Reworking Solder Alloy Mixtures of Lead-free and Tin-Lead Alloys

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ABSTRACT:

Recent moves in the industry away from using traditional SnPb solder towards Pb-free soldering technologies has raised the possibility of having mixed solders in joints that have been reworked or repaired. However, few data are available on joints fabricated using these mixed solders in terms of say, appearance, microstructure or strength. This report presents the results of an initial evaluation of these features on as-fabricated joints using combinations of five solders (SnAgCu, SnAgCuBi, SnCu, SnPbAg and SnPb) to produce joints on test vehicles using chip resistors, gull-wing SOICs, and leaded resistors. A comparison has been made with similar joints using a single solder paste.

The visual inspection evidence indicated that when a lead-containing solder is present in the mix, the surface finish of the joint becomes brighter and smoother with increasing levels of lead. No defects were identified that were specific to a particular solder or mixture.

Microsectioning of the joints confirmed that complex phases and intermetallics (e.g. Ag3Sn, Cu6Sn5 and Sn-Bi) were formed as a result of mixing the solders. The levels of these complex phases could be generally correlated with the appearance and shear strength of the solder joints. Their presence has a significant impact on joint strength and roughness of the solder, the effects becoming worse as the levels of the phases increased. Whilst small levels of bismuth increased the strength of the joints there was no observable impact on the microstructure.

Shear testing demonstrated that the strengths of all solder mixtures were quite acceptable when benchmarked against those for single solder joints. The strongest joints were those containing high levels of SnAgBiCu with SnAgCu solders in the mix, and the weakest were those containing high levels of SnCu or SnPbAg in the mix with SnPb and SnAgCu solders. Generally, lead-free solder mixtures outperformed lead-containing mixtures.

Further work will focus on the effect of thermal cycling on the appearance, microstructure and strength of joints having solder mixtures.
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1 INTRODUCTION

Recent trends in choosing lead-free alternatives have started to cause concern in the rework arena, with the potential mixing of a wide range alloys with no control or traceability on the solder compositions being used or created. This issue has arisen with the impending introduction of European legislation (Waste in Electrical and Electronic Equipment (WEEE), and the Restriction of Hazardous Substances (RoHS)) banning the use of lead in solder. Industry is therefore faced with a transitional period where there is move from lead-containing solders to lead-free solders. Where sub-assemblies are manufactured at various locations and possibly reworked or repaired with alternative solders, the possibility of creating solder mixtures has significantly increased. The consequence of creating alloys differing from the original specification will be that new phases and intermetallics may be formed that may enhance or degrade solder joint reliability. The material properties of such mixtures are unknown. In the work presented here five solders (SnAgCu, SnAgCuBi, SnCu, SnPbAg and SnPb) have been used to generate binary mixtures, and subsequently fabricate joints on chip resistors, SOICs and leaded resistors. In this initial phase of the work joints made using these mixed systems have been characterised in the as-fabricated state. A further phase of the work will be to thermally cycle the joints and evaluate their thermo-mechanical fatigue properties.

To characterise the solder joints three different evaluation techniques are used. These are:

- Visual Inspection
- Microsections and microscopy
- Shear strength testing.

**Visual inspection:**
Inspection was carried out from the basis of existing standards for SnPb solder. The inspection looked at the solder joint fillet morphology formed with mixed alloy combinations and compared this with the conventional appearance.

**Microscopy:**
Microstructural analysis was performed, as this is a direct indication of solder alloy strength and performance in service. [1]

**Shear strength tests:**
The use of shear strength testing is a method that has been used previously [2]. The measurement of strength is used here to discriminate between alloys. The technique can also be used to indicate the degree of fatigue cracking in thermally cycled samples, and hence the reliability of a particular solder.

The component choice is important in determining the effects of rework with mixed alloy combinations. For the surface mount components the two main termination forms were assessed, the discrete ceramic chip component, and the gull wing for which a SOIC component was used. Through hole components were also assessed, using a connector and resistors. For the shear strength measurements the component selected was chosen because it has the most susceptibility to failure and weakness within the
solder joint, and this was a surface mount 2512-type ceramic resistor[2]. Figures 1 and 2 show examples of the components.

![Figure 1: Example of TH-resistor](image1)

![Figure 2: Example of 2512-type ceramic resistor](image2)

The testing and inspection were carried out approximately 2 weeks after assembly.

2 EXPERIMENTAL

2.1 ASSEMBLY AND MATERIALS
The substrate material used in the study was FR4 epoxy laminate with bare copper and an OSP (organic solderability preservative) finish.

The PCB layout, shown in Figure 3, was a double-sided 1.6 mm thick FR4 board with Cu tracking. The design incorporated 20 off 2512-type resistors, 20 off 0805 type resistors, 10 SOICs and 10 TH-resistors (on the opposite side).
Figure 3: Test PCB layout/ design

The components used were:

**Chip resistors:** These components were chosen, since their rigid alumina bodies have a significantly different TCE (thermal coefficient of expansion) from the PCB base material, and hence are more prone to fail from stress accumulation in a rework environment. This type of joint was used primarily to facilitate easy shear testing, since it presents a 90° face to the shear tooling.

**SOIC:** The attachment design here is based on the gull wing, this being the most common type of lead attachment used in SM components. This was the principal component used for the visual inspection work, the main point of focus being the heel since it is an indicator of the wetting performance of a solder and hence the joint reliability. Due to its compliance, the reliability of this type of solder attachment is considered to be quite high, providing proper wetting characteristics are obtained[3].

**TH-resistor:** This component is shown in Figure 1, and was primarily used for metallographic examination combined with visual inspection of the joints. This type of resistor was assembled since there was a particular interest in a phenomenon known as “fillet-lifting” which is known to occur with bismuth-containing alloys[4].

There were five different solder alloys used in the experiment in combinations of two lead-based solders and 3 lead-free solders. Table 1 below lists the alloys together and their melting points.
Table 1: Solder alloy description

<table>
<thead>
<tr>
<th>Solder</th>
<th>Composition</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>63.1Sn/36.9Pb</td>
<td>183</td>
</tr>
<tr>
<td>B</td>
<td>95.8Sn/3.5Ag/0.7Cu</td>
<td>217</td>
</tr>
<tr>
<td>C</td>
<td>93.3Sn/3.7Ag/2.1 Bi/0.8 Cu</td>
<td>210</td>
</tr>
<tr>
<td>D</td>
<td>99.3Sn/0.7Cu</td>
<td>227</td>
</tr>
<tr>
<td>E</td>
<td>63Sn/37Pb/2Ag</td>
<td>~179</td>
</tr>
</tbody>
</table>

2.2 SOLDER MIXTURES

In the experiment it was necessary to produce mixtures of the alloys listed in Table 1 in proportions of 25%/75%, 50%/50% and 75%/25% of all the respective combinations of the three lead-free and two lead-based solders, giving a total of 29 mixtures of which 5 assemblies were manufactured for each combination. This was done by mixing solder paste in the correct ratio. All the components were tested after soldering without being thermally cycled. Table 2 below outlines the matrix of solder mixtures; half the table is blanked out as it repeats diagonally the bottom half. The occurrence of 5 in a cell indicates that 5 assemblies were built of this combination.

Table 2: Solder alloy combinations

<table>
<thead>
<tr>
<th>(%)</th>
<th>ID</th>
<th>A 25</th>
<th>A 50</th>
<th>A 75</th>
<th>B 25</th>
<th>B 50</th>
<th>B 75</th>
<th>C 25</th>
<th>C 50</th>
<th>C 75</th>
<th>D 25</th>
<th>D 50</th>
<th>D 75</th>
<th>E 0</th>
<th>D 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnPb</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnAgCu</td>
<td>B</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnAgBiCu</td>
<td>C</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCu</td>
<td>D</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>SnPbAg</td>
<td>E</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Taking the volume percentages of each solder combination, the percentages of each elemental species were calculated. These data are presented in Table 3.
Table 3: Volume percentages of all solder alloy combinations

<table>
<thead>
<tr>
<th>Solder1</th>
<th>Solder2</th>
<th>% of Solder 1</th>
<th>Sn</th>
<th>Pb</th>
<th>Ag</th>
<th>Cu</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>25</td>
<td>87.5</td>
<td>9.2</td>
<td>2.7</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
<td>50</td>
<td>79.4</td>
<td>18.4</td>
<td>1.8</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
<td>75</td>
<td>71.2</td>
<td>27.7</td>
<td>0.9</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>C</td>
<td>25</td>
<td>85.8</td>
<td>9.2</td>
<td>2.8</td>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>A</td>
<td>C</td>
<td>50</td>
<td>78.2</td>
<td>18.4</td>
<td>1.8</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>A</td>
<td>C</td>
<td>75</td>
<td>70.7</td>
<td>27.7</td>
<td>0.9</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>A</td>
<td>D</td>
<td>25</td>
<td>90.2</td>
<td>9.2</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>D</td>
<td>50</td>
<td>81.2</td>
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<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>D</td>
<td>75</td>
<td>72.2</td>
<td>27.7</td>
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<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>C</td>
<td>25</td>
<td>93.9</td>
<td>0.0</td>
<td>3.7</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>B</td>
<td>C</td>
<td>50</td>
<td>94.5</td>
<td>0.0</td>
<td>3.7</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>C</td>
<td>75</td>
<td>95.0</td>
<td>0.0</td>
<td>3.7</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>D</td>
<td>25</td>
<td>98.3</td>
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<td>0.9</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>D</td>
<td>50</td>
<td>97.4</td>
<td>0.0</td>
<td>1.8</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>D</td>
<td>75</td>
<td>96.5</td>
<td>0.0</td>
<td>2.7</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>E</td>
<td>25</td>
<td>70.6</td>
<td>26.9</td>
<td>2.3</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>E</td>
<td>50</td>
<td>78.9</td>
<td>17.9</td>
<td>2.8</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>E</td>
<td>75</td>
<td>87.2</td>
<td>9.0</td>
<td>3.2</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>D</td>
<td>25</td>
<td>97.8</td>
<td>0.0</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>D</td>
<td>50</td>
<td>96.3</td>
<td>0.0</td>
<td>1.8</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>D</td>
<td>75</td>
<td>94.8</td>
<td>0.0</td>
<td>2.8</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>C</td>
<td>E</td>
<td>25</td>
<td>70.0</td>
<td>26.9</td>
<td>2.3</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>E</td>
<td>50</td>
<td>77.8</td>
<td>17.9</td>
<td>2.8</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>E</td>
<td>75</td>
<td>85.6</td>
<td>9.0</td>
<td>3.2</td>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>D</td>
<td>E</td>
<td>25</td>
<td>71.5</td>
<td>26.9</td>
<td>1.4</td>
<td>0.2</td>
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</tr>
<tr>
<td>D</td>
<td>E</td>
<td>50</td>
<td>80.8</td>
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<td>0.9</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>E</td>
<td>75</td>
<td>90.0</td>
<td>9.0</td>
<td>0.5</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>63.1</td>
<td>36.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>95.8</td>
<td>3.5</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>93.3</td>
<td>0.0</td>
<td>3.7</td>
<td>0.8</td>
<td>2.1</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>99.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>62.2</td>
<td>35.9</td>
<td>1.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The investigation methods used, visual inspection, shear testing or microsectioning, were applied to selected component types as shown in Table 4.
Table 4: Component types and applied evaluation techniques

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Component types</th>
<th>Mixtures used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual Inspection</td>
<td>0805 type resistors, SOICs and TH-Resistors</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25%/75%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50%/50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75%/25%</td>
</tr>
<tr>
<td>Shear testing</td>
<td>2512 type resistors</td>
<td>25%/75%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75%/25%</td>
</tr>
<tr>
<td>Microsectioning</td>
<td>2512 type resistors</td>
<td>25%/75%</td>
</tr>
<tr>
<td></td>
<td>TH-Resistors</td>
<td>75%/25%</td>
</tr>
</tbody>
</table>

The details of the various techniques are given below.

2.3 VISUAL INSPECTION
Assemblies manufactured using mixtures of solder pastes were inspected, and photographed where appropriate. The assemblies included three joint types, SM resistor (chip), SOIC (gull-wing) and connector (TH). The inspection was carried out using a binocular zoom microscope with 10 to 40X magnification. A fibre optic ring illuminator provided illumination. Figure 4 below shows a typical inspection set up.
2.4 MICROSECTIONING

2.4.1 Sample Preparation.
Table 5 lists the components and the specific alloys used for the microsectioning work.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Solder combination</th>
<th>2512 resistor = A, TH- resistor = B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnAgCu/ 25% SnPb</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>SnAgCu/ 25% SnPb</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>SnAgCu/ 75% SnPb</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>SnAgCu/ 75% SnPb</td>
<td>B</td>
</tr>
<tr>
<td>5</td>
<td>SnAgBiCu/ 25% SnPb</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>SnAgBiCu/ 25% SnPb</td>
<td>B</td>
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<tr>
<td>7</td>
<td>SnAgBiCu/ 75% SnPb</td>
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</tr>
<tr>
<td>16</td>
<td>SnCu/ 75% SnAgCu</td>
<td>B</td>
</tr>
<tr>
<td>17</td>
<td>SnPbAg/ 25% SnAgCu</td>
<td>A</td>
</tr>
<tr>
<td>18</td>
<td>SnPbAg/ 25% SnAgCu</td>
<td>B</td>
</tr>
<tr>
<td>19</td>
<td>SnPbAg/ 75% SnAgCu</td>
<td>A</td>
</tr>
<tr>
<td>20</td>
<td>SnPbAg/ 75% SnAgCu</td>
<td>B</td>
</tr>
</tbody>
</table>

Samples were cut out individually from the boards using a liquid-cooled conventional diamond saw. This method of cutting was employed to ensure that the soldered joints remained cool and there were no consequential microstructural changes.

Once cut, the components were cleaned using conventional IPA (iso-propyl alcohol) to ensure that any residue present from the cutting stage had been sufficiently cleaned from the joint region. The samples were mounted in a cold curing epoxy.

2.4.2 Metallography.
Once cured, the samples were removed from their respective moulds to be ground and polished, using silicon carbide from 120 to 4000 grit paper on an automated machine, and polished with diamond-containing pastes/sprays 15 to 0.25µm in size. Diamond impregnation of the cloth was optimised in order to ensure that the best cutting rate of the surface had occurred. Final polishing of the samples was achieved by hand using a
Some of the samples were etched. For etching the lead-containing solder systems a solution containing 2 ml hydrochloric acid and 98 ml industrial methylated spirits was used. With this solution a polish-etch technique was achieved using 0.25 µm diamond pastes as the polishing medium. The lead-free alloys were etched using 2 ml nitric acid, 2 ml hydrochloric acid and 96 ml distilled water. A bismuth etch was not required as the microstructure could readily be seen after polishing with OP (oxide polishing) solution.

A standard Olympus optical bench microscope was used with Polaroid instant colour film (Polaplan 100) at magnifications of 200x-500x.

2.5 SHEAR TESTING

Figure 5 shows the 2512 components tested.

![Figure 5: Area of PCB used for shear testing](image)

The boards used were cut into smaller sections containing two or three components for testing, using the same method as described in Section 2.4.1. The smaller sections of board were cleaned to remove any contaminants/residues from the cutting process and dried using compressed air.
Figure 6 shows the experimental arrangement of the board placed within the jig ready for testing. The push-off tool was positioned directly behind the component (as shown). For each test the push-off tool, was pre-set at a height (centre of component) of 80 µm and driven at 200 µm/s. The outcome of a typical test is shown in Figure 7.

Figure 7: Typical joint break after failure

For each board 19 2512 type resistors were tested in order to compute an average of the joint strength.
3 RESULTS

3.1 VISUAL INSPECTION

Figures 8 to 62 show typical examples of joints from all the mixtures of the five solder alloys. For clarity all these Figures are in the Appendix. Figures 8 to 12 show chip resistor examples and Figures 18 to 22 show TH examples. For clarity, the remaining examples are all SOIC solder joints.

*Generally there were no defects noted that were specific to any alloy or mixture. Varying alloy composition does not change joint profile.*

3.2 MICROSECTIONING

Micrographs for various alloys are presented in Figures 64 to 84, and are again shown in the Appendix.

1) Figures 63-66 are for mixtures containing SnAgCu and SnPb in volume concentrations of 25% and 75% of each alloy.
2) Figures 67-70 are for mixtures containing SnAgBiCu and SnPb in volume concentrations of 25% and 75% of each alloy.
3) Figures 71-74 are for mixtures containing SnAgBiCu and SnAgCu in volume concentrations of 25% and 75% of each alloy.
4) Figures 75-78 are for mixtures containing SnCu and SnAgCu in volume concentrations of 25% and 75% of each alloy.
5) Figures 79-82 are for mixtures containing SnPbAg and SnAgCu in volume concentrations of 25% and 75% of each alloy.

The micrographs are organised to show both chip resistors and TH-resistor sections for each alloy combination.

3.3 SHEAR TESTING

Shear tests were conducted on 19 resistors (see Figure 5), for each alloy listed in Table 6. Figure 83 shows the shear strength results, an average for the 19 values for each alloy.

Table 6: Alloys selected for shear testing, and designator for Figure 83

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Alloy Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnAgCu/ 25% SnPb</td>
</tr>
<tr>
<td>2</td>
<td>SnAgCu/ 75% SnPb</td>
</tr>
<tr>
<td>3</td>
<td>SnAgBiCu/ 25% SnPb</td>
</tr>
<tr>
<td>4</td>
<td>SnAgBiCu/ 75% SnPb</td>
</tr>
<tr>
<td>5</td>
<td>SnAgBiCu/ 25% SnAgCu</td>
</tr>
<tr>
<td>6</td>
<td>SnAgBiCu/ 75% SnAgCu</td>
</tr>
<tr>
<td>7</td>
<td>SnCu/ 25% SnAgCu</td>
</tr>
<tr>
<td>8</td>
<td>SnCu/ 75% SnAgCu</td>
</tr>
<tr>
<td>9</td>
<td>SnPbAg/ 25% SnAgCu</td>
</tr>
<tr>
<td>10</td>
<td>SnPbAg/ 75% SnAgCu</td>
</tr>
</tbody>
</table>
4 DISCUSSION

4.1 VISUAL INSPECTION

4.1.1 Results for SnAgCu/SnPb mixtures:
Figures 8 to 22 show the solder joints that result for mixtures of SnAgCu and SnPb solder alloys. Generally the solder alloys which do not contain lead have a duller surface finish than would normally be expected from a SnPb eutectic alloy (Figures 8, 13 and 18). These non-Pb alloys generally also show a faceted surface. With all three types of joint, the Figures show that increasing the amount of lead in the joint causes the surface finish of the solder joint to brighten and smooth. There are no obvious changes in joint profile due to changes in alloy composition.

4.1.2 Results for SnAgCuBi/SnPb mixtures:
Figures 23 to 27 show the solder joints that result for mixtures of SnAgCuBi and SnPb solder alloys. Here, the issues are much the same as for the previous mixtures. The Figures show that increasing the amount of lead in the joint causes the surface finish of the solder joint to brighten and smooth. There are no obvious changes in joint profile due to changes in alloy composition.

4.1.3 Results for SnAgCuBi/SnAgCu mixtures:
Figures 28 to 32 show the solder joints that result for mixtures of SnAgCuBi and SnAgCu solder alloys. This is an alloy mixture without any lead content so all joints have a dull, faceted surface finish. Indeed there is very little difference in the joints as would be expected since the mixing of the alloys only changes the bismuth content.
from 1.6% to 0%. Similarly, there are no obvious changes in joint profile due to changes in alloy composition.

4.1.4 Results for SnCu/SnPb mixtures:
Figures 33 to 37 show the solder joints that result for mixtures of SnCu and SnPb solder alloys. As with the other mixtures of lead-free and Pb-containing alloys, the Figures show that increasing the amount of lead in the joint causes the surface finish of the solder joint to brighten and smooth. There are no obvious changes in joint profile due to changes in alloy composition.

4.1.5 Results for SnCu/SnAgCuBi mixtures:
Figures 38 to 42 show the solder joints that result for mixtures of SnCu and SnAgCuBi solder alloys. This is another alloy mixture without any lead content so all joints have a dull, faceted surface finish. Indeed there is very little difference in the joints as would be expected since the mixing of the alloys only changes the bismuth content from 0% to 1.6% and the silver content from 0% to 2.8%. Similarly, there are no obvious changes in joint profile due to changes in alloy composition.

4.1.6 Results for SnPbAg/SnAgCuBi mixtures:
Figures 43 to 47 show the solder joints that result for mixtures of SnPbAg and SnAgCuBi solder alloys. As with the other mixtures of Pb-containing and lead-free alloys, the Figures show that decreasing the amount of lead in the joint causes the surface finish of the solder joint to dull and become faceted. There are no obvious changes in joint profile due to changes in alloy composition.

4.1.7 Results for SnPbAg/SnCu mixtures:
Figures 48 to 52 show the solder joints that result for mixtures of SnPbAg and SnCu solder alloys. As with the other mixtures of Pb-containing and lead-free alloys, the Figures show that decreasing the amount of lead in the joint causes the surface finish of the solder joint to dull and become faceted. There are no obvious changes in joint profile due to changes in alloy composition.

4.1.8 Results for SnCu/SnAgCu mixtures:
Figures 53 to 57 show the solder joints that result for mixtures of SnCu and SnAgCu solder alloys. This is another alloy mixture without any lead content so all joints have a dull, faceted surface finish. Indeed there is very little difference in the joints as would be expected since the mixing of the alloys only changes the silver content from 0% to 2.7%. Similarly, there are no obvious changes in joint profile due to changes in alloy composition.

4.1.9 Results for SnPbAg/SnAgCu mixtures:
Figures 58 to 62 show the solder joints that result for mixtures of SnPbAg and SnAgCu solder alloys. As with the other mixtures of Pb-containing and lead-free alloys, the Figures show that decreasing the amount of lead in the joint causes the surface finish of the solder joint to dull and become faceted. There are no obvious changes in joint profile due to changes in alloy composition.
4.2 MICROSECTIONING
Microstructure is seen to be sensitive to both varying alloy content and composition, as highlighted in Figures 63 to 82. The observed morphology changes are a direct result of these compositional variations, and the consequent impact on the occurrence of particular phases and intermetallics. This experiment shows clearly that the microstructure will vary as alloys are mixed during rework.

Generally solders that contain tin and lead, form a Sn-rich and Pb-rich phases which consist of a eutectic equilibrium structure consisting of colonies of alternating lamellae of a Pb-rich alpha phase (face centered cubic) crystal structure and Sn-rich beta phase (body centered tetragonal) platelets. With Cu present intermetallics of Sn-Cu also tend to occur between the solder and the Cu situated in the pad area. This structure can be clearly seen in Figures 63-70. When Ag and Cu are both alloyed, a secondary intermetallic is formed, this is Ag₃Sn, which can be clearly seen as acicular needles in Figures 64 and 66. The Ag₃Sn needles appear to be more prevalent on the TH-resistor joints than the SM joints, and this could be a direct function of the different cooling rates. The SM 2512 type joints are shown in Figures 63 and 65. A globular phase is present in least concentrations in Figure 66. This phase is the Cu₆Sn₅ phase, and can be observed end on in the lower part of Figure 66.

Typical micro-sections of joints with mixtures of SnAgBiCu and SnPb are presented in Figures 67-70. The SnPb eutectic is widespread in Figure 69 where there is a higher concentration of lead within the solder mixture. Five different elements are present when SnAgBiCu and SnPb are mixed, which results in to many different phases or intermetallic combinations. Many of these cannot be seen optically. It has been shown that the primary phases to form are Sn-Pb eutectic, SnAgCu eutectic, Sn-Cu eutectic, Cu₆Sn₅ phase, Sn-Bi phase, SnAgBiCu quaternary and Ag₃Sn phase. To ascertain the detailed microstructure of such a complex alloy was outside the scope of this work. One common feature of all the joints is the pure tin matrix.

Typical micro-sections of joints with mixtures of SnAgCuBi and SnAgCu are presented in Figures 71 to 74. In essence these alloys are very similar, and have different ratios of the various components of SnAgBiCu. The microstructure in the Figures consists mainly of a Sn matrix with intermediate phases of Sn-Cu and Sn-Ag. A Bi-rich phase can be seen in the TH-resistor, Figure 74; toward the top part of the solder joint. It is interesting to note that the microstructure seen in the TH-Resistors is far more obvious optically than those of the 2512-type resistors, again reflecting the importance of cooling rate. The presence of voids can be seen in the SnAgBiCu / 25%SnAgCu TH-Resistor, shown in Figure 72, concentrated mostly near the resistor. These alloys are less compliant than other alloys and therefore less resistant to TCE mismatch stresses that can be caused by high cooling rates, which hence makes them susceptible to this type of voiding.

Typical micro-sections of joints with mixtures of SnCu and SnAgCu are presented in Figures 75 to 78. There are once again changes in volume concentrations of the ternary alloy SnAgCu. The phases formed were the same as seen in the ternary, i.e. Sn-Cu and Sn-Ag intermetallics. The Ag₃Sn acicular intermetallic can be seen in Figure 76 and 77, distributed within the Sn matrix.
Typical micro-sections of joints with mixtures of SnPbAg and SnAgCu are presented in Figures 79 to 82. These show the Sn-Pb eutectic and a globular like phase, which is more readily visible in the TH-Resistor shown in Figure 80. Generally the microstructure is quite coarse in nature. Again the difference between the TH and SM joints is evident, and the importance of cooling is again made. It is clear that the presence of Pb has a pronounced affect on microstructure, as was apparent in the shear testing.

4.3 SHEAR TESTING.
The results were presented in Figure 83. Mixtures of SnAgBiCu and SnAgCu produced the highest average shear strength values (samples 5 and 6), the highest strength for the mixture containing 75% of the SnAgBiCu alloy. The Bi-containing alloy always had high strength at 0 cycles and this was reflected in the more brittle failure. SnPb-containing mixtures (samples 1-4) all failed in a ductile fashion with relatively lower shear strengths. Pb-free alloys were generally stronger than the Pb-containing alloys. However, the SnCu and SnAgCu mixture had very similar strength to some of the Pb containing alloys.

Clearly the addition of Bi is significant in increasing the strength, although if Pb is present then the Bi concentration needs to be greater than 1.5% for this effect. The data presented here refer only to the visual microstructure, but it is clear from these shear results that Pb and Bi have very different effects on the Sn matrix. While Pb introduces ductility, the Bi induces the exact opposite in behaviour; the Sn matrix also appears to be more sensitive to Bi additions. Results from previous work also suggest that Pb-free alloys are generally stronger than Pb-containing alloys. [4].

5 CONCLUSIONS
This work set out to evaluate the appearance and behaviour of alloy mixtures that occur during rework. The three aspects that are readily quantified; the solder surface finish, the shear strength of the solder joint and the microstructure, have been investigated. Five alloys were used as the starting point and mixed to form 29 different binary alloys in various ratios. The following conclusions were found:

- Generally, there is very little difference in the visual appearance between joints made from Pb-free alloys and their mixtures. Their surface finish is dull and faceted but the joint profile is the same as that for lead-containing alloys. When the lead-containing alloys are added to these lead-free alloys, the surface finish is brighter and smoother with increasing amounts of lead. There were no defects noted that were specific to any alloy or mixture.

- Shear test results have concluded that mixtures containing SnAgBiCu alloy and SnAgCu alloy displayed the highest strengths. Generally, lead-free solder mixtures outperformed lead-containing mixtures. This was most marked when a higher volume of lead-free solders was used in the alloy mix, particularly when Bi was included. Shear strengths were quite acceptable for all alloy mixtures when compared to results obtained previously with the same type of joints with a single alloy [4].
Micro-sectioning studies show that Pb significantly influences the microstructure at the 25% level. The Ag$_3$Sn intermetallic occurs readily in the lead-free alloys, and this is consistent with the higher strength of these alloys. While small additions of Bi have been shown to increase the strength there is no impact on the microstructure at the scale studied here. Further work would be required to determine the number and amount of phases or intermetallics present using EDX and volume fraction analysis.

Further work is planned after these boards have been thermally cycled. Hence, the impact of mixing alloys during rework on the reliability will be assessed.

6 ACKNOWLEDGEMENTS

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7 REFERENCES

8 APPENDIX

8.1 VISUAL INSPECTION

Figure 8: R0603 chip resistor joint using 100% SnAgCu solder

Figure 9: R0603 chip resistor joint using 75%/25% SnAgCu/SnPb solder

Figure 10: R0603 chip resistor joint using 50%/50% SnAgCu/SnPb solder

Figure 11: R0603 chip resistor joint using 25%/75% SnAgCu/SnPb solder

Figure 12: R0603 chip resistor joint using 100% SnPb solder
Figure 13: SOIC joint using 100% SnAgCu solder

Figure 14: SOIC joint using 75%/25% SnAgCu/SnPb solder

Figure 15: SOIC joint using 50%/50% SnAgCu/SnPb solder

Figure 16: SOIC joint using 25%/75% SnAgCu/SnPb solder

Figure 17: SOIC joint using 100% SnPb solder
Figure 18: TH joint using 100% SnAgCu solder

Figure 19: TH joint using 75%/25% SnAgCu/SnPb solder

Figure 20: TH joint using 50%/50% SnAgCu/SnPb solder

Figure 21: TH joint using 25%/75% SnAgCu/SnPb solder

Figure 22: TH joint using 100% SnPb solder
Figure 23: SOIC joint using 100% SnAgCuBi solder

Figure 24: SOIC joint using 75%/25% SnAgCuBi/SnPb solder

Figure 25: SOIC joint using 50%/50% SnAgCuBi/SnPb solder

Figure 26: SOIC joint using 25%/75% SnAgCuBi/SnPb solder

Figure 27: SOIC joint using 100% SnPb solder
Figure 28: SOIC joint using 100% SnAgCuBi solder

Figure 29: SOIC joint using 75%/25% SnAgCuBi/SnAgCu solder

Figure 30: SOIC joint using 50%/50% SnAgCuBi/SnAgCu solder

Figure 31: SOIC joint using 25%/75% SnAgCuBi/SnAgCu solder

Figure 32: SOIC joint using 100% SnAgCu solder
Figure 33: SOIC joint using 100% SnCu solder

Figure 34: SOIC joint using 75%/25% SnCu/SnPb solder

Figure 35: SOIC joint using 50%/50% SnCu/SnPb solder

Figure 36: SOIC joint using 25%/75% SnCu/SnPb solder

Figure 37: SOIC joint using 100% SnPb solder
Figure 38: SOIC joint using 100% SnCu solder

Figure 39: SOIC joint using 75%/25% SnCu/SnAgCuBi solder

Figure 40: SOIC joint using 50%/50% SnCu/SnAgCuBi solder

Figure 41: SOIC joint using 25%/75% SnCu/SnAgCuBi solder

Figure 42: SOIC joint using 100% SnAgCuBi solder
Figure 43: SOIC joint using 100% SnPbAg solder

Figure 44: SOIC joint using 75%/25% SnPbAg/SnAgCuBi solder

Figure 45: SOIC joint using 50%/50% SnPbAg/SnAgCuBi solder

Figure 46: SOIC joint using 25%/75% SnPbAg/SnAgCuBi solder

Figure 47: SOIC joint using 100% SnAgCuBi solder
Figure 48: SOIC joint using 100% SnPbAg solder

Figure 49: SOIC joint using 75%/25% SnPbAg/SnCu solder

Figure 50: SOIC joint using 50%/50% SnPbAg/SnCu solder

Figure 51: SOIC joint using 25%/75% SnPbAg/SnCu solder

Figure 52: SOIC joint using 100% SnCu solder
Figure 53: SOIC joint using 100% SnCu solder

Figure 54: SOIC joint using 75%/25% SnCu/SnAgCu solder

Figure 55: SOIC joint using 50%/50% SnCu/SnAgCu solder

Figure 56: SOIC joint using 25%/75% SnCu/SnAgCu solder

Figure 57: SOIC joint using 100% SnAgCu solder
8.2 MICROSECTIONING
Figure 63. SnAgCu/ 25% SnPb 2512-resistor joint (x360).

Figure 64. SnAgCu/ 25% SnPb TH-Resistor joint (x390).
Figure 65. SnAgCu/ 75%SnPb 2512-resistor joint (x380).

Figure 66. SnAgCu/ 75%SnPb TH-resistor joint (x400).
Figure 67. SnAgBiCu/ 25% SnPb 2512-Resistor joint (x360).

Figure 68. SnAgBiCu/ 25% SnPb TH-Resistor joint (x440).
Figure 69. SnAgBiCu/ 75% SnPb 2512-Resistor joint (x380).

Figure 70. SnAgBiCu/ 75% SnPb TH-Resistor joint (x390).
Figure 71. SnAgBiCu/ 25% SnAgCu 2512-Resistor joint (x370).

Figure 72. SnAgBiCu/ 25% SnAgCu TH-Resistor joint (x400).
Figure 73. SnAgBiCu/75% SnAgCu 2512-Resistor joint (x360).

Figure 74. SnAgBiCu/75% SnAgCu TH-Resistor joint (x380).
Figure 75. SnCu/ 25%SnAgCu 2512-Resistor joint. (x383)

Figure 76. SnCu/ 25%SnAgCu TH-Resistor joint. (x395)
Figure 77. SnCu/ 75%SnAgCu 2512-Resistor joint. (x360)

Figure 78. SnCu/ 75%SnAgCu TH-Resistor joint. (x450)
Figure 79. SnPbAg/25% SnAgCu 2512-Resistor joint. (x387).

Figure 80. SnPbAg/25% SnAgCu TH-Resistor joint. (x410).
Figure 81. SnPbAg/ 75%SnAgCu 2512 Resistor joint. (x390)

Figure 82. SnPbAg/ 75%SnAgCu TH-Resistor joint. (x420).