

The Mechanics of Solder Alloy Interconnects

Edited by

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P International Thomson Publishing

New York • Albany • Boar • Boston • Cincinnati • Detroit • London • Madrid • Melbourne

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This printing published by Chapman & Hall, New York, NY

Printed in the United States of America

For more information contact:

Chapman & Hall 115 Fifth Avenue New York, NY 10003

Thomas Nelson Australia 102 Dodds Street South Molbourne, 3205 Victoria, Australia

International Thomson Efficares Campos Elineor 385, Piso 7 Col. Polanco 11560 Mexico D.F. Mexico

International Thomson Publishing Asia 221 Henderson Road #05-10 Henderson Building Singapore 0315 Chapman & Hall 2-6 Boundary Row London SE1 SEN England

Chapman & Hall GmbH Postfach 100 263 D-69442 Weinbeim Germany

International Thomson Publishing - Japan Hirakawacho-che Kyowa Building, 3F 1-2-1 Hirakawacho-che Chiyeda-ku, 102 Tokyo Japan

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2 3 4 5 6 7 8 9 XXX 01 00 99 98 97 96

Library of Congress Cataloging-in-Publication Data

The medianics of solder alloy interconnects / [edited by] Darrel Freer, Harold Morgan, and Steven Burchett

Includes index. ISBN 0-442-91505-4

SNDS OF STREET, 3-35-4 I. Solder and soldering: J. Freat, D. R. II. Morgan, Harold (Harold S.) III. Burvaett, Steven TV. Lau, John TSO10 M43 1991 93-30138 671.5'6-dc20 CIP

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Interfaces and Intermetallics

James L. Marshall, L. Ann Foster, and Jennifer A. Sees

3.1 INTRODUCTION

The American Welding Society defines soldering as a joining process wherein a coalescence between metal parts is produced by heating to temperatures below 800°F using filler metals (solders) having melting temperatures below those of the base metal [Fenton, 1959]. After its deposition, the solder is then evenly distributed between the properly fitted surfaces of the joint by capillary action. Solders act by (a) wetting the basis metal surfaces forming the joint; (b) flowing between these surfaces so as to fill the space between them; and (c) metallurgically bonding to the surfaces when solidified [Thwaites, 1982]. This metallurgical bonding occurs, in a solder joint, between the solder and the substrate at a boundary area termed the interface [Morris et al., 1991]. This interface consists of a thin layer of an alloy formed during the soldering process. The alloy—termed the intermetallic—is generated by metals from both the solder and the substrate [Morris et al., 1991]. Figure 3-1 shows a typical cross section of a solder joint displaying the intermetallic.

In this chapter we will characterize intermetallics and discuss their potential impact upon solder reliability. When intermetallics occur at the interface of a soldered surface, they can grow and increase in thickness. In large solder joints, which are properly soldered and which function in benign environments, intermetallics have no deleterious effect upon long-term reliability of solder joints. How-

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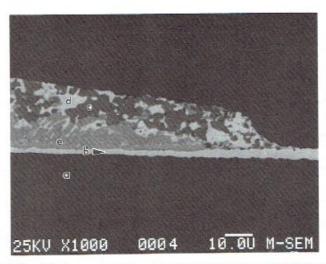


FIGURE 3-9 SEM of a cross section with excess original thickness of gold. The original gold layer was 5 µm thick, and in this solder joint has been reduced to 3 µm. Bottom, dark region: nickel substrate (a). White horizontal strip: gold layer (b). Solder: dark regions, tin (c); light regions, lead (d); gray regions, AuSn₄ (e). X1000, backscattered mode.

3.2.5 Intermetallic Growth

The effect of intermetallic growth within solder joints is not entirely understood. While the presence of intermetallic compounds are an indication that a good metallurgical bond has formed, the fact that these compounds are brittle may also make them deleterious to a joint's mechanical integrity. When these compounds form as continuous layers at the solder-substrate interface, the intermetallics can interrupt electrical currents with their high resistivity, effectively isolating the metals that were to be electrically joined [Brothers,1981]. In addition, if these intermetallic compounds become too thick, the reliability of the joint can be jeopardized due to cracking. This can be a problem especially if the joint is exposed to any mechanical forces, such as expansion or contraction of the printed wiring board (PWB) laminate caused by variations in temperature [Woodgate, 1983]. Exposure of these intermetallic compounds to the atmosphere via microtunnels formed through the solder during the tinning or aging process has also been recently postulated as allowing for the environmental degradation of the intermetallics located on the surface of the base metal [Marshall, 1991].

In extreme cases, the intermetallic compound growth reaches the surface of the solderable coating over a significant area of the sample and renders the joint unsolderable with mild fluxes [Brothers, 1981]. Finally, the interdiffusion processes

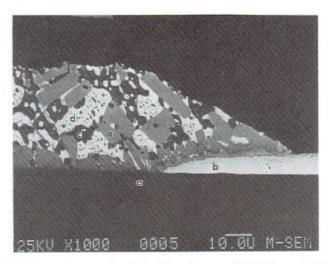


FIGURE 3-10 SEM of cross section of solder joint with excess original thickness of gold, and reflowed with excess solder in an attempt to scavenge all metallic gold from the substrate. However, large amounts of AuSn_d still adhere to the substrate. Bottom, dark region: nickel substrate (a). White horizontal tongue, leading from right: gold layer (b). Solder: dark regions, tin (c); light regions, lead (d); gray regions, AuSn₄ (e). X1000, backscattered mode.

which produce the intermetallic layers can also produce Kirkendall porosity (voids) which can also degrade the mechanical properties of the connection [Romig et al., 1991].

It appears that there is some optimal thickness of these intermetallies, below which a good metallurgical bond has not been achieved, and above which they become a liability to the system. A study by Davis et al. [1982] indicates that solderability can be reduced when intermetallic compound growth between Cu and Sn on Sn/Pb protective coatings reaches a thickness of 2 to 4 µm, especially when there is little remaining coating after aging. At the same time, it is evident that the parameters by which solderability is judged are also improved if a thicker remaining coating is present after high-temperature exposure. The application of a sufficient thickness of solder as a protective coating tends to enhance solderability, even when exposure to elevated temperatures is involved.

An understanding of their phase formation is important because of the important contribution that the various intermetallics make to the stability of the solder connection. The solder/substrate reaction falls into one of two categories: molten solder/substrate reactions and solid state growth of intermetallic compounds [Romig et al., 1991]. During wetting, molten solder comes into contact and reacts with the solid substrate. At this point, two processes occur simultaneously: the base

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FIGURE 3-11 SEM of a cross section of the bulk of a well-soldered joint to gold-plated substrate. The AuSn₄ lamellae have drifted well into the bulk of the solder. Dark regions: tin (a). Light regions: lead (b). Gray regions: AuSn₄ (c). X1000, backscattered mode.

metal dissolves into the molten metal, and the active constituent in the solder reacts with the base metal. Both processes will form intermetallic compounds in the interfacial region between the molten solder and the base metal.

The amount of base metal that dissolves into the molten solder is dependent on its solubility in that material, while the intermetallic compound formation is dependent on the solubility of the active element in the base metal [Romig et al., 1991]. Many studies have been published that examine the reaction between the molten solder and substrate [Romig et al., 1991; Okamoto, 1986; Saperstein and Howes, 1968; Howes and Saperstein, 1969; Bader, 1969].

The solid state growth of intermetallic compounds is generally more complex and includes the problem of long term growth of intermetallic layers at the solder/substrate interface during the service life of the connection. The solid state growth of intermetallics can be inhibited either by the use of diffusion barriers or by changing one or more constituents in the solder alloy or the base metal in order to slow growth [Romig et al., 1991].

3.2.6 Kinetics of Intermetallic Growth

As described above, tin-based solders on a copper substrate form two Cu/Sn intermetallic compounds with two distinct stoichiometries at room temperature:

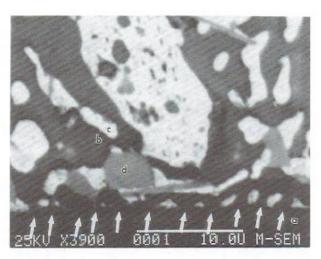


FIGURE 3-12 SEM of a cross section of well-soldered joint to gold-plated substrate, including the interface. The gold-tin intermetallics have drifted far from the interface (see Figure 3-9), leaving the tin to form the normal tin-nickel intermetallic at the interface (arrows). Bottom, horizontal dark area: nickel substrate with nickel-tin intermetallic (a). Solder: dark areas, tin (b); light areas, lead (c); gray areas, AuSn₄ (d). X3900, backscattered mode.

Cu $_6$ Sn $_5$ (η-phase) and Cu $_3$ Sn (ϵ -phase) [Hansen, 1958]. In a typical manufacturing solder operation, if the solder joint is cross-sectioned by the analytical laboratory and studied by optical microscopy or scanning electron microscopy, only a Cu $_6$ Sn $_5$ layer is observed, because Cu $_6$ Sn $_5$ grows much faster than Cu $_3$ Sn in the molten state. In optical microscopy, Cu $_6$ Sn $_5$ appears as a creamy-white layer, about 1 μ m (micrometer) thick, scarcely contrasting visually with the metallic white solder. The Cu $_3$ Sn layer is visible only upon prolonged heating as a pastel blue layer, and can be used as a sleuth for a high-temperature history of a solder joint. Even though only the Cu $_6$ Sn $_5$ intermetallic is observed in freshly-soldered joints by optical and electron microscopy, at higher magnification some Cu $_3$ Sn can be observed. Recent transmission electron micrographs with greatly increased resolution show that there in fact exists a very thin layer of Cu $_3$ Sn in a newly formed solder joint, a few hundred angstroms thick, Figure 3-13.

Two types of solid state growth are distinguished: linear and parabolic growth kinetics. Linear growth implies that the growth rate is limited by the reaction rate at the growth site (reaction controlled). Parabolic growth implies that growth is limited by bulk diffusion of elements to the reaction interface (diffusion controlled). Systems consisting of Cu substrates in contact with Sn/Pb solder alloys

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The activation energy for growth of Cu₃Sn on polycrystalline copper was found to be 1.27 eV and 0.47 eV for Cu₆Sn₅. Diffusion couples showed that Cu₃Sn and Cu₆Sn₅ had lower activation energies for growth on the copper (110) face than on either the copper (100) or the copper (111) faces. This effect of copper orientation on growth was not explained. Again, intermetallic growth appeared to be diffusion controlled.

Finally, a study of Sn/Pb solder on a copper substrate [Dirnfeld and Ramon, 1990] revealed typical Cu/Sn intermetallic conclusions: two distinct phases were identified, time-at-temperature dependence of layer thickness was found to obey t^{1/2} kinetics, and very thin and relatively thick intermetallic compound layers were associated with mechanically weaker joints. In addition, crystallographic morphologies of the intermetallic compounds were identified by electron diffraction analysis using TEM.

3.2.7 Physical Properties of Intermetallics

The physical properties of intermetallics contrast significantly with those of the solder or the base metal—intermetallics are less ductile, and less thermally and electrically conductive. Physical properties of Cu/Sn and Cu/Ni intermetallics are included in Table 3-1 [Frederiske et al., 1991; Fields et al., 1991]. The intermetallic material used to generate this data was produced by rapid solidification by supersonic, inert gas, metal atomization, and resulted in single-phase, fine-grained material. Other literature values for intermetallics are in general agreement—elastic properties [Cabaret et al., 1949; Subrahmanyan, 1972; Ostrovskaya et al., 1985], microhardness [Olsen et al., 1975; Wassink, 1989; Revay, 1977; Dunn, 1989], toughness [Hoyt, 1987], and coefficient of expansion [Reichenecker,

TABLE 3.1 Room Temperature Physical Properties of Intermetallics

Property	Cu_6Sn_5	Cu_3Sn	Ni ₃ Sn ₄
Vickers Hardness (kg/mm,2)	378±55	343±47	365±7
Toughness MPa*m ^{-1/2}	1.4±0.3	1.7±0.3	1.2±0.1
Youngs Modulus GPa	85.56±1/65	108.3±4.4	133.3±5.6
Shear Modulus GPa	50.21	42.41	45.0
Thermal Expansion x10 ⁻⁶ /°C	16.3±.03	19.0±0.3	13.7±0.3
Thermal Diffusivity cm ² /sec	0.145±0.015	0.24±0.024	0.083±0.008
Heat Capacity J/gm/deg	0.286±0.012	0.326±0.012	0.272±0.012
Resistivity µohm-cm	17.5±0.1	8.93±0.02	28.5±0.1
Density gm/cc	8.28±0.02	8.9±0.02	8.65±0.02
Thermal Conductivity watt/cm-deg	0.341±0.051	0.704±0.098	0.196±0.019

1981]. However, in these previous examples, generally bulk samples were obtained by casting and annealing, probably producing a coarse, multiphase material, sometimes with defects. Hence, the data of Table 3-1 [Frederiske et al., 1991; Fields et al., 1991] is considered more reliable.

To gain an appreciation of the significance of the values of Table 3-1, selected properties are presented in Table 3-2 for copper, tin, and nickel [Lynch, 1989]. The hardness is greater for the intermetallics, indicating their greater brittleness. With these high values of hardness for the intermetallics, no plastic deformation should be expected under normal levels of stress in solder joints. The elastic modulus is likewise greater for the intermetallics, giving rise to a lower ductility.

The thermal coefficient of expansion for the intermetallics is similar to that of metals, and therefore it would seem that the intermetallics would expand much like their associated substrate material.

Thermal and electrical conductivities are generally lower for the intermetallics, but for a thin intermetallic layer should pose minimal problems.

All these properties of intermetallics—mechanical, thermal, and electrical should give rise to no significant difficulties in a solder joint wherein the thickness of intermetallic is low compared with that of the solder. It is possible, however, as solder joints miniaturize, that these physical properties could impact the performance of circuitry.

3.3 EFFECT OF INTERMETALLICS ON THE INTEGRITY OF SOLDER JOINTS

3.3.1 Solderability Issues

Normally, the intermetallic does not play a role in the failure of a solder joint [Morris et al., 1991]. However, if a solder joint is improperly soldered because of poor wetting, then failure can occur directly at the interface. That this failure

TABLE 3.2 Room Temperature Physical Properties of Elements

Property	Cu	Sn	NI
Vickers Hardness Kg/mm ²	30	100	15
Youngs Modulus GPa	117	41	213
Thermal Expansion x10 ⁻⁶ / ¹ C	17.1	23 (solder 20-29)	12.9
Heat Capacity J/gm/deg	0.385	0.227	0.439
Resistivity µohm-cm	1.7	11.5	7,8
Density gm/cc	8.9	7.3	8.9
Thermal Conductivity watt/cm-deg	3.98	0.67	0.905