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Fracture mechanism of brass/Sn–Pb–Sb solder joints and the effect of production variables on the joint strength

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The effect of various processing parameters on the strength of brass/Sn–Pb–Sb solder joints containing 0–10% Sb have been determined and the fracture mechanism examined by microscopical techniques. Soldering times up to 1 h at 300° C caused the greatest decrease in the strength of joints with solder containing 3% Sb. After 1 h joints with solders containing 0, 3, 5 and 10% Sb all had a similar strength. Cooling rates after soldering (from water quenching to furnace cooling) and joint gap thickness (from 0.05 to 0.20 mm) had a negligible effect on joint strength. Fracture occurs through a region of high porosity in the solder at the brass/solder interface. The presence of Sb and/or cuboids of SnSb in the solder increases the number and size of the pores and the cuboids tend to physically locate the pores at the interface.

1. Introduction

Antimony is sometimes added to Sn–Pb solder to replace the more expensive tin and so reduce the cost of soldering [1], and it has been concluded that Sn–Pb–Sb alloys are an effective alternative to Sn–Pb alloys to provide stronger fillets at a reduced cost [2]. The general properties of Sn–Pb–Sb solder joints have been surveyed [3]. Such joints have a reputation for poor reliability [1]. The presence of 2.2% Sb* in brass/Sn–Pb joints resulted in greater scatter in the strength properties [4] and more detailed work on brass 2% antimonial Sn–Pb ring-and-plug joints have shown the degree of scatter in the fatigue properties to be much less than those in the strength and creep properties [1]. These contrasts with recent data [5] when the presence of 10% Sb resulted in a variable and occasionally very low fatigue resistance. However, these results are not necessarily contradictory since 2% Sb would be in solid solution in the solder whereas 10% Sb results in large cuboids of SnSb in the microstructure. Many of the unreliable aspects of brass/antimonial solder joints had previously been considered to be due to a brittle ZnSb compound but no evidence has been found for its presence in soldered joints [1, 6]. Intermetallic phases of other types are commonly observed to grow at the interface [1, 5, 6] and as the amount of antimony in the solder increases the thickness and hardness of the intermetallic layer increases, and at and above about 4% Sb cuboids of SnSb form in the solder [5]. Additions of up to 3% Sb increases the shear strength of solder joints, but further additions up to 10% Sb causes the strength to progressively decrease [5]. Lower strengths sometimes observed with a 2% Sb solder is considered to be probably due to shrinkage voids [1]. Other work has shown that up to 3% Sb always has a strengthening effect and that the presence of voids were not considered to play a crucial part in the fracture process.

It is clear that there is a lack of information and also much disagreement on the effect of antimony on the properties of brass/tin–lead solder joints. The solder joint is essentially an interdiffused and then quickly cooled casting, and the properties of the joint depend on the composition of the solder, substrate and flux, the reaction time and temperature, and hence the amount of interdiffusion, the cooling rate, internal stress, joint thickness and geometry, and the method of testing; it is the large number of these factors which make identification of the process controlling the strength of the solder joint difficult. Previous work [5] has shown that a simple lap joint gives reproducible and meaningful results. The present work aims to examine the effect of the time of soldering at the reaction temperature, the cooling rate after soldering, and the gap thickness on the strength of lap joints, and to consider in detail the structure of the fracture surface on brass/Sn–Pb–Sb joints containing up to 10% Sb.

2. Experimental details

Alloys weighing about 0.1 kg were made from a 1 kg Sn–40.0% Pb master alloy. All details of melting and fettling the solders, the $ZnCl_2/NH_4Cl$ flux, and the brass substrates were as given previously [5]. The solder alloys were of nominal composition 0.0, 3.0, 5.0 and 10.0 wt % antimony. These alloys are coded 0, 3, 5 and 10, respectively.

In order to maintain a constant joint gap and overlap, brass specimens were prepared to a dry 600 grit finish, degreased in acetone, fluxed and then placed in a jig to provide an overlap area of 14 mm × 15 mm. Two small Nichrome wires, 0.17 mm diameter, were placed lengthwise in the joints about 2 mm from the

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*All compositions are in wt % unless given otherwise.

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edge. The joint was then wrapped and tightly bound with Nichrome wires. Such wire-spacers have been used sucessfully with ring and plug joints [7] and present tests with lap joints showed the wires to have a negligible effect. A rack of thick steel wire capable of holding 42 specimens was designed to fit into an air circulation furnace. Tests with a thermocouple attached to the joint showed that the heating rate for all positions in the rack was similar. In practice the fluxed specimens had extra flux applied to the joint and a 12 mm × 12 mm square of solder was rolled and placed against the joint step. Typically, four specimens of each solder type were placed about the rack, and any empty rack spaces were filled with dummy specimens to maintain a constant thermal load. The furnace was heated to 300 ± 1° C and then the loaded rack was placed in the furnace and the temperature monitored with a thermocouple clipped to a dummy specimen. When the temperatures had reached 300° C batches corresponding to soldering times of 5, 10, 15, 20 and 60 min were soldered, and then the rack removed and cooled in a strong air blast to give similar cooling throughout the rack. Some batches were soldered at 300° C for 10 min and then cooled at various rates by quenching in water, quenching in oil, and furnace cooling. To measure the effect of joint gap the Nichrome wire was replaced by very small pieces of steel cut from feeler gauges to provide gaps of 0.05, 0.07, 0.10, 0.15 and 0.20 mm.

Tensile testing at a strain rate of 5 mm min^{-1} and general metallographic, SEM and EDAX techniques were detailed previously [5]. In addition a "Dapple System Image Plus" image analyser was used to measure the porosity on a metallographically polished section.

3. Results and discussion

Scatter is an important indication of the reliability of joint strength. Previous work [5] determined a minimum sample size of 10 to enable a change of 1.2 MPa to be detected at the 95% confidence level. In the present case the larger number of variables tested makes such a large sample size unrealistic and we typically use a sample size of 4. This is small in terms of using a statistical parameter of scatter and so the full results are given in Tables I to III and a plot of the mean values in Figs. 1 to 3. The values for soldering for 5 min at 300° C and air cooling (Table I and Fig. 1) are within 5% of the values obtained previously [5] using a technique without wire-spacers and soldering joints one at a time. Thus the present use of wire spacers and the batch method of soldering have a negligible effect on the joint shear strength. Looking at the data overall (Figs. 1 to 3), and considering the large changes in soldering time, cooling rate and gap thickness, it is seen that for any solder composition the effect of these production variables is relatively small. A feature of the soldering time (see Fig. 1) is the common value of about 16 MPa for joints made by solders of all compositions after 1 h at 300° C. Thus

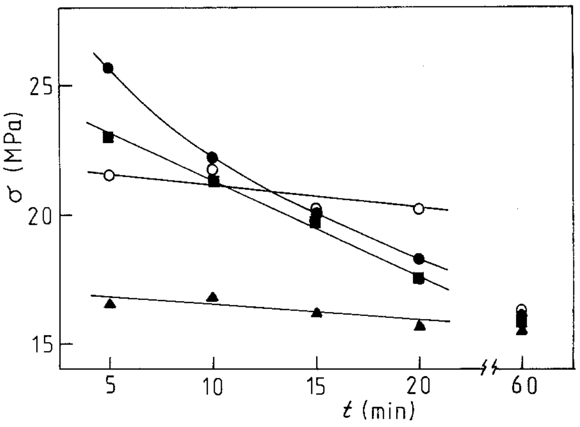

Figure 1 Effect of soldering time at 300° C on the shear strength of brass/Sn–Pb–Sb joints. Joint gap 0.17 mm; cooled by blown air. Symbols: ○ zero, ● 3, ■ 5 and ▲ 10 wt % Sb.

TABLE I Effect of soldering time at 300° C on the shear strength of brass/Sn–Pb–Sb joints. Joint gap 0.17 mm; cooled by blown air

Sb (%)	Time (min)	Shear strength (MPa)			
		1	2	3	Average
0	5	22.9	21.5	20.6	21.6
0	10	22.8	21.7	20.6	21.7
0	15	19.6	19.4	21.7	20.3
0	20	19.4	21.3	20.1	20.3
0	60	16.3	–	–	16.3
3	5	26.7	24.4	26.2	25.7
3	10	22.1	22.9	21.7	22.2
3	15	20.1	18.7	22.1	20.3
3	20	19.1	17.1	18.7	18.3
3	60	16.1	–	–	16.1
5	5	24.4	21.3	23.3	23.0
5	10	22.3	22.1	19.4	21.3
5	15	19.6	21.3	18.3	19.8
5	20	18.6	15.8	18.1	17.5
5	60	15.9	–	–	15.9
10	5	15.2	17.6	17.1	16.7
10	10	17.1	17.3	16.3	16.9
10	15	16.3	17.4	15.2	16.3
10	20	16.4	15.2	15.5	15.7
10	60	15.7	–	–	15.7

TABLE II Effect of cooling rate after soldering time at 300° C for 10 min on the shear strength of brass/Sn–Pb–Sb joints. Joint gap = 0.17 mm; WQ = water quenched, OQ = oil quenched, AB = air blown, FC = furnace cooled

Sb (%)	Cooling method	Shear strength (MPa)			
		1	2	3	Average
0	WQ	17.6	19.5	18.3	18.5
0	OQ	20.0	24.3	21.9	20.1
0	AB	18.3	19.8	22.9	20.3
0	FC	19.4	19.8	20.3	19.8
3	WQ	18.6	19.5	19.0	19.0
3	OQ	20.0	20.9	20.4	21.1
3	AB	21.7	22.9	22.1	22.2
3	FC	19.0	20.9	19.9	19.7
5	WQ	22.3	19.5	20.5	20.8
5	OQ	20.9	22.9	20.6	21.5
5	AB	22.9	19.7	21.6	21.4
5	FC	19.6	16.4	20.5	18.8
10	WQ	15.2	17.1	16.6	16.3
10	OQ	16.4	19.0	18.1	17.8
10	AB	15.8	17.3	17.1	16.8
10	FC	16.4	17.6	17.6	17.2

TABLE III Effect of joint gap on the shear strength of brass/Sn–Pb–Sb joints soldered at 300° C for 10 min and cooled by blown air

Sb (%)	Gap (mm)	Shear strength (MPa)			
		1	2	3	Average
0	0.05	19.6	23.0	20.4	21.0
0	0.07	18.5	20.8	21.9	20.4
0	0.10	19.0	21.9	21.1	20.7
0	0.15	22.3	19.0	20.0	20.4
0	0.20	17.8	22.9	20.9	20.5
5	0.05	20.1	23.5	24.8	22.8
5	0.07	22.9	22.5	19.8	21.7
5	0.10	22.5	22.9	21.9	23.4
5	0.15	20.6	20.5	23.8	21.7
5	0.20	19.0	20.5	18.7	19.4
10	0.05	16.0	16.3	17.5	16.6
10	0.07	18.7	17.1	17.8	17.9
10	0.10	19.0	17.1	16.7	17.6
10	0.15	17.6	17.0	17.1	17.3
10	0.20	16.2	15.2	15.0	15.5

the relatively poor strength with 10% Sb solder is maintained whereas the values with the 3% Sb solder falls substantially. The cooling times in Fig. 2 were obtained from a thermocouple fixed to a dummy specimen and noting the time to cool from 300 to about 25° C. For water quenching, oil quenching, blowing in air (a strong air blast), and furnace cooling, the times were 5 sec, 1 min, 5 min and 6 h, respectively. These times are approximate but nevertheless indicate the cooling rates over a wide range. Overall the effect of cooling rate is small. Also the effect of joint gap in the range 0.05 to 0.20 mm has only a minor effect (Fig. 3). This consistent with the negligible effect of changes in the range 0.03 to 0.22 mm of the gap in ring-and-plug brass/Sn–Pb joints [7], and in contrast to data on simple brass/Sn–Pb lap joints where a marked change in joint strength for different joint gap thickness has been reported [3]. The present results do show a small effect of gap thickness on joints made with solder containing 5 and 10% Sb (see Fig. 3). These solders contain cuboids of SnSb [5] and it is possible that the cuboid morphology in solders within different gap thickness is the origin of the small effect noted.

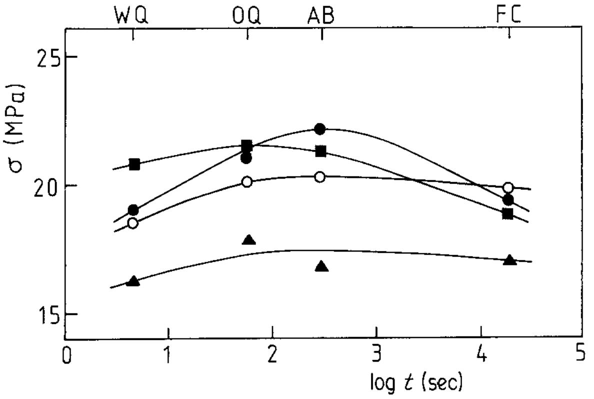

Figure 2 Effect of cooling rate (the time to cool from 300 to 25° C) on the shear strength of brass/Sn–Pb–Sb joints. Joint gap 0.17 mm. Symbols: ○ zero, ● 3, ■ 5 and ▲ 10 wt % Sb. WQ = water quenched, OQ = oil quenched, AB = air blown, FC = furnace cooled.

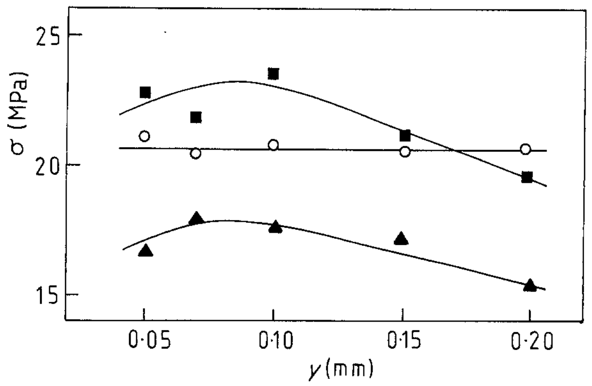

Figure 3 Effect of joint gap on the shear strength of brass/Sn–Pb–Sb joints, soldered at 300° C for 10 min and cooled by blown air. Symbols: ○ zero, ■ 5 and ▲ 10 wt % Sb.

Fracture of a soldered joint always occurred at the brass/solder interface within the solder, and the fracture faces of joints made with various solders at 300° C for 10 min and air-cooled are shown in Fig. 4. The most significant features of these factographs is the presence of large holes. These are most apparent in the solders containing antimony, and as the amount of antimony in the solder increases the number and size of the pores increases. Fig. 5 emphasizes the localized distribution of the pores. The crack had been propagated in the plane, T (Fig. 5) which is in the solder adjacent to the solder/intermetallic layer interface. The crack then crossed to the corresponding plane B, next to the other brass substrate. It is seen that many large pores occur in the fracture faces T and B next to the intermetallic layers, but in the fracture wall W. corresponding to the centre of the solder region no large pores are visible. The region C (Fig. 5) is where the crack had partly separated the solder body from the brass. The observations from Fig. 5 are quantified in Fig. 6. As viewed on a metallographic cross-section, there are many tiny pores (or perhaps microdepressions in the surface) in the centre of the solder corresponding to a cross-section on the crack wall W (see Fig. 5), but about the cross-section close to the intermetallic layer there are fewer but much larger pores. It is clear that an important factor in the fracture process is the size and distribution of pores in the solder near the brass interface, and as the amount of antimony in the solder increases the size of the pores about the interface increases.

A metallographic section showing pores at the interface of a binary Sn–Pb solder/brass joint is shown in Fig. 7. This is after soldering for 1 h and so the pores are much larger than apparent in Fig. 4a. With the largest pore (Fig. 7) there appears to be strain markings around and normal to the pore surface as if stresses had been induced sufficient to cause local plastic deformation. These pores are clearly intimately related to the intermetallic layer. A section of a 10% Sb solder joint is shown in Fig. 8. Here a large cuboid of SnSb has formed at the interface. It is seen that the relatively pore-free cuboid has localized the porosity at the brass/solder interface. Also there is an outline of a pre-existing pore which has been enveloped and then almost filled in by the growing cuboid. This suggests that the pore existed at the reaction

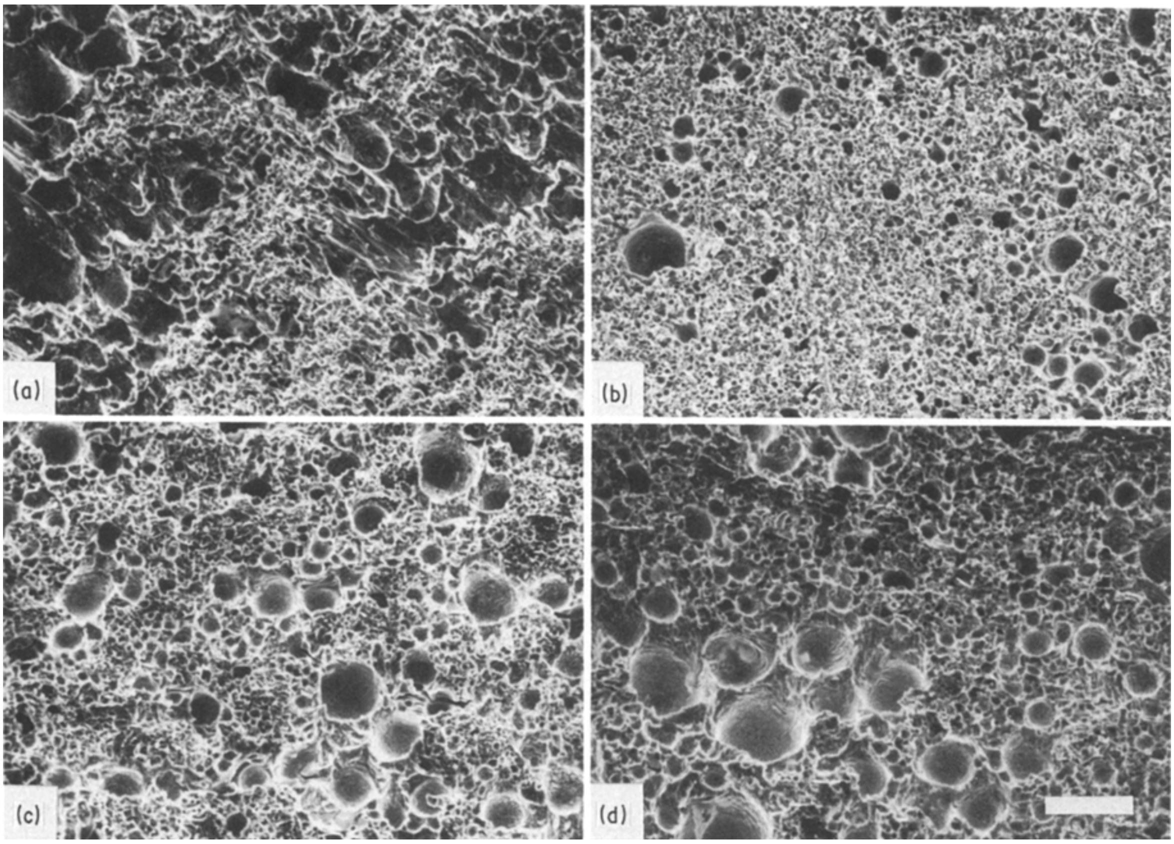

Figure 4 Fracture faces of brass/Sn–Pb–Sb joints soldered at 300° C for 10 min then cooled by blown air. Gap 0.17 mm. Solder containing antimony: (a) 0%, (b) 3%, (c) 5%, (d) 10%. Marker = 25 μm.

temperature and is not due to shrinkage on cooling. The spherical shape also indicates that surface tension had been present when the pore formed. What is commonly referred to as the intermetallic layer is really more complex. The microstructure between the substrate and solder typically consists of a thin continuous interdiffusion layer contiguous with the metal and then a thicker region where irregular intermetallic protrusions into the solder have broken away to form basically a two-phase compound and solder zone. It is in this zone that the largest pores are most evident. It seems impossible to show clearly both regions by etching. Light etching shows only the details of the two-phase zone (see Fig. 5). The nature of the continuous interdiffusion zone is discussed later with respect to Fig. 9. The irregular and complex nature of the "intermetallic" zone clearly makes characterization of its thickness ambiguous.

Some results of an EDAX study are shown in Fig. 9 and Table IV. The step (at point A) in the tin and zinc traces of Fig. 9 show the difference between the interdiffused continuous layer and the intermetallic compound that has broken away. From Table IV we calculate the inner layer has an empirical formula $Cu_6(Sn, Zn)_{5.28}$ and we assume this to be a solid solution based on Cu_6Sn_5. The small copper and zinc peaks at B (Fig. 9) suggests that the intermetallic compound as it floats away into the solder redissolves. The continuous layer in the 10% Sb joint (Table IV) may be interpreted as either $Cu_6(Sn, Sb, Zn)_{6.0}$ or $(Cu, Zn)_6$ $(Sn, Sb)_{2.67}$ but

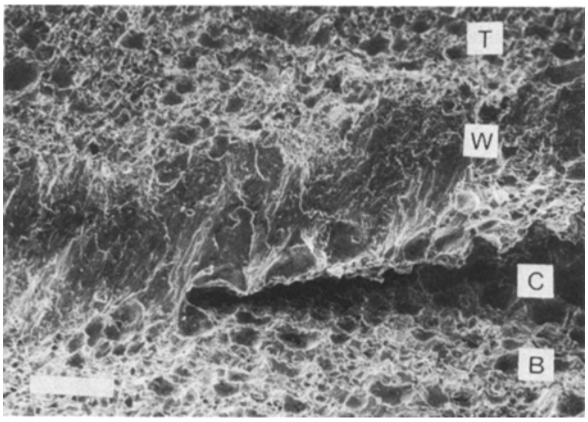

Figure 5 Fracture path along the brass/solder interfaces of a 5% Sb joint soldered at 300° C for 1 h then cooled by blown air. Gap = 0.17 mm. B = botton face, T = top face, W = crack wall. Marker = 100 μm.

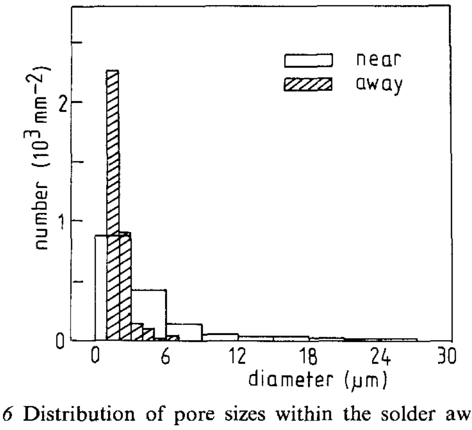

Figure 6 Distribution of pore sizes within the solder away from (cross-hatched) and near (plain) the solder/brass interface. Measured on a 3% Sb joint section soldered at 300° C for 20 min then cooled by blown air.

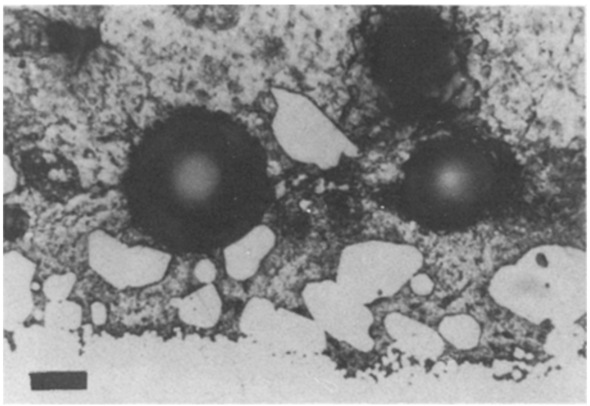

Figure 7 Intermetallic layers and porosity at the brass/Sn–Pb interface on a joint soldered at 300° C for 1 h then cooled by blown air. Etched: dilute acetic acid/hydrogen peroxide. Marker = 10 μm.

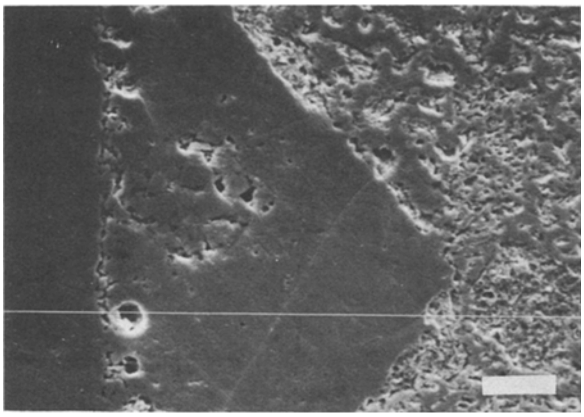

Figure 8 Cuboid at the brass/solder interface of a 10% Sb joint soldered at 300° C for 10 min then cooled by blown air. Gap = 0.17 mm. Marker = 10 μm. SEM micrograph.

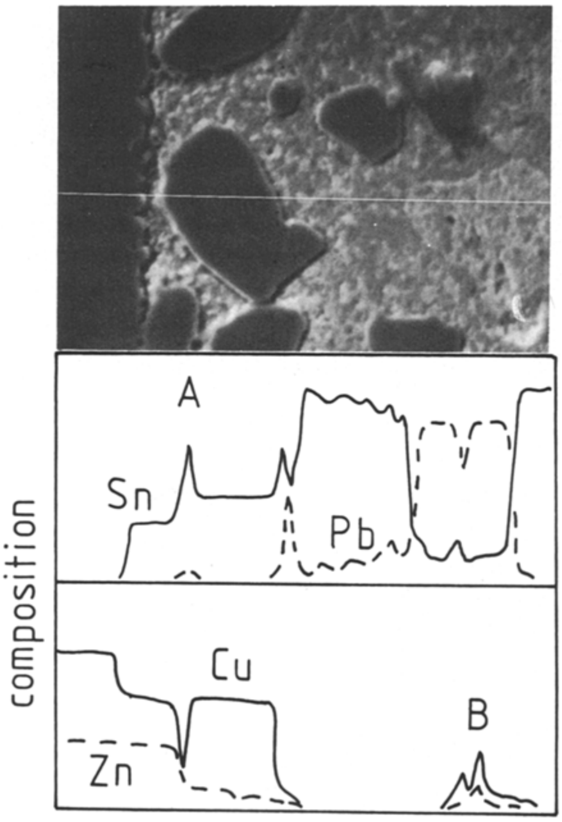

Figure 9 Intermetallic layers and composition line scans at the brass/Sn–Pb interface on a joint soldered at 300° C for 10 min then cooled by blown air. Gap = 0.17 mm. Marker = 5 μm.

TABLE IV Composition (wt %) of phases in the intermetallic layer formed on brass/Sn–Pb–Sn joints at 300° C for 1 h and cooled by blown air

Sample, Sb (%)	Cu	Zn	Sn	Pb	Sb
0	47.6	29.1	23.3	ND	–
10, inner region	37.7	9.3	49.3	ND	3.7
10, outer region	36.5	6.2	52.1	ND	5.2
10, cuboid	–	–	52.0	5.3	42.7

ND = not detected.

on the basis of the formula $Cu_6(Sn, Zn)_{5.28}$ observed on the 0% Sb solder joint we assume that zinc again acts like tin and the compound formed is based on Cu_6Sn_5. The cuboids have the empirical formula $Sn_{1.16}(Sb, Pb)$. From a number of line scans on the 0, 3 and 10% Sb alloy joints the main feature that emerged was the variability of the phases and the two-phase zone. In paricular, during reaction to form the intermetallic layer, the outer layers move away into the solder and start to redissolve.

A previous study summarized the fracture behaviour of brass/Sn–Pb–Sb solder joints [5]. Antimony up to 3% causes solid solution strengthening of the joint. Above 4% Sb there is a fall in strength associated with the presence of SnSb in the solder, and at the 8 and 10% Sb levels fracture occurs in the intermetallic layer. From the present work we make two further comments. First the reference at the 8 and 10% Sb levels to fracture in the intermetallic layer is really fracture at the intermetallic/solder (now cuboid) interface as seen in Fig. 8. Second it appears that it is not so much the presence of cuboids that changes the fracture process and lowers the strength of the joint, but the effect the antimony and/or cuboids have on the number, size and distribution of pores at the interface. It appears that above about 4% Sb, the presence of cuboids increases the number and size of the pores and localize the pores at the brass/solder interface. It appears that some of the larger pores may be due to gas porosity but the origin of the pores in general is not clear.

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