

Report

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**Measurements of Copper
Dissolution in Lead-Free Sol-
der Alloys**

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C Hunt**

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Industry and Innovation Division

ABSTRACT

The transition from tin-lead to lead-free has increased the tendency for copper dissolution in molten solders. PCB land and plated through holes can be eroded or dissolved away in the presence of molten solder rendering the PCB non-functional. Significant dissolution can potentially occur with certain tin-rich alloys due to increased solubility of copper, which is further exacerbated by higher process temperatures. Clearly this phenomenon represents a serious risk to circuit reliability. To determine the dissolution rate of copper in lead-free solders, a well defined and efficient technique has been developed to compare solder performance.

The first phase of this project developed a measurement method for copper dissolution rates under a variety of conditions and with many different commercial and reference alloys. Here a special PCB design and erosion timing technique was developed. This methodology provided repeatable measurements that allowed the various experimental parameters to be isolated. These findings were tested in a second phase using a circuit board with assembled parts to assess the copper thickness after selective and hand soldering processes performed using various commercial alloys.

The second part of this research aimed at verifying the potential impact on copper dissolution during soldering PCBs of the same type used in production, using single lead-free solder alloys and cored solder wires.

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by Dr M G Cain, Knowledge Leader, Materials Team
authorised by Director, Industry and Innovation Division

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1 LITERATURE REVIEW

1.1 INTRODUCTION

During soldering there is a reaction between the solder and the metallisation of the substrate. The dissolution process occurs through an intermediate phase, an intermetallic that forms at the interface. As the copper is soluble in the tin, the intermetallic forms and grows into the copper substrate, at a rate determined by temperature and Cu concentration at the interface.

This is an essential stage in forming a joint between the two metals. Copper is frequently used as an interconnect on printed wiring boards (PWB) and in component terminations. The dissolution process is temperature and solder alloy dependent. The solubility of copper in the new lead free alloys with tin compositions of at least 95% tin is higher than that of tin-lead solder. The higher melting points of the lead-free alloys also dictate higher processing temperatures, and unusually higher contact times, as the components take longer to heat up to the higher processing temperature. Hence there are a number of factors that contribute to make copper dissolution a more critical problem.

It is appropriate to clarify some terminology; copper dissolution is often referred as copper erosion or copper leaching. In this report the term "copper dissolution" will be referred to as the general phenomenon by which solid copper leaves the bulk when in contact with molten solder, independent of the cause. Copper erosion strictly refers to the purely mechanical removal of copper, whilst copper leaching is a chemical-based dissolution. Copper dissolution is not caused by a single phenomenon but is the effect of a mixture of causes and variables.

1.2 INTERFACIAL PHENOMENA

When a copper substrate is in contact with a molten solder, atoms of the solder will tend to diffuse into the copper, whilst atoms of copper will tend to diffuse into the molten metal. The Nernst Brunner equation, often referred as Dybkov's analysis was found to be valid to explain this part of the dissolution process.

$$\frac{dc}{dt} = k \frac{S}{V} (c_s - c) \quad (1)$$

where c_s is the solubility of copper in the molten solder at the specific temperature, c is the concentration of copper in the solder, S is the surface area of the copper, V is the volume of the molten solder and k is a constant [1, 2, 3]. The solubility of copper (function of temperature) is the first of a long series of variables that are important for the dissolution phenomenon.

The copper dissolution process forms a boundary layer, or intermetallic, on the copper, which is an alloy of copper and tin. Diffusing copper atoms form the intermetallic with tin atoms diffusing in from the solder. The first intermetallic to form is Cu_6Sn_5 (η). Underneath this layer another intermetallic forms, Cu_3Sn (ϵ phase) due to reaction of copper with η phase. This second ϵ layer however will be thinner and the η phase will constitute most of the intermetallic layer thickness. The microstructure of these two compounds is also different: η has a scalloped morphology, whilst ϵ forms an undulated

layer [5]. Microstructure plays a role in copper diffusion, with a coarsening of the η grains reducing the number of grain boundaries, therefore decreasing possible diffusion paths for copper [1]. Grain boundary diffusion is the predominant mechanism for intermetallic growth and has a great influence on the copper dissolution rate [2]. The morphology of the intermetallic is important, and can fully, or just partially cover the copper [6].

The intermetallic growth rate will be dependent on the copper diffusion rate [7]. The Cu-Sn atoms in the intermetallic are soluble in the solder due to the thermal energy and their relatively high diffusivity [8]. The η intermetallic phase has a higher melting point than that of tin or eutectic Sn/Cu, and hence has a lower dissolution rate. This suggests that a uniform layer of this phase at the interface can reduce the formation rate of further intermetallic, and hence reduce copper dissolution [9].

The balance between the intermetallic formation, its microstructure and morphology is probably the most limiting step in controlling the whole dissolution process.

1.3 THE EFFECT OF THE SOLDER

The type of solder used in the process has an important effect on the dissolution rate of copper. From equation 1, it can be observed that increasing the amount of copper in the solder, the dissolution rate will be reduced because of diffusion effects [1, 3]. If the amount of solder is limited and the bath condition is static the amount of copper in the solder will increase more rapidly and further dissolution will decrease.

Lead-free solder alloys contain mainly tin and a small amount of various elements such as Cu, Ag, Ni, Bi, In, Zn, Sb and small amounts of Pb. Many of these can form intermetallics that can attach to the surface of the copper intermetallic. For example Ag, which is commonly used in the SAC alloys, forms the Ag_3Sn intermetallic. This tends to precipitate near the interfacial intermetallic and be "absorbed" by this layer, hence reducing the interfacial energy. It has been observed that in presence of Ag_3Sn the intermetallic layer does not grow as thick as that formed with just Sn/Cu [2].

It has been suggested that elements such as Sb and Bi could reduce the dissolution by diluting the tin-rich solder [4]. The other elements are likely to affect the intermetallic layer as well, but the effect of each of these has not been reported in literature in a detailed way.

Different solder compositions will have different melting temperatures; hence the optimal operating temperature for each alloy will be different and the copper dissolution rate will be affected. Typically for higher temperatures, the copper dissolution rate is greater for two main reasons: firstly, the saturated copper concentration increases with temperature; secondly the dissolution rate follows Arrhenius behaviour:

$$K = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where K is the dissolution rate, A a constant independent of temperature, E_a the activation energy and R the gas constant [4, 3].

1.4 THE EFFECT OF FLOW RATE

It is reasonable to think that in a bath where the solder is static the concentration of copper in the solder near the interface increases with time and hence the dissolution rate decreases due to reduced diffusion. In flowing solder the dissolved copper will be continuously swept away from the interface, leaving the copper concentration $c_s - c$ of equation 1 unchanged.

The flow rate of solder is an important parameter, and it has been observed that copper dissolution rate is highly dependent on flow conditions [10]. In fact, a highly turbulent flow generates mechanical erosion of the copper surface (or more accurately of the intermetallic)[11]. The flow rate and flow type in the solder bath depend on many different variables, such as machine geometry and type, pump speed and solder viscosity. Different types of soldering machines, for example rework fountains and wave soldering systems, present very different types of flow, depending on their construction and operating conditions. For this reason, dissolution rates can be very dissimilar, even when operating at the same temperature. Varying the pump speed is the easiest way to change the flow rate and type, however not all machines allow this to be controlled. If the pump speed is fixed, then the flow rate can be varied only by changing the operating temperature, and hence the solder viscosity. Figure 1 shows the viscosity of tin dependence with temperature.

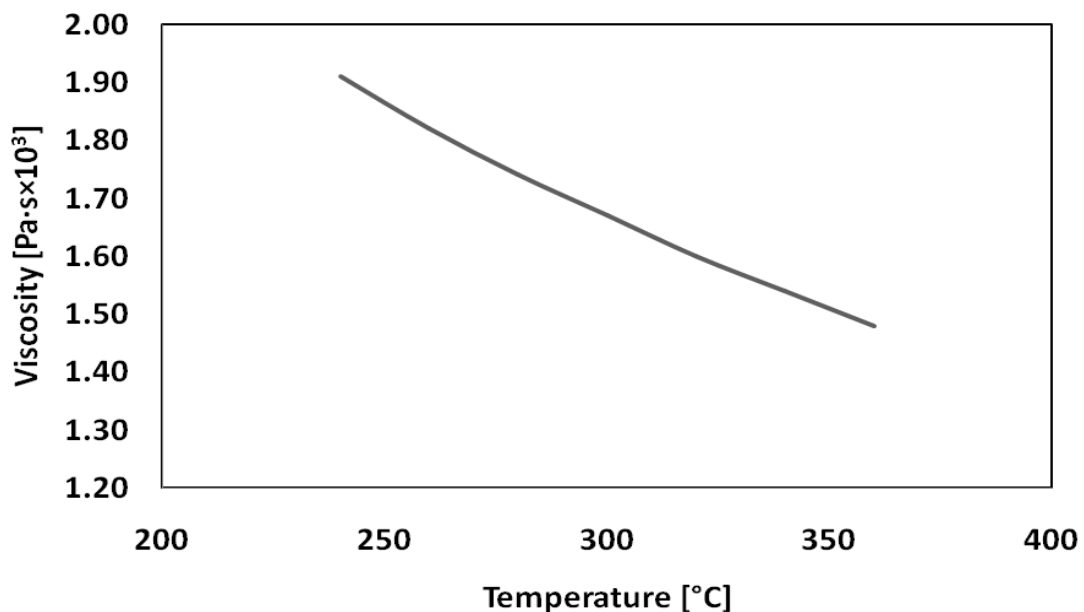


Figure 1: Viscosity of tin as a function of temperature (from “The Absolute Measurement of The Viscosity Of Liquid Tin” A J Lewis 1936
Proc. Phys. Soc. 48 102-110 doi: 10.1088/0959-5309/48/1/315)

1.5 COPPER RELATED VARIABLES

The form of the copper and how it is presented to the molten solder, can affect its dissolution rate. An important consideration is preheating, which can reduce dissolution by reducing the solder contact time. Hamilton *et al.* however found preheat had little impact in influencing dissolution [11], but this finding assumed a constant soldering time.

Copper geometry has been found to be significant, as this affects the solder flow and thermal conditions in specific regions of the PCB. It was found in particular that dissolution rate is highest at the knee of a plated through hole (PTH), lower on the pad and lowest on the inner barrel. Variability in dissolution rates was found due to the position of the PTH relative to the component. PTHs more central to the component were generally found to be more susceptible to dissolution due to an increased turbulent flow in this region [11, 12].

Potentially the type of copper microstructure can affect its dissolution resistance. Despite large variations in the performance of different copper types being observed [13], not many researchers have investigated this factor. Some early findings however, seem to suggest that there is no correlation between microstructure/mechanical properties and dissolution propensity [13,14].

Copper is often protected with a surface finish. It is reasonable to suppose that this can have an effect in protecting the copper delaying initial dissolution. It has been observed that a Ni plated finish could reduce the occurrence of copper dissolution [4, 11]. The presence of flux before soldering can affect the early stages of the reactions, by removing the surface oxide on the copper and making the surface very active with the formation of kink sites, which will preferentially adsorb tin [8]. The activity of the flux must then play a role in the early stages of the dissolution as it contributes to the activation of the copper surface.

1.6 FINAL CONSIDERATIONS

A summary of the factors influencing copper dissolution, and their complex relationships is shown in Figure 2. In this figure, an arrow pointing from one factor to another indicates that the first factor influences the second factor. The figure clearly shows a study of this phenomenon is complex, particularly since the variables are not independent of each other. While many variables are temperature dependent (such as intermetallic formation/dissolution, and solubility of copper) others are not (e.g. geometry of the copper, solder type). Many authors consider time as a variable. However all the phenomena involved in this process are time dependent. For this reason the rate of copper dissolution rate is studied here, eliminating time as a variable.

Optimising a soldering process to take into account all these variables, although difficult, would be possible. A complete analysis would consider soldering machine types, and consider the effect of the chosen conditions on solderability and mechanical performance of the solder joints, but falls beyond the scope of this research.

Instead, this work focuses on some of the key variables, utilising the development of a simple testing system that permits a quantitative comparison of the performance of different alloys.

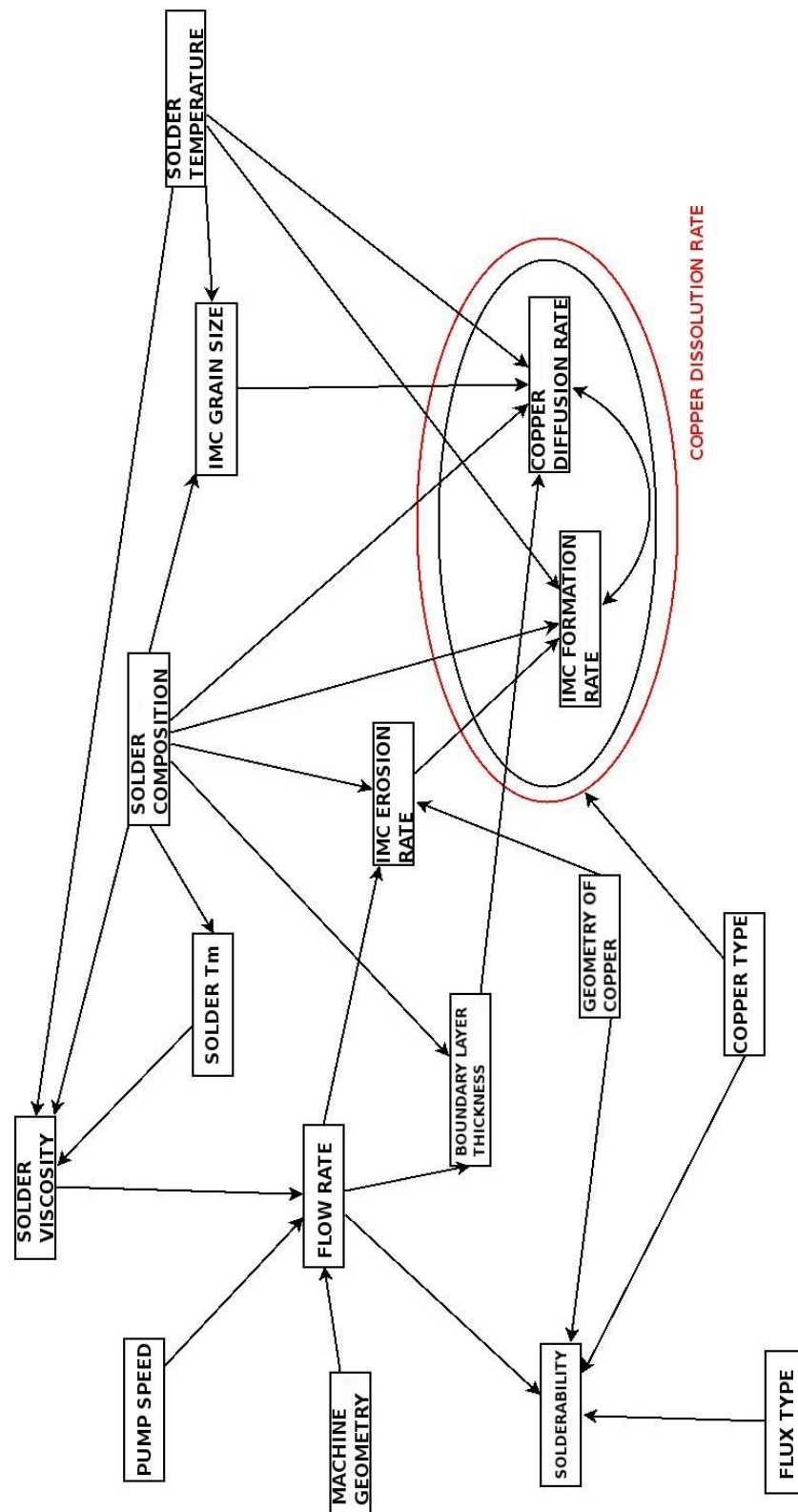


Figure 2: The factors influencing copper dissolution.

2 DISSOLUTION TESTS ON COPPER WIRES AND FOILS IN A STATIC AND FLOWING SOLDER

2.1 INTRODUCTION

Initially the effect of temperature on copper dissolution with common binary alloys was studied, using simple geometries of copper wires and foils. This provided the opportunity to develop the experimental set up and repeatability.

2.2 EXPERIMENTAL SETUP

2.2.1 Description of the soldering equipment

The soldering machine used for the tests was an ACE Automated Soldering Machine - KISS 102TM. A photograph of this equipment is shown in Figure 3.



Figure 3: ACE soldering machine used for copper dissolution tests.

The manufacturer describes the machine as an automated, simple to use, low cost bench-top selective soldering machine using a travelling mini-solder wave. A large number of parameters can be computer controlled including immersion depth, pre-heat dwell, travel distance and speed, solder temperature and wave height. The operator places the PCB onto the location rails and starts the automated cycle. The cycle begins by applying flux (optional) to all the programmed sites. During the next phase, the mini solder wave moves under the component to be soldered. The pot, which can contain 13 kg of solder, rises to “wet” the first pins. The solder wave travels the length of the component, soldering all the through hole leads on the component to the PCB. At the completion of the travel the solder pot lowers and moves to the next site. The solder pot is fed with nitrogen gas to minimise dross formation. Different nozzle sizes could be chosen and the solder flow from the nozzle can be observed using a camera system.

2.2.2 Samples and experimental conditions

For these preliminary experiments the following samples were used:

- Copper foils: 12, 18, 36 mm thick
- Copper wires: 0.1, 0.3, 0.5 mm in diameter

Three nominal eutectic alloys were used for these tests to act as a benchmark for future commercial alloys:

- SnPb
- Sn3.5Ag
- SnCu

The tests were performed at three fixed temperatures: 260, 275, 300 °C. The pump speed of the solder fountain was kept at a fixed value (indicated value of 720 on the machine's display).

2.3 EXPERIMENTAL PROCEDURE

The experimental arrangement for copper foils and wires is shown in Figures 4 and 5. The foils were held in simple clamps. The wire was fixed on one side, with a weight attached to the other side, holding the wire taught and provided an easy indication of complete dissolution.

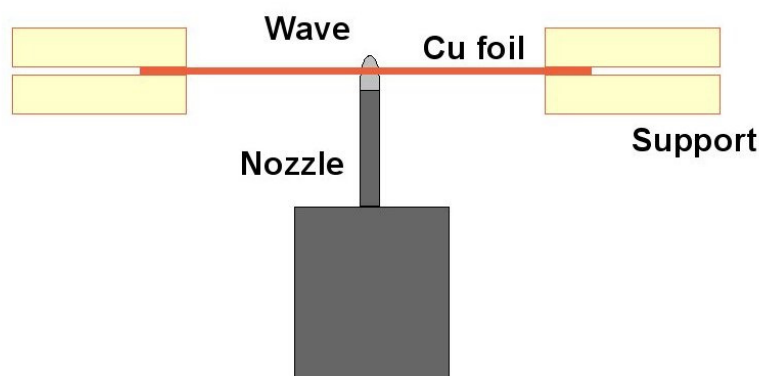


Figure 4: Experimental setup for testing copper foils

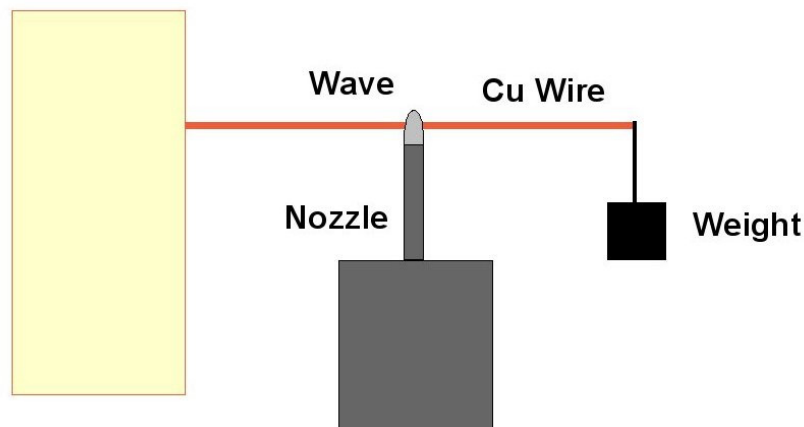


Figure 5: Experimental setup for testing copper wires

The experimental procedure for both copper foils and copper wires was very similar. A water-based flux was first applied to the samples, which were then introduced to the wave. At this point a timer was started. The solder wave progressively dissolved the copper causing the rupture of the wire or the erosion of a hole in the foil. Each solder was tested with the wire and foil samples, and there were 5 repeat measurements at each set temperature.

2.4 EXPERIMENTAL RESULTS

Results of the dissolution times for the copper foils and wires are shown in Figure 6. The left column shows the results for the copper foils and the right column refers to the copper wires. Experimental data are tabulated in Table 1.

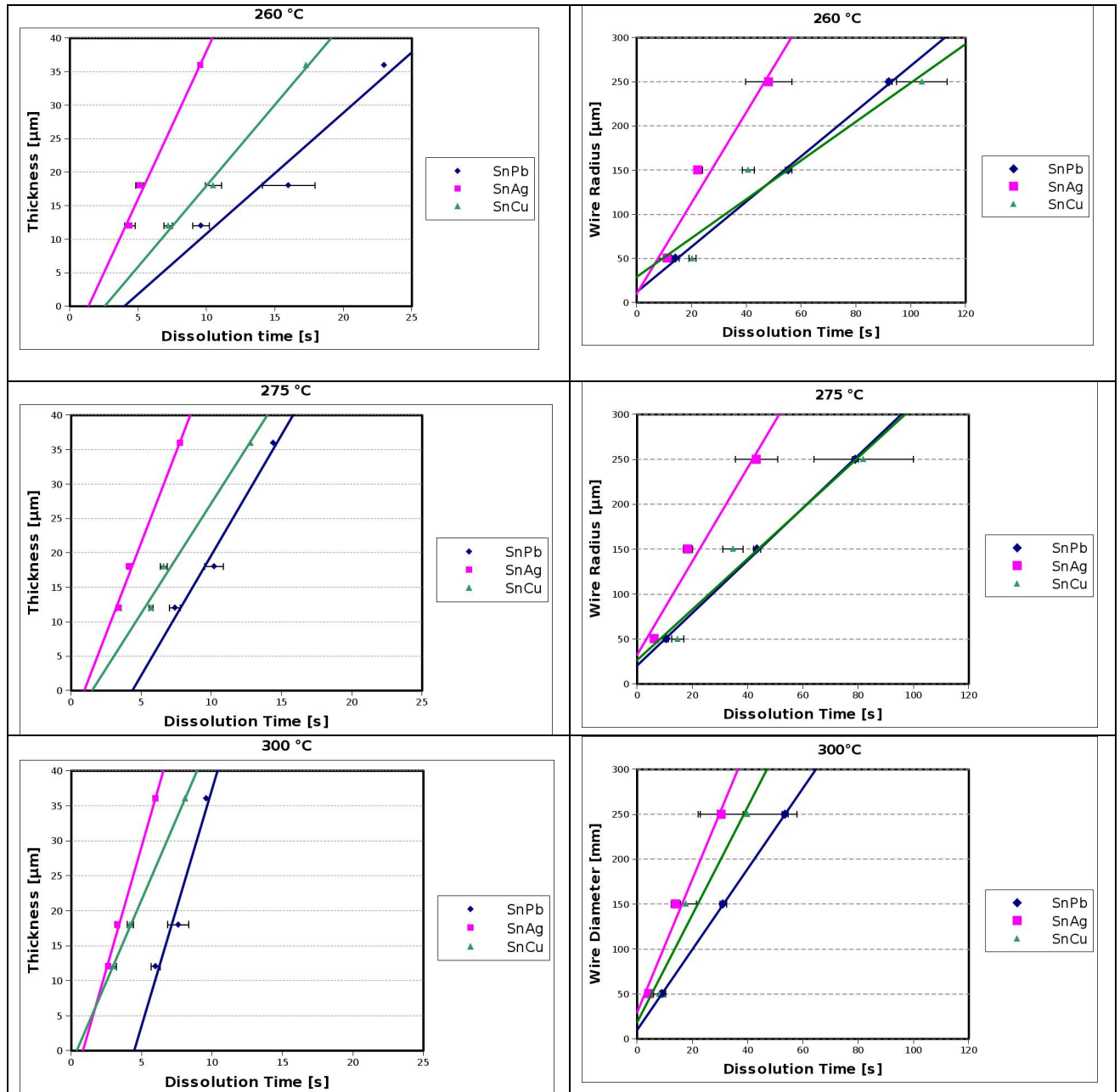


Figure 6: Dissolution times for copper foils (left) and copper wires (right) SnPb, SnAg, SnCu.

Table 1a: Dissolution times (seconds) for copper foils

SnPb/ Thickness	12μm	18μm	36μm
260 °C	9.6 ± 0.6	16 ± 1.9	23 ± 1.2
275 °C	7.4 ± 0.4	10.2 ± 0.7	14.4 ± 3.6
300 °C	6 ± 0.3	7.6 ± 0.7	9.6 ± 0.9
SnAg/ Thickness	12μm	18μm	36μm
260 °C	4.4 ± 0.4	5.1 ± 0.3	9.6 ± 0.2
275 °C	3.4 ± 0.2	4.1 ± 0.1	7.8 ± 0.6
300 °C	2.6 ± 0.2	3.3 ± 0.1	6 ± 0.3
SnCu/ Thickness	12μm	18μm	36μm
260 °C	7.2 ± 1.2	10.5 ± 1.9	17.3 ± 1.0
275 °C	5.7 ± 0.8	6.6 ± 1.2	12.8 ± 1.1
300 °C	3.0 ± 0.7	4.2 ± 1.5	8.1 ± 0.7

Table 1b: Dissolution times (seconds) for wires.

SnPb/ Diameter	100 μm	300 μm	500 μm
260 °C	14.2 ± 1.2	55.4 ± 1.2	92.2 ± 1.0
275 °C	10.6 ± 0.8	43.4 ± 1.2	79 ± 1.1
300 °C	9 ± 0.7	31.2 ± 1.5	53.6 ± 0.7
SnAg/ Diameter	100 μm	300 μm	500 μm
260 °C	11.2 ± 2.8	22.4 ± 1.6	48.2 ± 8.5
275 °C	6.2 ± 1.0	18.4 ± 1.7	43.2 ±
300 °C	4.2 ± 0.2	14 ± 0.1	30.6 ± 0.3
SnCu/ Diameter	100 μm	300 μm	500 μm
260 °C	20.3 ± 1.3	40.8 ± 2.2	104.1 ± 9.2
275 °C	14.8 ± 2.2	34.7 ± 3.7	82.0 ± 7.9
300 °C	8.2 ± 0.6	17.8 ± 0.6	39.9 ± 7.3

2.5 DISCUSSION

The slope of dissolution time/thickness, dissolution time/radius curves (for the foils and the wires respectively) gives the dissolution rate (apart from some geometry corrections). The dissolution rates obtained from the tests are shown in Figure 7. The SnAg curves are very similar for both foils and wires but that is not the case for SnPb and SnCu. The reason for this discrepancy is not clear. The instrument was used with the same setting for pump speed for all tests. However it became apparent analysing these results and checking the experimental setup that the solder volume in the pot was not the same in all cases. It was later observed that for this reason, different solder flow rates were occurring, causing additional variability. The important points from these experiments were:

- Dissolution rate increases with temperature and has a linear behaviour, independent of the two geometries used.
- The SnAg alloy has the highest copper dissolution rate, at all the temperatures tested.
- When making dissolution measurements the solder flow rate should be kept constant when comparing different alloys.

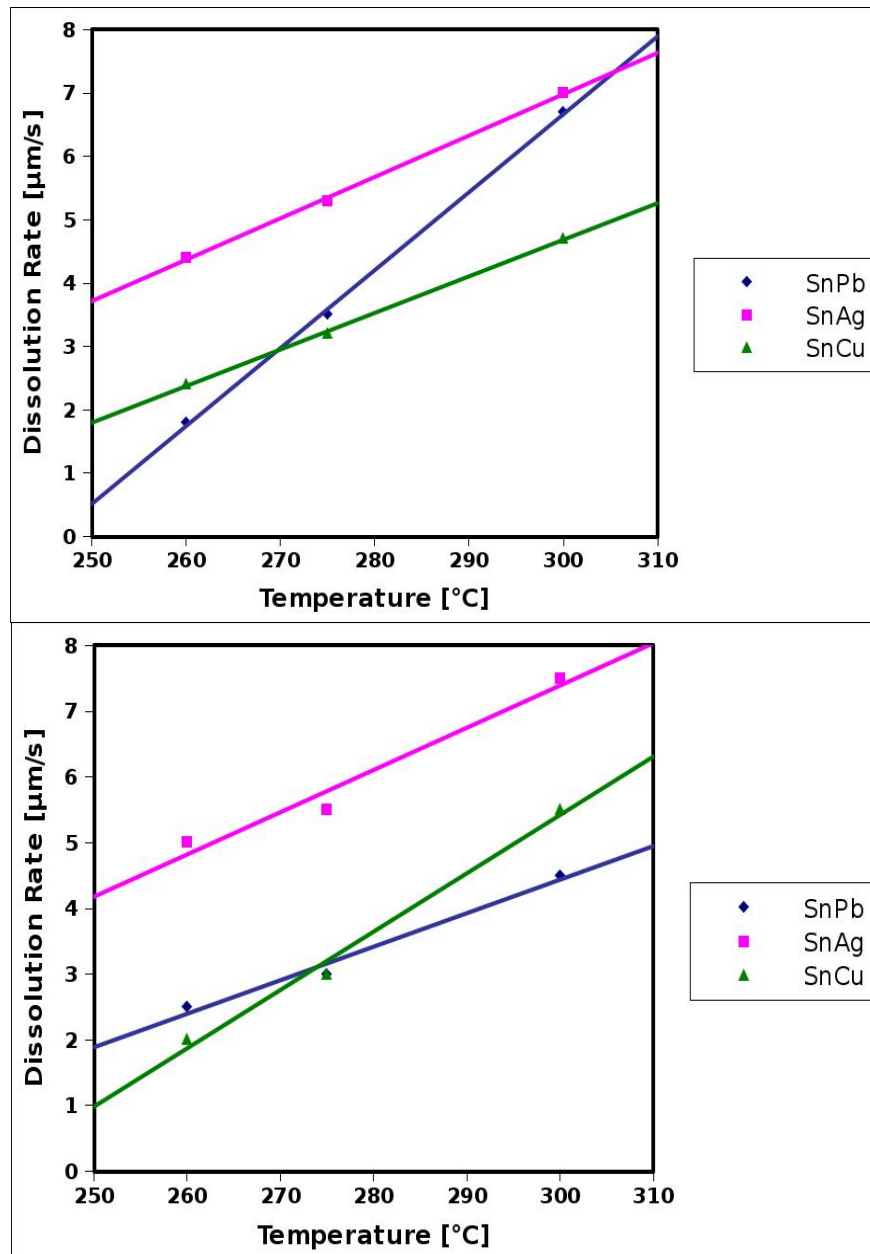


Figure 7: Dissolution rates for copper foils (above) and wires (below) on SnPb, SnAg, SnCu.

3 PCB DESIGN AND TESTS ON THE EFFECT OF FLOW RATE

3.1 INTRODUCTION

One of the aims of this study is the development of a simple testing method that can be universally employed in a variety of conditions and with different soldering processes. In order to perform the study on a sample similar to that used in industry, a special test PWB was designed, as shown in Figure 8. The PCB was a 2.5 mm thick FR4, with 10 copper test pads on the underside. The test pads can also be accessed from the top side through holes on the PCB. The bottom side shows small dimples where the copper is unsupported, and the hole can be clearly seen from the top view. Another requirement of the testing method was an automated detection of the dissolution time, minimising errors. The contact for the timing probe can easily be inserted into the hole, ensuring the sensor is always at the same height.

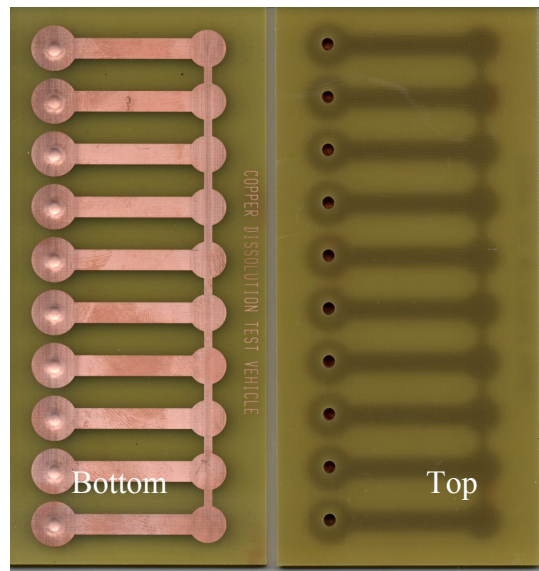


Figure 8: Test Vehicle

3.2 TESTING PROCEDURE

A schematic of the test set up is shown in Figure 9. The timing sensor was attached to the top of the PCB using a block and a screw. The screw was adjusted to be less than 1mm from the back of the copper pad. This assembly is connected to pin 6 of a serial port. This is also connected to pin 4 through a $2.2\text{k}\Omega$ resistor. Pin 5 of the serial port corresponds to ground and if the computer is powered by the mains, this is at the same value as the solder pot. The copper plating on the PCB is connected to pin 8 of the serial port.

A simple software program initially sets pin 6 and 8 to be high, using pin 4. When the solder touches the copper pad, pin 8 is grounded and starts the timer. When the solder penetrates through the copper and touches the screw, pin 6 is grounded and this signal stops the timer.

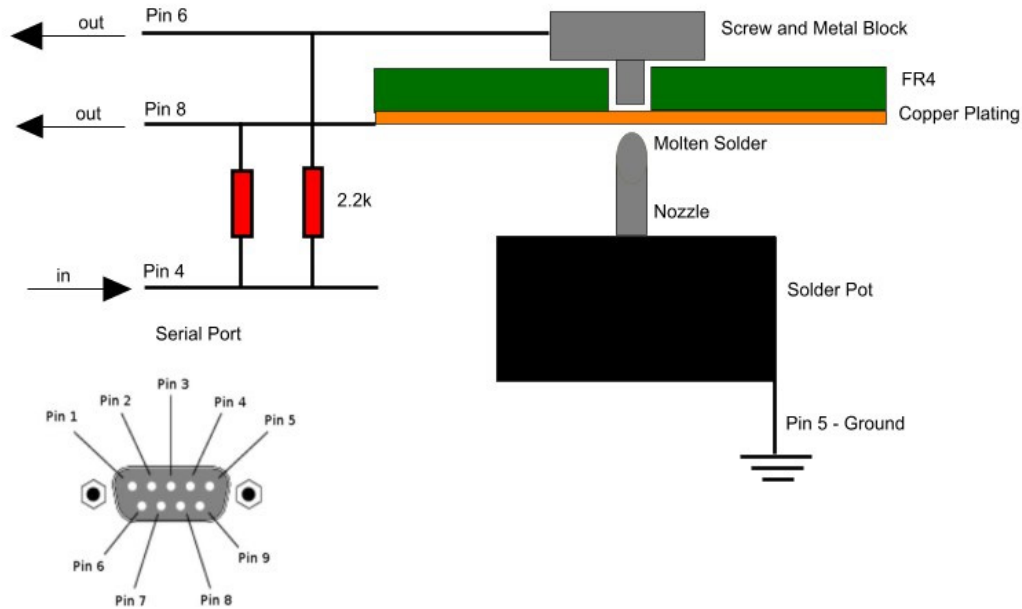


Figure 9: Experimental set up of timing method

3.3 THE EFFECT OF FLOW RATE ON COPPER DISSOLUTION

In Section 2.4 it was deduced that the molten solder flow rate plays an important role in the copper dissolution process. This is mainly due to the erosion effect on the intermetallic and the transport of dissolved copper away from the interface. Here quantitative measurements were performed to study the effect of increasing flow rate on copper dissolution.

3.3.1 Samples and Experimental Conditions

The flow rate tests were performed using the SnAg alloy with a PCB coupon in position. Two sets of tests were performed: First at a constant temperature of 275 °C and variable pump speeds. Second, sets of experiments were performed at 255, 275 and 300 °C, with three machine pump speed settings of 700, 730 and 760 (arbitrary units).

For these experiments the flow rate was measured by collecting the solder over fixed time intervals, and weighing the collected solder. The experimental set up is shown in Figure 10.

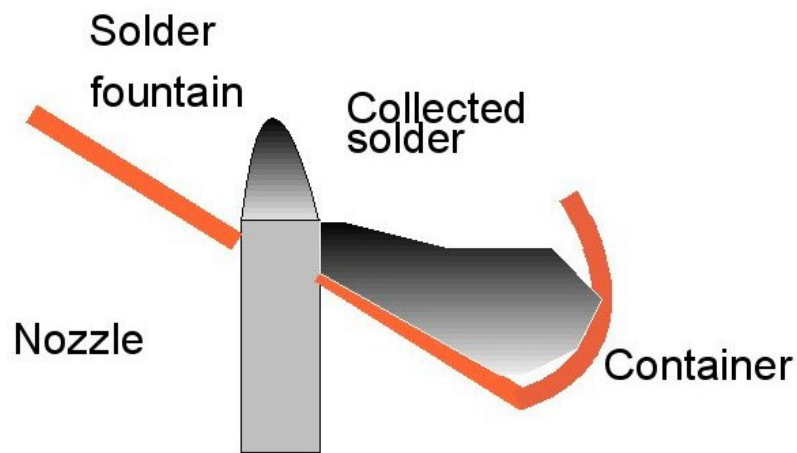


Figure 10: Solder collection for measuring the flow rate.

3.3.2 Experimental Procedure

The testing procedure described in Section 3.2 was used for this test. Before testing each board was fluxed using a water based flux. One board, and hence 10 test pads, was used for each test condition.

3.3.3 Results

The dissolution rates for the tests of the SnAg solder at 275°C and different pump speed settings are shown in Figure 11. The rate was calculated using an average copper thickness of 34 μm . Figures 12 and 13 show flow rate effects at 255, 275 and 300 °C.

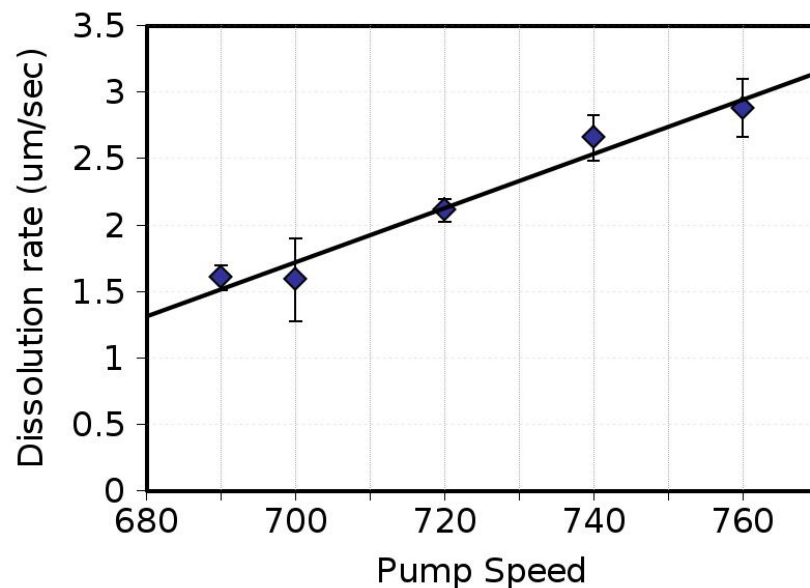


Figure 11: Dissolution rate of copper in SnAg versus pump speed at 275°C.

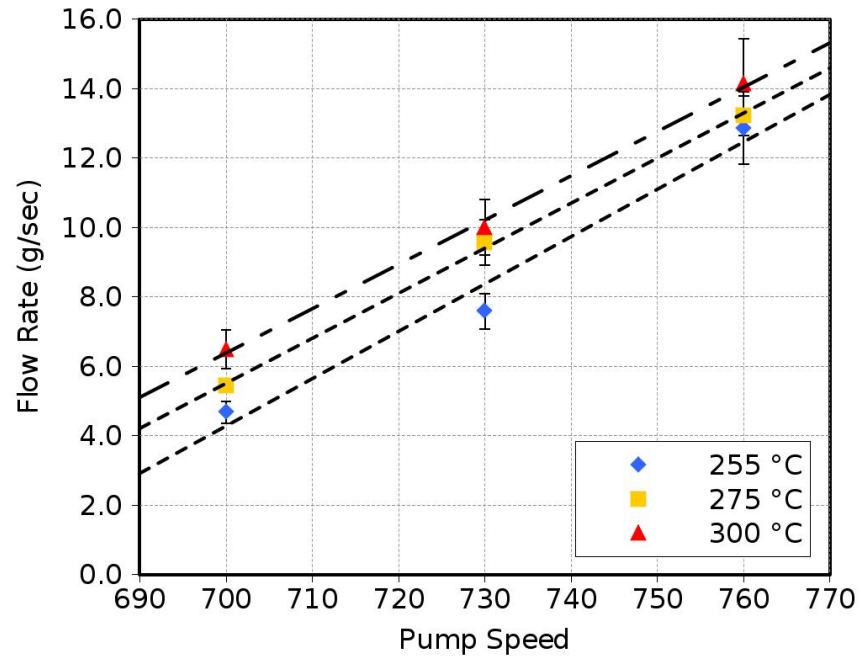


Figure 12: Flow rate dependency with pump speed.

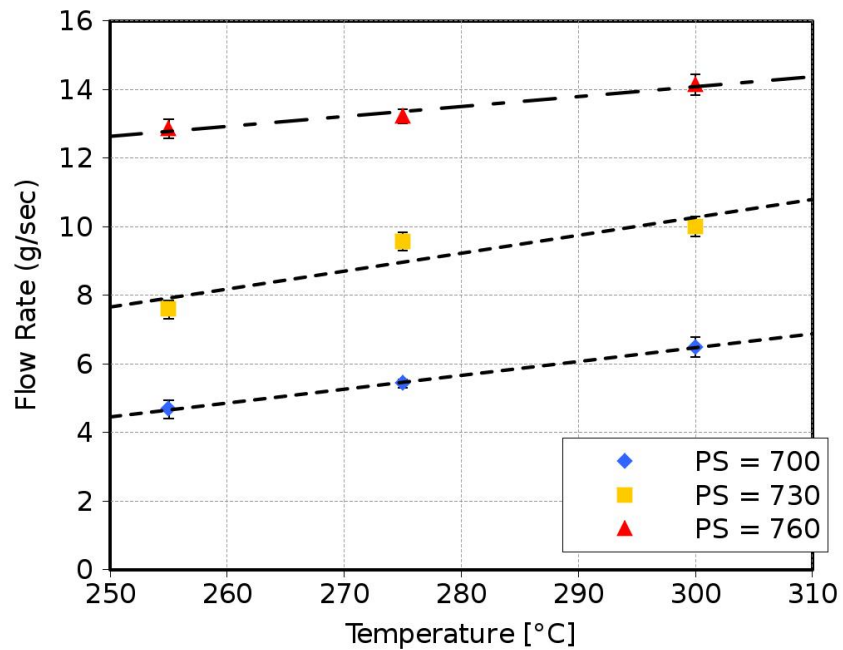


Figure 13: Flow rate dependency with temperature.

3.4 DISCUSSION

Figures 11, 12 and 13 show that:

- The dissolution rate increases linearly with pump speed.
- Flow rate increases linearly with pump speed and temperature.

The flow rate was found to have a significant influence on dissolution rate. Figures 11 and 12 show that a change in pump speed from 700 to 760 has an effect on copper dis-

solution that is as dramatic as changing the temperature from 260 to 300 °C (see Figure 7). Pump speed setting alone is not enough to determine the flow rate, as this is dependent on temperature and solder alloy composition. Compositional changes will cause the melting temperature to change, and hence variations in viscosity. We note here that if a larger nozzle was used and the same flow rate maintained, there will be a change in velocity. Solder velocity will be even more difficult to measure than flow rate, but may give a better correlation with dissolution, especially when comparing results between different machine types.

Some commercial machines use the solder wave height as a measure for flow rate. This approach will only be relevant for a specific machine type, since machine issues such as nozzle design will be specific to the machine, and the wave height will also be a function of the alloy fluidity. **Generally, no solder machines measure or indicate flow rate, a key parameter for copper dissolution.**

4 TESTS OF DISSOLUTION RATES ON COMMERCIAL LEAD-FREE SOLDER ALLOYS

4.1 INTRODUCTION

The test methodology developed in the previous section was now broadened to study a range of commercially available alloys to demonstrate that the approach developed could be used to quantify copper dissolution rates across a wider range of alloys.

4.2 SAMPLES AND EXPERIMENTAL CONDITIONS

Several commercial alloys were tested in this phase (indicated with the letters A-G). An elemental analysis of these alloys was performed by Butterworth Laboratories ¹ using inductively coupled plasma – atomic emission spectroscopy (ICP-AES).

Tests were performed at 3 temperatures: 255, 275 and 300 °C. Before performing the actual test, the flow rate behaviour of each alloy was measured at each temperature and at 3 different pump speed settings, 700, 730, 760, as described in 3.3.1. A flow rate of 1.35 cm³/s was selected, and was found to work well with all alloys and corresponded to a typical wave, as suggested by the selective soldering machine manufacturer, achieving the necessary height, without being too turbulent.

¹ Butterworth Laboratories Limited. 54-56 Waldegrave Road, Teddington, TW11 8NY, UK.
www.butterworth-labs.co.uk

%	Ag	Bi	Cu	Co	Ni	Pb	Sb	Al	Cd	Fe	In	Zn
A (before)	0.050	<0.01	0.626	0.050	<0.01	0.050	0.020	<0.01	<0.01	<0.01	<0.01	<0.01
A (after)	0.050	<0.01	0.630	0.060	<0.01	0.050	0.020	<0.01	<0.01	<0.01	<0.01	<0.01
B (before)	0.024	<0.01	0.513	0.081	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B (after)	0.020	<0.01	0.520	0.014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
C (before)	1.90	<0.01	0.748	<0.01	<0.01	0.030	0.560	<0.01	<0.01	<0.01	<0.01	<0.01
C (after)	1.90	<0.01	0.840	<0.01	<0.01	0.030	0.570	<0.01	<0.01	<0.01	<0.01	<0.01
D (before)	0.030	<0.01	0.660	<0.01	0.053	0.018	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
D (after)	0.030	<0.01	0.660	<0.01	0.053	0.018	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
E (before)	0.338	<0.01	0.720	<0.01	<0.01	0.030	0.011	<0.01	<0.01	<0.01	<0.01	<0.01
E (after)	0.262	<0.01	0.735	<0.01	<0.01	0.030	0.011	<0.01	<0.01	<0.01	<0.01	<0.01
F (before)	3.700	<0.01	0.730	<0.01	<0.01	0.030	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
F (after)	3.600	<0.01	0.715	<0.01	<0.01	0.030	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
G (before)	0.301	0.090	0.682	<0.01	<0.01	0.016	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
G (after)	0.307	0.092	0.682	<0.01	<0.01	0.016	0.017	<0.01	<0.01	<0.01	<0.01	<0.01
H (before)	0.210	<0.01	0.683	<0.01	0.040	0.030	0.010	<0.01	<0.01	<0.01	<0.01	<0.01
H (after)	0.280	<0.01	0.690	<0.01	0.040	0.030	0.010	<0.01	<0.01	<0.01	<0.01	<0.01
SnPb	<0.01	<0.01	<0.01	<0.01	<0.01	39.66	0.010	<0.01	<0.01	<0.01	<0.01	<0.01
SnAg	4.100	<0.01	<0.01	<0.01	<0.01	0.012	0.018	<0.01	<0.01	<0.01	<0.01	<0.01

Table 2. Composition of the alloys used for the tests (most alloys were tested before and after the test).

4.3 EXPERIMENTAL RESULTS

The results in Figure 14 show the pump speed setting for each alloy at each temperature. The results show that a linear progression was not always observed. This maybe due to variations in the solder volume in the reservoir, as noted earlier.

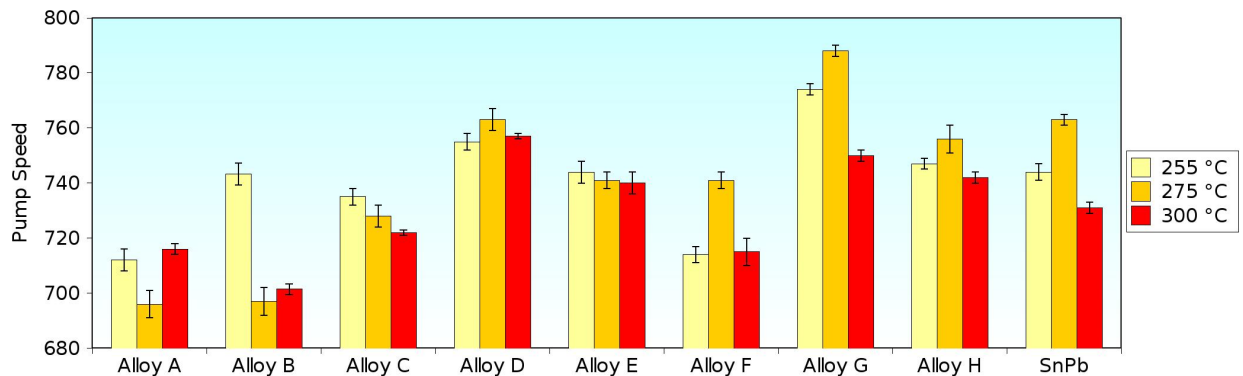


Figure 14: Pump speed used for the tests on commercial alloys.

The dissolution rates for the various alloys can be seen in Figures 15, 16 and in Table 3.

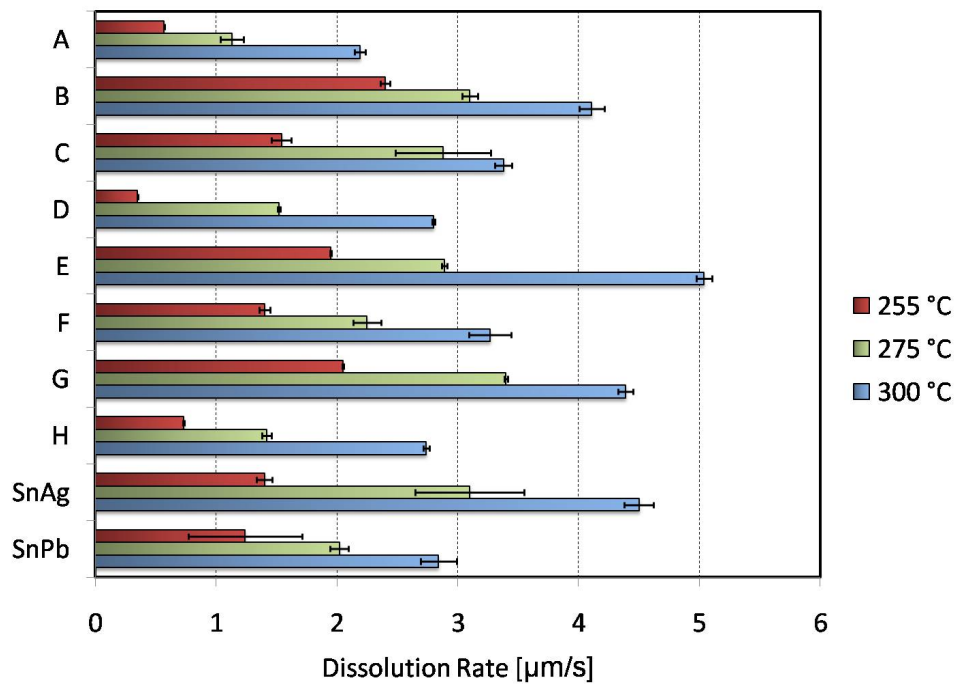


Figure 15. The dissolution rate of the alloys at the temperatures of 255, 275 and 300 °C.

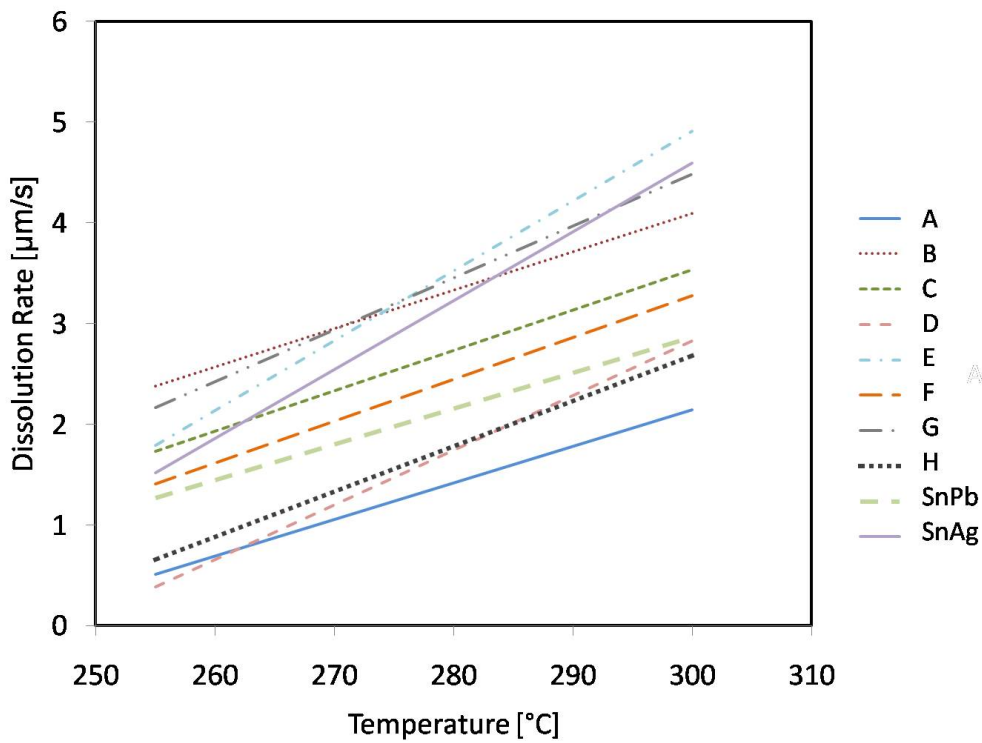
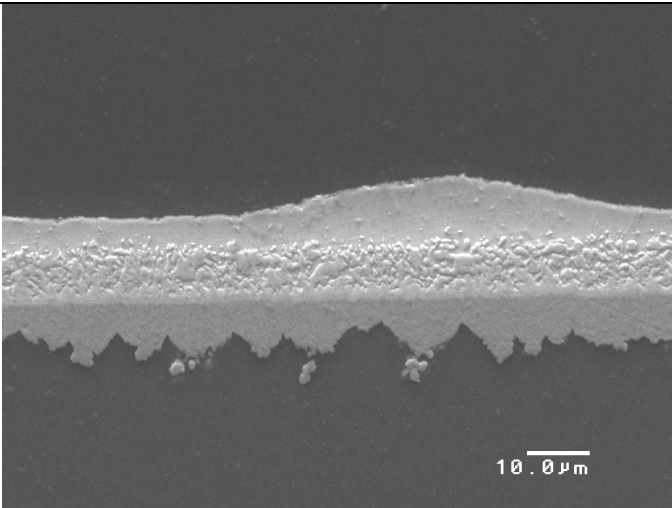
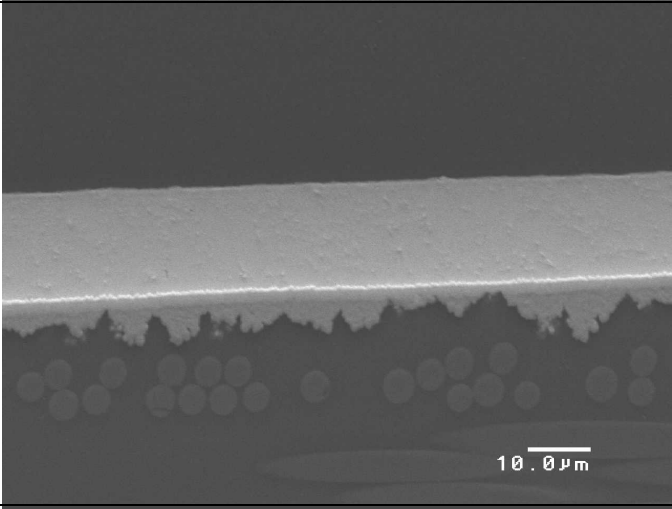
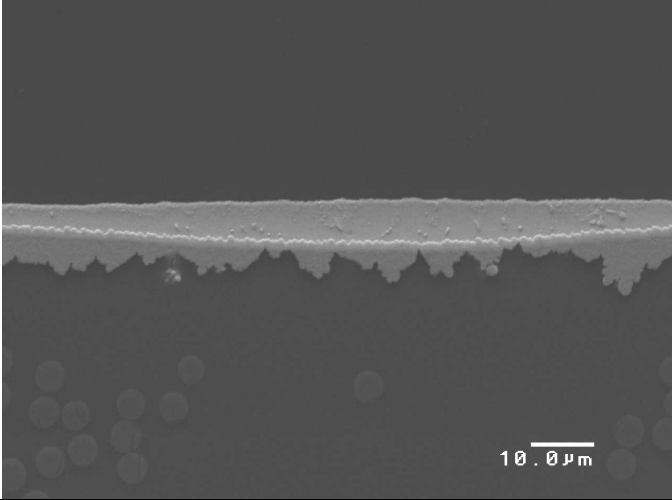


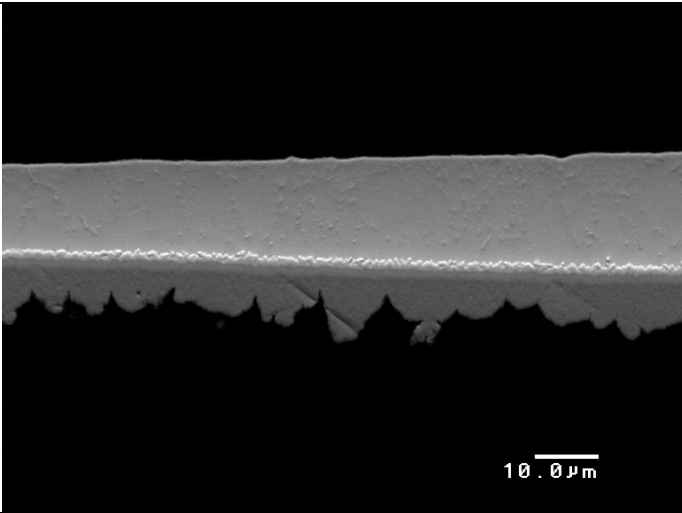
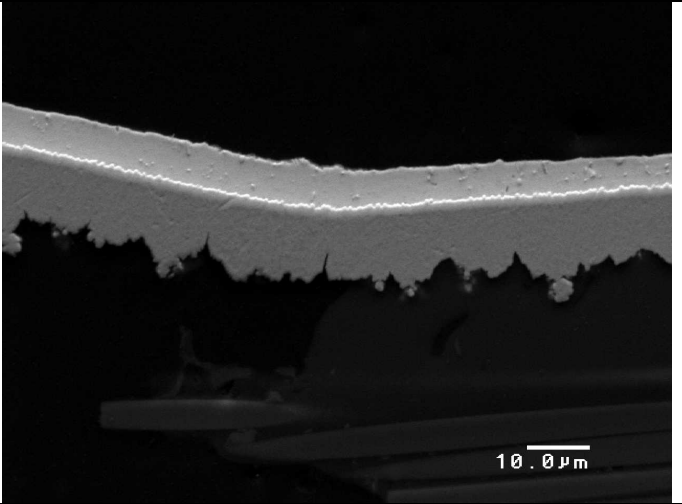
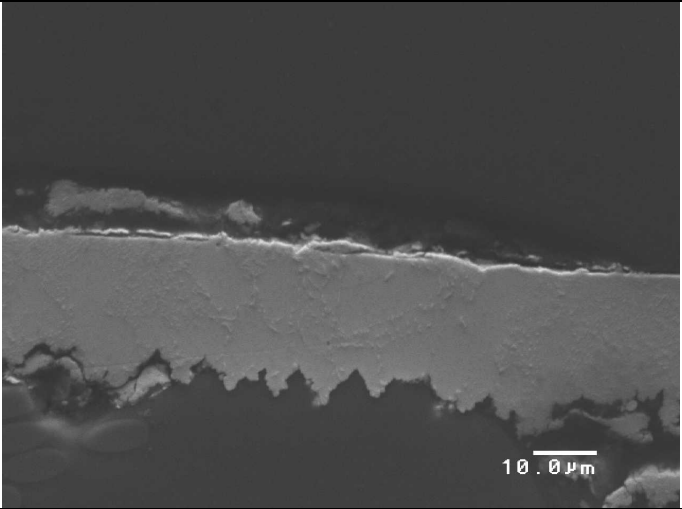
Figure 16. Linear fitting of the dissolution rate of the solder alloys.

Table 3: Dissolution rates of the commercial alloys tested here (mean and standard error are shown).

Alloy	255 °C [$\mu\text{m/s}$]	275 °C [$\mu\text{m/s}$]	300 °C [$\mu\text{m/s}$]
Alloy A	0.57 $\pm$ 0.01	1.13 $\pm$ 0.19	2.19 $\pm$ 0.09
Alloy B	3.10 $\pm$ 0.01	4.13 $\pm$ 0.50	5.28 $\pm$ 0.10
Alloy C	1.54 $\pm$ 0.16	2.88 $\pm$ 0.20	3.38 $\pm$ 0.14
Alloy D	0.35 $\pm$ 0.01	1.52 $\pm$ 0.02	2.90 $\pm$ 0.02
Alloy E	1.95 $\pm$ 0.01	2.89 $\pm$ 0.05	5.04 $\pm$ 0.13
Alloy F	1.40 $\pm$ 0.09	2.25 $\pm$ 0.23	3.27 $\pm$ 0.35
Alloy G	2.05 $\pm$ 0.01	3.40 $\pm$ 0.03	4.39 $\pm$ 0.12
Alloy H	0.73 $\pm$ 0.01	1.42 $\pm$ 0.08	2.74 $\pm$ 0.05
SnPb	1.24 $\pm$ 0.94	2.02 $\pm$ 0.15	2.84 $\pm$ 0.30

Microsections of samples after testing were undertaken and backscattered SEM images used to measure intermetallic thickness (see Figure 17). These are summarised in Figure 18.

Alloy A	 Scanning electron micrograph (SEM) showing a cross-section of Alloy A. The image displays a layered structure with a dark, granular top layer, a lighter, more uniform middle layer, and a dark, jagged bottom layer. A scale bar in the bottom right corner indicates 10.0 μm.
Alloy B	 Scanning electron micrograph (SEM) showing a cross-section of Alloy B. The image displays a layered structure with a dark, granular top layer, a lighter, more uniform middle layer, and a dark, jagged bottom layer. A scale bar in the bottom right corner indicates 10.0 μm.
Alloy C	 Scanning electron micrograph (SEM) showing a cross-section of Alloy C. The image displays a layered structure with a dark, granular top layer, a lighter, more uniform middle layer, and a dark, jagged bottom layer. A scale bar in the bottom right corner indicates 10.0 μm.

Alloy D	
Alloy E	
Alloy F	

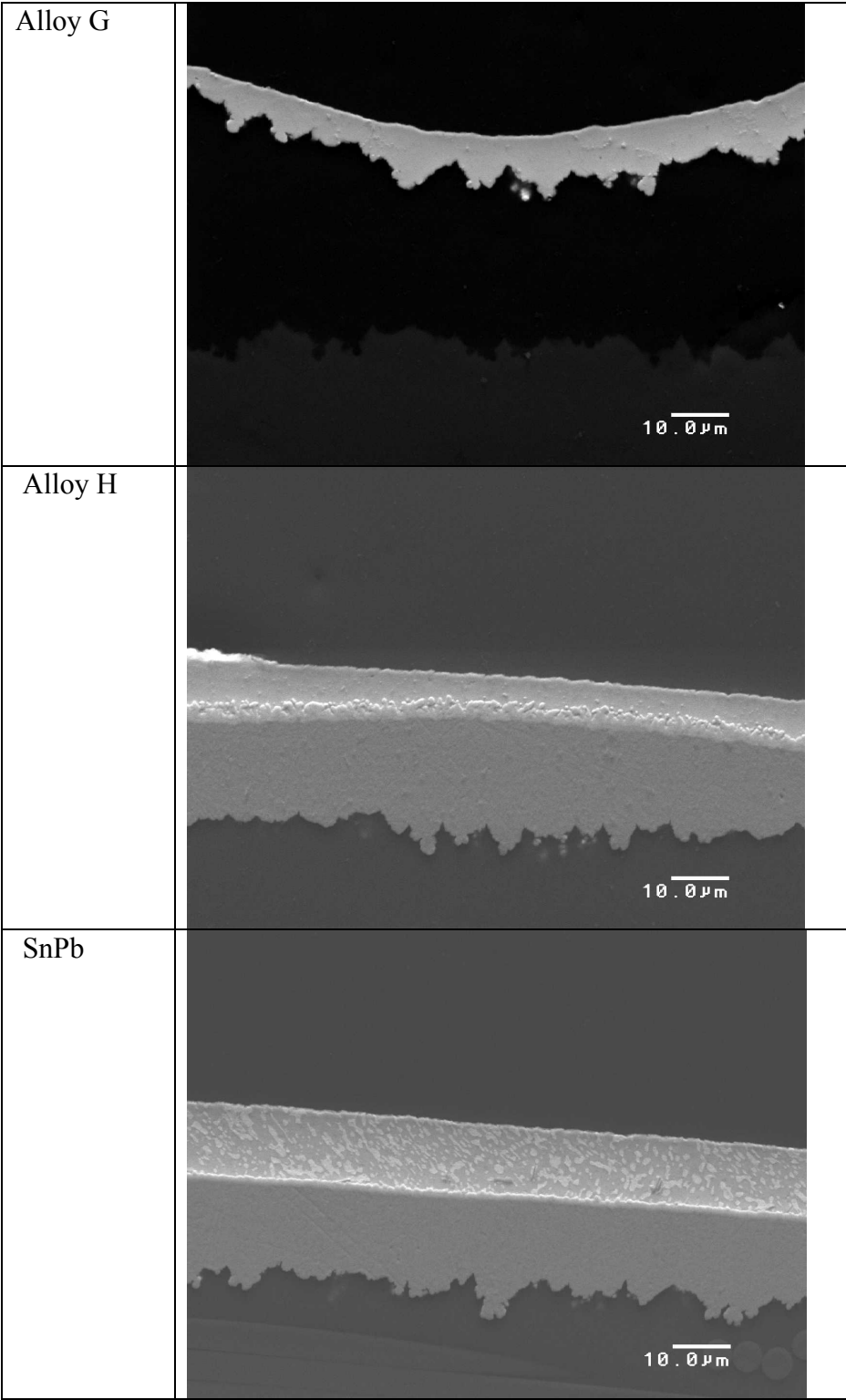


Figure 17. Examples of SEM micrographs that were used for measuring the intermetallic thickness.

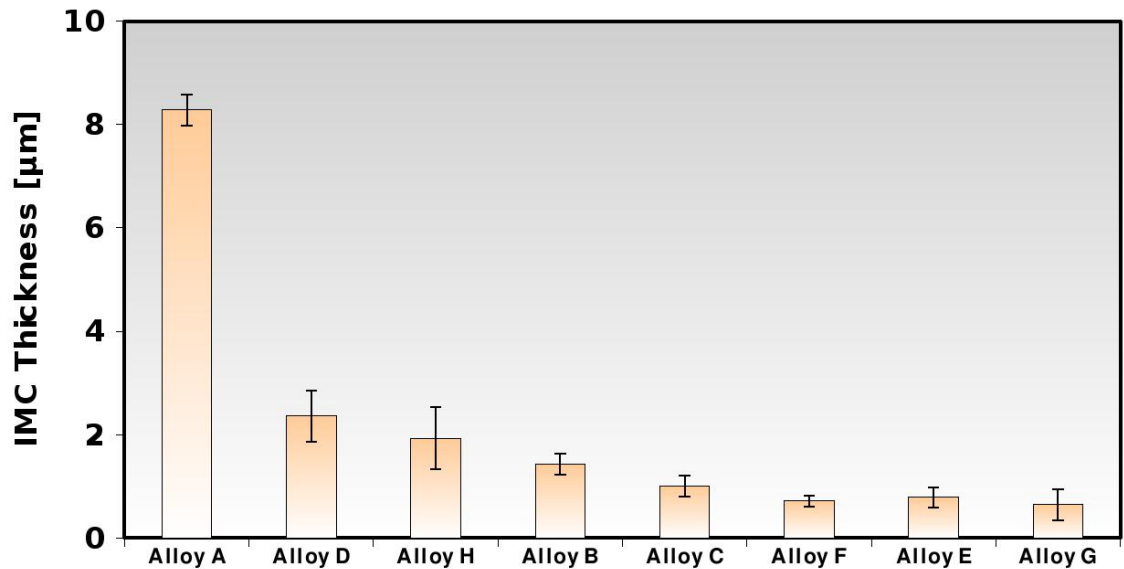


Figure18. Average thickness of the intermetallic layer (275 °C).

The intermetallic thickness, normalised with the dissolution time at 275 °C, was plotted against the measured dissolution rates, and this is presented in Figure 19. A normalised value for the thickness was used because samples were tested for different times (time required to dissolve the copper). The thickness of the IMC does not grow linearly with time; during soldering a dynamic process is established, IMC forms at a certain speed and some of it will dissolve again in the molten solder with a lower speed. This process stabilises after about 60 seconds and the IMC thickness does not vary much with time any more[15].

This shows that increasing intermetallic thickness correlates with reducing dissolution rates.

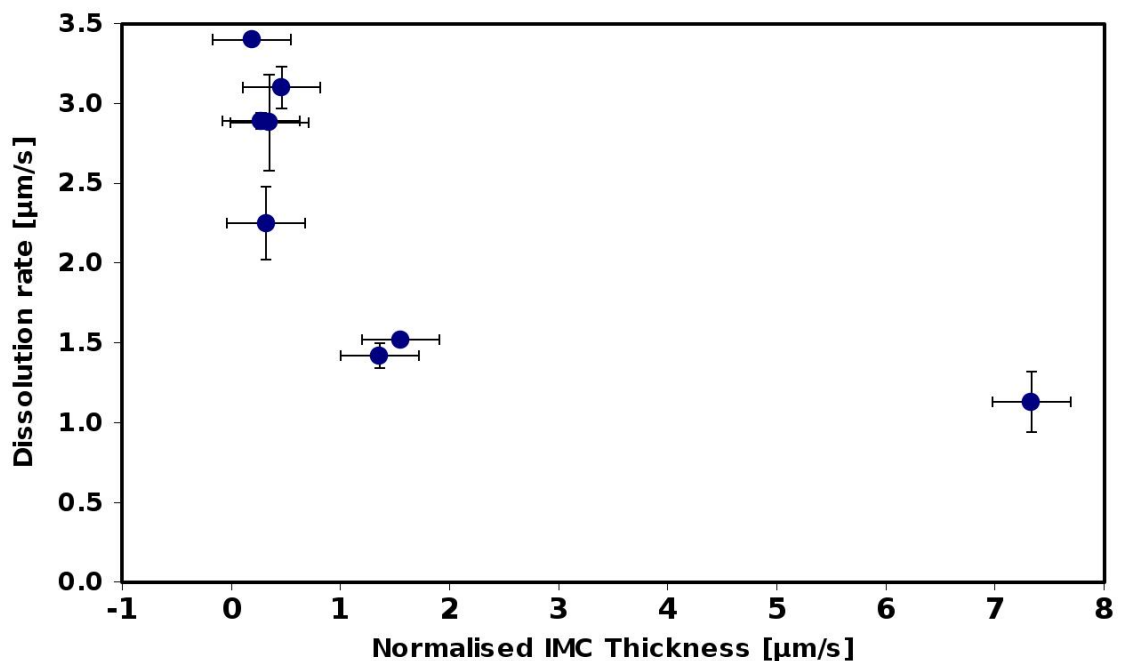


Figure 19: Dissolution rate and normalised intermetallic thickness trend.

4.4 DISCUSSION

The following observations are noted:

- Great variability in dissolution rate was observed among the different alloys.
- The dissolution rate increases linearly with temperature for all alloys.
- The SnPb alloy is not the alloy with the lowest dissolution rate at typical soldering temperatures.
- Alloys with less than 0.3% Ag have a slower dissolution rates than SnPb.
- The rate of change of dissolution rate with temperature was found to be very similar (less than 10% variation) especially for Alloy A, B, C, F, H and SnPb.
- A higher temperature dependence was found with alloy E, alloy D and alloy G (indicating that more care should be taken if raising the operating temperature).
- In general it was found that the thicker the intermetallic layer, the smaller the copper dissolution. This is reasonable because the intermetallic acts as a barrier for copper diffusion. The thicker intermetallic also indicates that it has reduced solubility. Variations in intermetallic microstructure may also influence the process and reflect the range of results.

5 TESTING WITH DIFFERENT EQUIPMENT

The method used to measure copper dissolution with the commercial alloys in Section 4, is easily applicable with different types of equipment. To verify this, tests with a SnCu alloy were performed on a Seho² soldering bath and also on the ACE machine used in previous tests. The Seho machine was based on a different design and consisted of an electromagnetic pump, a solder pot, a ring-type heater, an inerting hood and a wave nozzle. For the comparison, the flow rate of the Seho machine was measured in the same manner as described in section 3.1. The flow rates with the Seho machine were higher than those found with the ACE machine. Previously a flow rate of 10 g/s was used (Note: earlier the flow rate was quoted in volume terms to accommodate the difference between the lead-free alloys and SnPb). The Seho machine was unable to operate at this low flow rate due to the larger nozzle size. For the tests a flow rate of 50 g/s was used for both machines.

The samples used in the tests and the experimental conditions are shown in Table 4.

Table 4: Experimental Conditions for the comparison test.

Alloy	SnCu (see Appendix I)
PCB	PCB coupon described in section 1
Temperatures	255, 275, 300 °C
Flow Rate	50 g/s
Flux	Water based

The dissolution rates for the machine tests are presented in Figure 20. The results show that the maximum difference between the two sets is below 10% and hence within the

² <http://www.sehouk.com/>

experimental error due to the different geometries (in particular different heating systems).

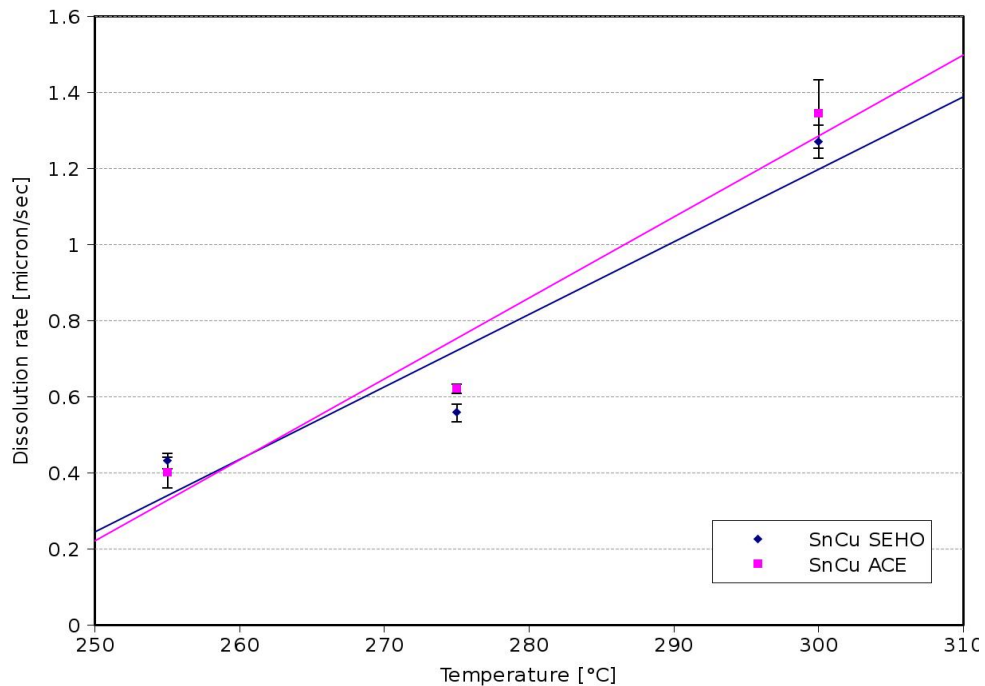


Figure 20: Comparison of copper dissolution flow rates using two different machines (ACE and Seho) in the same experimental conditions.

6 COPPER DISSOLUTION ON DIFFERENT TYPES OF COPPER

6.1 INTRODUCTION

The various copper types found on a PWB may influence the dissolution rate, and may well depend on the manufacturer. This suggests that the microstructure may play an important role in the dissolution process. Hence, here different copper types are studied and the dissolution rates compared.

6.2 EXPERIMENTAL SETUP

The effect of the copper type was studied using the SEHO machine described previously. The experimental conditions used were the following:

- Solder: SnCu
- Temperatures: 255, 275, 300 °C
- Flow Rate: 1.35 cm³/s (this unit was used rather than g/s to take into account the higher density of SnPb).
- Copper types: 0.5 oz Electrodeposited, 2 oz Electrodeposited, Reverse Treated 0.5 oz, Electroplated 30 μm (1oz ≈ 18μm)
- The above copper types were used on the PCB coupon shown in Figure 8.

6.3 EXPERIMENTAL RESULTS

The dissolution time of the various copper types was measured and results are shown in Figure 21.

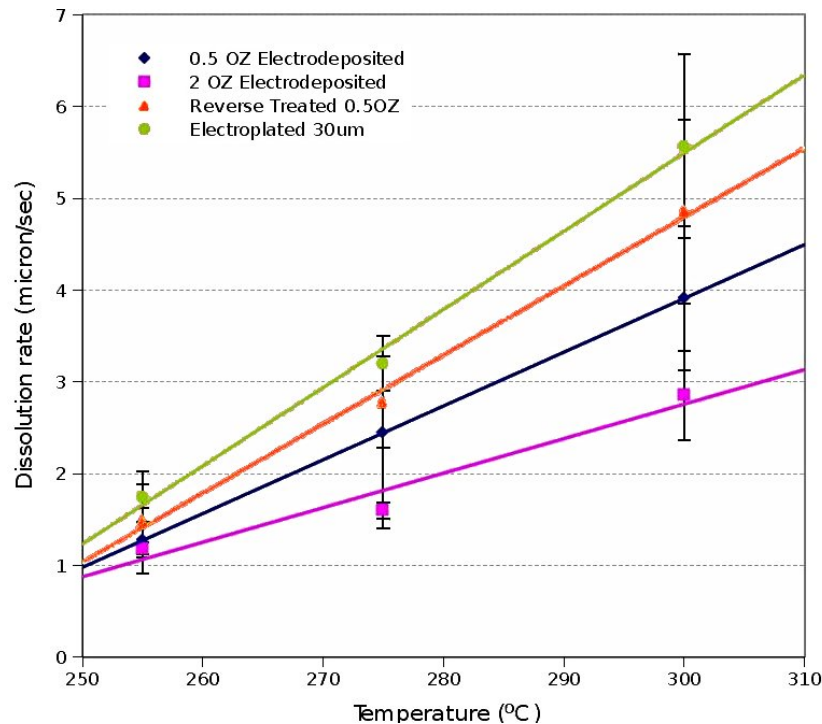


Figure 21: Dissolution rate of different copper types.

6.4 COPPER CHARACTERISATION

6.4.1 Electron Backscatter Diffraction (EBSD) measurements

EBSD was used to compare the microstructure of the different types of copper. Images obtained with this technique are shown in Figure 22. EBSD requires very flat and smooth surfaces, and these were produced by electropolishing. Electropolishing of the electrodeposited copper was not successful and no images were obtained from this sample. The grain size distribution obtained from the image analysis is shown in Figure 23. It can be observed that reverse treated copper tends to have larger grain size than the electroplated copper. From Figure 21 this may indicate that larger grains will tend to minimise copper dissolution.

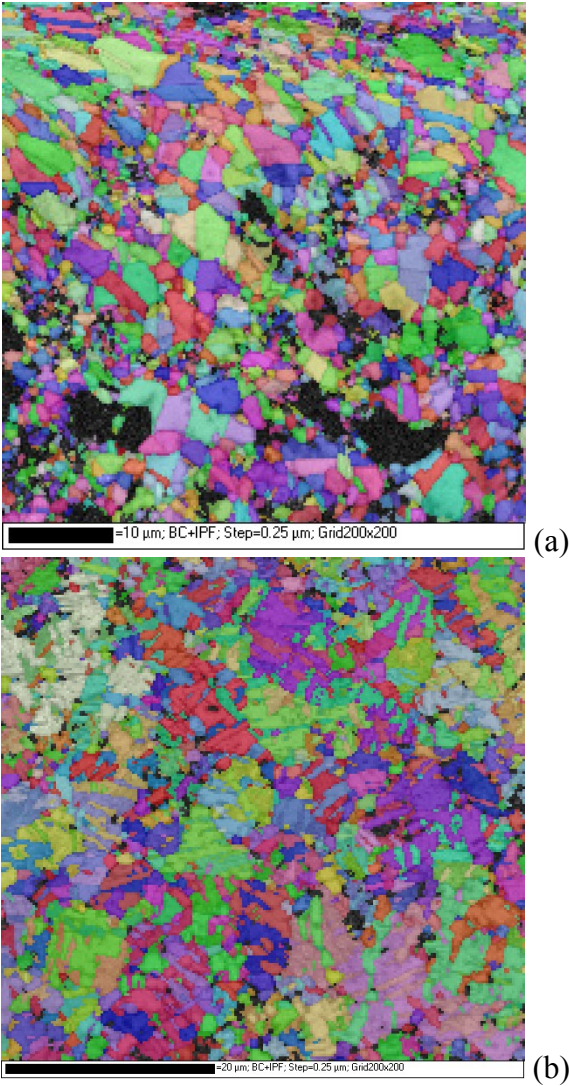


Figure 22. EBSD analysis of electroplated (a) and reverse treated copper (b)

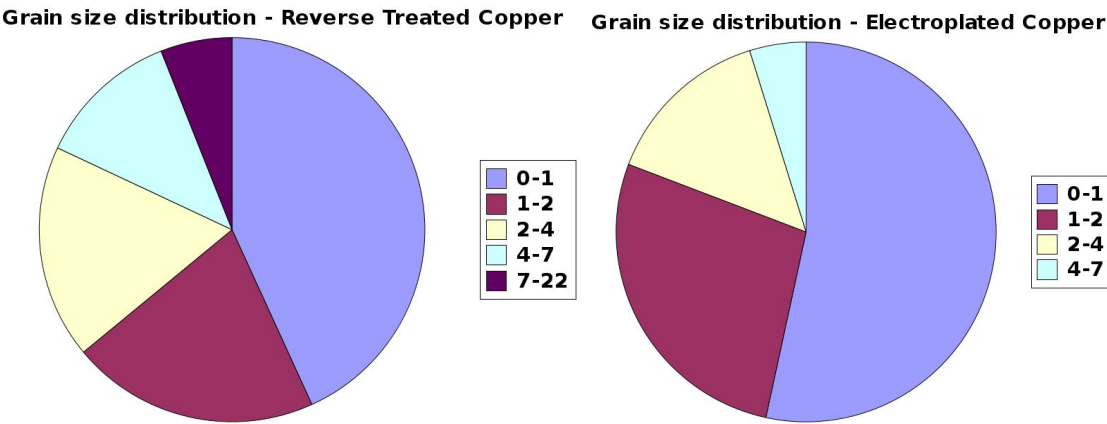


Figure 23. Grain size distributions for electroplated copper and reverse treated copper. Size is in micrometers.

6.4.2 Dynamic Mechanical Analysis (DMA) of copper foils

DMA was performed on electrodeposited (0.5 and 2oz) and electroplated copper. The graph in Figure 24 shows the change in elastic modulus for the 3 materials against the temperature. It is interesting to observe that the two electrodeposited copper samples despite being nominally the same material show very different behaviour.

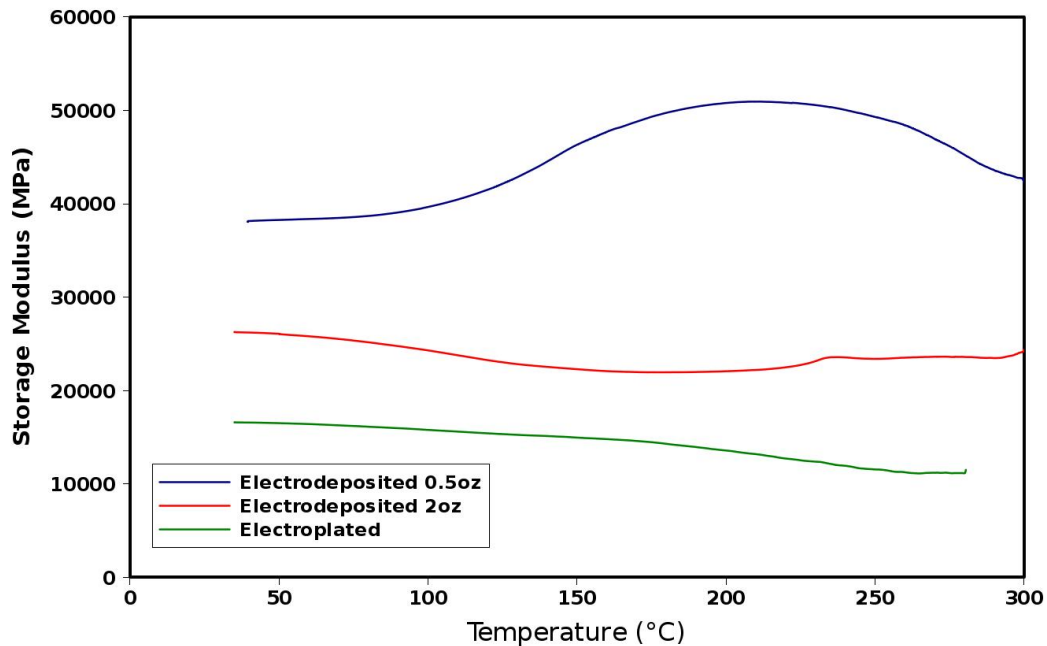


Figure 24: Elastic modulus of electrodeposited copper 0.5oz, electrodeposited copper 2oz and electroplated copper.

6.5 DISCUSSION

It can be observed that the two electrodeposited foils of different thickness have different Cu dissolution rates. This is probably due to the influence of the thermal mass on dissolution rate, caused by the different copper thickness. Differences were also found between the tested samples both in terms of grain size and elastic modulus. Unfortunately it was not possible to correlate these differences with the copper dissolution behaviour and more studies would be required in this area.

7 PRINTED CIRCUIT BOARDS TRIALS

7.1 INTRODUCTION

The second part of this research was aimed at verifying the potential impact of copper dissolution during hand and selective soldering of PCBs with lead free solders.

Three alloys were tested (two only with soldering/de-soldering) and their composition of these solder alloys was tested by Butterworth Laboratories Limited³ and can be

³ Butterworth Laboratories Limited. 54-56 Waldegrave Road, Teddington, TW11 8NY, UK.

found in Table 5. These alloys were nominally the same as those analysed in Table 2, but here these were the used in the selective soldering machines, and as such were physically distinct.

Cored solder wire was 0.8 mm with a single core of flux.

Table 5: Composition of the alloys used for the trials and soldering/de-soldering tests.

Alloys	Ag	Al	As	Au	Bi	Cd	Cu	Fe	In	Ni	Pb	Sb
Alloy D	0.030	<0.01	<0.01	<0.01	<0.01	<0.01	0.600	<0.01	<0.01	0.047	0.019	0.043
Alloy E	0.290	<0.01	<0.01	<0.01	<0.01	<0.01	0.717	<0.01	<0.01	<0.01	0.034	0.003
Alloy F	3.700	<0.01	<0.01	<0.01	<0.01	<0.01	0.733	<0.01	<0.01	<0.01	0.027	0.003

7.2 EXPERIMENTAL METHOD

The printed circuit board, shown in Figure 25, used for testing had the following construction.

- Laminate Type ISOLA DE 104i
- Outer copper foil thickness 12um
- Black hole direct metallisation (McDermid)
- PTH copper plating (Shloetter)
- Inner layer copper 1oz 36um
- PCB finish immersion silver (Alpha)
- Solder mask finish (Electra EMP110)
- PCB six layer (1.6mm thickness) construction

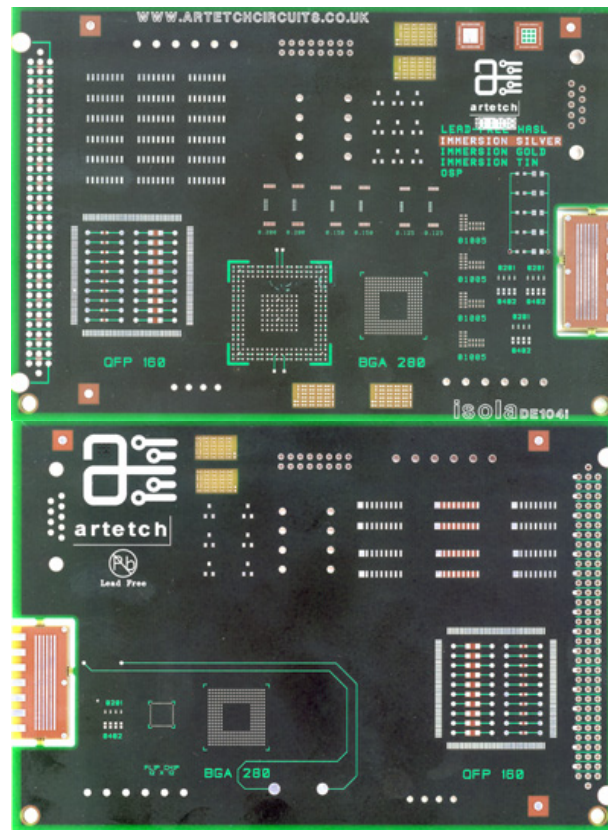


Figure 25: Photograph show the printed circuit board design used in these trial.

The circuit boards where produced by Artetch Limited.

The 96 way edge connectors, presented in Figure 26, were provided by Harting, Germany. The design rules for the PCB and connector location consisted of the following:

- Hole size 0.045" (1.14mm)
- Pad size 0.060" (1.52mm)
- Pin size 0.030"x 0.010" (0.76 x 0.25mm)
- Pin pitch 0.100" (2.54mm)
- High temperature plastic body
- Pin termination tin plated

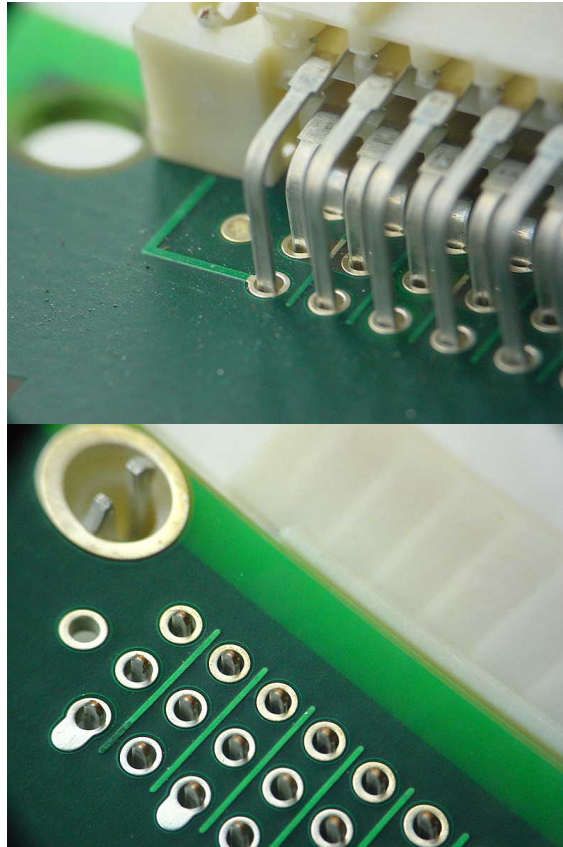


Figure 26: Photograph shows the connector and circuit board location used for the trials

Evaluating the rate of copper dissolution during production testing consisted of exposing four multilayer circuit boards to selective soldering operations. The dissolution rate of copper from the printed board during soldering was determined by measurement of the copper on the top pads of the plated through hole after soldering and masked adjacent pads that had not been exposed to solder.

The selective soldering trials were conducted at Vitronic Soltec demonstration facility in Holland between 5 and 9th May 2008. Trials were conducted on a Soltec MySelective 6745 system, shown in Figure 27, using two set-point soldering temperatures of 280 and 320°C. The solder alloy was provided as bar stock, and was placed in a new solder bath to avoid cross contamination issues. The resources available for the experiments restricted the number of alloys under test to three alloys, (alloy D, E and F).



Figure 27: Vitronic Solttec 6745 system used during the trials

The selective soldering operation consisted of fluxing, preheats and automated soldering using a fixed width nozzle. Fluxing was achieved during multiple passes; the soldering operation was conducted during a single pass of the board assembly over the solder nozzle. The process parameters for selective soldering remained constant for all testing, with the exception of soldering temperature. This was changed from 280 to 320°C for soldering the sample boards. The selective soldering machine/process parameters are listed below:

- Flux type: IF 2005M Interflux
- Fluxing parameters: Track speed 12mm/s
- Distance from board: 60mm
- Nozzle/PCB speed: 2mm/s
- PCB angle: 10°
- Separation speed: 5mm/s
- Nozzle size: 12mm
- Nozzle distance: 1.8mm
- solder pump speed: 385 rpm (May vary slightly as the bath or alloy changes)
- Solder temperature: 280 °C and 320 °C (Confirmed with a independent thermocouple in the solder wave)
- Preheat time: 40seconds
- PCB height above pre-heat surface: 70mm
- Preheat set-point: 45%

Preheat profiles are provided for each of the two soldering temperatures. The locations of the thermocouples are shown in Figure 28. The results of thermal profiling are given in Figures 29 and 30.

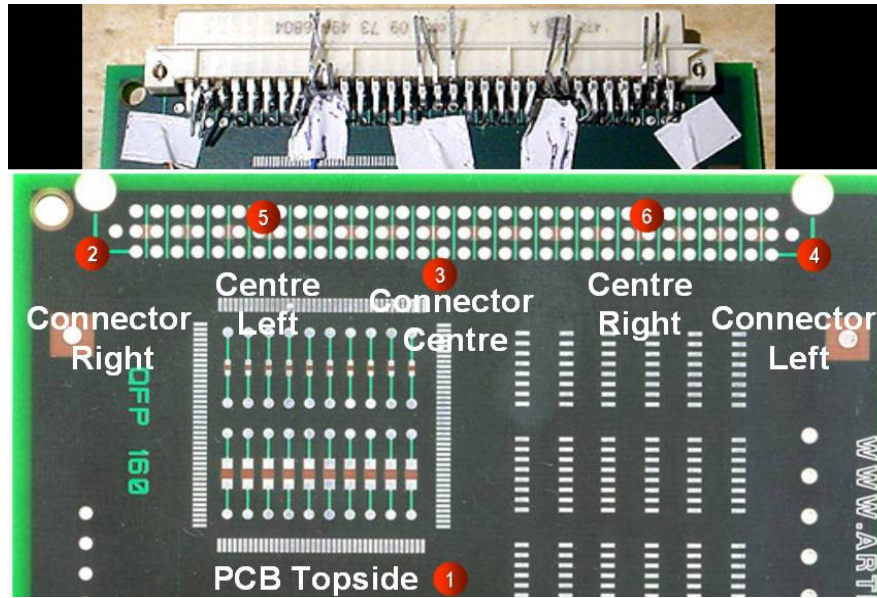


Figure 28: Thermocouple locations, and insert a picture of attached thermocouples and connector pins bent out of the way.

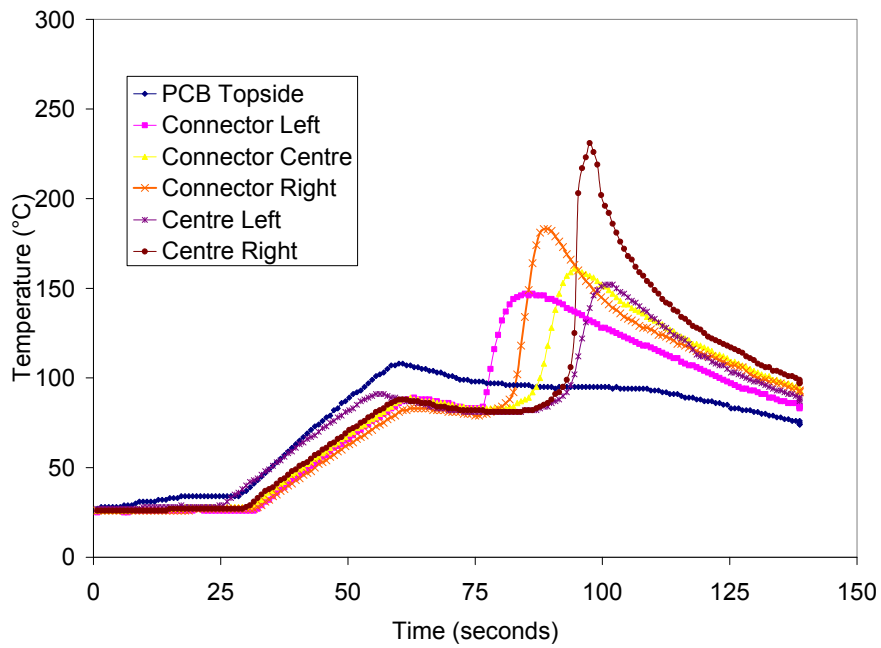


Figure 29: Temperature profile for selective soldering of boards at 280°C. Measurements are for locations shown in Figure 28.

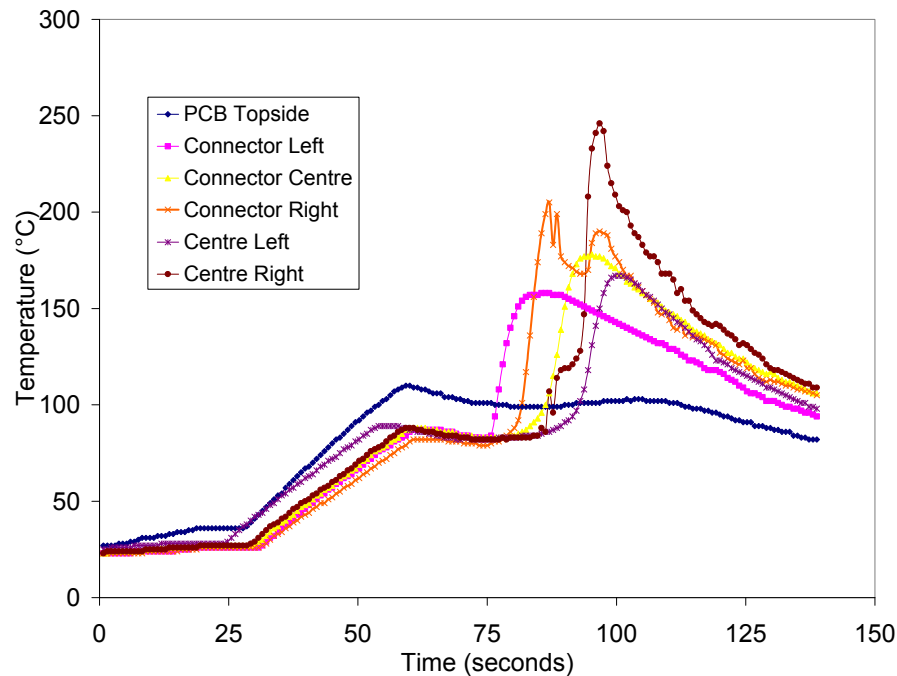


Figure 30: Temperature profile for selective soldering of boards at 320°C. Measurements are for locations shown in Figure 28.

Although a new solder bath was used for this evaluation a solder sample was taken for reference from solder flowing out of the nozzle after it had been operating for 10 minutes, the results of the analysis are shown in Table 5:

Microsections were taken from the test boards after the soldering trials. The section size was selected based on the number of different through-hole connection points. As previously discussed, the inner layer thermal/electrical connections were varied to examine the impact of heat loss to the joint during the soldering operation and the subsequent solder solidification. Micro-sections were prepared so that the final section position used for measurements was at the centre line on the base of the hole, as indicated in Figure 29.

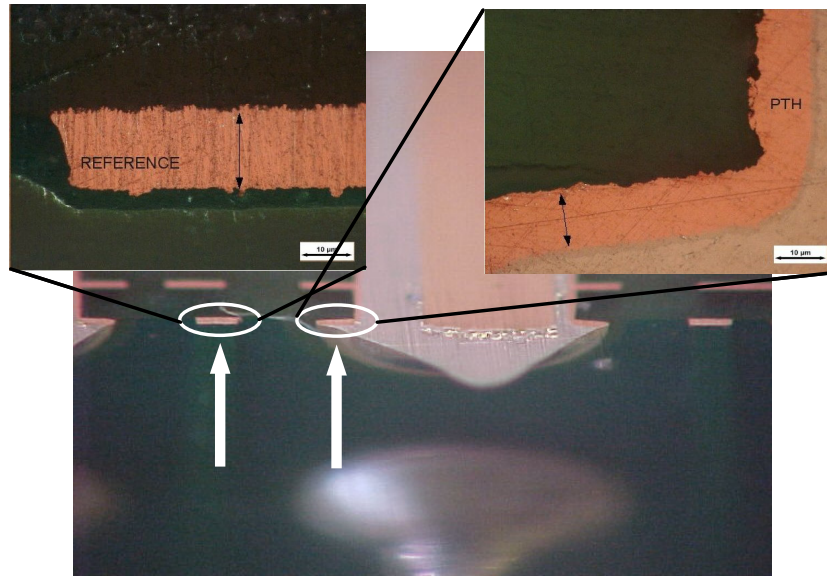


Figure 29: Example of section view where measurements were taken on the reference track and the through hole/pad (10µm bars).

Measurements of the copper plating were taken from the track adjacent to the plated through hole, this was coated with solder mask and was not subjected to contact with the soldering alloy during soldering. Measurements were taken from the pad and plated through hole after the soldering operation for comparison.

7.3 EXPERIMENTAL RESULTS

The soldering results on each of the test boards was satisfactory with solder penetration on each of the plated through holes, even with the design changes intended to increase the thermal demand of the board. The soldering exceeded the minimum IPC soldering standards defined in IPC 610 level 3. The solder created positive solder fillets on the topside of the board during the trials, as demonstrated in Figures 32 and 33.

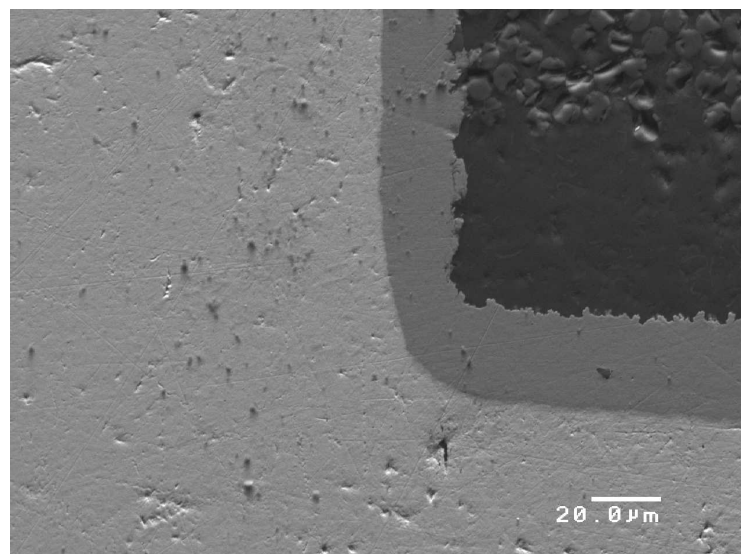


Figure 32: Photograph shows an SEM image of a selected through hole after selective soldering at 320°C

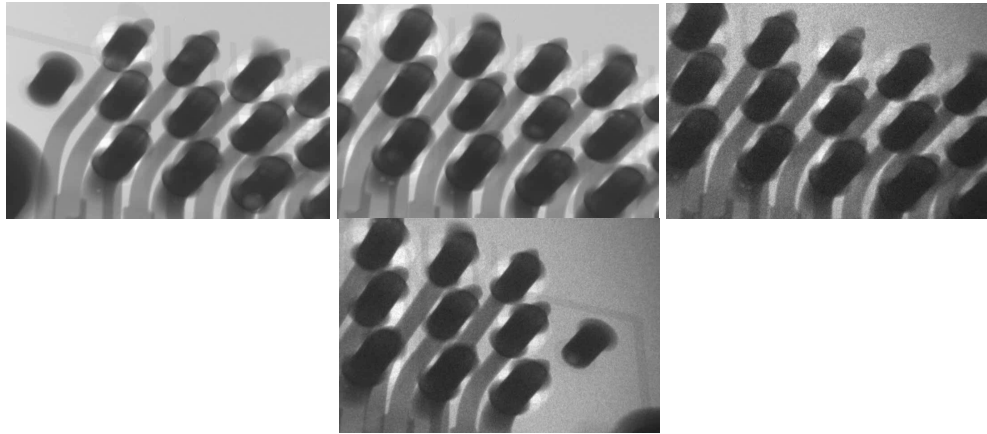


Figure 33: Selected X-ray images revealing uniform solder fill

Based on the trials and the soldering performance on the test board it is clear that in a production environment with a similar design the process parameters could have been further optimised to increase through-put speed and reduce the solder bath temperatures. Further trials on the preheat setting would have allowed further optimisation of the process.

The copper thickness on the PCBs after soldering was measured and compared to the reference pad. The remaining copper on the pad for the various alloys is shown in Figure 34.

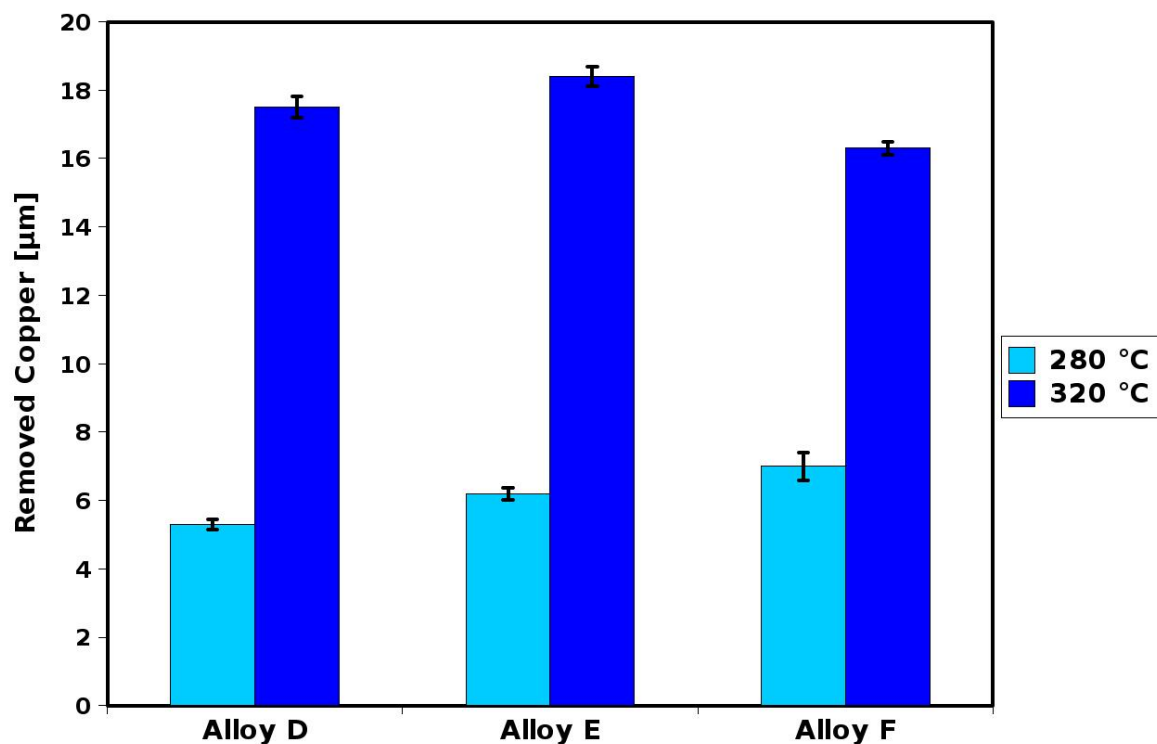


Figure 34: Removed copper on the PCBs after soldering.

7.4 DISCUSSION

It was observed that:

- The variability in copper thickness between the boards was too high to assume that they all had the same initial value. Hence a reference was needed close to the measurement point, and a convenient pad covered in solder mask was used. The measurements in the plated through hole could not be used, as there was no reference.
- It was not possible to measure or control the solder flow rate when testing. The solder height was set to a typical profile, and the setting was held constant as described above. This lack of knowledge of flow rate has probably caused the greatest variability, and prevents a detailed comparison with the measurements in section 4.
- Alloy D proved to be the best alloy at 280°C as expected from the previous tests, however the amount of removed copper at 320°C was much higher than what the previous tests would suggest. This maybe due to the uncontrolled flow rate during the tests.
- Alloy F was found to have the worst performance at 280°C as expected from the previous tests, but at 320°C the worst alloy was Alloy E.

7.5 HAND SOLDERING AND DE-SOLDERING TRIALS

Hand soldering and de-soldering trials were conducted using an Ersa Icon2 and CU100A compressor unit with a set-point of 400°C. The tips used were 102CDLF 1.6 for manual soldering, the de-soldering tip was a 722EN1020. The hand soldering/de-soldering time was approximately 4 seconds per joint. The soldering iron tip surface was approximately 1.6mm x 3.0mm. The de-soldering tip size was selected based on the printed circuit board hole and pad size plus the size of the connector pin to maximise heat transfer and vacuum force. A typical arrangement is shown in Figure 35.



Figure 35: Photograph of the manual soldering tools used during trials

Normally the outer tip diameter is equal to or smaller than the pad size, the hole size in the nozzle is slightly larger than the pin size which allows maximum vacuum on the solder in a liquid state. It also allows pin movement to be determined without mechanical contact with the pad surface. Pin movement indicates to the operator that complete solder reflow has occurred in the barrel of the plated through hole.

7.5.1 Results from hand soldering

Manual soldering and through hole solder fill was specifically influenced by the different thermal connections to selected plated through holes. It was not possible to fill all plated through holes to meet the minimum requirements of the IPC 610 specification due to thermal demand issues. If this board design was encountered in a production environment preheating prior to manual soldering or de-soldering would be required. This would have allowed better hole fill and optimisation of the process and possible reduction of the peak soldering temperature. Measurements of copper thickness were taken on sample holes where satisfactory through hole fill was achieved to IPC 610. Results from the measurements are shown in Figure 36 (unfortunately alloy E wire was not available for this test).

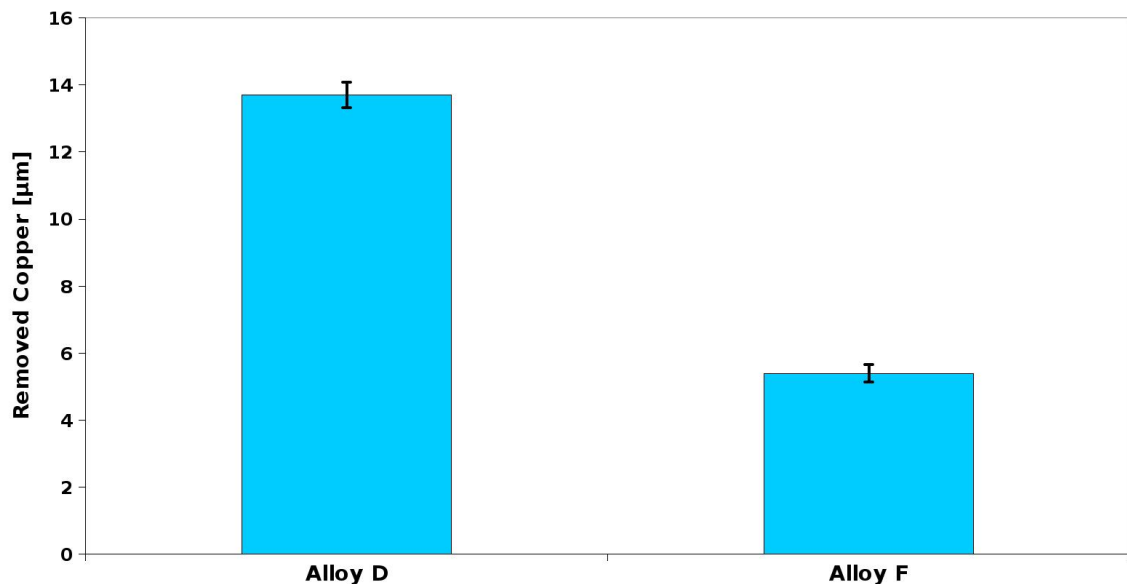


Figure 36: Results from hand soldering and de-soldering tests.

7.5.2 Discussion of hand soldering results

It was observed that

- Alloy D had a much higher amount of removed copper than alloy F, despite it resulted to be amongst the best alloys in the previous tests.
- The amount of copper removed was much higher than what would be expected from a static test (see section 1 of this report).

Based on these results de-soldering and then re-soldering a through-hole joint will lead to further dissolution of copper.

It is inevitable that some companies will adopt board preheating to aid hand soldering and de-soldering operations possibly decreasing actual soldering times/temperatures. This will increase the possibility of meeting inspection standards for through hole fill and minimise copper dissolution. Preheating has been standard practice for reworking large surface mount components but not for soldering/reworking through hole components manually or with semi automatic solder fountains.

Inspection criteria in the future may be modified, but currently through hole fill is not mandatory. Reduced fill of plated through hole boards is allowed under IPC 610 level 2 where thermal connections on ground and power planes make hole fill extremely difficult. However, it is not unusual to encounter inspectors expecting and often demanding evidence of fill to be visible from the topside of the board.

8 CONCLUSIONS

Copper dissolution is an essential part of forming a solder joint, but can become an issue if too much copper is removed, as has been observed with some lead-free soldering processes. Copper dissolution is more an issue with lead-free soldering for two reasons. Firstly the higher melting points of these alloys resulted in higher processing temperatures, and hence faster dissolution, and secondly the higher solubility of copper in the certain lead-free solder alloys.

This work has shown that copper dissolution with the new generation of alloys is significantly lower than the first alloys to be introduced. Silver has been highlighted as particularly problematic at concentrations above 0.3%. Certain new alloy types tested at the same temperatures can out perform SnPb. Clearly the design of new alloys and the addition of minor elements have significant influence on dissolution rates.

The measurement methodology developed here highlighted the interaction of many parameters influencing copper dissolution rates. Of specific interest is the flow rate of the solder, which can have as large influence on dissolution rates as temperature. Most soldering machines do not have a method for calibrating the flow rate. Optimisation of soldering conditions can therefore be problematic if temperature and alloys are being varied.

- Over the temperature range studied here dissolution increased linearly with temperature.
- Dissolution increased linearly with flow rate, which is as significant a factor as temperature in affecting dissolution rate.
- Differences in dissolution rate with different solders have been found to broadly follow an inverse correlation with the final intermetallic thickness.
- The form of the copper on the PWB was significant. Copper from one supplier was sampled and here it was found that electroplated copper resulted in the highest dissolution rate, whereas electrodeposited had a lower dissolution rate.

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