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The mechanical properties and microstructures of copper and brass joints soldered with eutectic tin–bismuth solder

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The mechanical properties and microstructures of copper and brass soldered with eutectic tin–bismuth solder have been determined and the joints examined using metallographic techniques. Joints made with copper were stronger than those made with brass. At the copper/solder interface a uniform layer 2 μm thick of $Cu_{5.2}Sn_5$ was formed and at the brass/solder interface a uniform layer 2 μm thick of $(Cu, Zn)_{2.9}Sn$ and an irregular layer 2 to 5 μm thick of $(Cu, Zn)_{5.7}Sn_5$ were formed. Copper joints fractured at the copper/solder interface and brass joints fractured in the intermetallic layer. Copper joints soldered with eutectic Sn–Bi were stronger than copper joints soldered with eutectic Sn–Pb and the reverse was true for brass joints. Results are also given for the effect of thermal shock on copper and brass joints soldered with Sn–Bi and Sn–Pb solders, and also for the fatigue and creep behaviour of joints soldered with eutectic Sn–Bi solder.

1. Introduction

Soldering is a process whereby a molten metal wets two components and which on solidifying forms a bond and a continuous metal body between the two components. During the automatic soldering of printed circuit boards a considerable strain is produced in the board by the imposed temperature gradients [1], and also there is a continuous outgassing of the laminates which interferes with the formation of a good solder bond [2]. Both these effects depend on the temperature of the soldering bath and they may be reduced by using a lower melting point solder. Eutectic Sn–Pb solders melt at 183° C and eutectic or near-eutectic Sn–Pb solders are almost universally used in soldering electronic components because of their excellent wetting, solderability, and physical properties [3].

Eutectic Sn–Bi alloys melt at 139° C and the use of eutectic Sn–Bi solders with printed circuit boards may be considered as a possible replacement for Sn–Pb alloys. The effect of composition changes and impurities on the wetting behaviour of eutectic Sn–Bi solders have been investigated in detail, with the main conclusions that satisfactory wetting occurred, but that the Sn–Bi solder was less tolerant than Sn–Pb solder to the impurities commonly found in soldering [4]. The properties of eutectic Sn–Bi alloys are generally superior to those of eutectic Sn–Pb alloys [4] but there is little detailed knowledge of the properties of eutectic Sn–Bi solder joints. The present work determines the mechanical properties of copper and brass joints soldered with a eutectic Sn–Bi alloy. For comparison, some tests were also made using a eutectic Sn–Pb solder.

2. Experimental details

Alloys containing Sn–40% Pb and Sn–58% Bi were made by weighing and melting commercially pure (nominally 99.9%) metals. Each alloy weighed 1 kg. Details of the melting, fettling and rolling of the Sn–Pb solder, the $ZnCl/NH_4Cl$ flux, and the manufacture of the copper and 70–30 brass substrates (680 mm × 15 mm × 2 mm) have been given previously [5, 6]. The Sn–Bi alloy was made in a similar way except that it was melted at 400° C for 15 min. The Sn–Bi ingot could not be cold or hot rolled because of extensive cracking, but it was readily pressed to sheet 2 mm thick and blocks 12 mm × 2 mm × 2 mm were cut for use in soldering.

Full details of manufacturing the soldered joints, and the testing procedures in tension, creep and fatigue have been published [5, 6] and only an outline and any differences are given here. Simple lap joints of contact area 14 mm × 15 mm and joint thickness 0.20 mm (maintained with nichrome wire spacers) were held in a rack and soldered in batches of 42 in a pre-heated air circulating furnace. All soldering times were 10 min and the temperatures were 190 and 250° C for the Sn–Bi and Sn–Pb joints, respectively. Tensile testing used a crosshead speed of 5 mm min^{-1}, and fatigue testing used a crosshead speed of 50 mm min^{-1} between load limits of 1.75 and 2.50 kN. For creep testing the overlap was reduced to 10 mm and the width reduced to 6 mm, and a load of 50 kg (equivalent to about 80% of the tensile yield stress) was applied. To assess the effect of thermal shock a lap joint was heated in an air-circulating furnace for 10 min at 125° C and then quickly immersed in liquid nitrogen (− 196° C) for 2 min. This was repeated ten times on each specimen before tensile testing. Some tensile tests with a crosshead speed of 5 mm min^{-1} were also made on the bulk solder using a 40 mm circular section and a reduced length of 38 mm. Various metallographic, low-power

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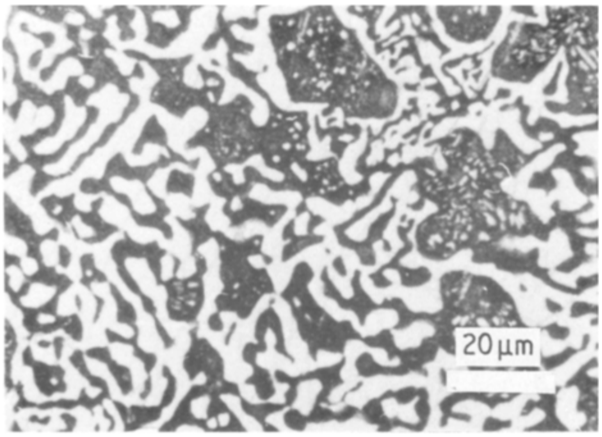

Figure 1 Microstructure of cast Sn–Bi alloy. Etched nital.

stereoscopic and optical microscopy, SEM and EDAX techniques were also used [5, 6].

3. Results and discussion

The cast structures of the tin–bismuth and tin–lead solder alloys were metallurgically sound and essentially of a eutectic composition. The microstructure of the Sn–Bi alloy is shown in Fig. 1 and the mechanical properties of both alloys are presented in Table I. The tensile strength (72.9 MPa) and elongation (16.6%) of the Sn–Bi alloy compares with the values of 55.1 MPa and 30%, respectively, reported by Mackay and Voss [4], and the difference probably reflects the increased strengthening effect of the impurities in the less-pure metals used in the present work. The properties of the Sn–Bi alloy agree closely with results reported by other workers [4]. It is seen (Table I) that the Sn–Bi alloys are substantially stronger and the ductility much reduced compared with the Sn–Pb alloys, although the 16.6% elongation of the Sn–Bi alloys may be considered more than adequate for many purposes.

Single lap joints of copper and brass soldered with Sn–Bi and Sb–Pb solders were tested in tensile shear in the as-soldered condition and after thermal shocking, and the results are presented in Table II. We first and mainly consider the tensile shear properties of copper and brass joints soldered with Sn–Bi in the as-soldered condition. Two points are clear from Table II. The first is that Sn–Bi solder joints are much stronger with a copper substrate than with a brass substrate (23.7 MPa compared with 16.8 MPa), and the second is that Cu/Sn–Bi joints are stronger than Cu/Sn–Pb joints whereas the reverse is true for brass substrates. These two points, along with the data from Table I, indicates that neither the property of the solder itself nor the property of the basis metal itself determines the property of the joint, but rather some reaction between the basis metal and the solder. We may also note that there is a much greater scatter in the properties of the Sn–Bi joints compared with those of the Sn–Pb joints, and that all the joints have an acceptable toughness, and hence ductility, as indicated by the work to fracture (Table II).

Fracture surfaces of the joints soldered with Sn–Bi, when examined under a low-power stereoscopic microscope, showed that good wetting and capillary penetration had occurred during soldering. Figs 2 and 3 show the fractured surfaces in more detail. At a relatively low magnification the fracture surfaces of the copper and brass joints have a similar appearance (Figs 2a and 3a, respectively) and a roughness characteristic of tearing and plastic deformation. At higher magnification and in more detail there is a significant difference between the two fracture surfaces (Figs 2b and 3b). The microstructure of the fracture face on the copper (Fig. 2b) is very similar to the microstructure of the cast Sn–Bi solder, whereas the fracture surface of the brass joint (Fig. 3b) has morphological features on the same size scale, but the (relatively) discontinuous phase appears, in part at least, to be more faceted and of a different character (cf. Figs 2b and 3b) indicating a less ductile nature. This is consistent with

TABLE I Properties of cast eutectic solders

Solder	Tensile strength (MPa)		Work to fracture (Nm)		Elongation (%)		Vickers hardness (5 kg)	
	Mean*	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Sn–Bi	72.9	3.4	16.9	3.5	16.6	3.4	23.2	0.5
Sn–Pb	47.5	6.1	51.0	6.3	169.1	87.0	19.4	0.3

*Tensile properties on four results, hardness properties on ten results.

TABLE II Tensile shear properties of lap joints

Substrate	Solder	Joint condition	Strength (MPa)		Work to fracture (Nm)	
			Mean	S.D.	Mean	S.D.
Copper	Sn–Bi	As-soldered*	23.7	5.6	9.1	3.2
Copper	Sn–Bi	Thermally shocked†	13.9	2.6	11.9	2.2
Copper	Sn–Pb	As-soldered	18.0	1.9	12.8	4.2
Copper	Sn–Pb	Thermally shocked	14.8	0.6	13.0	1.5
Brass	Sn–Bi	As-soldered*	16.8	4.7	6.4	3.8
Brass	Sn–Bi	Thermally shocked	15.1	6.3	5.8	4.1
Brass	Sn–Pb	As-soldered	18.7	1.8	9.1	1.9
Brass	Sn–Pb	Thermally shocked	29.5	6.3	17.5	5.7

*Average of ten results; other data average of four results.

†Heated 125° C, 15 min, quenched liquid nitrogen 2 min; repeated ten times.

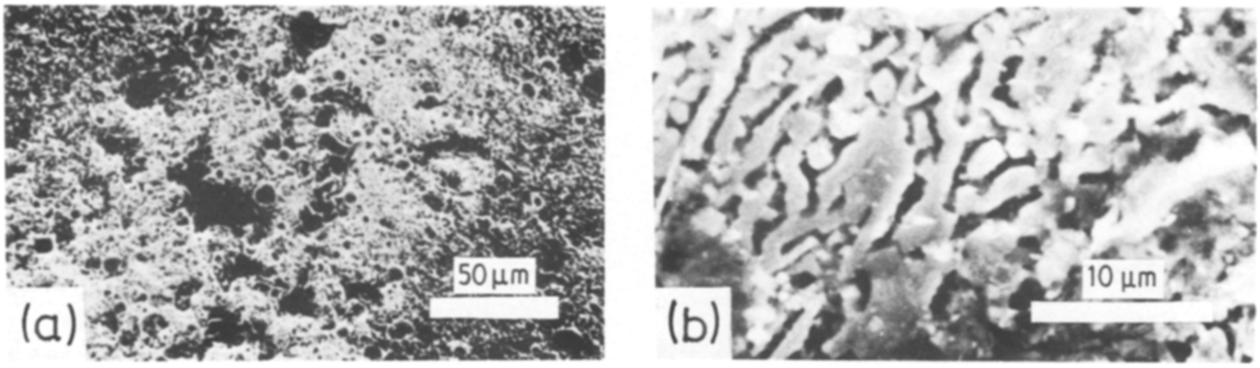

Figure 2 Fracture faces of copper joints.

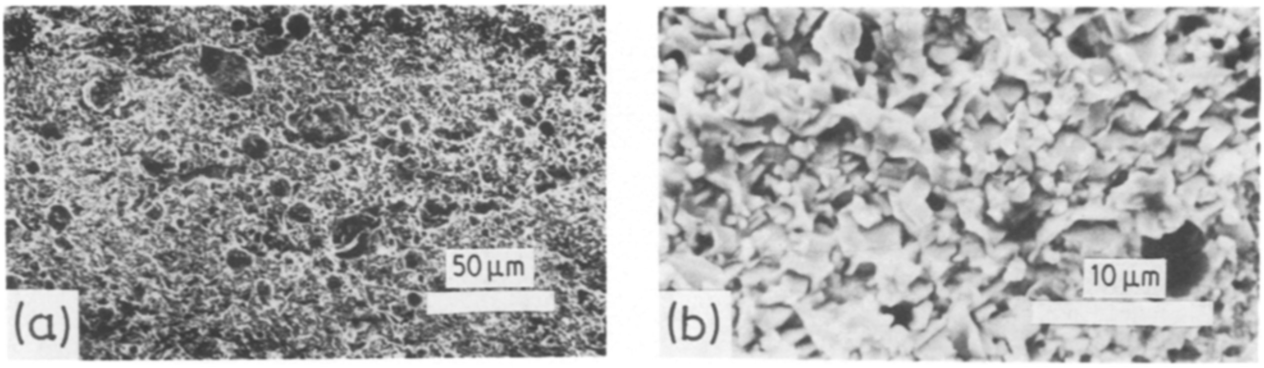

Figure 3 Fracture faces of brass joints.

the tensile shear results which show the Cu/Sn–Bi joints to be stronger than the brass/Sn–Bi joints (Table II).

Metallographic examination by optical microscopy of sections of joints soldered with eutectic Sn–Bi solder showed clearly a thin intermetallic zone. On the copper the intermetallic layer was approximately 2 μm thick and relatively uniform in thickness with the intermetallic layer compound/solder interface only slightly corrugated. On the brass there were two intermetallic layers, the inner layer (next to the brass) was approximately 2 μm thick and relatively uniform in thickness, and the outer layer varied from 2 to 5 μm thick and had a very irregular interface with the solder. Scanning electron micrographs of the interphase regions are shown in Figs 4 and 5. Unfortunately, at the high magnifications shown, contrast between the phases is poor, and so the marker is used to define the intermetallic thickness at the point of the associated EDAX trace. The important features of the EDAX traces across the intermetallic layer on copper are the large concentration gradient of copper and the small, but detectable, amount of bismuth in the compound. A point analysis within the layer gave the compositions presented in Table III, and while these results may be considered only semi-quantitative they give an empirical formula $Cu_{5.2}Sn_5$, and we assume the compound to be based on Cu_6Sn_5.

Two layers are clearly resolved from the EDAX traces across the intermetallic zone formed on brass (Fig. 5). These layers are thicker than those formed on copper and the concentration profiles are more distinct. Composition values from point analyses are given in Table III. If we assume the zinc substitutes for copper in the compounds, then we calculate from Table III the empirical formulae $(Cu, Zn)_3Sn$ and (Cu,

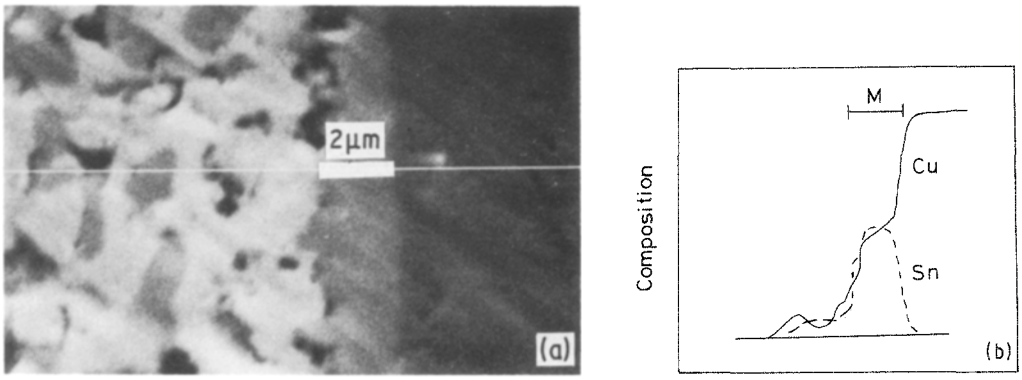

Figure 4 Section of a copper/Sn–Bi interface. On the micrograph (a), the scale bar defines the position of the intermetallic layer and of the EDAX traces. On the EDAX traces (b), M shows the scale bar position, and bismuth is not shown.

TABLE III Composition of a representative point in the intermetallic layers formed on joints soldered with eutectic Sn–Bi solder

Substrate	Thickness (μm)	Composition (wt %)			
		Cu	Sn	Zn	Bi*
Copper	2	35.4	64.6	–	< 1.0
Brass (inner layer)	2	39.9	39.0	21.1	trace
(outer layer)	2–5	33.7	62.0	4.3	< 1.0

*Estimated from a line scan.

$Zn)_{5.7}Sn_5$, and we assume these are based on the compounds Cu_3Sn and Cu_6Sn_5, respectively.

In order to define the fracture path in a brass/Sn–Bi joint an attempt was made to determine by point analysis the composition of the two fracture faces, one of the solder side and the other of the metal side, similar to that shown in Fig. 3b. On the solder side the composition ranges (wt %) were: Cu 15 to 28, and Zn 4 to 6; and on the metal side Cu 34 to 41, and Zn 7 to 30. The roughness of the surface (which introduces large errors) and the fineness of the microstructure (which tends to give an average of two phases) clearly makes these results, at best, only very approximate. Nevertheless, they do indicate that fracture has occurred, at least partly, within the outer, i.e. Cu_6Sn_5, intermetallic layer.

It would therefore appear from the present results that fracture of Cu/Sn–Bi solder joints occur at the Cu_6Sn_5/solder interface, or in the solder very close to the interface (see Fig. 2b). This process is aided by the relatively uniform thickness of the intermetallic compound (Fig. 4). With brass/Sn–Bi joints the presence of zinc promotes the formation of a much thicker duplex intermetallic layer containing substantial amounts of zinc (Table III) and an irregular $(Cu, Zn)_6Sn_5$/solder interface (Fig. 5), and the fracture passes, in part at least, through the intermetallic layer. Thus the zinc from the brass by changing the composition (and presumably the properties), amount, and morphology of the intermetallic compounds has lowered substantially the strength of the joint (Table II).

Finally, we report and comment briefly on limited results obtained to assess the susceptibility of joints soldered with eutectic Sn–Bi solder to thermal shock, fatigue and creep. The effect of thermal shock on the tensile properties of lap joints is included in the data of Table II. Overall, thermal shocking has no drastic effect on the properties of any of the soldered joints examined. But a striking feature of the data is that the scatter in the strength and work to fracture of copper joints, soldered with Sn–Bi and Sn–Pb, is always reduced by thermal shocking whereas the scatter in brass joints is always increased (Table II). This points to a fundamental role of the basis metal in the soldering and fracture process, and in the present case to the effect of zinc in brass. No metallographic studies of the fracture in thermally shocked joints were made, but the increase in scatter in the brass joints could well be caused by the thermally induced strains generating cracks in the irregular intermetallic/solder interface.

TABLE IV Fatigue life of copper and brass soldered with eutectic Sn–Bi alloy (maximum load 2.50 kN, minimum load 1.75 kN, extension rate 50 mm min^{-1})

Specimen	Cycles to failure	
	Copper	Brass
1	500*	57
2	500*	106
3	500*	211
4	47	3
5	2	4
6	191	21
7	500*	17
8	242	–
Mean	319	59

*No failure occurred.

Some fatigue results are presented in Table IV. These show again the embrittling effect of zinc on the strength of joints soldered with eutectic Sn–Bi solder. We note the occasionally very low number of cycles to failure, particularly in the copper joints. This is due to the quite high value of the maximum and minimum loads chosen to accelerate the test, and the larger range of values of the copper joints (Table IV) is clearly related to the greater scatter in the strengths of the Cu/Sn–Bi joints, as previously shown in Table II where we see that the standard deviation in the strengths of copper and brass joints were 5.6 and 4.7, respectively.

Creep data for Cu/Sn–Bi joints at 60 to 100°C are shown in Fig. 6 and the second stage creep rates in Table V. From the Arrhenius function we calculate an activation energy of 30 kJ mol^{-1}.

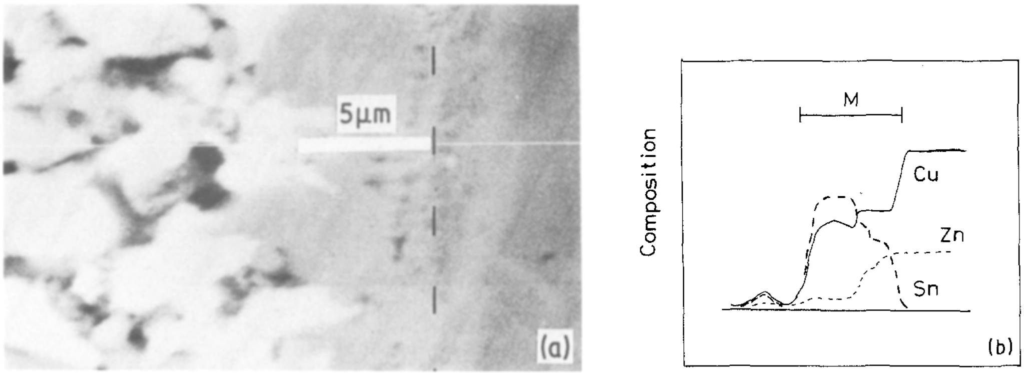

Figure 5 Section of a brass/Sn–Bi interface. On the micrograph (a), the scale bar defines the position of the intermetallic layer and of the EDAX traces and the dashed line shows the position of the Cu_3Sn/brass interface. On the EDAX traces (b), M shows the scale bar position, and bismuth is not shown.

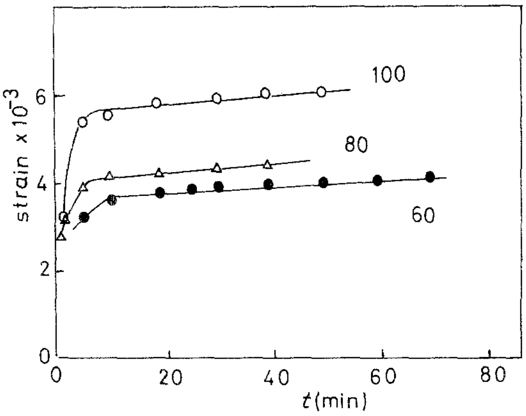

Figure 6 Creep of copper joints soldered with eutectic Sn–Bi solder at 60 to 100° C. Load 50 kg, joint area 60 mm^2.

In a Sn–38% Pb alloy, at strain rates below 10^{-5} sec^{-1}, the creep behaviour had an activation energy consistent with a process of lattice self-diffusion [7]. More recent work on the stress-relaxation of Sn–Pb alloys showed that the process is mainly influenced by the lead-rich α-portion of the alloy with an activation energy of 67 kJ mol^{-1} [8]. The activation energy of creep of bismuth in 47 kJ mol^{-1} [9] and that for creep of tin is about 70 kJ mol^{-1} [10]. The present results (30 kJ mol^{-1}) indicate that the creep process in Cu/Sn–Bi joints is mainly influenced by the bismuth-rich portion of the solder.

The main feature of the present work is that eutectic tin–bismuth solder forms joints with copper and with brass that have mechanical properties similar or superior to joints formed with eutectic Sn–Pb solders. The major restriction in the use of Sn–Bi solders is the low ductility of the joints, which, although limited, may nevertheless be more than adequate in joints of suitable design.

TABLE V Stage 2 creep rates for copper lap joints soldered with eutectic Sn–Bi solder

Temperature (° C)	Strain rate (sec^{-1})
60	9.67×10^{-8}
80	2.48×10^{-7}
100	3.06×10^{-7}

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