As originally published in the IPC APEX EXPO Proceedings.

A Test Methodology for Copper Dissolution in Lead-Free Alloys

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Abstract

Lead-free selective soldering can result in extended times at high temperatures, which in turn can result in excessive dissolution of exposed copper, such as plated through holes. This phenomenon is more severe with lead-free, since the alloys have higher melting points, hence requiring longer times for the PTH to reach the higher temperatures, and the alloys typically have a greater capacity to dissolve copper.

This paper discusses a test method that characterises the dissolution rate of copper from PWBs. A PWB design was created that allowed the time for the dissolution of a copper pad to be measured. With this quantitative method a soldering process or an alloy can be characterised in terms of dissolution rates at specific conditions of temperature and flow rate. This methodology provided repeatable measurements that allowed the various experimental parameters to be isolated. Particular attention was paid at the flow rate of the molten solder. In fact, different alloys at the same temperature can have considerably different flow rates, due to the different viscosity at that temperature. The performances of seven lead-free alloys and a typical 60/40 Sn-Pb alloy were compared at three temperatures.

NPL worked with a number of partners using different alloys and copper types to measure the relative rate of copper dissolution. This work shows that some of the current alloy developments now offer superior performance to SnPb at the same temperature. Interestingly intermetallic formation between the alloy systems varies considerably. The copper type on the PWB is also influential, with significant differences between electroplated, electrodeposited and reverse treated.

Introduction

The advent of lead-free soldering has resulted in the introduction of a number of high tin solder alloys, which for selective soldering applications typically means solders with melting temperatures in excess of 220°C. The higher melting points of the lead-free alloys also dictate higher processing temperatures, and usually higher contact times, as the components take longer to heat up to the higher processing temperature. The copper 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 potentially higher than that of tin-lead solder. Hence, the higher temperature and solubility effects can significantly increase the risk of damaging copper dissolution. Exposed surface copper can be removed, disconnecting the land from the track.

The formation of a solder joint during soldering requires a reaction between the solder and the metallisation of the substrate. This reaction involves a dissolution process, which occurs through an intermediate phase, an intermetallic that forms at the interface. The intermetallic itself is soluble in molten solder, and hence the intermetallic substrate interface proceeds into the substrate with time. The nature of this intermetallic and its thickness will be significant in controlling the overall copper dissolution process. A number of alloys are now available where additions significantly below 1% affect a number of material properties, of which the solubility of copper is an important parameter.

Factors Affecting Dissolution of Copper

When a copper substrate is in contact with molten solder, atoms of copper will tend to diffuse into the molten metal and a diffusion zone is created on top of the copper surface [1]. The Nernst Brunner equation, often referred as Dybkov's analysis was found to be valid to explain this part of the dissolution process:

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

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 [2, 3, 4].

The diffusion of copper atoms into the molten solder, favours the formation of intermetallic layers, such as the scalloped Cu_6Sn_5 (η) and the planar Cu_3Sn (ε) [5]. The microstructure of these two compounds plays a role in copper diffusion; a coarsening of the η grains reduces the number of grain boundaries, decreasing possible diffusion paths for copper [2]. Grain boundary diffusion is the predominant mechanism for intermetallic growth and has a great influence on the copper dissolution rate [4]. The morphology of the intermetallic is important, and can fully or just partially cover the copper [6]. Furthermore, 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 [7]. The balance between the intermetallic formation, its microstructure and morphology is significant in controlling the whole dissolution process.

The type of solder used in the process has an important effect on the dissolution rate of copper. This is related to the elements contained in lead-free alloys, both alloying and trace elements, such as Cu, Ag, Ni, Bi, In, Zn, Sb and small amounts of Pb. All these can form intermetallics that can attach to the surface of the copper. For example Ag, used in 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 was observed that in presence of Ag_3Sn, the intermetallic layer becomes thinner than that formed with just Sn/Cu [4]. Also, it is expected that a higher amount of Cu in the solder will reduce the dissolution process [8].

Different solder compositions will have different melting temperatures; hence the optimal operating temperature for each alloy will be different, and this temperature change will impact on copper dissolution. Typically the higher the temperature the higher the copper dissolution rate, for two principal reasons: Firstly the saturated copper concentration increases with temperature; secondly the dissolution rate follows Arrhenius behaviour:

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

Where K is the dissolution rate, A is a constant independent of temperature, E_a is the activation energy and R is the gas constant [3, 9].

In a solder bath the solder is static and the concentration of copper in the solder near the interface can be expected to increase with time and hence the dissolution rate decreases due to concentration and solubility effects. In flowing solder the dissolved copper will be continuously swept away from the interface, leaving the $c_s - c$ difference of equation 1 unchanged.

The flow rate of solder is another important parameter, and it has been observed that copper dissolution rate is highly dependent on flow conditions [10]. In fact, a high turbulent flow generates a mechanical erosion effect of the copper surface (or actually of the intermetallic) [11]. The flow rate and flow type in the solder bath are dependent on many variables, such as the machine geometry and type, the pump speed and solder viscosity. Different types of soldering machines, for example the rework fountain and wave soldering 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 of flow, however not all machines allow this to be controlled. If the pump speed is fixed, then the flow rate can be varied by changing the operating temperature, and hence the solder viscosity. Figure 1 shows how the viscosity dependence of tin with temperature [12].

Potentially the type of copper microstructure can affect its dissolution resistance. Large variations have been observed in the performance of different copper types [13, 14], however this dependency has not been investigated fully. Work to demonstrate a correlation between microstructure/mechanical properties with dissolution propensity was not successful [15], and the effect of microstructure and factors within the copper, such as composition, need to be studied further.

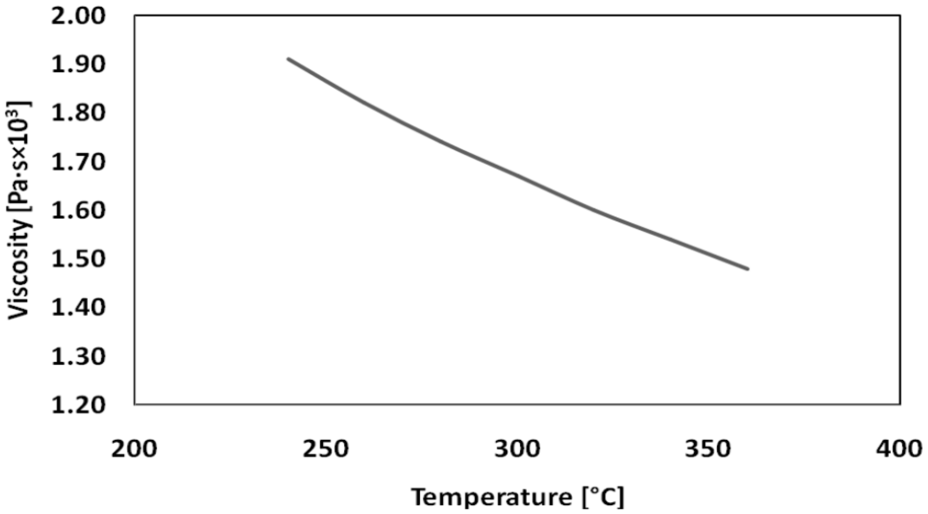

Figure 1: Dependence of viscosity with temperature for pure tin (adapted from [12]).

Materials and Experimental Set Up

One of the aims of this study is the development of a simple testing method that can be universally employed for evaluating a number of variables. For this study a typical PCB construction was used in industry, using a specific design of copper pad. This is shown in Figure 2. The PCB was a 2.5 mm thick FR4, with 10 copper test pads, further details of this are given in reference [14]. The test pads can also be accessed from the bottom side through a hole. The topside shows small dimples where the copper is unsupported, and the hole can be clearly seen from the bottom view. Another requirement of the testing method is an automated detection of the dissolution time. A contact for the timing probe can easily be inserted into the hole to sense when the solder penetrates the copper foil and contacts the pin.

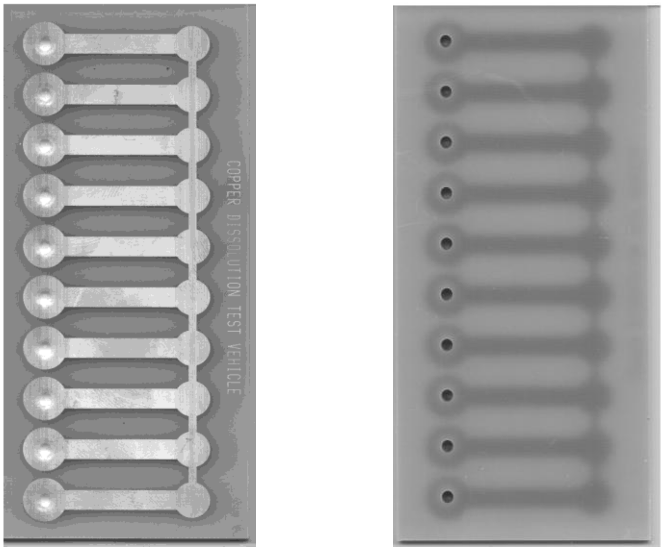

Figure 2: The top and bottom side of the PCB (left and right respectively) coupon used for the tests.
The holes on the bottom side correspond to the unsupported part of the copper pads seen on the top side.

The soldering machine used for the tests was an ACE Automated Soldering Machine - KISS 102^{TM} . This machine is an automated selective soldering machine using a travelling mini–solder fountain. An image of this equipment showing the solder pot and nozzle is shown in Figure 3.

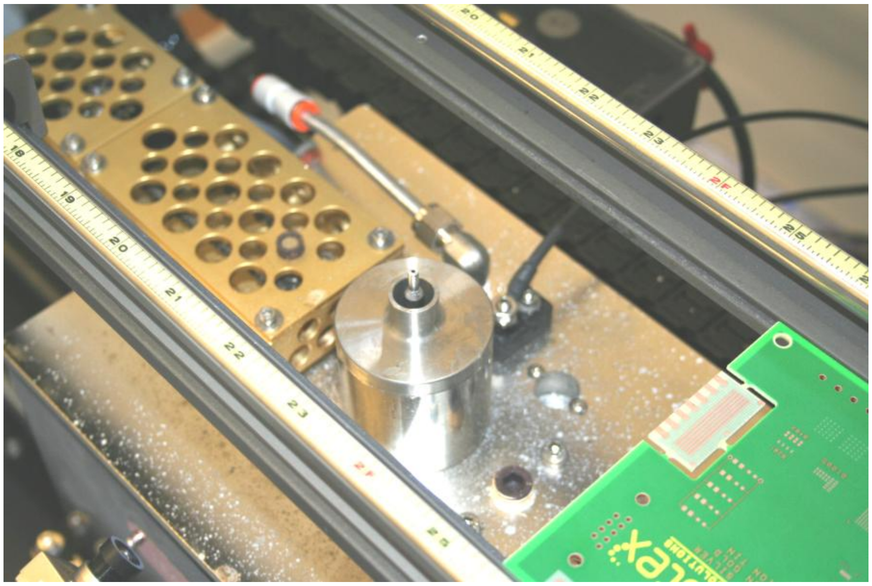

Figure 3: Solder pot and nozzle of the soldering equipment used.

This machine can be computer controlled and programmed. A large number of parameters can be controlled including immersion depths, pre-heat dwells, travel distances and speeds, solder temperature and pump speed. During the soldering procedure, the mini solder fountain moves under the component to be soldered. The solder pot can be fed with nitrogen gas to minimise dross formation.

In the introduction it was noted that the 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 solder to the interface. Flow rate was measured here, by collecting the solder over fixed time intervals, and weighing the collected solder.

Alloys with composition close to those commercially available were tested here. The analysis of their composition, done by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) is shown in Table 1.

Table 1: Composition of the alloys used for the tests (weight %).
The remaining contribution is from tin

%	Ag	Bi	Cu	Co	Ni	Pb	Sb
A	0.050	<0.01	0.626	0.030	<0.01	0.040	0.020
B	0.024	<0.01	0.510	0.081	<0.01	0.005	0.008
C	2.520	<0.01	0.748	<0.01	<0.01	0.030	0.700
D	<0.01	<0.01	0.660	<0.01	0.050	0.018	0.017
E	0.338	<0.01	0.594	<0.01	<0.01	0.006	0.011
F	3.700	<0.01	0.730	<0.01	<0.01	0.015	0.017
G	0.301	0.090	0.682	<0.01	<0.01	0.016	0.017
H	0.210	<0.01	0.690	<0.01	0.040	0.030	0.010
SnPb	<0.01	<0.01	<0.01	<0.01	<0.01	60.340	0.010
SnAg	4.100	<0.01	<0.01	<0.01	<0.01	0.012	0.018

Experimental Results

In order to verify the effect of flow rate on the dissolution of copper, tests were performed at temperatures of 255, 275 and 300 °C and the pump speed were varied. Results obtained using the test boards described before are shown in Figures 4 and 5. It can be observed that the relationship between the flow rate and the pump speed is linear.

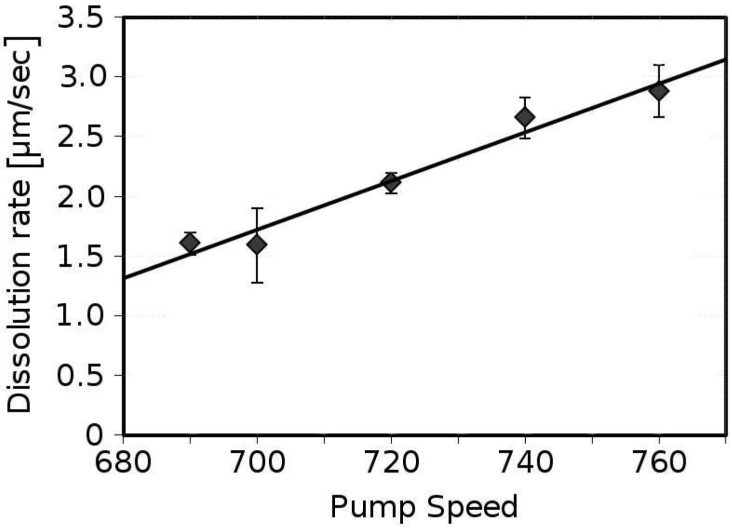

Figure 4: Dependency of the dissolution rate of copper in SnAg with variation of the pump speed (arbitrary units) at 275 **°C.**

Copper dissolution tests of the different alloys were performed at 3 temperatures: 255, 275 and 300 °C. Before performing these tests, the flow rate behaviour of each alloy was determined at each temperature. Since the compositional changes will cause the melting temperature to change, variations in viscosity were expected. Therefore to compare the dissolution rate for different alloys, the pump speed setting was varied as shown in Figures 4 and 5 for all alloys described in Table 1, so that the same flow rates were used for all the alloys at the given temperatures.

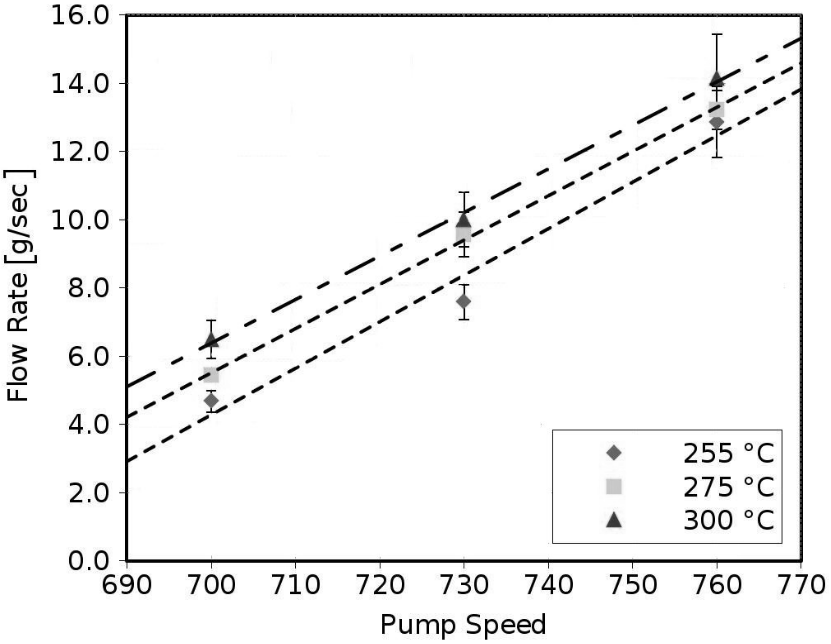

Figure 5: Dependency of flow rate for SnAg with variation of pump speed (arbitrary units) and temperature.

A flow rate of 1.35 cm^3/s was selected for the tests, as it was found to work well with all alloys and corresponded to a typical solder fountain profile, as suggested by the selective soldering machine manufacturer, achieving the necessary height and without being turbulent. The correct pump speed to apply during the dissolution tests could be calculated from the flow rate/pump speed relationship using linear interpolation. The dissolution rate of the alloys tested at the temperatures of 255, 275 and 300 °C is shown in Figure 6.

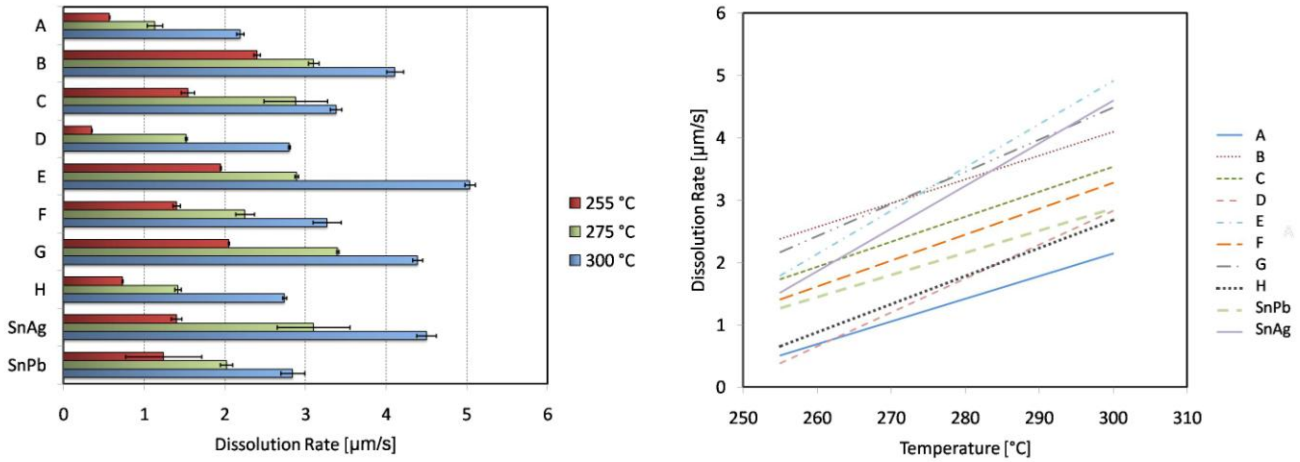

Figure 6: The dissolution rate of the alloys at the temperatures of 255, 275 and 300 °C.

Discussion

Controlling the flow rate during the test was seen to be important step to insure a better comparison between the different solder alloys. An important distinction must be made here, that is between the flow rate emerging from the nozzle and the flow rate across the surface of copper, or surface velocity. The same solder surface velocity across the copper could be achieved by a high machine flow rate through a wide nozzle, or a low machine flow rate through a small nozzle. Clearly interpretation of flow rate in should be in terms of solder flow across the copper surface. In this work the machine flow rate was measured because it is a simpler parameter to measure practically. A good approximation of the surface velocity can be obtained by dividing the flow rate by the nozzle size. For the flow rate and nozzle size used here (1350 mm^3/s and 12.6 mm^2 respectively) and hence a velocity of 107 mm/s is obtained. This could be used to compare the results obtained here with similar experiments performed with different machines and conditions.

The dissolution rate, which was found to increase linearly with temperature, varied between the different alloys. This demonstrated the role that the composition of the alloys plays in this phenomenon. It was observed that the SnPb alloy was not the alloy with the lowest dissolution rate within the temperature interval used here (see Figure 6). In general, it was found that, alloys with less than 3% Ag have a better performance than SnPb.

The slope of the dissolution rate curves of Alloys A, B, C, F, H and SnPb were very similar. The curves for alloys D, E and SnAg had a higher slope, indicating a higher dependence of the dissolution rate with temperature. The alloys that presented the highest copper dissolution rates in the commonly used for soldering temperature range 275-300 °C, were alloys E, G and SnAg. Finding SnAg in this group was expected, because of the high solubility of Cu in Sn3.5Ag (Yu, 2005). Alloys E and G are very similar in composition (see Table 1), so a similar behaviour is to be expected. However, it is not clear why their copper dissolution behaviour is poor. The relatively high Cu content should have a positive effect compared to SnAg, but this was not observed. The alloys that showed the lowest copper dissolution rates were alloys A, D and H. It is likely that the good performance of alloys D and H is due to their Ni content. In presence of Ni, complex Ni-based IMCs tend to form instead of Cu_6Sn_5. The Ni IMC acts as a superior barrier, protecting the underlying copper [9].

It was previously observed that the characteristics of the intermetallic layer play an important role in the dissolution rate. Cross sections of the tested samples were made and observed using an SEM, in order to measure the IMC thickness. In general it was found that the thicker the intermetallic layer, the smaller the copper dissolution rate, as shown in Figure 7. This is consistent with the intermetallic acting as a barrier for copper diffusion, and explains why alloy A shows the lowest dissolution rate of copper. Variations in intermetallic microstructure may also influence the dissolution process and reflect the range of results, but further research would be necessary to confirm this.

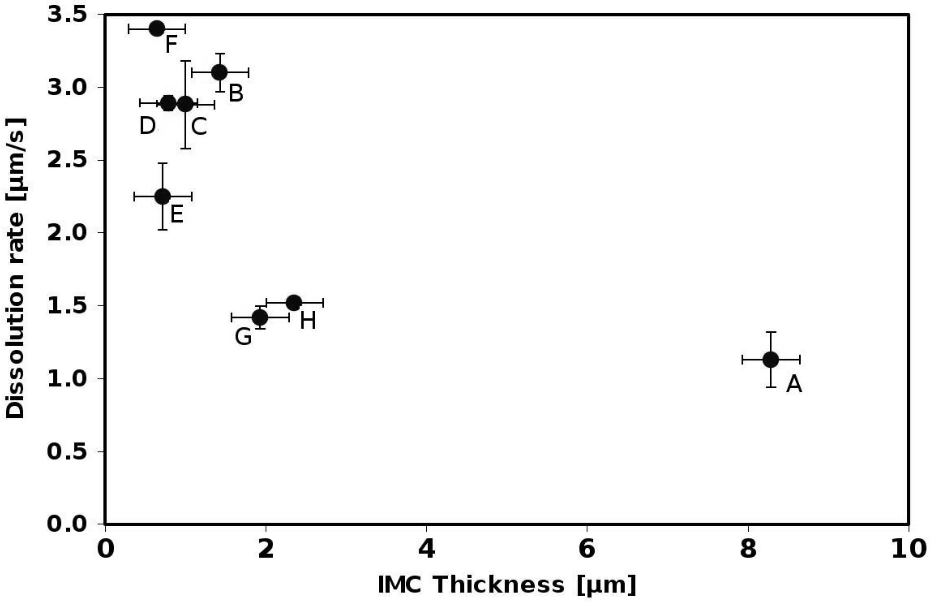

Figure 7: Dissolution rate of copper in the solder alloys and IMC thickness relationship (275 °C).

The Effect of Copper Type on Copper Dissolution

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.

This investigation used SnCu solder, at 255, 275, 300 °C, with a solder flow rate: 1.35 cm3/s, and the following copper types were investigated: 0.5 oz electrodeposited, 2 oz electrodeposited, reverse treated 0.5 oz, and electroplated 30 µm. These copper types were used with the PCB coupon design shown in Figure 8. The dissolution time of the various copper types was measured and is shown in Figure 10.

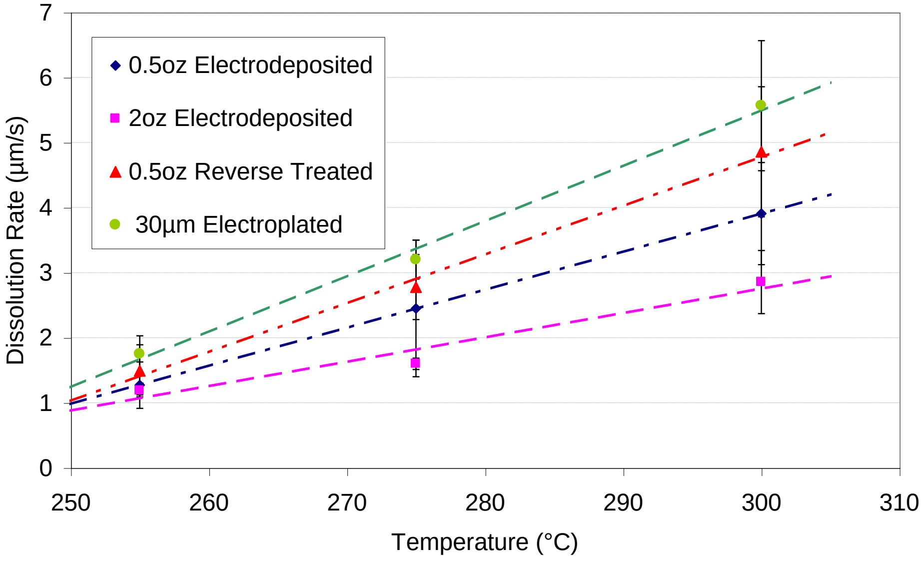

Figure 8: Dissolution rate of different copper types.

The results show that the electrodeposited foils gave measurably lower dissolution rates than the other copper foils. The difference in results between the electrodeposited foils is probably due to the influence of the thermal mass on dissolution rate, given by the different copper thickness. Measurements were made of grain size and elastic modulus, and differences were observed between the samples, but unfortunately it was not possible to correlate these differences with the copper dissolution behaviour and more studies would be required in this area.

Conclusions

The various factors that influence the dissolution of copper in molten solder were investigated and the important parameters were found to be: temperature, solder composition and flow rate.

A method was developed for comparing the dissolution rate of copper with different solder alloys. The method developed here, presents many advantages. First of all, the detection of the dissolution time was instrumented, hence improving repeatability. This method removes the need for cross sectioning to measure the dissolution rate, and hence the measurement process is very quick, and potentially real time within the machine setup process. Ten copper pads can be tested automatically in rapid succession, insuring constant conditions and repeatability of the results. The procedure is also very flexible and can be adapted and used for different types of soldering machines and providing the same conditions are used, comparables results should be obtainable.

These features make the procedure described here an important tool for future testing in the copper dissolution area. In particular studies that investigate the effect of different copper types could benefit from the flexibility and ability to obtain a large number of results in a short period of time.

Acknowledgments

We would like to thank the Department for Innovation, Universities and Skills (DIUS) for funding contributions to this research. We would also like to acknowledge Milos Dusek for his help in setting up some of the experiments.

We would also like to acknowledge the support of the following project partners included (in alphabetical order), in particular the support of Artetch Circuits in the development of the test vehicle: Artetch Circuits, Celestica, Cookson Electronic Assembly, DKL Metals, Dolby Laboratories, European Space Agency, Falcon Metals, Henkel Technologies, Hewlett-Packard Co, Indium Corporation of Europe, MBDA (UK), Photomechanical Services (Essex) Ltd, Rockwell Collins, Seho, Vitronics Soltec BV

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