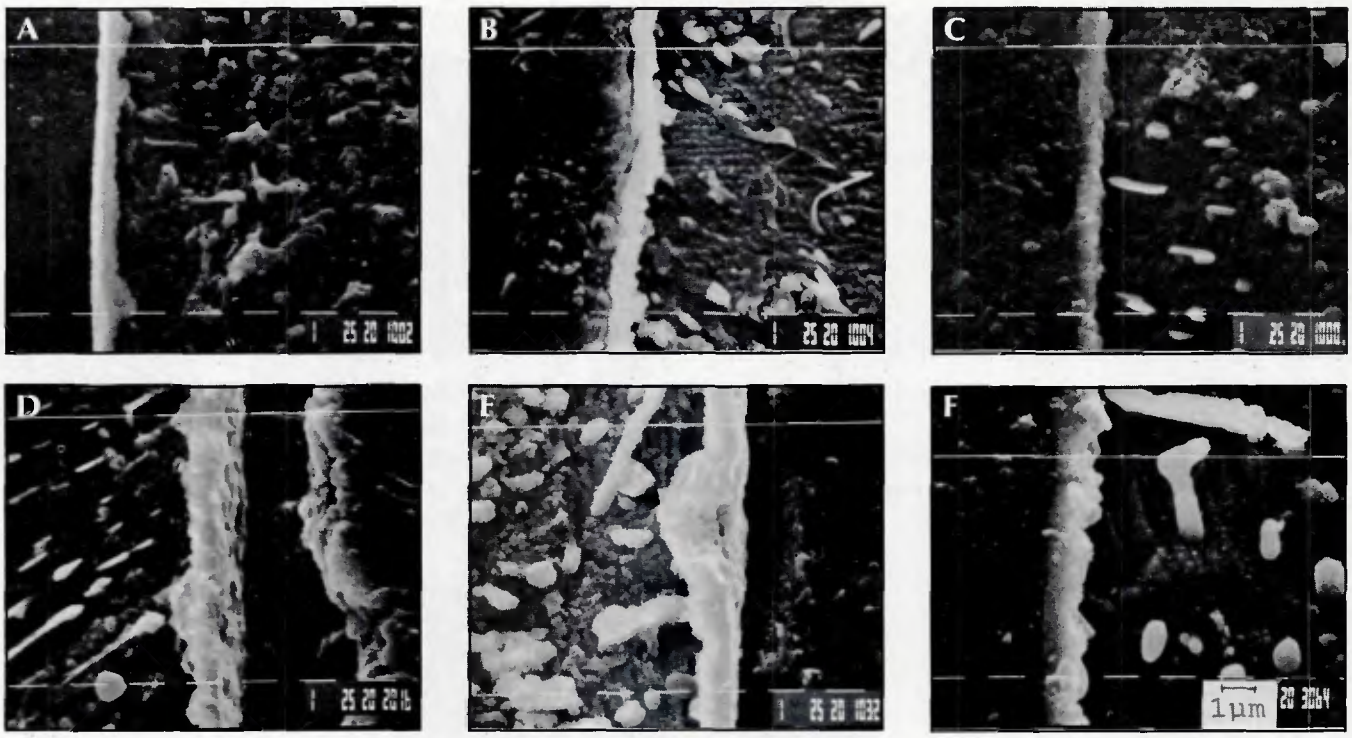

Fig 9—SEM micrographs of the intermetallic layer at successive interaction times: A—2 s; B—4 s; C—B s; D—16 s; E—32 s; F—64 s.

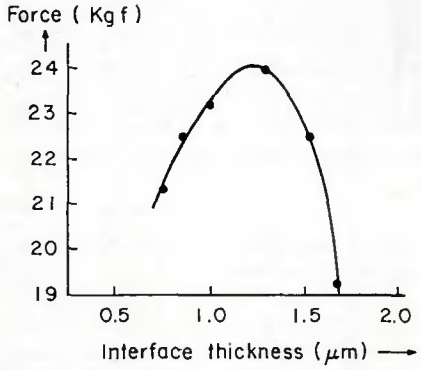

Fig 10—Shearing force vs. intermetallic layer thickness.

nesses formed after various interaction times are given in Table 1, showing the $t^{1/2}$ dependence. Results of shear strength as a function of soldering time are presented in Table 2.

From the above measurements, the relevant thickness/strength relationship was deduced—Fig. 10. Shear strength is around 3 kg/mm^2 (4.3 ksi), typical of the common 30Sn soft soldered joints as previously measured by us (Ref. 2), and is in agreement with results obtained elsewhere (Refs. 3, 4); this shear strength level represents the strength of the solder material itself. As the intermetallic builds up to a thickness of about 1.3 μm, the shear strength increases by about 20% and reaches a peak—Fig. 10. In our work this buildup took about 30 s (at the soldering temperature: 310°C). In electric assemblies operating at 70°C, the same thickness is achieved after about one month—Fig. 11. On further buildup, the shear stress increasingly acquires a tensile character, the brittleness of the layer begins to manifest itself, and the strength curve plunges, the joint losing strength as the

Fig 11—Buildup of intermetallic layer at different temperatures (Ref. 1).

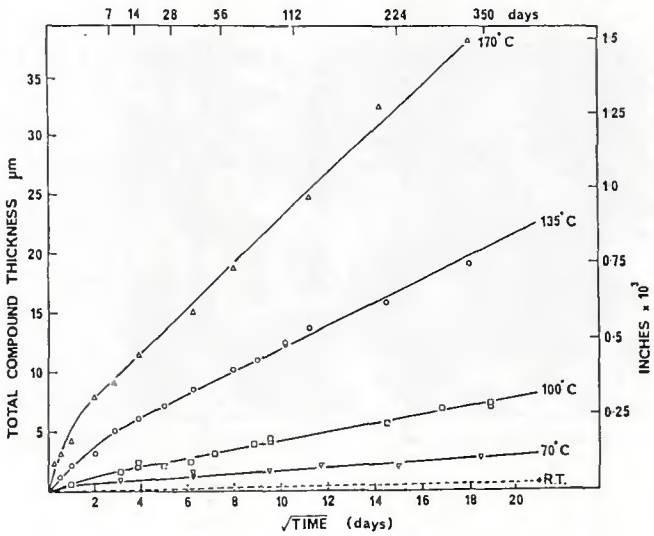

Table 1—Intermetallic Layer Thickness vs. Interaction Time at Soldering Temperature

Time (s)	Thickness (μm)
2	0.75
4	0.80
8	1.0
16	1.2
32	1.3
64	1.6

Table 2—Shear Force Required to Tear Specimens Soldered at Prolonged Interaction Times

Time (s)	Shear Strength (kg/mm^2)
2	2.68
4	2.85
8	3.01
16	3.13
32	2.96
64	2.65

layer thickness increases. The shear strength is impaired to such an extent, that it falls below that of the bulk solder itself. The strength loss upon longer soldering times has been observed also by Saperstein and Howes (Ref. 5). They have measured the peel strength (which is a measure of fracture propagation resistance) of soldered joints using longtime isothermal holding at various temperatures.

Conclusion

Several aspects of the process of copper-tin intermetallic compounds formation were investigated. Cu_6Sn_5 and Cu_3Sn are the two phases identified, differentiated and characterized. Analysis by energy-dispersive x-ray fits the assigned stoichiometry; electron diffraction analysis in TEM yields their crystallographic morphology, and elemental line scans by SEM, the extent of their growth. A relationship was established among soldering time, thickness of the intermetallic layer and shear strength of the soldered joint. Although the results reflect only the specific conditions employed, we conclude that exposure to high temperatures favors excessive buildup of the intermetallic layer, with undesirable consequences, indicating the preference of low-tin solders in critical applications.

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