JOURNAL OF MATERIALS SCIENCE 22 (1987) 2416–2420

The shear strength of copper and brass soldered with Sn–40% Pb containing 0 to 10% Sb and/or 0 to 15% Zn

W. J. TOMLINSON, P. A. ROGERS
Department of Materials, Coventry Polytechnic, Coventry CV1 5FB, UK

The single lap shear strength of copper and brass soldered with Sn–40% Pb containing 0 to 10% Sb and/or 0 to 15% Zn has been determined and the microstructure examined using metallographic techniques. For any solder composition, brass joints were stronger than copper joints. The strength of copper joints decreased monotonically with the increase of antimony in Sn–Pb solder, and the strength of brass joints increased to a peak with about 3% Sb in the solder and thereafter decreased on further additions of antimony. With less than a few per cent antimony in the solder, 1% Zn in the solder decreased the strength of both copper and brass joints; with more than 1% Zn in the solder the strengths of both copper and brass joints were increased substantially. Fracture occurs mainly in the Cu_6Sn_5. The microstructure and the presence of zinc in the intermetallic compounds were determined, and the results are discussed.

1. Introduction

Copper and brass are the two most common substrates that are joined by soldering, and Sn–Pb alloys are the most common solders. The solder joint is essentially an interdiffused and then quickly cooled casting. An important feature of such joints, observed and measured by many workers, is the formation by reaction diffusion of the intermetallic compounds Cn_6Sn_5 and Cu_3Sn in the interphase region between the substrates and the solder. The detailed structure and properties of the joint are complex and depend upon a wide range of variables, and much work has been done to determine the structure and properties of copper and brass joints soldered with tin-based alloys [1–9]. But, despite the work done and the importance of the subject, there is still a considerable uncertainty in the microchemistry, microstructure, properties, and fracture of soldered joints. Two major areas of uncertainty are the effects of zinc in the brass (and hence the differences between copper and brass joints), and the effect of antimony in Sn–Pb solder on the structure and properties of copper and brass joints.

Saperstein and Howes [9] and Stone and co-workers [3] both reported that copper and brass joints have similar properties when soldered with Sn–Pb and tin–lead based alloys. In contrast, Thwaites and McDowall [4] reported that for ring and plug joints soldered with Sn–60% Pb alloy and tested at 50 mm min^{-1}, copper joints were much stronger (40 MPa) than brass joints (30 MPa). Again in contrast, Nightingale and Hudson [1] reported that joints made of brass were stronger than those made of copper, probably because of the strengthening caused by the zinc which had diffused from the brass into the solder. Accumulation of zinc to the extent of a few per cent has been observed in the compound Cu_6Sn_5 formed on brass, but the presence or otherwise of zinc in the compound Cu_3Sn was not reported [4]. Zinc [4, 7] and copper [4] have also been detected in the solder of brass substrates. The presence of the zinc in the solder has been associated with a higher porosity and its location at the solder/intermetallic compound interface in the solder, and it is suggested to be the cause of the lower strength of brass joints [4].

Antimonial Sn–Pb solders and the general properties of antimonial solder joints have been surveyed by Manko [2]. A few percent antimony in a Sn–Pb solder increases the strength of brass joints [1, 4, 5], and further additions thereafter cause a progressive loss in strength [1, 2, 5], until at 10% Sb there has been a loss in strength of about 10% [5]. Thwaites and McDowall also observed that it was the combined presence of antimony in the solder (a few per cent) and zinc in the solder (diffused from the brass) that was the most likely cause of scatter in the strength of brass joints soldered with antimonial Sn–Pb solders [4]. Recent work has brought attention to the presence and possible effects of porosity in the solder near the solder/metal interface on the strength of soldered joints [4, 5], but the effects of porosity and its relation with other factors like the presence of antimony and zinc, is as yet unclear.

Thus there is only a small amount of detailed information on the effects of antimony in Sn–Pb solder on the properties of copper and brass joints, and much of the information is contradictory. In addition, the redistribution, presence, and effects of zinc on the structure and properties of the joints are little understood. Many of these deficiencies are due in a large measure to the complexity of the soldered joint and

0022–2461/87 $03.00 + .12

TABLE I Composition (wt %) of the solders made from a base metal of Sn–40% Pb solder containing Sb

Sb (wt %)	Zn (wt %)		
0.00	1.02	5.04	15.02
3.01	1.04	5.02	15.02
10.02	1.00	5.00	15.03

the many variables that influence its structure, properties and testing. Previous work by the present authors have shown that a single lap joint gives reproducible and meaningful results [5, 6]. The present work uses the lap joint to determine the shear strengths of copper and brass joints soldered with a Sn–40% Pb solder containing a wide range of antimony and/or zinc.

2. Experimental details

Full details of the melting, fettling, and fabrication of the solders, manufacture and mechanical testing of the joints, and the experimental techniques used to examine the joints have been given previously [5, 6] and only an outline will be given here along with any additional methods used. A 1 kg master alloy of Sn–40.0% Pb was made by melting the components, casting and rolling to 3 mm sheet. Antimonial solders were made by melting the antimony and then adding the master alloy to make solders containing 3.01, 5.00, and 10.03 wt % Sb, casting and rolling to 0.25 mm sheet. Solders containing zinc were made by melting the base solder (the master alloy containing 0, 3.0 or 10.0% Sb) and adding zinc, casting and rolling to 0.25 mm sheet. The weighted components were taken to be the nominal composition, and these are presented in Table I. Copper and brass (Cu–30% Zn) were cut from the same copper or brass sheet and machined to 80 mm × 15 mm × 2 mm. All the solder components were nominally 99.9% pure and the copper and brass were commercially pure. A zinc chloride/ammonium chloride/HCl flux (specification DTD 87 1953) was used.

TABLE II Shear strength of copper/Sn–Pb–Sb–Zn joints

Sb (%)	Zn (%)	Shear strength (MPa)				
		1	2	3	4	Average
Set A						
0	0	17.0	17.8	–	–	17.4
3	0	14.8	16.1	–	–	15.5
5	0	14.4	14.2	–	–	14.3
10	0	13.9	13.8	–	–	13.9
Set B						
0	0	16.2	15.7	14.8	14.8	15.4
0	1	15.3	13.9	–	–	14.6
0	5	19.7	20.4	–		20.0
0	15	21.0	19.9	–	–	20.5
3	0	18.6	15.7	15.7	14.3	16.1
3	1	13.8	12.3	–	–	13.1
3	5	13.0*	16.0	–	–	16.0
3	15	19.2	17.6	–	–	18.4
5	0	14.8	16.1	15.1	13.3	14.8
10	0	13.2	11.6	13.5	15.2	13.4
10	1	10.1	11.7	–	–	10.9
10	5	14.5	13.8	–	–	14.2
10	15	15.8	15.5	–	–	15.7

*Judged from the load–extension curve to be a low value and so disregarded.

TABLE III Shear strength of brass/Sn–Pb–Sb–Zn joints

Sb (%)	Zn (%)	Shear strength (MPa)				
		1	2	3	4	Average
0	0	25.6	18.1	23.3	23.3	22.6
0	1	20.6	20.4	–	–	20.5
0	5	24.8	22.8	–	–	23.8
0	15	26.9	25.4	–	–	26.2
3	0	25.2	26.8	27.6	24.2	26.0
3	1	20.4	21.7	–	–	21.1
3	5	20.5	20.5	–	–	20.5
3	15	22.3	27.4	–	–	24.9
5	0	19.0	17.4	19.4	18.1	18.5
10	0	16.0	15.5	18.2	17.8	16.9
10	1	18.4	17.3	–	–	17.9
10	5	18.6	16.9	–	–	17.8
10	15	–	–	–	–	–

Joints were manufactured from strips with a 10 mm overlap and a spacing of 0.2 mm fixed by two nichrome wires of diameter 0.2 mm and length 10 mm placed in the joint area approximately 2 mm from each edge and parallel to the long edge of the strip. The method included cleaning and fluxing [5, 6]. A 12 mm × 12 mm piece of solder was rolled and placed against the joint step. The joint was held in a rack holding 42 specimens and placed in a pre-heated air circulating furnace at 300° C for 10 min and then air-cooled. All solder joints were made in this way. Standard tensile testing (5 mm min^{-1} at room temperature) and metallographic techniques were used [5, 6].

3. Results and discussion

Single lap shear strengths of soldered joints show a significant amount of scatter and previous work [5, 6] has determined a minimum sample size of 10 to enable a change of 1.2 MPa to be detected at the 95% confidence level. Such large numbers of samples are unrealistic in the present work where a wide range of variables are investigated and to indicate clearly the scatter the full results are presented in Tables II and III and in Figs 1 and 2. In Table II Set A are some early results and Set B are the main results and considering the scatter in the data, the agreement between the Set A and Set B is quite close. Before we consider the results in detail we make two general points. Firstly, despite the scatter in the results, there is a clear pattern of behaviour, and secondly, for all the solder compositions of Sn–40% Pb containing 0 to 10% Sb and/or 0 to 15% Zn, for a given solder, brass joints were always stronger than copper joints.

In more detail, we consider first the strength of copper and brass joints soldered with binary Sn–Pb solder. The present results show (Fig. 1) that Sn–Pb solder brass joints (22.6 MPa) are substantially stronger than copper joints (average 16.1 MPa). This is consistent with the older work of Nightingale and Hudson [1], and is in contrast to more recent work that concluded both types of joint have similar properties [3, 9], or that copper joints were much stronger than

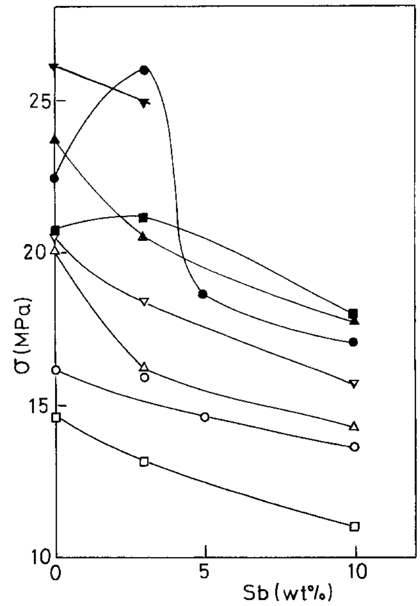

Figure 1 Average shear strength of single lap joints of copper and brass soldered with Sn–40% Pb solder containing antimony and/or zinc at 300° C for 10 min and then air-cooled. (○□△▽) copper; (●■▲▼) brass; solder, wt % Zn, (○●) nil, (□■) 1%, (△▲) 5%, (▼▽) 15%.

brass joints [4]. The greater strength of brass joints compared with copper joints when soldered with the binary Sn–Pb solder is clearly consistent with the strength of brass and copper joints soldered with a series of solders based on Sn–40% Pb alloys (Fig. 1).

Unbroken joints were examined metallographically in cross-section at magnifications up to × 800. Except for a very occasional large gas void the joints were sound and free from defects. Some examination of the fracture faces by SEM showed a number of circular structures (of the kind shown in Fig. 8 in connection with another system). These have been observed previously on brass [5, 6] and now clearly exist in copper joints. Focusing on the fracture surface at × 500 using optical microscopy showed that the majority, if not all, of the circular regions were holes. Some of the fracture faces were copper plated and the polished and etched cross-section examined under the optical microscope. At magnifications up to × 800 there was no indication of the presence of any solder and so the fracture path must be in the intermetallic layer, at the interface, or in the solder very close to the interface. Scanning electron microscope results are shown in Figs 3 and 4. It is seen from these that the intermetallic compounds Cu_6Sn_5 and Cu_3Sn are very variable in thickness, and we note the large, almost filamentary protrusion of the intermetallic layer into the solder (Fig. 3). Energy dispersion X-ray analysis (EDAX) traces showed that a few per cent zinc has been incorporated in the intermetallic compounds and it seems that this, through a strengthening of the intermetallic compound, is the cause of the greater strength of brass joints compared with copper joints.

Antimony in Sn–Pb solders progressively increases the strength of brass joints with a maximum strength occurring at about 3% Sb. Further additions of antimony then causes a progressive decrease in strength (Fig. 1). The effect has been discussed

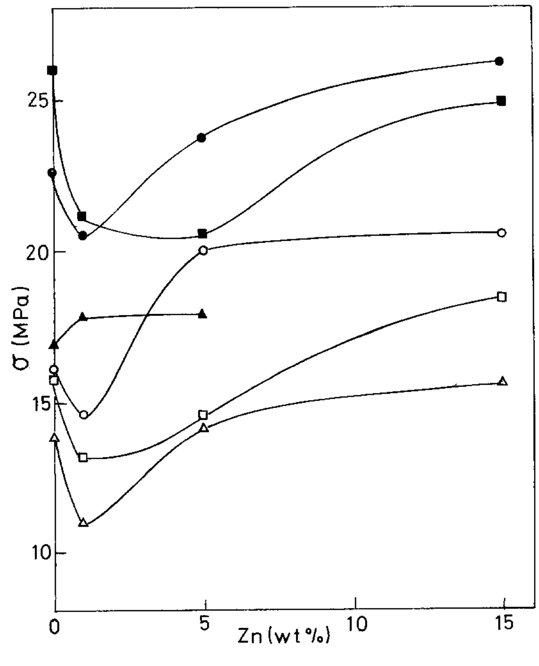

Figure 2 Average shear strength of single lap joints of copper and brass soldered with Sn–40% Pb solder containing antimony and/or zinc at 300° C for 10 min and then air-cooled. (○□△) copper; (●□▲) brass; solder, wt % Sb, (○●) nil, (□■) 3 %, (△▲) 10%.

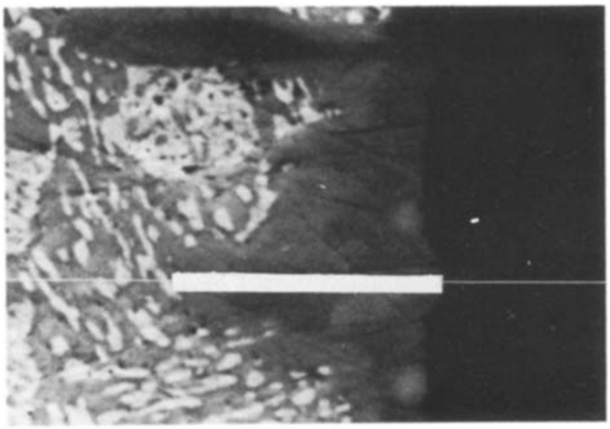

Figure 3 Intermetallic compounds formed on copper soldered with Sn–40% Pb solder. The marker $16\,\mu m$ shows the position of the compounds.

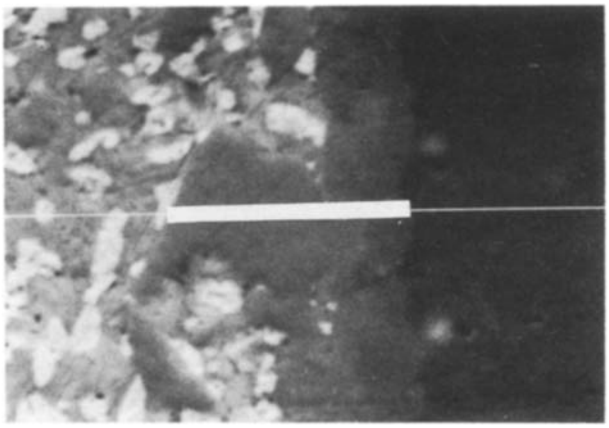

Figure 4 Intermetallic compounds formed on brass soldered with Sn–40% Pb solder. The marker $13\,\mu m$ shows the position of the compounds.

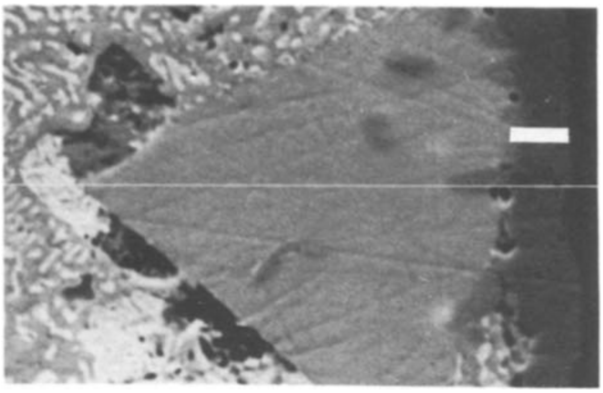

Figure 5 Intermetallic compounds and cuboid of SnSb formed on copper soldered with Sn–Pb–10% Sb solder. The marker, 7 μm, shows the position of the intermetallic compounds (mainly Cu_3Sn). Note the extensive porosity at the cuboid/intermetallic compound interface.

previously [5, 6]. But in contrast, copper joints are not strengthened by the presence of antimony in the solder; rather they show a small and progressive decrease in strength (Fig. 1). All copper and brass joints soldered with Sn–Pb–Sb alloys were examined in section (unbroken) and on the fracture faces by optical and scanning electron microscopy. Some results are collected in Table IV and some features illustrated in Fig. 5. Cuboids of SnSb (Fig. 5) occupy about 5 and 10% of the solder interface in joints with solders containing 5 and 10% Sb, respectively. Only patchy remnants of the Cu_6Sn_5 layer remain (Fig. 5), and a line of porosity is associated with the cuboid/intermetallic compound interface (Fig. 5). These features are similar to those observed in brass joints observed and discussed previously [5]. Copper plating and examination of the fracture surfaces in section, as with the Sn–Pb solders, showed that the fracture did not occur in the solder.

The solid solubility of antimony in tin is about 7% and since antimony is virtually insoluble in lead, cuboids of SnSb occur in the microstructure of a Sn–40% Pb alloy above about 4% Sb [2]. In association with the peak in the strength of brass joints at about 3% Sb (Fig. 1), this has been taken to mean that the strengthening effect of brass joints by antimony is due to solid solution hardening of the tin in the solder [2, 5]. However, this now appears unlikely since if the effect is due solely to changes in the solder then a similar effect should occur in copper (or any other metal) joints. Since antimony in the solder does not strengthen copper joints (Fig. 1) we conclude that solid solution strengthening of tin in Sb–Pb solder by antimony is not the cause of the increased strength of brass joints. EDAX analysis showed the presence of a few per cent zinc in the intermetallic layer in brass joints and since fracture does not occur through the solder (see above), it seems likely that this is the cause, through strengthening of the intermetallic layer, of the increased strength of brass/Sn–Pb–Sb joints. But why the maximum strength of the joint occurs at, or near, 3% Sb is unknown.

TABLE IV Thickness* of the intermetallic compounds formed on copper and brass with a Sn–40% Pb solder containing Sb ($\eta = Cu_6Sn_5$, $\varepsilon = Cu_3Sn$)

Thickness (μm)	Sb in solder (%)							
	0		3		5		10	
	η	ε	η	ε	η	ε	η	ε
On copper	3	3	4	5	2	4	< 1	7
On brass	3	2	5	2	9	3	6	2

*The general thickness of layers are given and not the value of the occasional protuberance (see for example Fig. 3).

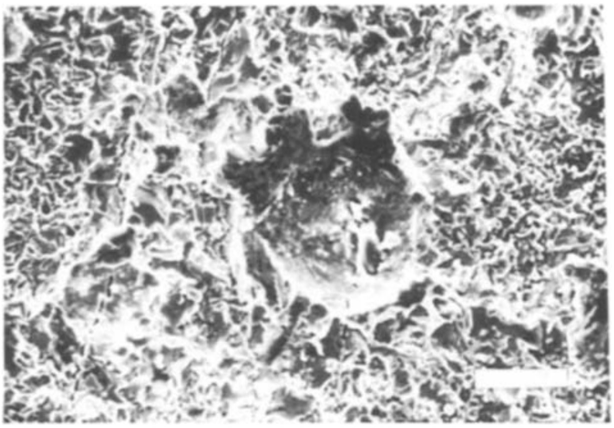

Figure 6 A void in the fracture of a copper/Sn–Pb–10% Sb solder joint away from the region of cuboids. Marker 22 μm.

A void in the solder face of a Cu/Sn–Pb–10% Sb joint (away from the presence of a cuboid) is shown in Fig. 6. Allowing for errors due to the roughness of the surface, an EDAX analysis of the void and the surrounding face showed them to be of the same composition. Two small cracks are seen to cross the solder face. These indicate clearly the weakness of the intermetallic layer or intermetallic compound/solder interface compared with bulk solder.

Zinc in Sn–Pb and Sn–Pb–Sb solder has a complicated effect on the shear strength of copper and brass joints (Fig. 2). We consider first the Sn–Pb–Zn soldered joints. When the solder contains no antimony, the effect of zinc in the solder causes similar increases in the strength of both copper and brass joints. The addition of 1% Zn decreases the strength of both kinds of joints; further addition of zinc increases the strength, with a decrease in effectiveness above about 5% Zn (Fig. 2). Only a limited metallographic study was made of these joints. Fig. 7 shows the fracture face of a Cu/Sn–Pb–5% Zn joint. This is similar to the fracture faces observed in joints without zinc in the solder and so the fracture mechanism appears to be similar. Fig. 8 shows a section of a Cu/Sn–Pb–Zn joint where it is seen that the characteristic two intermetallic compounds occur but, most notably, the Cu_6Sn_5/solder interface is smooth. An EDAX analysis showed clearly that the intermetallic compounds (e.g. Fig. 8) have incorporated a substantial amount of zinc and we assume that it is this zinc dissolved in the intermetallic compound that is mainly responsible for the increased strength of Cu/Sn–Pb–Zn joints. This can not be the only reason since even high additions of zinc to the solder does not raise the strength of copper joints to that of brass joints (Fig. 2), and it may be that the difference is related to the inter-

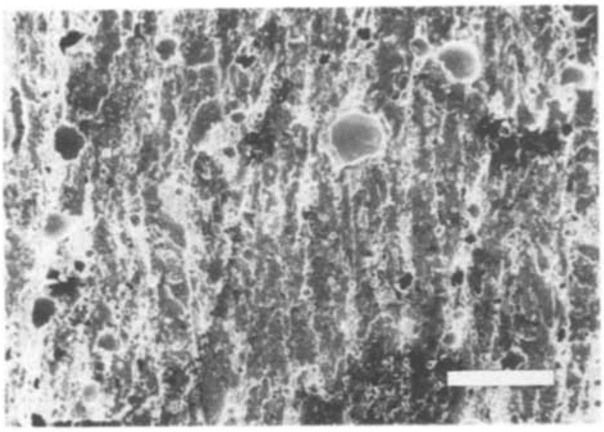

Figure 7 Fracture face of a copper/Sn–Pb–5% Zn solder joint. Marker 100 μm.

locking Cu_6Sn_5/solder interface of the brass joints (cf. Figs 4 and 8).

The combined effect of both antimony and zinc in the solder on the strength of joints is difficult to identify. This is mainly because: on brass, there is the zinc from the brass in addition to the zinc in the solder; with Sn–Pb–Sb solders the nature of the peak in strength at 3% Sb is unclear; and on both brass and copper, provided the antimony content of the solder is 3% or less, then the presence of 1% Zn in the solder decreases the strength of the joints whereas more than about 1% Zn increases the strength of the joints. Clearly there is some interaction between the components in the solder and the substrate but the nature of these are unknown.

The present results then, give a broad view of the shear strength and microstructure of copper and brass joints soldered with Sn–Pb–Sb–Zn alloys. They show that fracture occurs mainly in the Cu_6Sn_5 intermetallic compound, and support the view that this compound is strengthened by the presence of zinc. But this does not fully explain the strength behaviour of soldered joints inasmuch as the strength of copper joints could not be raised to the strength of brass joints by addition of zinc to the solder. Indeed, for small amounts (less than a few per cent) of antimony in the solder, the first 1% Zn in the solder always caused a decrease in strength. It also seems that the origin of the zinc, whether from the brass or from the solder, may influence the morphology of the $(Cu, Zn)_6Sn_5$/solder interface and hence the properties of the joint. It further seems that the maximum strength of brass joints at about 3% Sb is not due to solid solution hardening of the tin in the solder by antimony, but is associated with an increased amount of zinc in the intermetallic compound. Although not investigated or considered in detail in the present work, the presence of porosity and cuboids of SnSb are expected to increasingly influence the fracture process as the amount of antimony in the solder increases [5, 6].

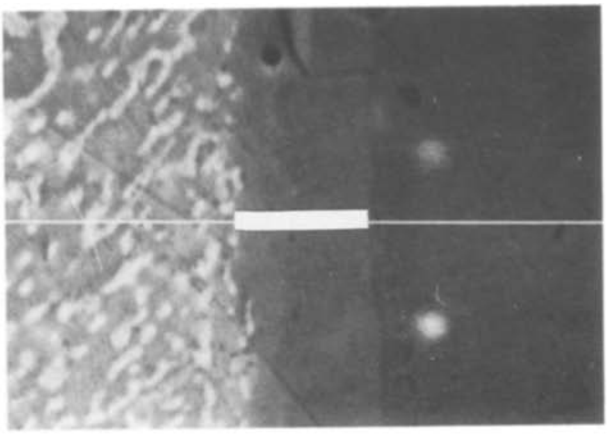

Figure 8 Intermetallic compounds formed on copper soldered with Sn–Pb–5% Zn solder. The marker 8 μm, shows the position of the intermetallic layer. Note the uniform thickness of the intermetallic layer.

Acknowledgements

The authors wish to thank Dr R. Carey and C. Dawson for the SEM/EDAX results.

References

1. S. J. NIGHTINGALE and O. F. HUDSON, "Research Monograph No. 1" (British Non-Ferrous Metals Research Association, London, 1942).
2. H. H. MANKO, in "Solders and Soldering", 2nd Edn (McGraw-Hill, New-York, 1979) p. 101.
3. K. R. STONE, R. DUCKETT, S. MUCKETT and M. WARWICK, *Brazing and Soldering*, No. 4 (1983) 20.
4. C. J. THWAITES and D. McDOWALL, *ibid.* No. 6 (1984) 32.
5. W. J. TOMLINSON and N. J. BRYAN, *J. Mater. Sci.* **21** (1986) 103.
6. W. J. TOMLINSON and G. A. COOPER, *ibid.* **21** (1986) 1730.
7. W. R. COLEMAN, in Proceedings in Technological Progress, National Electronic Packaging and Production Conf., Anaheim, Calif. 26–28 February, 1980, New York, 17–19 June 1980, Vol. 1. (Industrial Scientific Conference Management Inc., New York, 1980) p. 542.
8. E. W. BROTHERS, *Western Electric Eng.* **25** (1981) 49.
9. Z. P. SAPERSTEIN and M. H. HOWES, *Welding J. Research* Suppl. 48 (1969) 317s.

Received 24 July
and accepted 3 December 1986