Dissolution in Service of the Copper Substrate of Solder Joints

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Abstract

It is well known that during service the layer of Cu_6Sn_5 intermetallic at the interface between the solder and a Cu substrate grows but the usual concern has been that if this layer gets too thick it will be the brittleness of this intermetallic that will compromise the reliability of the joint, particularly in impact loading. There is another level of concern when the Cu-rich Cu_3Sn phase starts to develop at the Cu_6Sn_5/Cu interface and an imbalance in the diffusion of atomic species, Sn and Cu, across that interface results in the formation at the Cu_3Sn/Cu interface of Kirkendall voids, which can also compromise reliability in impact loading. However, when, as is the case in some microelectronics, the copper substrate is thin in relation to the volume of solder in the joint an overriding concern is that all of the Cu will be consumed by reaction with Sn to form these intermetallics. This paper reports an investigation into the kinetics of the growth of the interfacial intermetallic, and the consequent reduction in the thickness of the Cu substrate in solder joints made with three alloys, Sn-3.0Ag-0.5Cu, Sn-0.7Cu-0.05Ni and Sn-1.5Bi-0.7Cu-0.05Ni. A simple model developed for the reduction of the Cu thickness as a result of the diffusion controlled reaction with Sn to form Cu_6Sn_5 was found to fit the experimental data well. The results reported in this paper provide an example of the way in which microstructural features that can affect joint reliability are affected by small alloying additions.

Introduction

Several of the major trends in electronics are driving the industry towards thinner Cu substrates. The desire for thinner packages is putting pressure on the Z-axis dimension of semiconductor packages [1] (Figure 1). Also, new applications such as wearable electronics are increasing the need for circuitry with thinner Cu substrates that allow the required flexibility.

It has always been known that Sn, which is a constituent of most solder alloys, reacts with Cu substrates to form intermetallic compounds (IMC), Cu_6Sn_5 and Cu_3Sn. In fact the formation of Cu_6Sn_5provides visual evidence that the substrate has been wetted and an electrically and thermally conductive metallurgical bond established. It is not always appreciated, however, that in forming those intermetallic compounds some metallic Cu is lost from the substrate. And the physical properties of these IMC that influence the performance and reliability of the solder joint are generally inferior to those of Cu they replace (Table 1). However, possibly the most catastrophic consequence of the reaction between Sn and a Cu substrate is the complete disappearance of metallic Cu. It is the bond between the metallic Cu and the substrate that in most cases provides the basic mechanical integrity of the assembly.

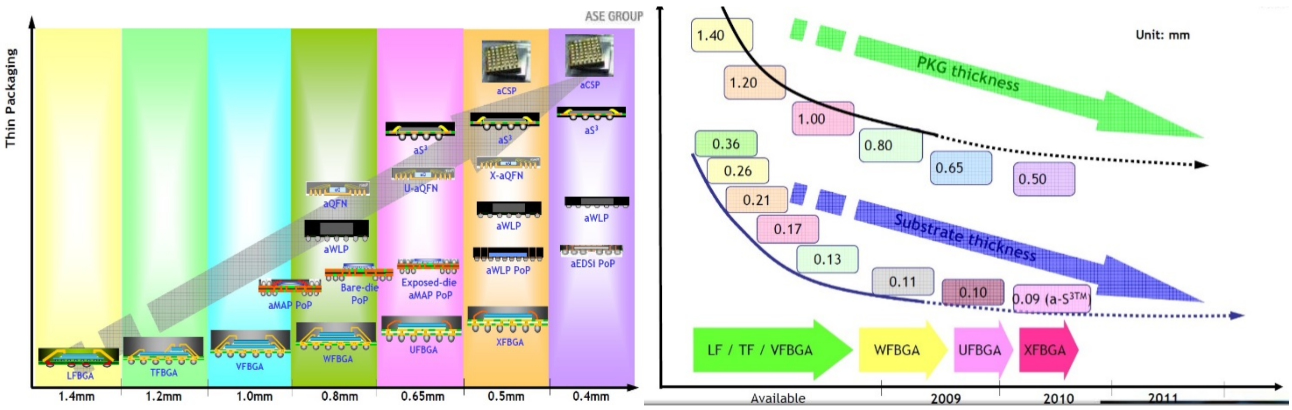


Fig 1. Trends in semiconductor package thickness [1]

Table 1. Comparison of IMC properties with those of Cu

Property	Cu_6Sn_5[2]	Cu_3Sn[2]	Cu[3]
Resistivity ($\mu\Omega$.cm)	17.5±0.10	8.93±0.10	0.01678
Thermal Conductivity (W/cm.K)	0.341±0.051	0.707±0.098	4.01
Young's Modulus (GPa)	85.56±1.65	108.3±4.4	110-128
Vickers Hardness (Kg/mm^2)	378±55	343±47	343-369
CTE (ppm/K)	16.3±0.3	19.0±0.3	16.5

From a thermodynamic point of view, a joint made to Cu substrates with Sn-based solder is in a metastable state. The phase diagram for the mix of elements present in the joint, including substrates would in many cases predict that when the system reached thermodynamic equilibrium there would be no metallic Cu left. All the Cu would have reacted with Sn to form intermetallic compounds.

In this paper the authors report:

- A case in which the consumption of the Cu substrate of a component was considered to have compromised the reliability in service of a consumer device
- An experiment that was carried out to obtain quantitative data on the rate of Cu consumption in three solder alloys that could be used to provide design guidelines for Cu substrate thickness.
- A simple model for IMC growth and Cu consumption

Case Study

The component in which the reduction in Cu substrate thickness was observed is a FOWLP (Fan-Out Wafer Level Package) in which the initial thickness of the Cu substrate was 9µm. After soldering with the Sn-3.0Ag-0.5Cu alloy ("SAC305") the Cu thickness had been reduced by 44% to 4µm (Figure 2). There was concern that there would be a further reduction in the thickness when the solder remelted during the reflow soldering of the component into the final assembly with a possible negative effect on the reliability of the joint in service.

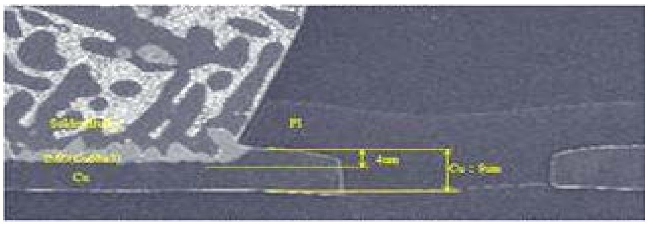


Figure 2. Reduction in Cu thickness after reflowing solder bump

Experimental

In order to quantify the consumption of the Cu substrate by dissolution during the soldering process and subsequent IMC growth a series of experiments were carried out under controlled conditions. The test vehicle consists of a 250x190mm panel with 182 9x9 area arrays (Figure 3).

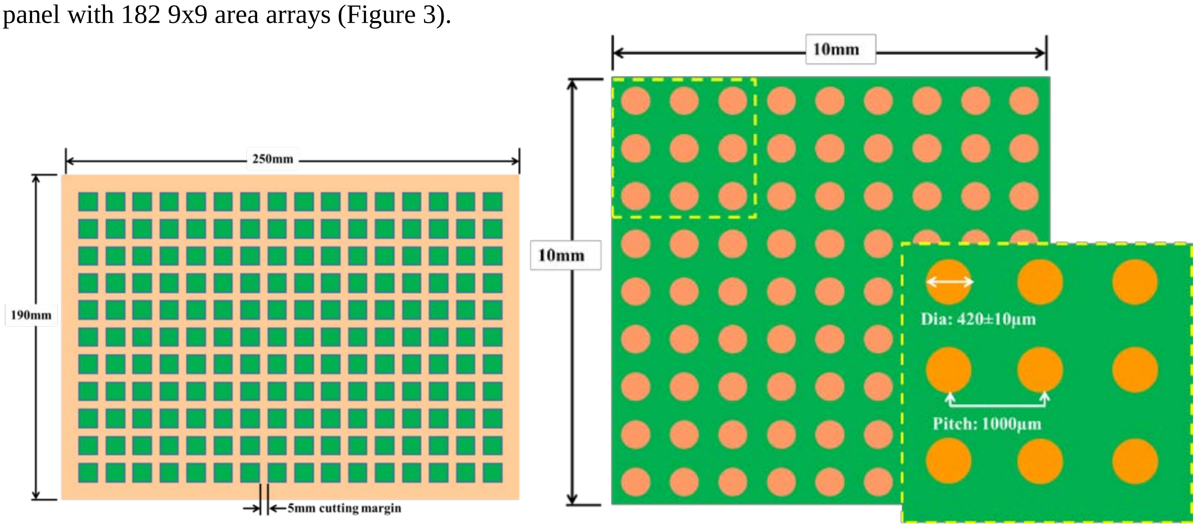


Figure 3. Test vehicle

The pad construction is shown in Figure 4.

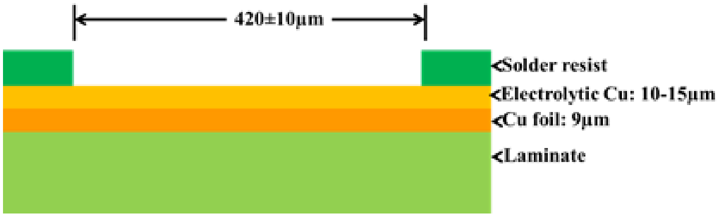


Figure 4. Pad construction

In addition to the solder alloy used for the assembly reported in the case study two other alloys were included in the experiment to determine the extent to which the solder alloy composition affected the total Cu consumption. The nominal composition of the three solder alloys is listed in Table 2.

Table 2. Nominal composition of alloys tested

Alloy	Nominal Composition				
	Sn	Ag	Cu	Ni	Bi
Sn-3.0Ag-0.5Cu	Rem.	3.0	0.5		
Sn-0.7Cu-0.05Ni	Rem.		0.7	0.05	
Sn-0.7Cu-0.05Ni-1.5Bi	Rem.		0.7	0.05	1.50

Ni is recognized as having a significant effect in slowing the rate of dissolution of Cu, slowing IMC growth and inhibiting the formation of Cu_3Sn [4,5, 6, 7]. It has been reported that Bi slows Cu dissolution and IMC growth [8, 9].

The 500µm solder balls were hand placed and reflow soldered in air to solder mask defined (SMD) pads (Figure 4) with a proprietary mildly activated rosin flux and the reflow profile used is shown in Figure 5

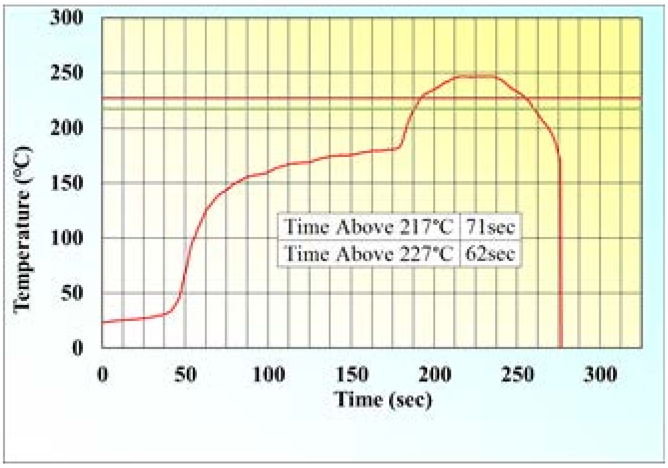


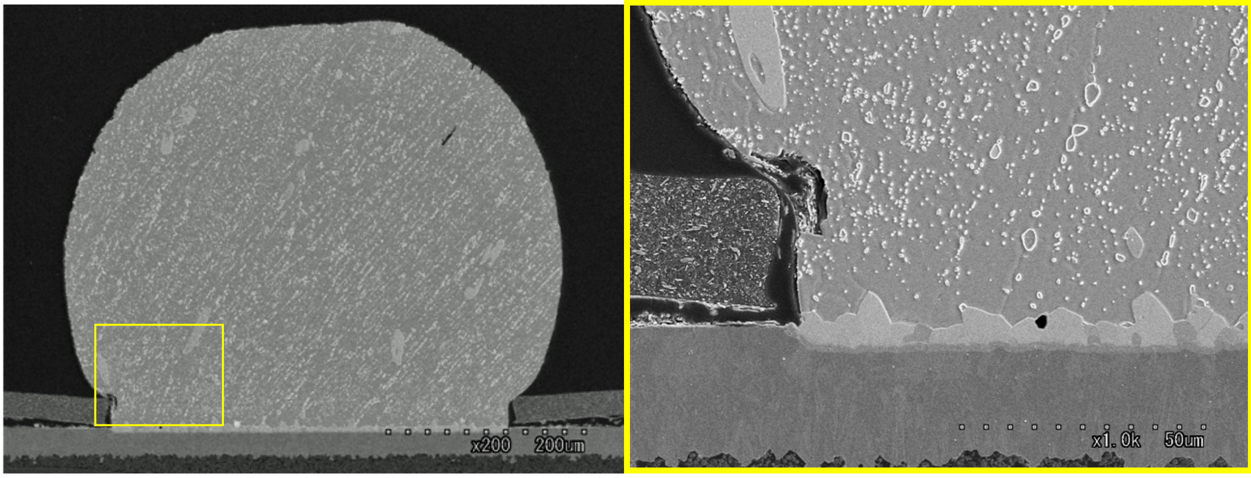
Figure 5. Reflow profile

After soldering the flux residue was removed with dichloromethane (DCM).

The test vehicles were then aged at 150°C in an air atmosphere for times up to 1008 hours.

Representative solder-bumped pads were removed from the test vehicle, mounted in Epoxy resin and sections prepared for SEM examination by mechanical polishing, ion milling and the application of vapour-deposited Pt. A typical cross-section of a reflowed and aged Sn-3.0Ag-0.5Cu sphere is shown in Figure 6.

A typical cross-section of the solder/substrate interface is shown in Figure 7 with the points at which the Cu_3Sn IMC thickness was measured indicated. The area of the IMC in a fixed length of the cross-section was measured using a tool that is part of the operating software of the SEM (yellow outline in Figure 7). The extent of Cu consumption was measured in an area adjacent to the solder resist where the original thickness of the Cu is protected by the solder resist (Figure 2).



(a) (b)

Figure 6. (a) Typical profile of Sn-3.0Ag-0.5Cu reflowed and aged solder ball. (b) Higher Magnification detail showing consumption of Cu substrate and IMC formation after reflow soldering and 1008 hours ageing at 150°C.

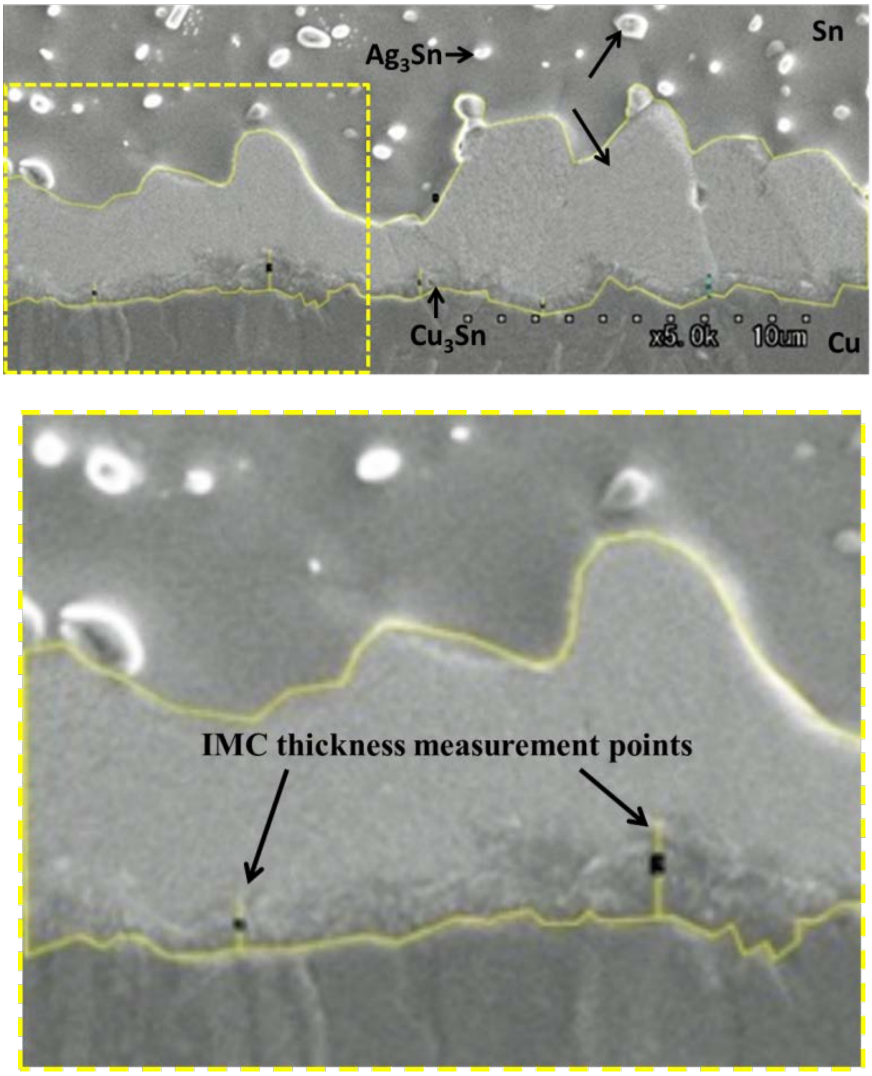


Figure 7. Total IMC area and Cu_3Sn thickness measurement in Sn-3.0Ag-0.5Cu alloys

Results

The trend of growth in the IMC (Cu_6Sn_5 + Cu_3Sn) as a result of the soldering process and subsequent ageing is apparent in Figure 8.

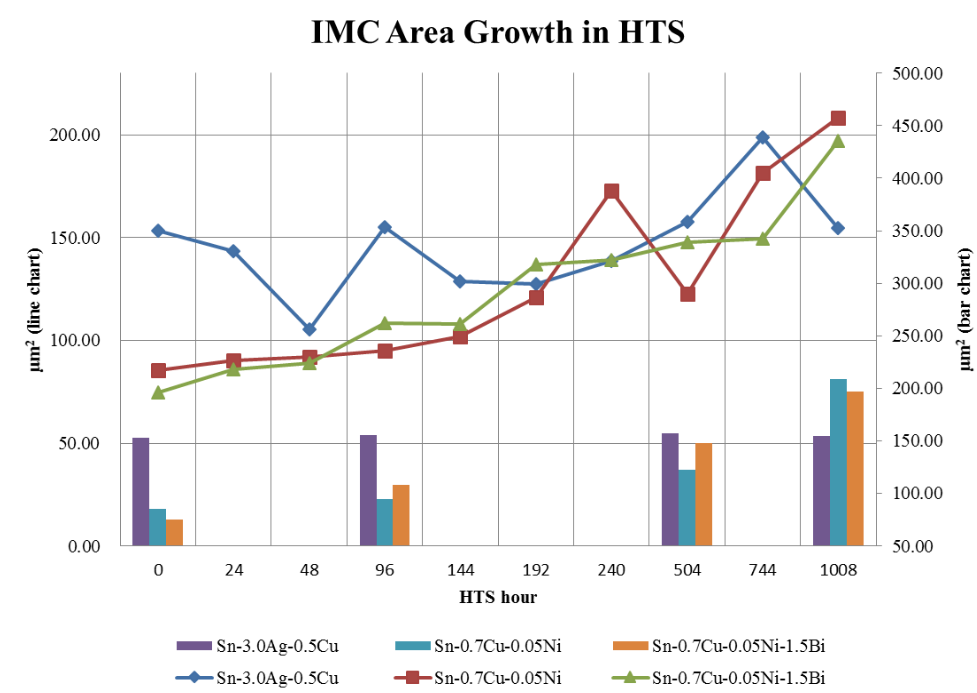
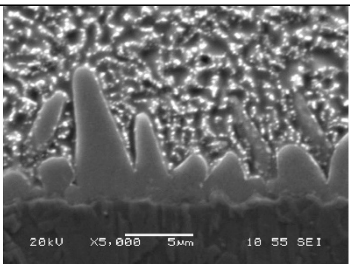
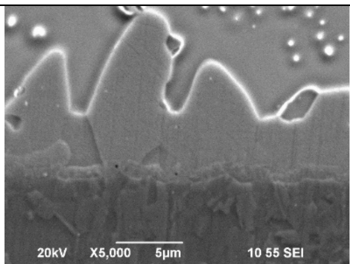
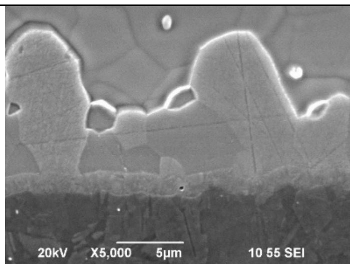
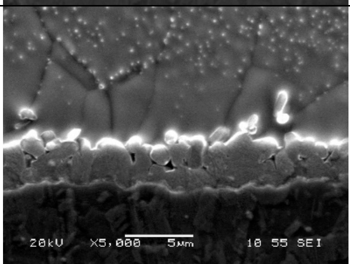
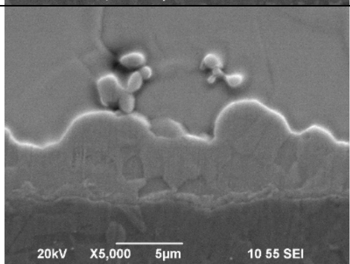
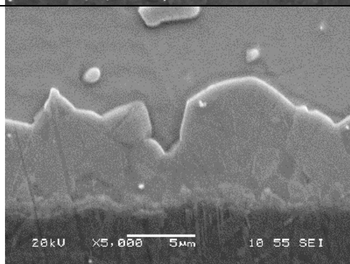
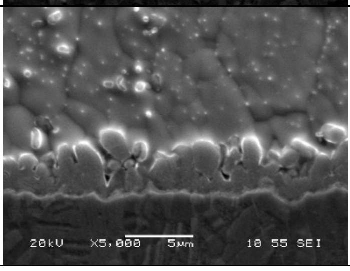
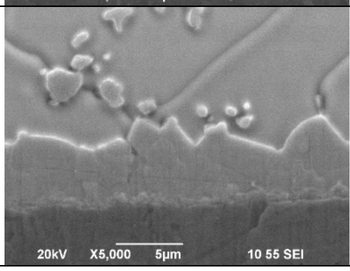
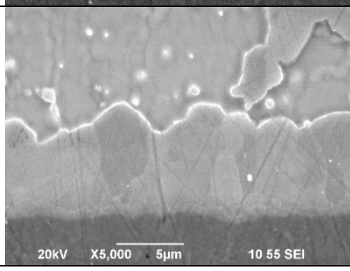


Figure 8. Area of Total IMC (Cu_6Sn_5 +Cu_3Sn) in cross-section as a function of ageing time at 150°C.

The change in the morphology, thickness and makeup of the IMC layer (Cu_6Sn_5 and Cu_3Sn) with alloy and ageing at 150°C is apparent in Table 3.

Table 3. Solder/Cu interface as a function of alloy and ageing time at 150°C

Alloy	As Reflowed	504 h	1008 h
Sn-3.0Ag-0.5Cu			
Sn-0.7Cu-0.05Ni			
Sn-0.7Cu-0.05Ni-1.5Bi			

There is considerable scatter in the data and on the basis of these measurements there appears to be no significant difference between the alloys in the total volume of IMC formed. Since most of the Cu required to form the IMC apparent in Figure 8 comes from the substrate it is not unexpected that there is no significant difference in reduction in thickness of that substrate (Figure 9).

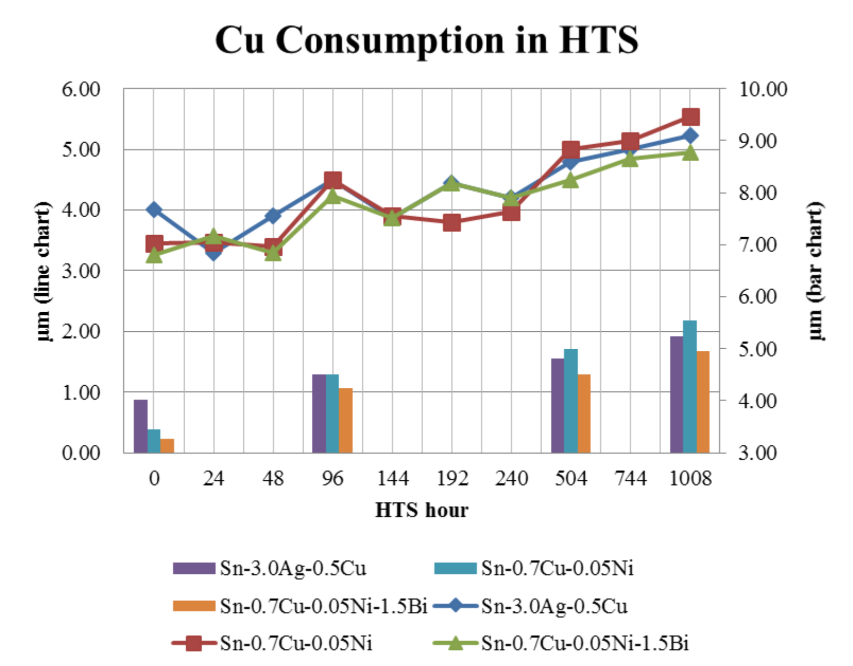


Figure 9. Thickness of Cu consumed by IMC growth as a function of ageing time at 150°C

However, a significant difference was found in the thickness of Cu_3Sn formed in Sn-3.0Ag-0.5Cu alloy and that formed with the other two alloys tested (Figure 10). Cu_3Sn forms at the interface between the Cu substrate and the Cu_6Sn_5 (Figure 7).

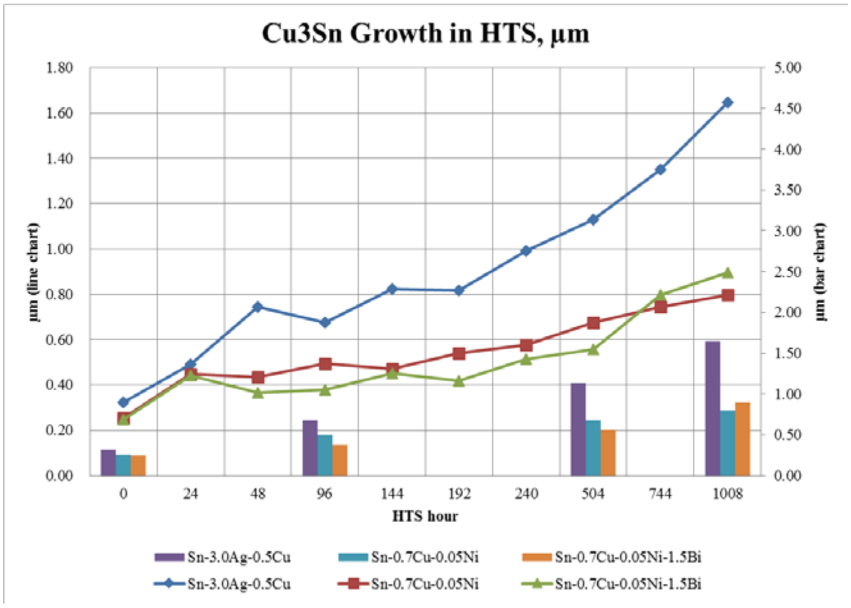


Figure 10. Thickness of Cu_3Sn as a function of ageing time at 150°C.

Modelling

There are two processes that contribute to the dissolution of Cu from the substrate:

1. The Cu that dissolves into the molten solder and forms IMC during reflow
2. The Cu loss to the formation of Cu_6Sn_5 (and later Cu_3Sn) during ageing

These two stages are illustrated schematically in Figure 11.

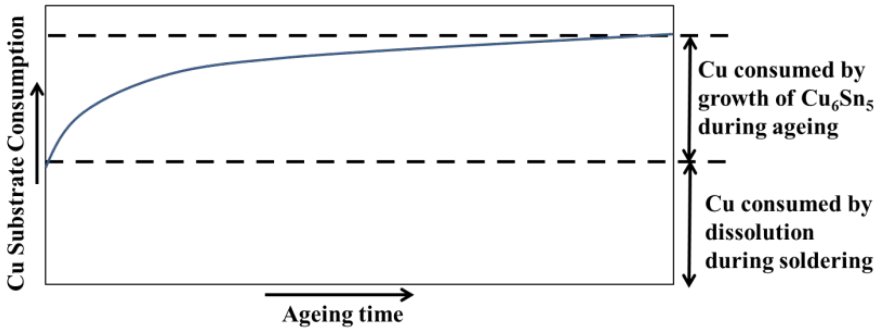


Figure 11. Schematic representation of the two Cu consumption mechanisms

The similarity between Figure 11 and the general trend in Figure 9 is apparent. Because the Sn-3.0Ag-0.5Cu alloy is unsaturated with respect to Cu and because it does not contain the Ni that is known to slow Cu dissolution there is a little more Cu dissolved by that alloy during soldering than the other two alloys (Figure 12).

In considering a possible model for predicting Cu consumption it was realised that it would be better based on the thickness of IMC than the area of IMC exposed in a cross-section. In the first stage model proposed in this paper account is taken only of the contribution of Cu_6Sn_5 to Cu consumption, which means that the prediction of Cu consumption will be a little less than if Cu_3Sn growth were also included. A model that includes the separate effects of the growth of both Cu_6Sn_5 and the Cu_3Sn on Cu consumption will be considered in the next stage of this study.

Thickness measurements were made on the samples in the as-reflowed condition and after 504 hours and 1008 hours ageing at 150°C and the results are plotted in Figure 12. In these measurements, the inhibiting effect of Ni on IMC growth is clearer and the additional inhibiting effect of Bi apparent. The data in Figure 12 was used as the basis for model development.

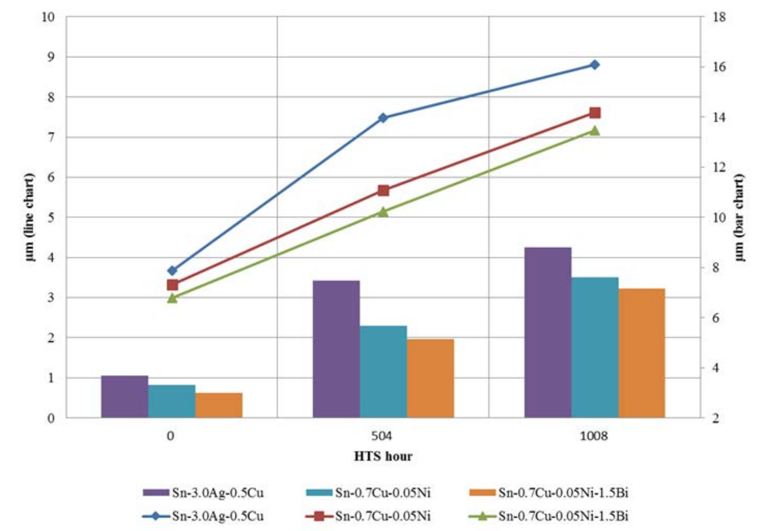


Figure 12. IMC thickness (Cu_6Sn_5 + Cu_3Sn) as a function of alloy and ageing

If in the second stage of Cu consumption it is assumed that:

- All the Cu in the Cu_6Sn_5 layer comes from the substrate
- No Cu_3Sn is formed
- There is an infinite supply of Sn

The formation of 1 mole of Cu_6Sn_5 requires 6 moles of Cu from the substrate so the theoretical thickness of the Cu_6Sn_5 layer (L_{Cu6Sn5}) depends on the thickness of the dissolved Cu (L_{Cu}) according to the equation:

$$L_{Cu6Sn5} = \frac{L_{Cu} \cdot \rho_{Cu} \cdot M_{Cu6Sn5}}{\rho_{Cu6Sn5} \cdot 6M_{Cu}}$$

Inserting values for the densities of the phases and their molar masses gives the thickness of Cu dissolved as a function of the Cu_6Sn_5layer thickness:

$L_{Cu} = 0.36 \cdot L_{Cu6Sn5}$ (Eq. 1)

Assuming that IMC layer growth occurs at a constant temperature during solid state ageing and that IMC growth is controlled by volume diffusion through the Cu_6Sn_5 layer, the rate at which the IMC thickens is inversely proportional to the layer thickness. This means that, after integration with appropriate limits, the thickness is given by:

$$L_{Cu6Sn5} = \sqrt{{L_0}^2 + k^2 t} \qquad \text{(Eq. 2)}$$

Where L_0 is the layer thickness at the start of ageing and k can be expressed as:

$$k^2 = {k_0}^2 e^{-\left(\frac{Q}{RT}\right)}$$

It has been reported that for Sn-0.6Cu-0.05Ni[4]:

$$k^2 = 2.02641\times10^{-9} e^{-\left(\frac{7986.4}{T}\right)} \mathrm{m^2/s} \qquad \text{(Eq. 3)}$$

Combining Eq. 2 and Eq. 3

$$L_{Cu6Sn5} \approx \sqrt{{L_0}^2 + \left(2\times10^{-9} e^{-\left(\frac{7986.4}{T}\right)} t\right)} \text{(Eq. 4)}$$

Combining Eq. 1 and Eq. 4 gives an approximate expression for the thickness of Cu consumed during isothermal ageing:

$$\Delta L_{Cu} = 0.36 \cdot (\ L_{Cu6Sn5} \ - \ L_0\ )\mathrm{m} \quad \text{(Eq,5)}$$

Inserting the ageing temperature (423.15K), the maximum ageing time (3,628,800 s) and the Cu_6Sn_5 layer thickness prior to ageing for Sn-0.7Cu-0.05Ni/Cu (3.3µm), this model predicts a Cu_6Sn_5 layer thickness after ageing at 150°C for 1008 hours of 7.6µm (i.e. a change of thickness during ageing of 4.3µm).

Using Eq. 5, the thickness of Cu consumed during ageing is 1.6µm giving a total thickness of Cu consumed of5.1µm (3.45µm + 1.6µm), which is in reasonable agreement with the experimental results considering the simplicity of this first stage model(Figure 13).

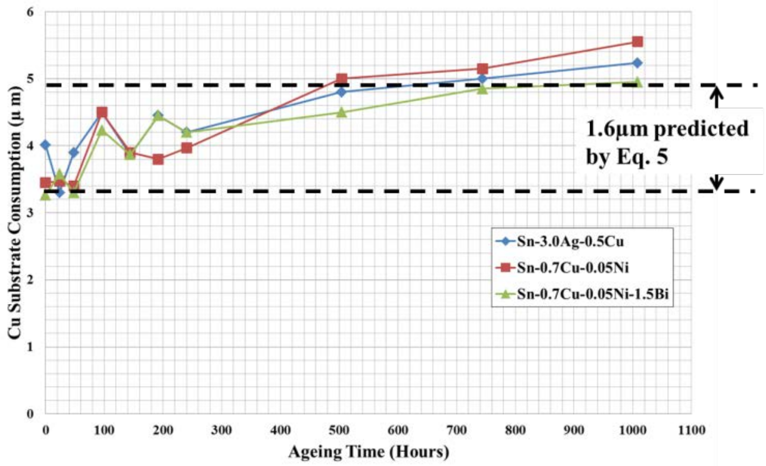


Figure 13. Fit of prediction model to experimental data

Discussion

The well-established inhibiting effect of Ni on Cu dissolution in molten solder and subsequent IMC growth was not clear in the first set of measurements of IMC area (Figure 8) and Cu consumption (Figure 9). On the basis of the simple model proposed this suggests that the critical factors in the model, two constants that depend on the diffusivity of atomic species through Cu_6Sn_5, are not as strongly affected by the composition of the alloys tested as might be expected on the basis of reports in the literature [4-9].

However, an effect of Ni was observed in the apparent inhibiting effects of Ni and Bi on Cu_3Sn growth, which is perhaps more sensitive to their diffusion inhibiting effects. Since the formation of the Cu-rich Cu_3Sn is an intermediate stage in the formation of Cu_6Sn_5 by reaction between Sn in the solder and Cu in the substrate it could be expected that in the longer term there would be less formation of Cu_6Sn_5 so that the total volume of IMC formed (Cu_6Sn_5 + Cu_3Sn) would be less. The consequence would be less Cu consumption than if there were no Ni present.

The stronger evidence of effects of Ni and Bi on IMC grow thin the subsequent measurements of average total IMC thickness (Figure 12) suggests that further study of the use of these alloying additions to manage Cu consumption is worth pursuing.

Future work
It is clear from the attempt to develop a predictive model for the reduction in the thickness of Cu substrates during soldering processes with Pb-free solders based around the Sn-Cu eutectic and subsequent ageing that more work needs to be done to identify the contribution of each process to the net effect. *In situ* observation of the interaction between the reflowing solder and the Cu substrate [10] appears to offer the prospect of identifying the separate contributions to the formation of the intermetallic layer and is an avenue of investigation that will be pursued.

On the basis of this additional information an attempt will be made to develop a prediction model that will take account of both IMC that contribute Cu consumption.

References
1. Solid State Technology® 2012 Archive p3 "Insights from Leading Edge http://electroiq.com/insights-from-leading-edge/2012/page/3/

2. RJ Field, SR Low III, GK Lucey Jr "Physical and mechanical properties of intermetallic compounds commonly found in solder joints. Metal Science of Joining, Proceedings of TMS Symposium, Cincinnati, Oct 24, 1991

3. Wikipedia https://en.wikipedia.org/wiki/Copper

4. JY Tsai, YC Hu, CM Tsai, CR Kao, "A study on the reaction between Cu and Sn3.5Ag solder doped with small amounts of Ni", Journal of Electronic Materials, Vol. 32, No. 11, 2003

5. JW Yoon, YH Lee, DG Kim, HB Kang, SJ Suh, CW Yang, CB Less, JM Jung, CS Yoo, SB Jung "Intermetallic compound layer growth at the interface between Sn-Cu-Ni solder and Cu substrate", Journal of Alloys and Compounds 381 (2004) 151-157

6. H Nishikawa, Jin Yu Piao, T Takemoto, Interfacial reaction between Sn-0.7Cu (-Ni) solder and Cu substrate, Journal of Electronic Materials, Vol. 35, No. 5 2006

7. MJ Rizva, C Bailey, YC Chan, MN Islam, H Lu, "Effect of adding 0.3wt% Ni into Sn-0.7wt% Cu solder, Part II, Growth of intermetallic layer with Cu during wetting and ageing, Journal of Alloys and Compounds, 438 (2007) 122-128

8. Jie Zhao, Lin Qi, Lai Wang, "Effect of Bi on the kinetics of intermetallic growth in Sn-3Ag-0.5Cu/Cu Solder Joint", Proceedings of HDP'06 (High Density Microsystem Design and Packaging and Component Failure Analysis)

9. M He, VL Acoff, "Effect of Bi on the interfacial reaction between Sn-3.7Ag-xBi solders and Cu", Journal of Electronics Materials, Vol.37, No. 3, 2008.

10. MAA Mohd Salleh, SD McDonald, CM Gourlay, SA Belyakov, H Yasuda, K Nogita, "Effect of Ni on the Formation and Growth of Primary Cu_6Sn_5
Intermetallics in Sn-0.7 wt.%Cu Solder Pastes on Cu
Substrates During the Soldering Process". Journal of ELECTRONIC MATERIALS, Vol. 45, No. 1, 2016
DOI: 10.1007/s11664-015-4121-x

Dissolution in Service of the Copper Substrate of Solder Joints

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Michihiro Sato	Nagase & Co., Ltd., Japan
Christopher Gourlay Sergey Belyakov	Imperial College London, UK

Project triggered by a customer concern

Objectives

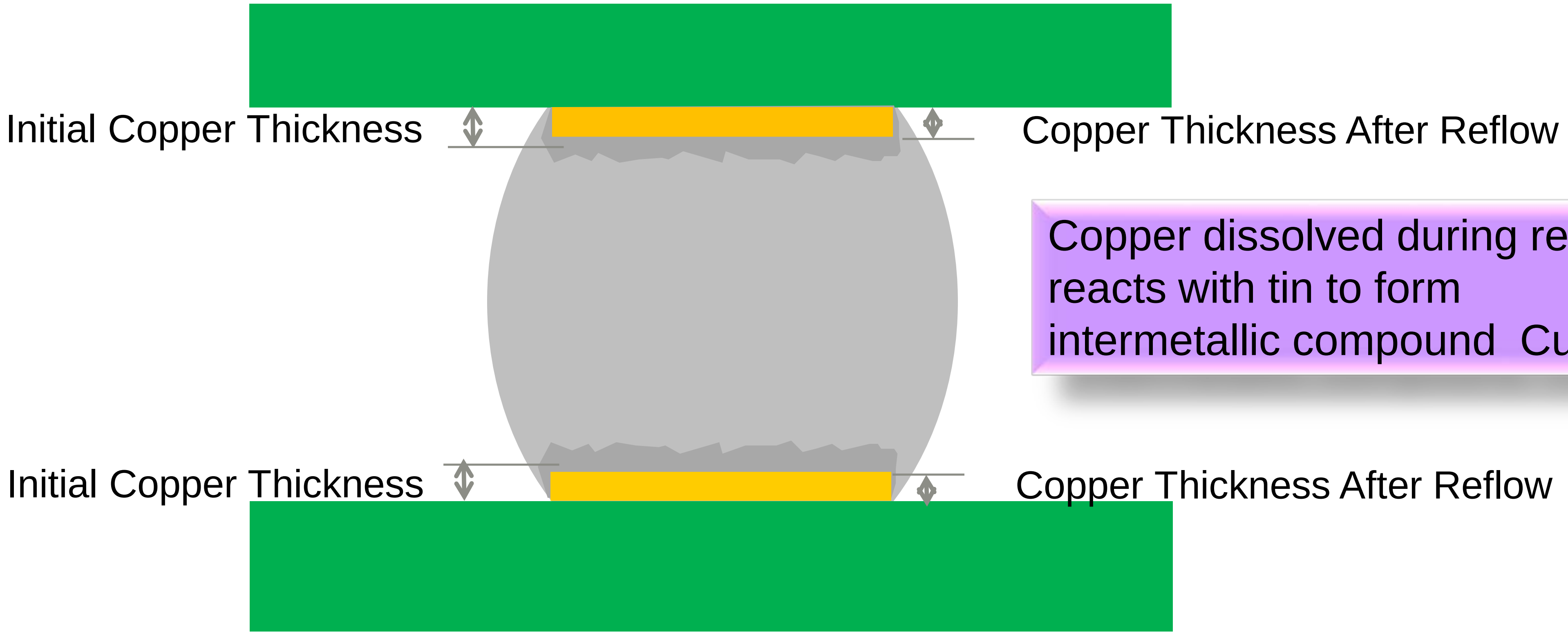
Provide a reminder that:

- The system that is a solder joint is not in thermodynamic equilibrium but in a metastable state
- The conditions of normal service provide an opportunity for the system to move toward thermodynamic equilibrium
- Metallic copper might not be a part of the system when it has reached thermodynamic equilibrium

- **Copper loss is an issue in all solder joints**
- **But the risk is greatest with thin substrates**

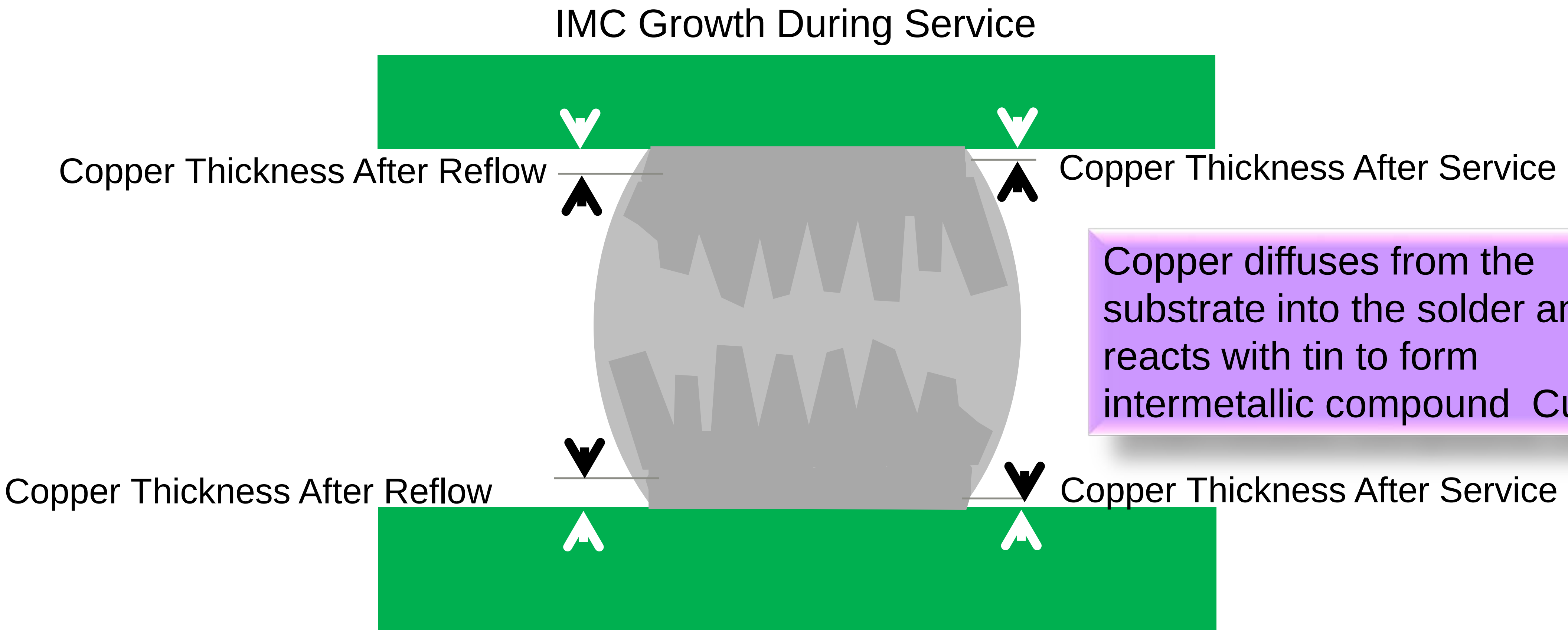
A Solder Joint as a Metastable System

IMC Growth During Reflow



Copper dissolved during reflow reacts with tin to form intermetallic compound Cu_6Sn_5

A Solder Joint as a Metastable System

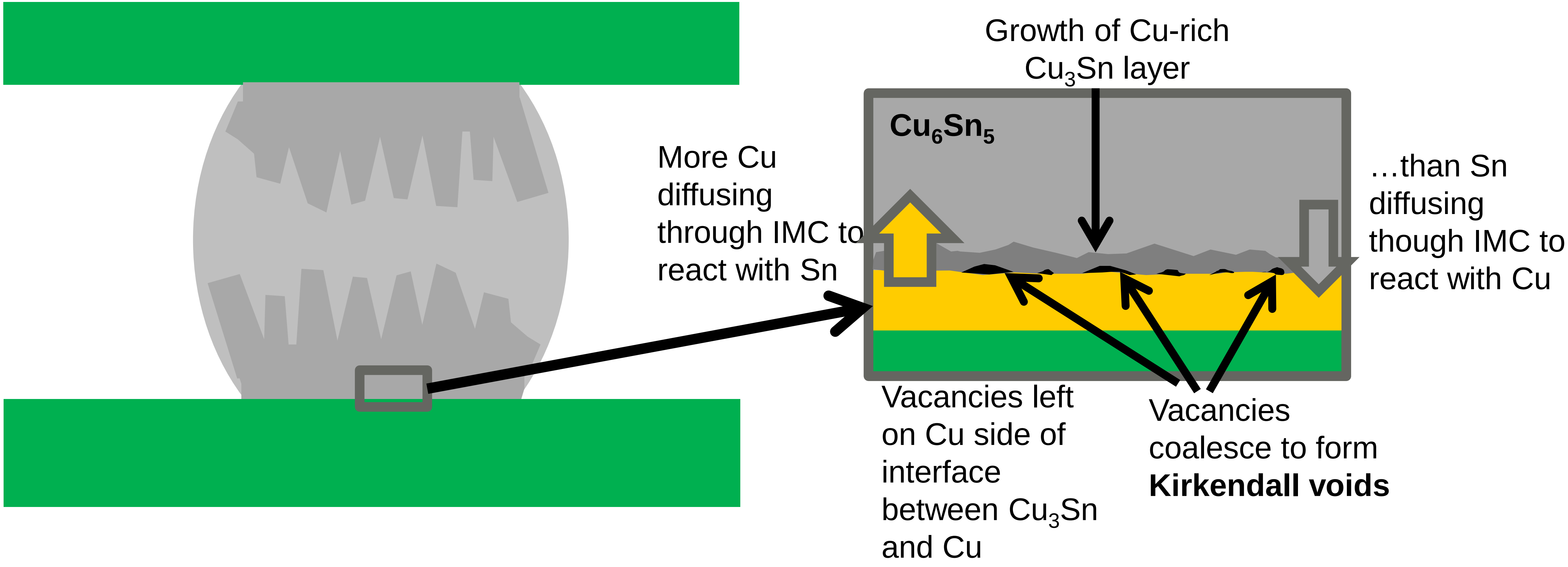


Copper diffuses from the substrate into the solder and reacts with tin to form intermetallic compound Cu_6Sn_5

The Case of the Disappearing Copper

A Solder Joint as a Metastable System

Cu_3Sn formation and Kirkendall voids at the Cu/Cu_6Sn_5 interface



Effect of Replacing Copper by IMC

Property	Cu_6Sn_5	Cu_3Sn	Cu
Resistivity (μΩ.cm)	17.5±0.10	8.93±0.10	0.01678
Thermal Conductivity (W/cm.K)	0.341±0.051	0.707±0.098	4.01
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Vickers Hardness (Kg/mm^2)	378±55	343±47	343-369
CTE (ppm/K)	16.3±0.3	19.0±0.3	16.5

Loss of Electrical and Thermal Conductivity as Cu is replaced by IMC

2. RJ Field, SR Low III, GK Lucey Jr "Physical and mechanical properties of intermetallic compounds commonly found in solder joints. Metal Science of Joining, Proceedings of TMS Symposium, Cincinnati, Oct 24, 1991
3. Wikipedia https://en.wikipedia.org/wiki/Copper

Trends in Electronics …

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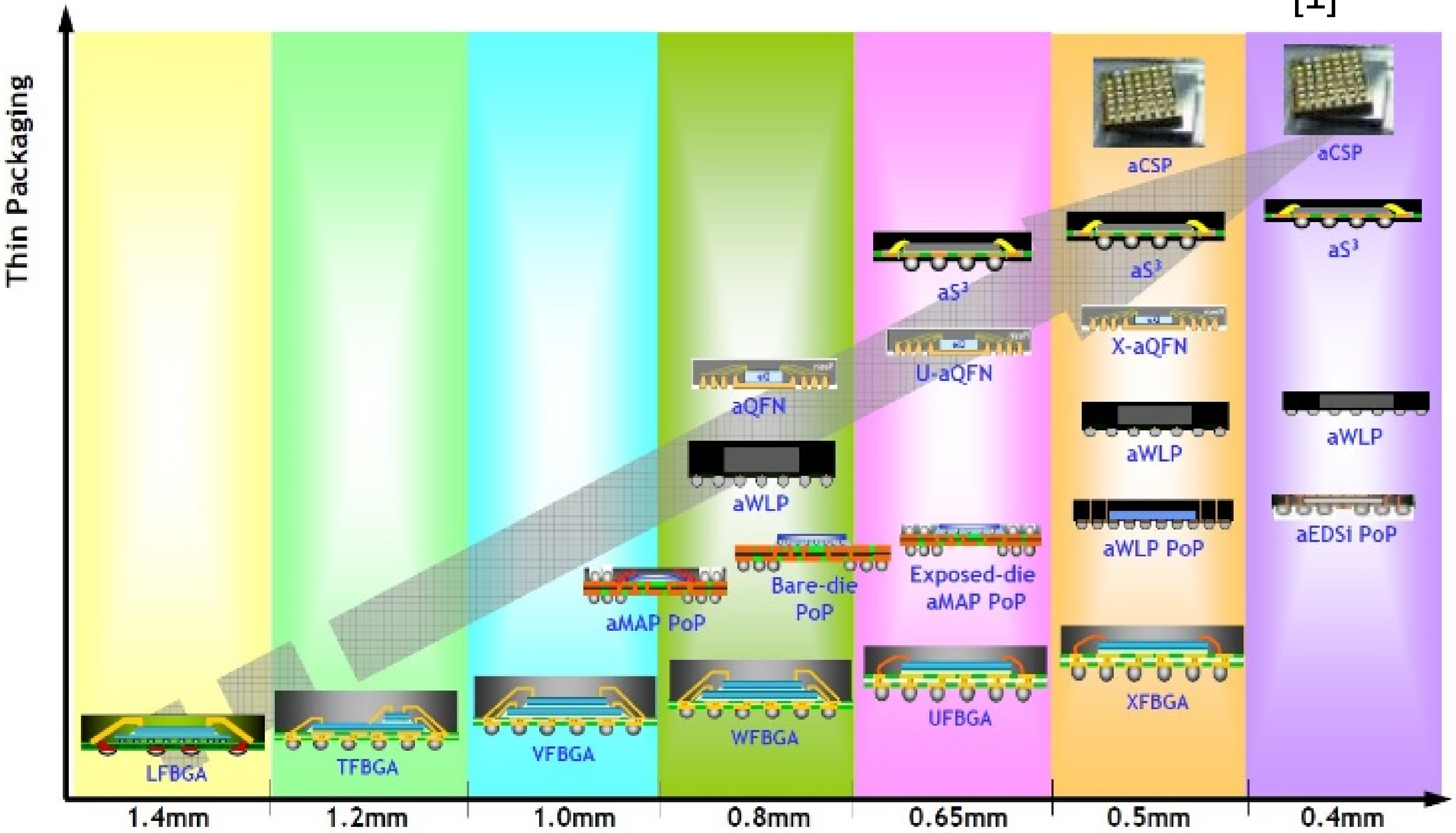

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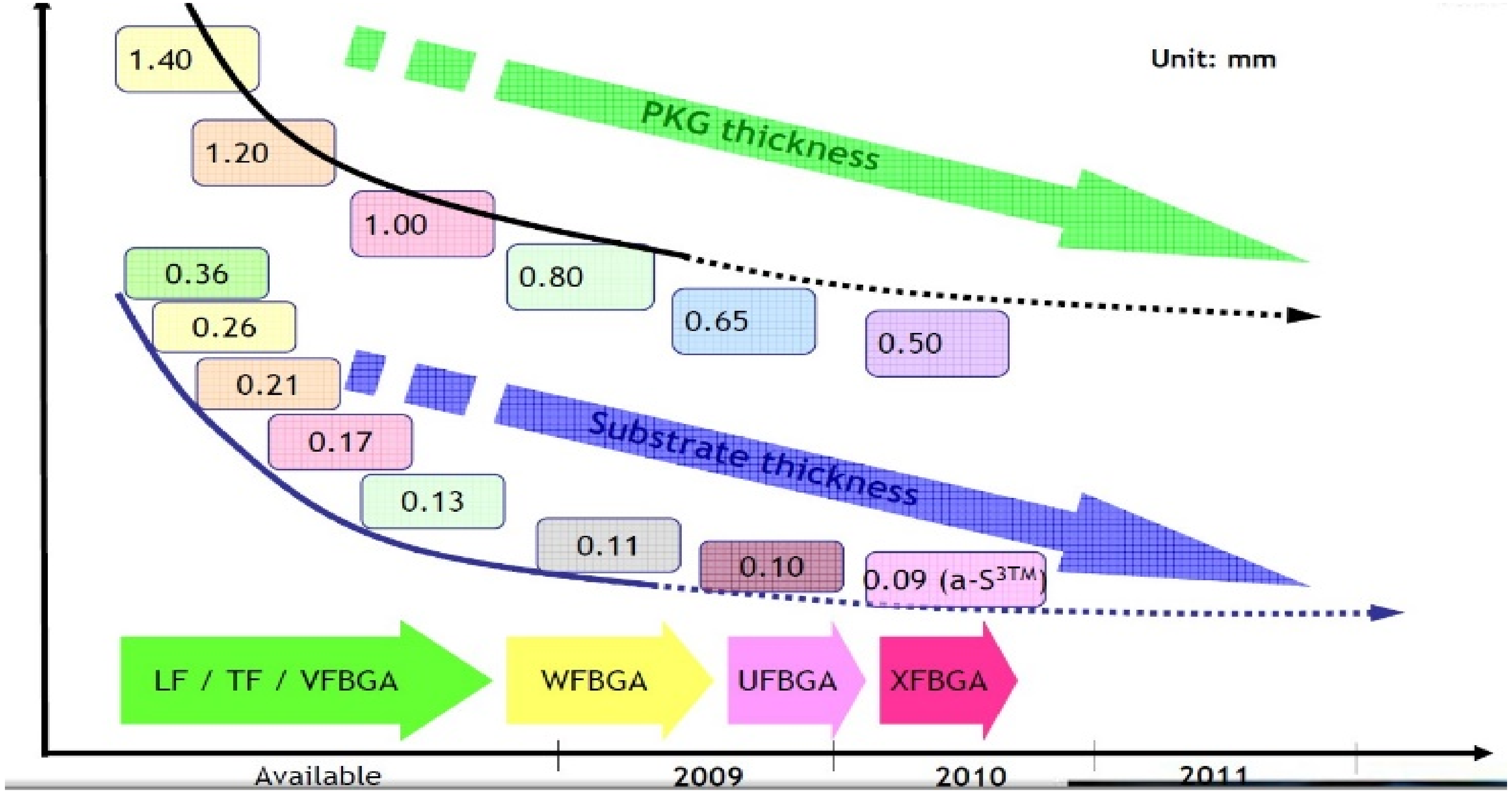
Trends in Electronics Reflected in Reducing Substrate Thickness



Increasing likelihood of copper substrate being completely lost to IMC formation

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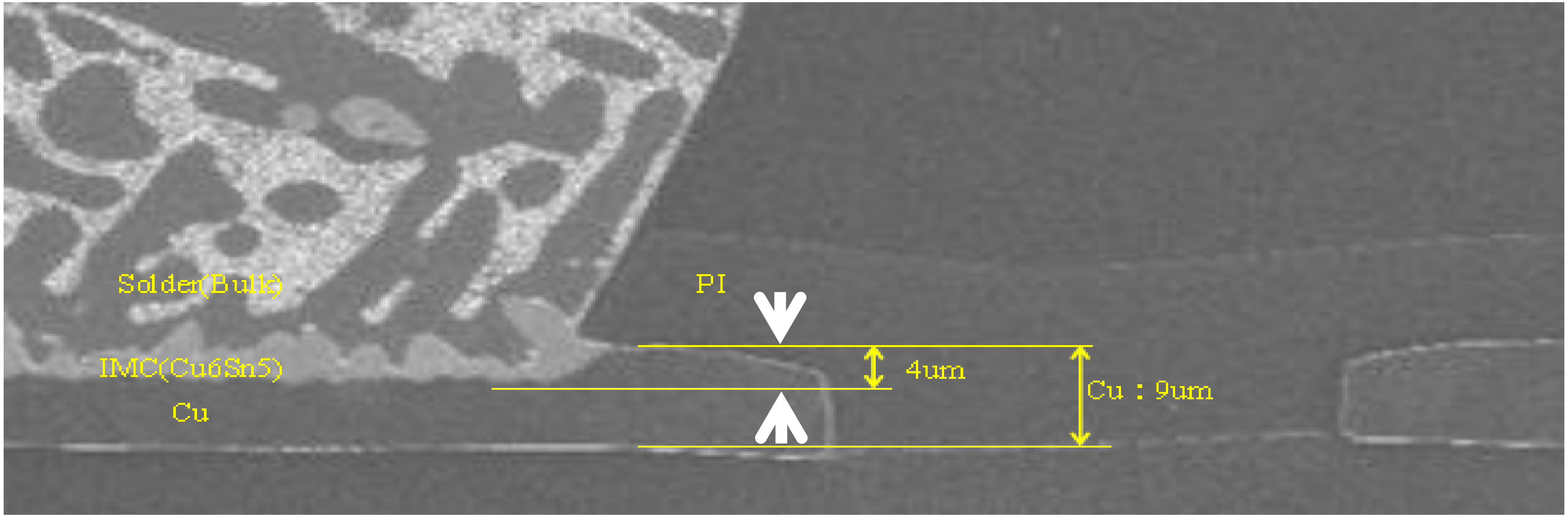
A Case Study

FOWLP (Fan-Out Wafer Level Package) Reflow Soldered with Sn-3.0Ag-0.5Cu

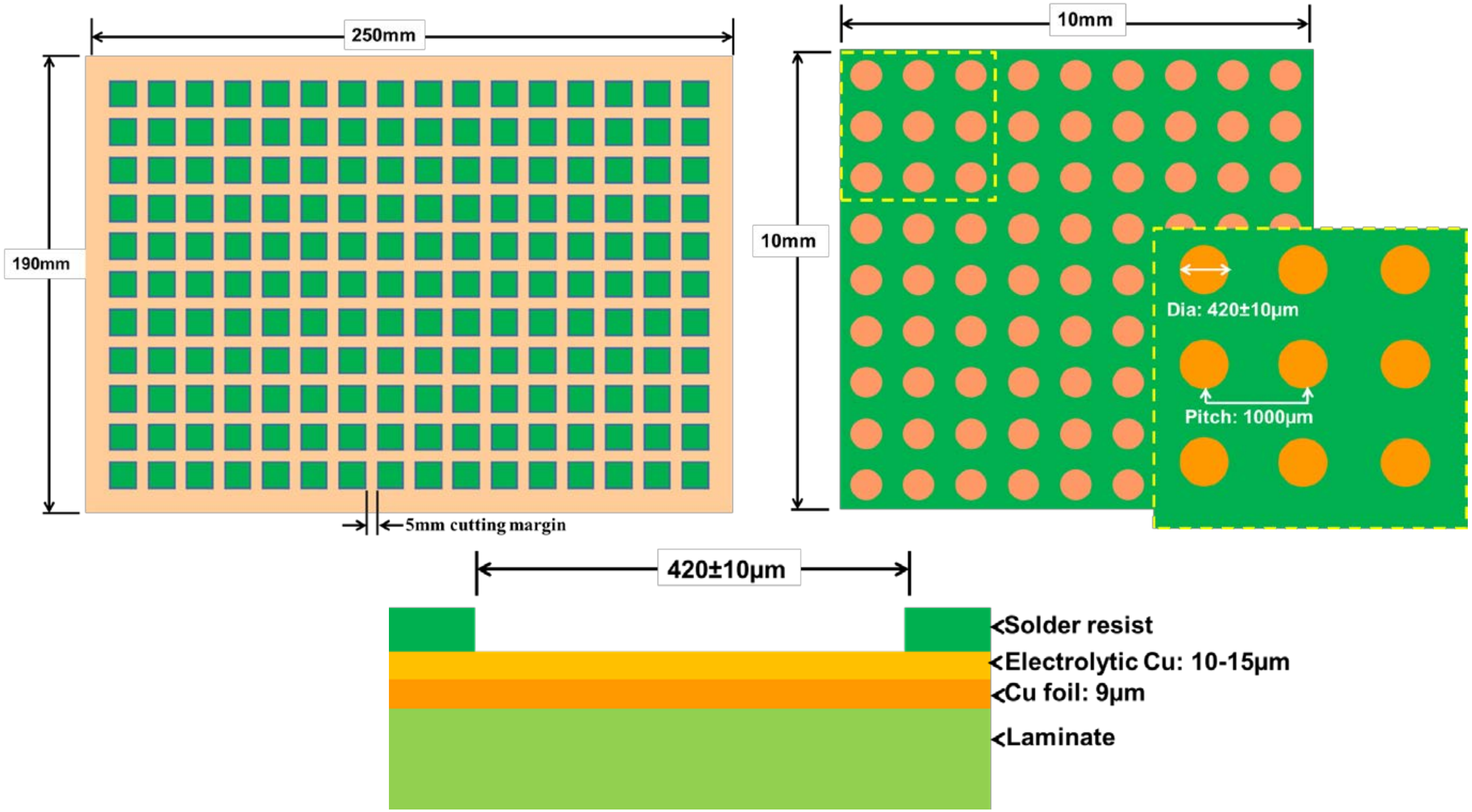


44% reduction in copper thickness (9µm to 5µm)!

Enough to prompt an investigation…

An Experiment

The Test Vehicle: 250mm x190mm panel with 182 9x9 area arrays



An Experiment

Solder Alloys Tested

Alloy	Nominal Composition				
	Sn	Ag	Cu	Ni	Bi
Sn-3.0Ag-0.5Cu	Rem.	3.0	0.5		
Sn-0.7Cu-0.05Ni	Rem.		0.7	0.05	
Sn-0.7Cu-0.05Ni-1.5Bi	Rem.		0.7	0.05	1.50

Ni reported to suppress Cu dissolution

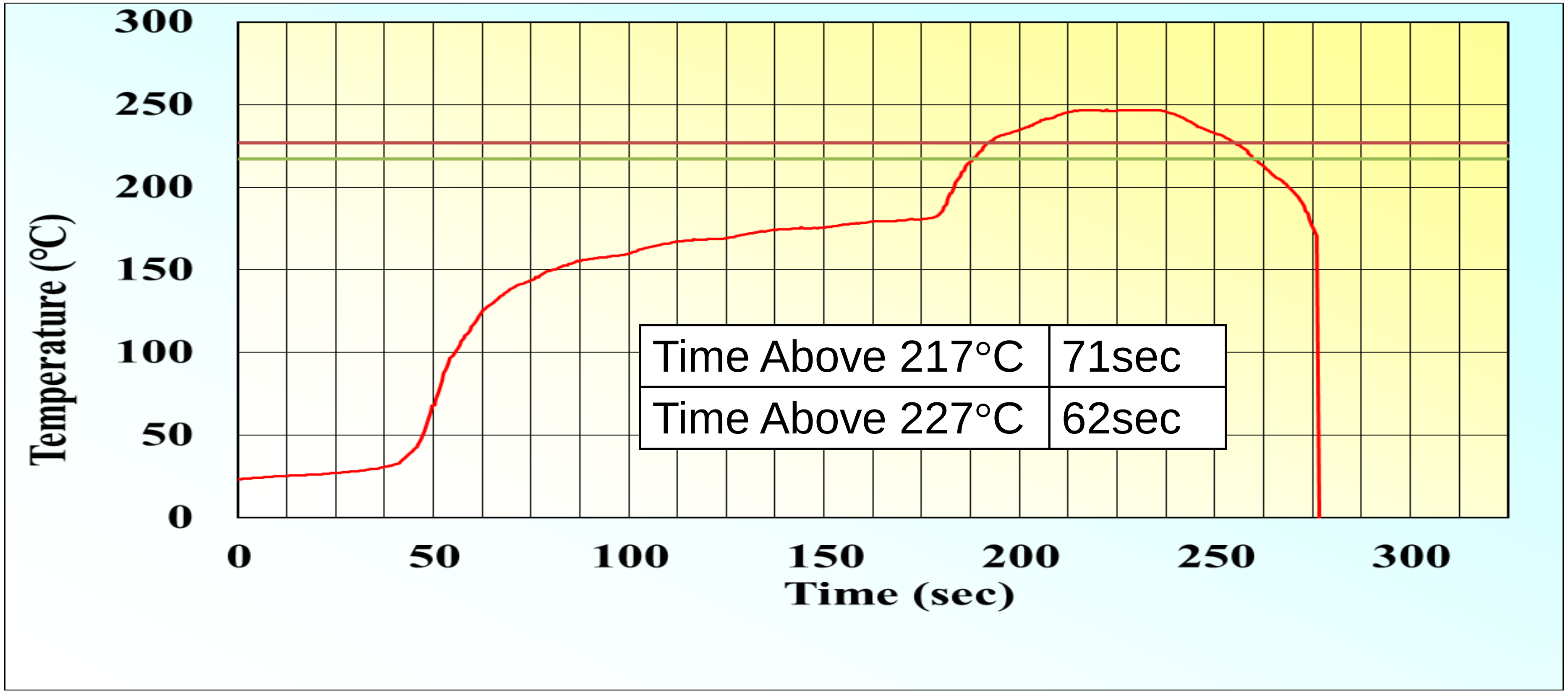
JY Tsai et al. "A study on the reaction between Cu and Sn3.5Ag solder doped with small amounts of Ni", Journal of Electronic Materials, Vol. 32, No. 11, 2003
JW Yoon et al. "Intermetallic compound layer growth at the interface between Sn-Cu-Ni solder and Cu substrate", Journal of Alloys and Compounds 381 (2004) 151-157
H Nishikawa, "Interfacial reaction between Sn-0.7Cu (-Ni) solder and Cu substrate, Journal of Electronic Materials, Vol. 35, No. 5 2006
MJ Rizva et al. "Effect of adding 0.3wt% Ni into Sn-0.7wt% Cu solder, Part II, Growth of intermetallic layer with Cu during wetting and ageing, Journal of Alloys and Compounds, 438 (2007) 122-128

Bi reported to suppress Cu dissolution

Jie Zhao et al. "Effect of Bi on the kinetics of intermetallic growth in Sn-3Ag-0.5Cu/Cu Solder Joint", Proceedings of HDP'06 (High Density Microsystem Design and Packaging and Component Failure Analysis)
M He,"Effect of Bi on the interfacial reaction between Sn-3.7Ag-xBi solders and Cu", Journal of Electronics Materials, Vol.37, No. 3, 2008.

An Experiment

Reflow Profile

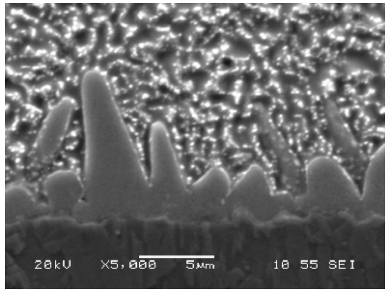
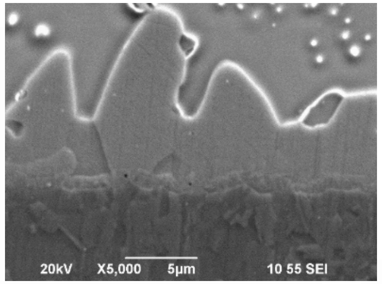
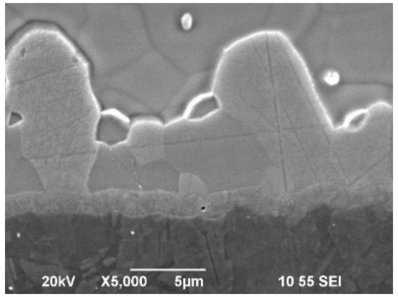
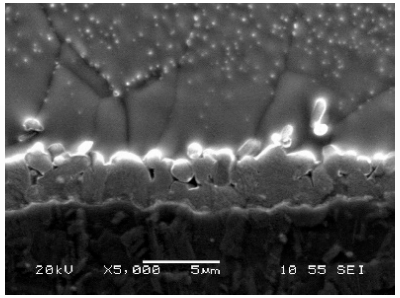
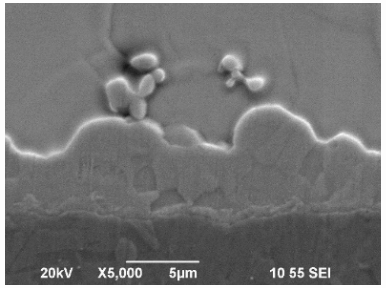
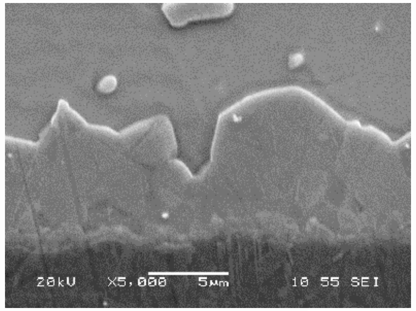
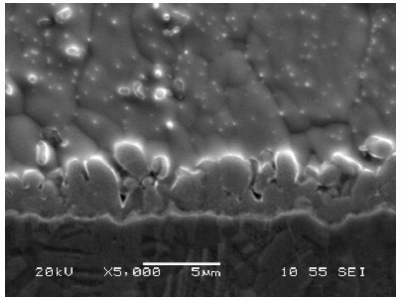
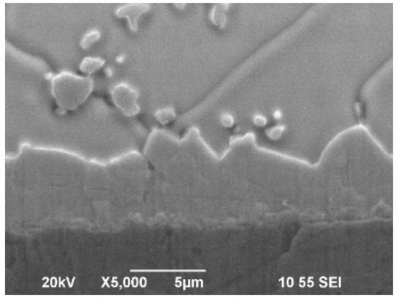
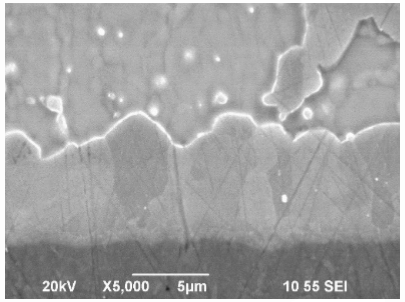


Time Above 217°C	71sec
Time Above 227°C	62sec

Age at 150°C in air atmosphere for up to 1008 hours (42 days)

An Experiment

Result: Solder/Cu Interface as a Function of Alloy and Ageing Time at 150°C

Alloy	As Reflowed	504 h	1008 h
Sn-3.0Ag-0.5Cu			
Sn-0.7Cu-0.05Ni			
Sn-0.7Cu-0.05Ni-1.5Bi			

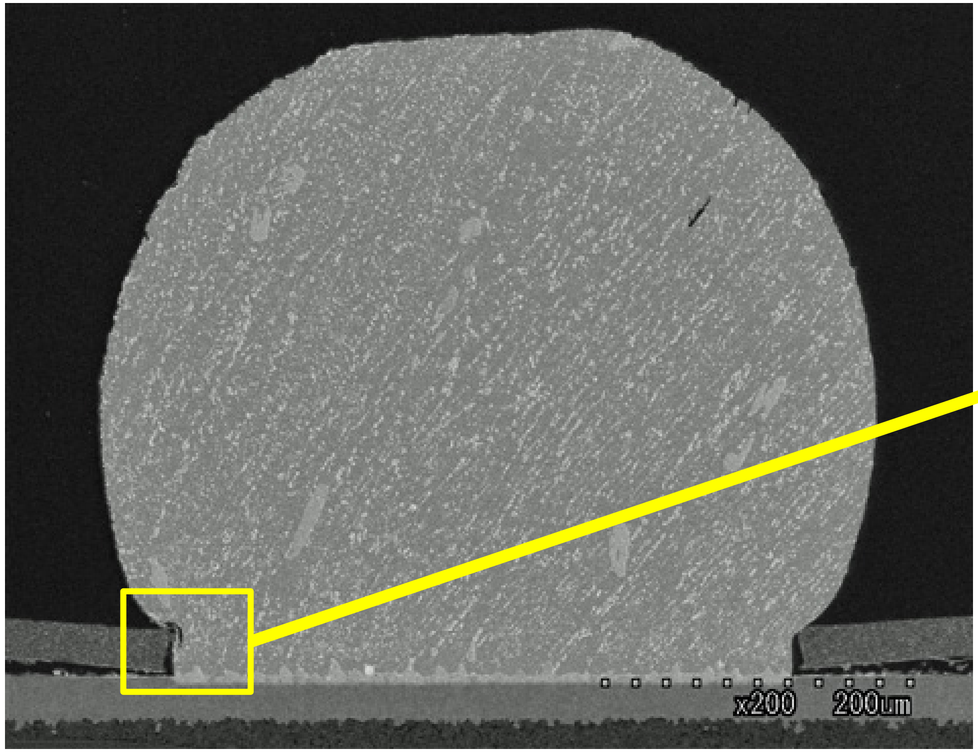
Tendency to columnar morphology

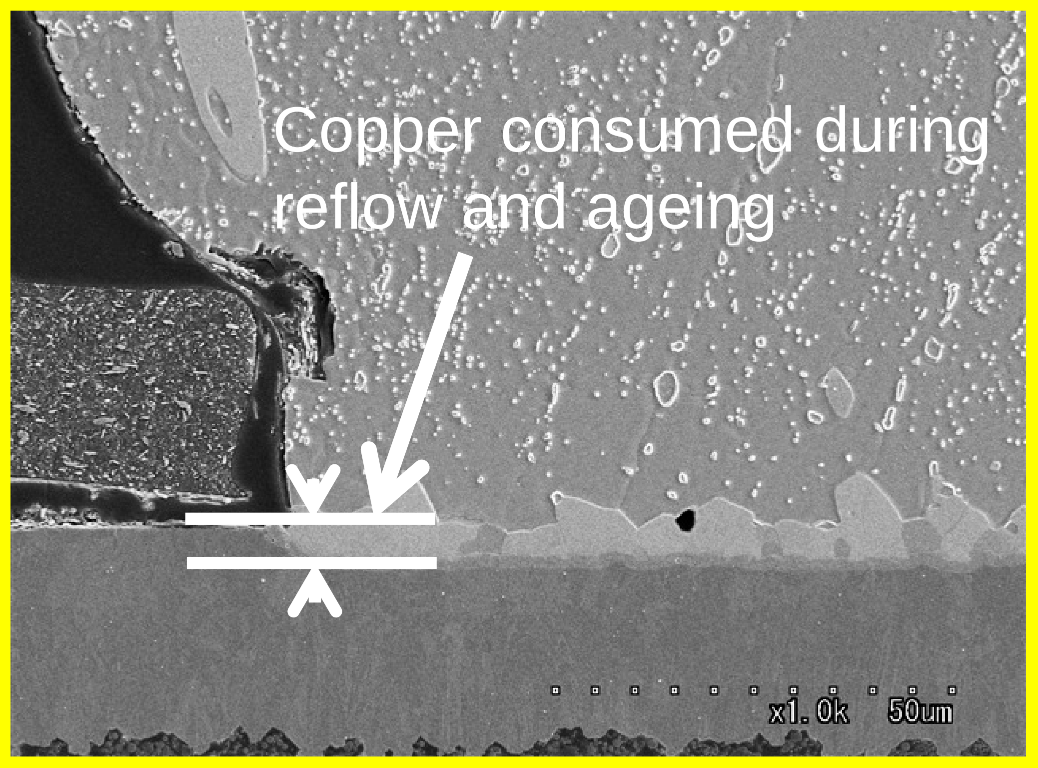
Generally smoother solder/IMC interface

Further smoothing of solder/IMC interface

An Experiment

Typical cross-section of Sn-3.0Ag-0.5Cu reflowed and aged solder ball

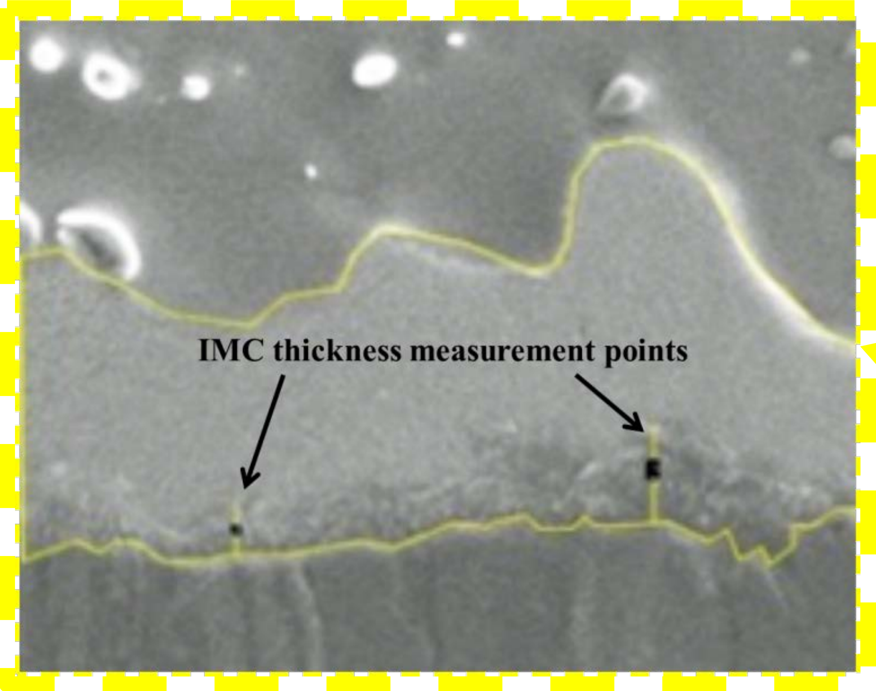




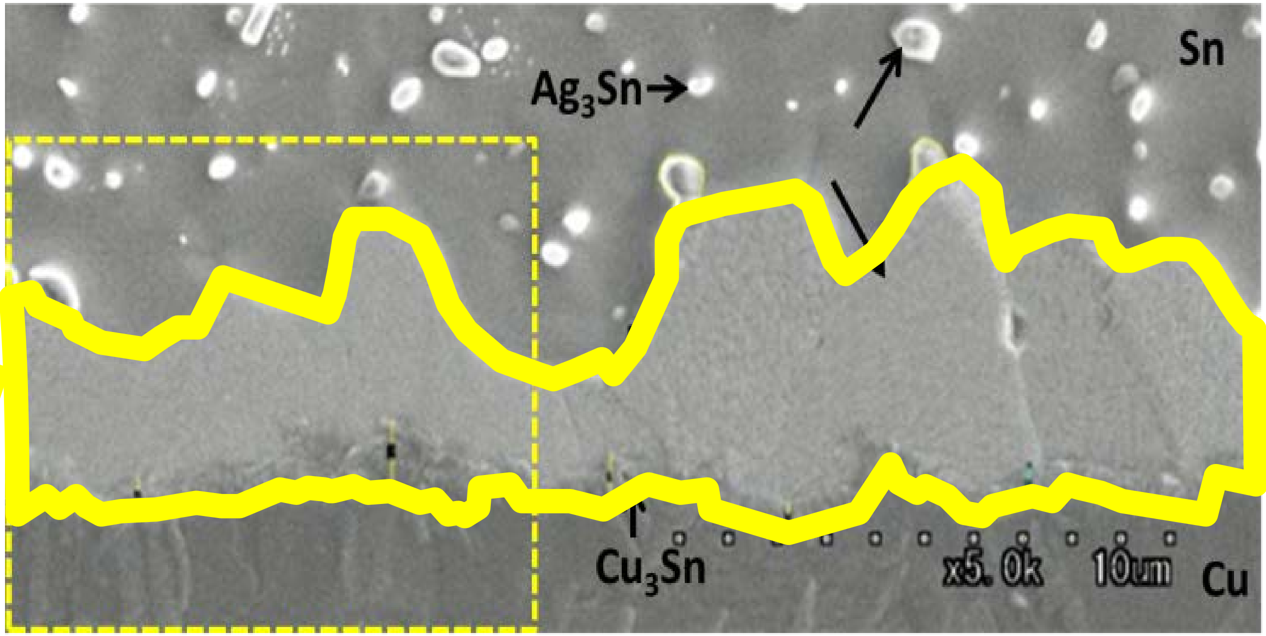
An Experiment

Total IMC area and Cu_3Sn thickness measurement in Sn-3.0Ag-0.5Cu alloys

Measure thickness of Cu_3Sn



Use image analysis software to measure the area of IMC

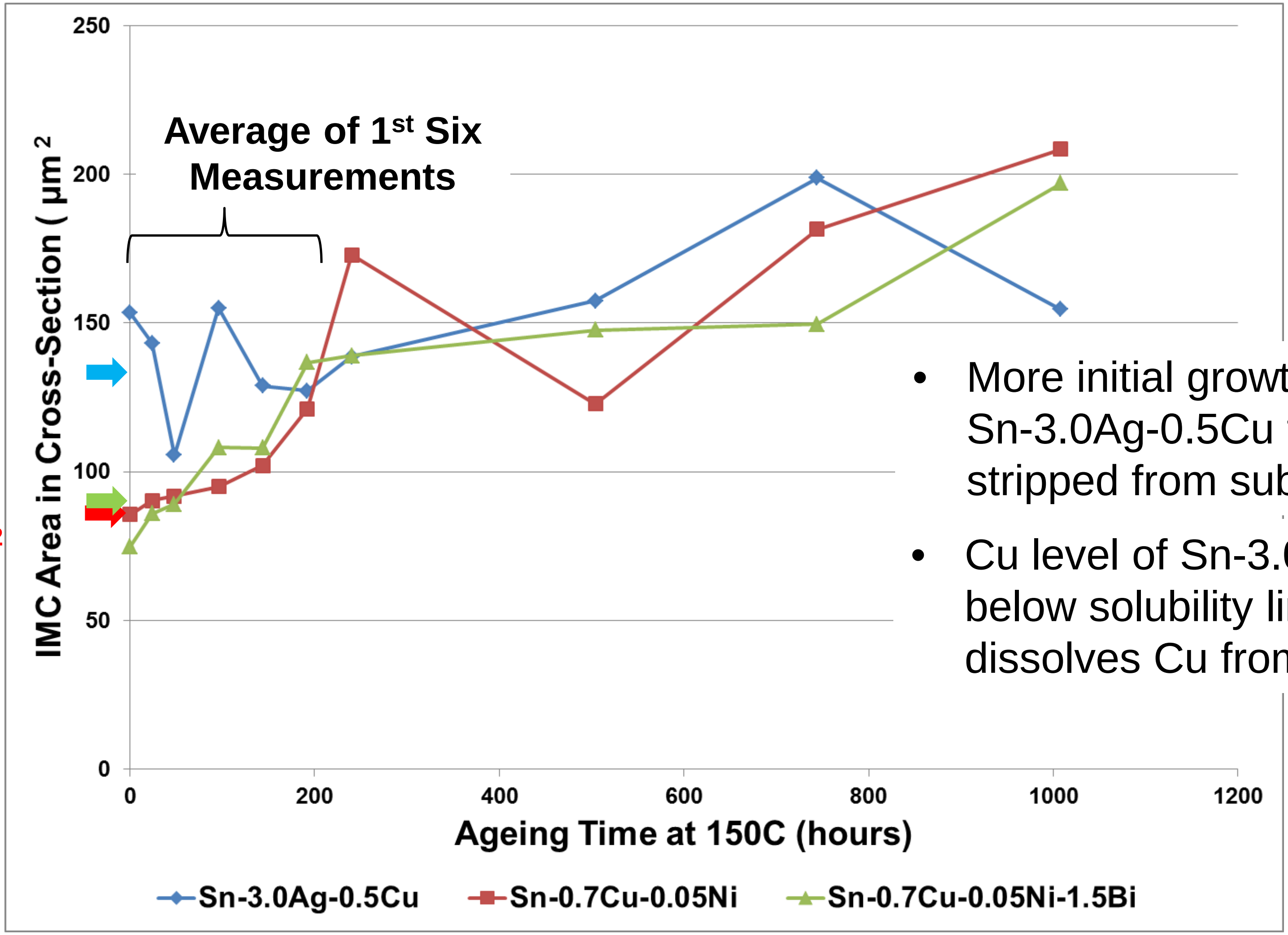


RESULT: Area of Total IMC in Cross –Section as a Function of Ageing time at 150°C

Sn-3.0Ag-0.5Cu: 1372μm²

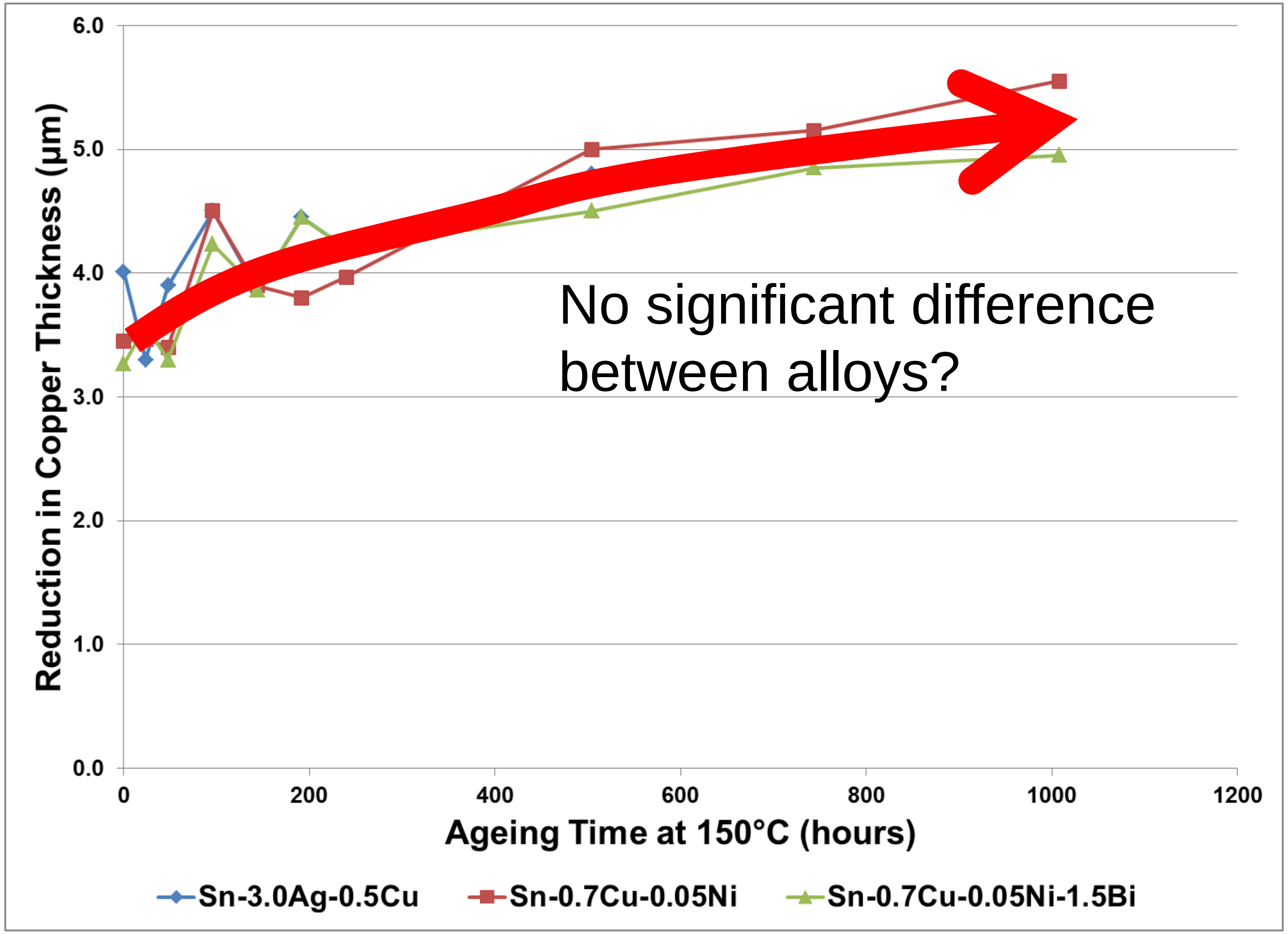
Sn-0.7Cu-0.05Ni-1.5Bi: 93.2μm²

Sn-0.7Cu-0.05Ni: 92.9μm²

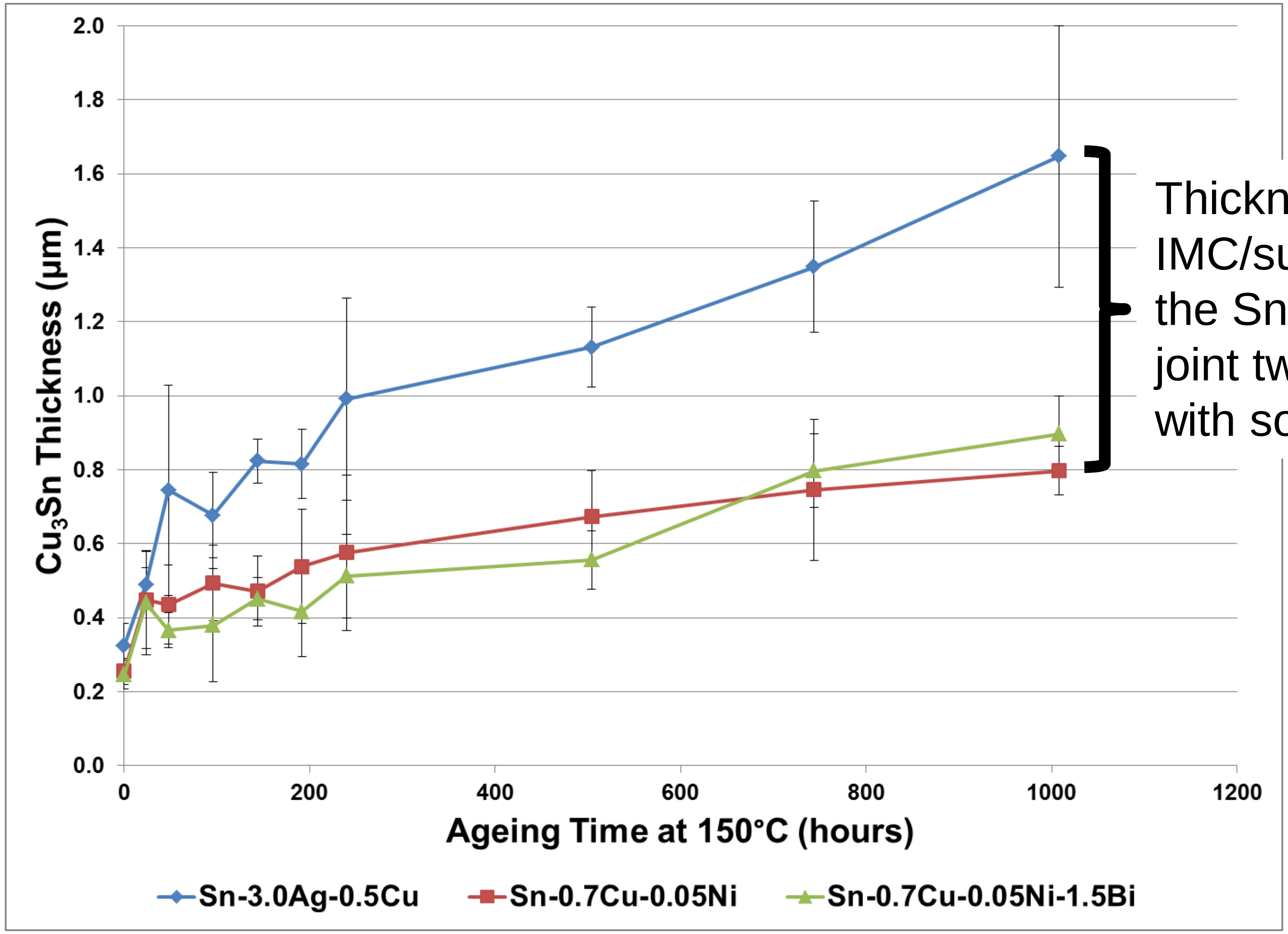


- More initial growth of IMC with Sn-3.0Ag-0.5Cu from Cu stripped from substrate.
- Cu level of Sn-3.0Ag-0.5Cu is below solubility limit and so dissolves Cu from substrate rapidly.

RESULT: Thickness of Copper Consumed by IMC growth as a Function of Aging Time at 150°C



RESULT: Thickness of Cu_3Sn as a Function of Ageing Time at 150°C

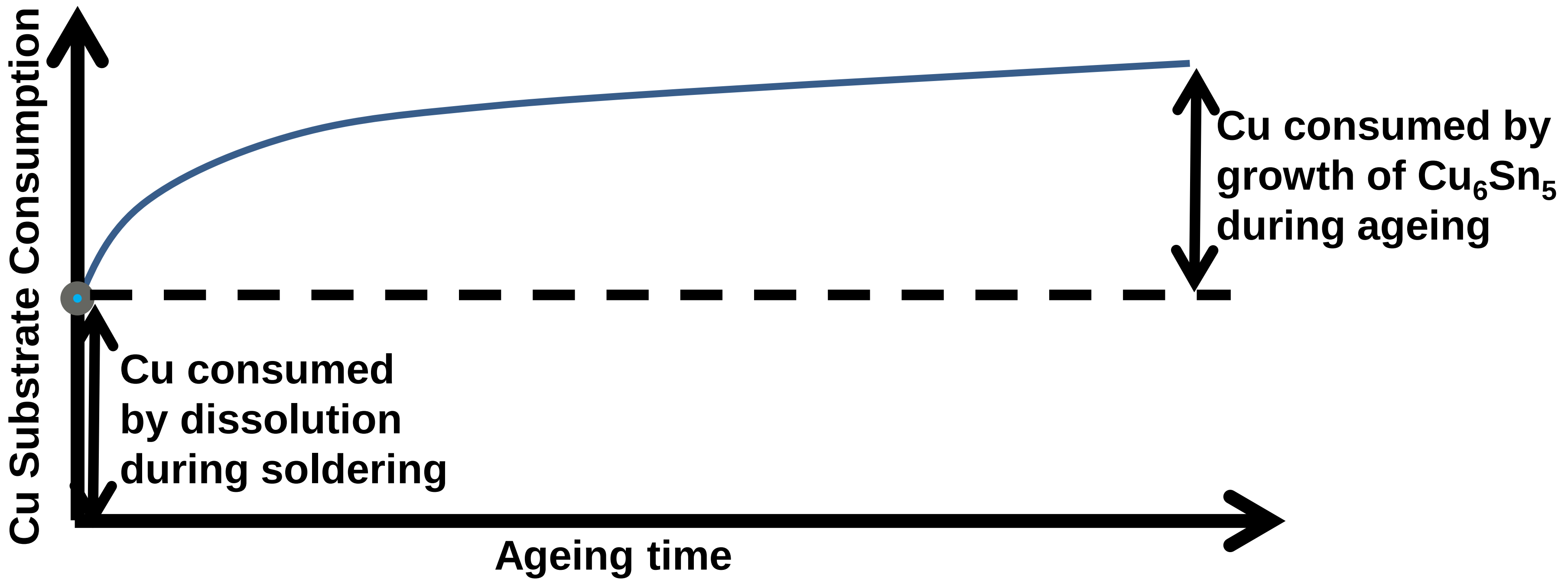


Thickness of Cu_3Sn at the IMC/substrate interface in the Sn-3.0Ag-0.5Cu joint twice that in the joints with solders containing nickel

A Model

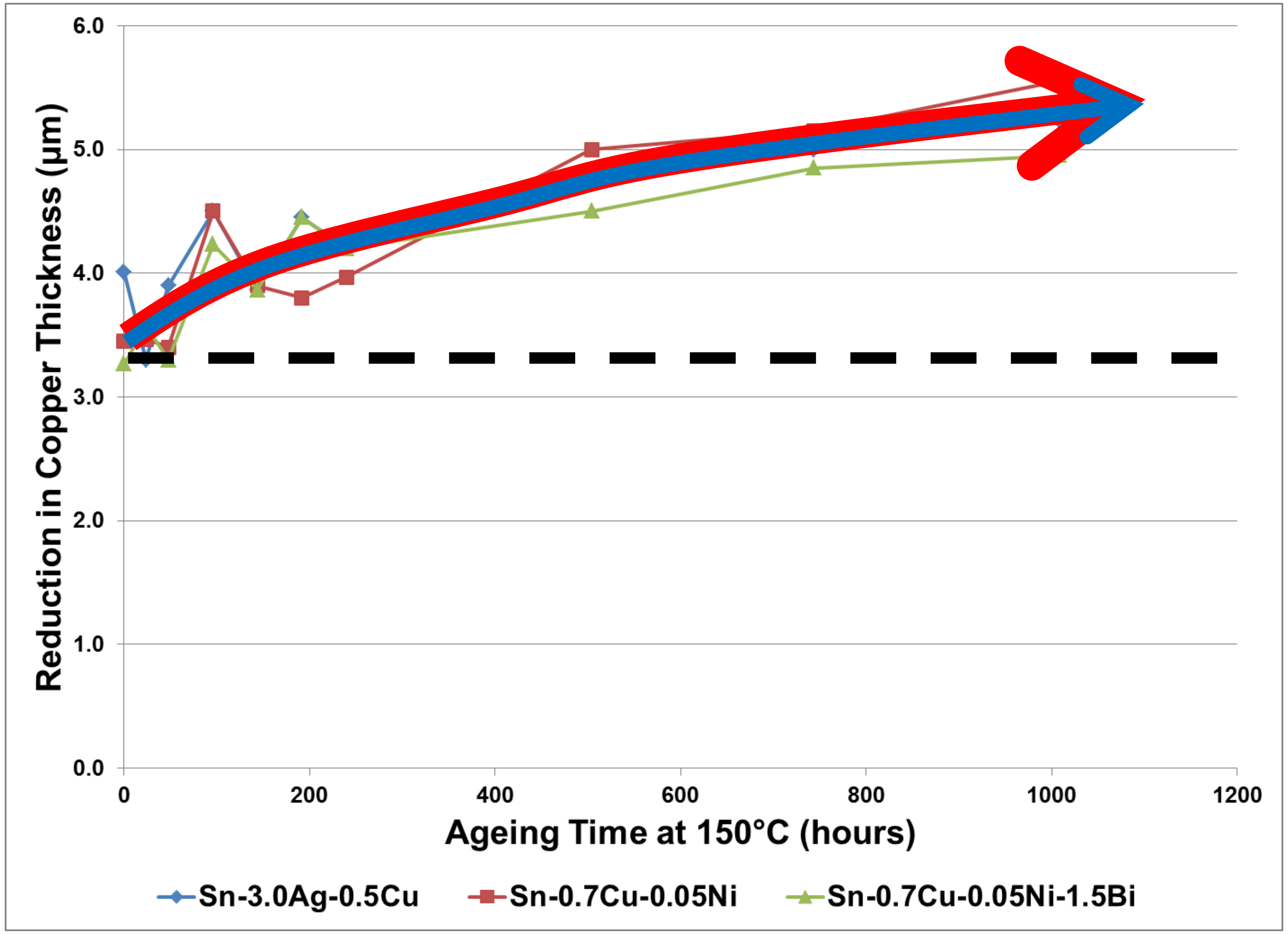
The two processes that contribute to the dissolution of Cu from the substrate
:

- The Cu that dissolves into the molten solder and forms IMC during reflow
- The Cu loss due to the formation of Cu_6Sn_5 (and later Cu_3Sn) during ageing



Reference: Slide 18

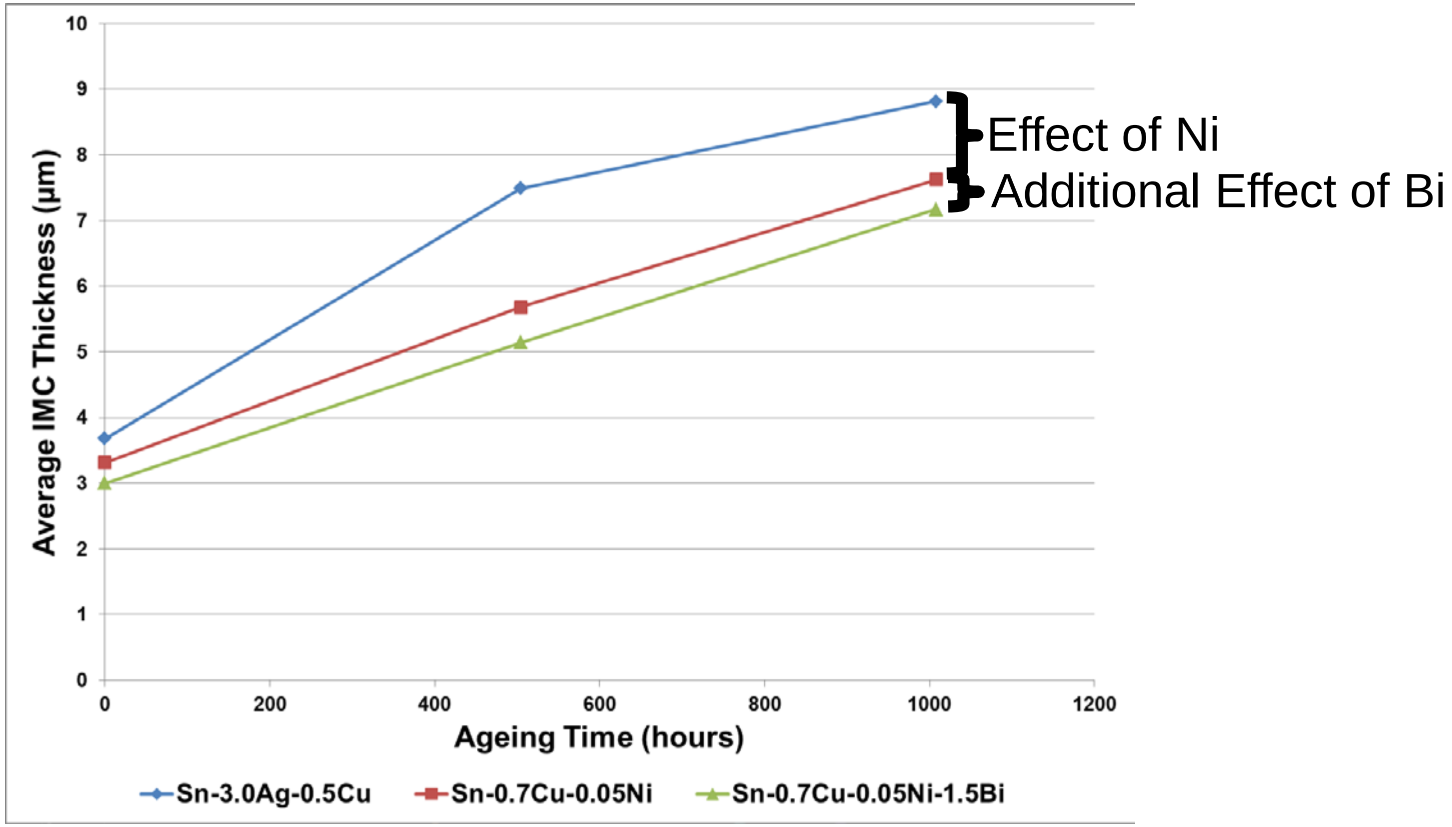
Result: Thickness of Copper Consumed by IMC growth as a Function of Aging Time at 150°C



A Model

Base model on IMC thickness rather than area exposed in a cross-section

Test pieces re-examined to measure IMC thickness



A Model

Consider only the contribution of Cu_6Sn_5 growth to consumption of substrate copper

Assume that in the second stage of consumption:

- All the Cu in the Cu_6Sn_5 layer comes from the substrate
- No Cu_3Sn is formed
- There is an infinite supply of tin

The formation of 1 mole of Cu_6Sn_5 requires 6 moles of Cu from the substrate

The theoretical thickness of the Cu_6Sn_5 layer (L_{Cu6Sn5}) depends on the thickness of the dissolved Cu (L_{Cu}) according to the equation:

$$L_{Cu6Sn5} = \frac{L_{Cu} \cdot \rho_{Cu} \cdot M_{Cu6Sn5}}{\rho_{Cu6Sn5} \cdot 6M_{Cu}}$$

A Model

Inserting values for the densities of the phases and their molar masses gives the thickness of Cu dissolved as a function of the Cu_6Sn_5 layer thickness:

$$L_{Cu} = 0.36 \cdot L_{Cu6Sn5} \qquad \text{(Eq. 1)}$$

Assuming that IMC layer growth occurs at a constant temperature during solid state ageing and that IMC growth is controlled by volume diffusion through the Cu_6Sn_5 layer, the rate at which the IMC thickens is inversely proportional to the layer thickness. This means that, after integration with appropriate limits, the thickness is given by:

$$L_{Cu6Sn5} = \sqrt{{L_0}^2 + k^2 t} \qquad \text{(Eq. 2)}$$

A Model

Where L_0 is the layer thickness at the start of ageing and *k* can be expressed as:

$$k^2 = {k_0}^2 e^{-\left(\frac{Q}{RT}\right)}$$

It has been reported* that for Sn-0.6Cu-0.05Ni :

$$k^2 = 2.02641 \times 10^{-9} e^{-\left(\frac{7986.4}{T}\right)} \ \text{m}^2/\text{s} \qquad \text{(Eq. 3)}$$

Combining Eq. 2 and Eq. 3

$$L_{Cu6Sn5} \approx \sqrt{{L_0}^2 + \left(2 \times 10^{-9} e^{-\left(\frac{7986.4}{T}\right)} t\right)} \qquad \text{(Eq. 4)}$$

* JY Tsai, YC Hu, CM Tsai, CR Kao, “A study on the reaction between Cu and Sn3.5Ag solder doped with small amounts of Ni”, Journal of Electronic Materials, Vol. 32, No. 11, 2003

A Model

Combining Eq. 1 and Eq. 4 gives an approximate expression for the thickness of Cu consumed during isothermal ageing:

$$\Delta L_{Cu} = 0.36 \cdot (L_{Cu6Sn5} - L_0) \text{ m} \quad \text{(Eq,5)}$$

Inserting:

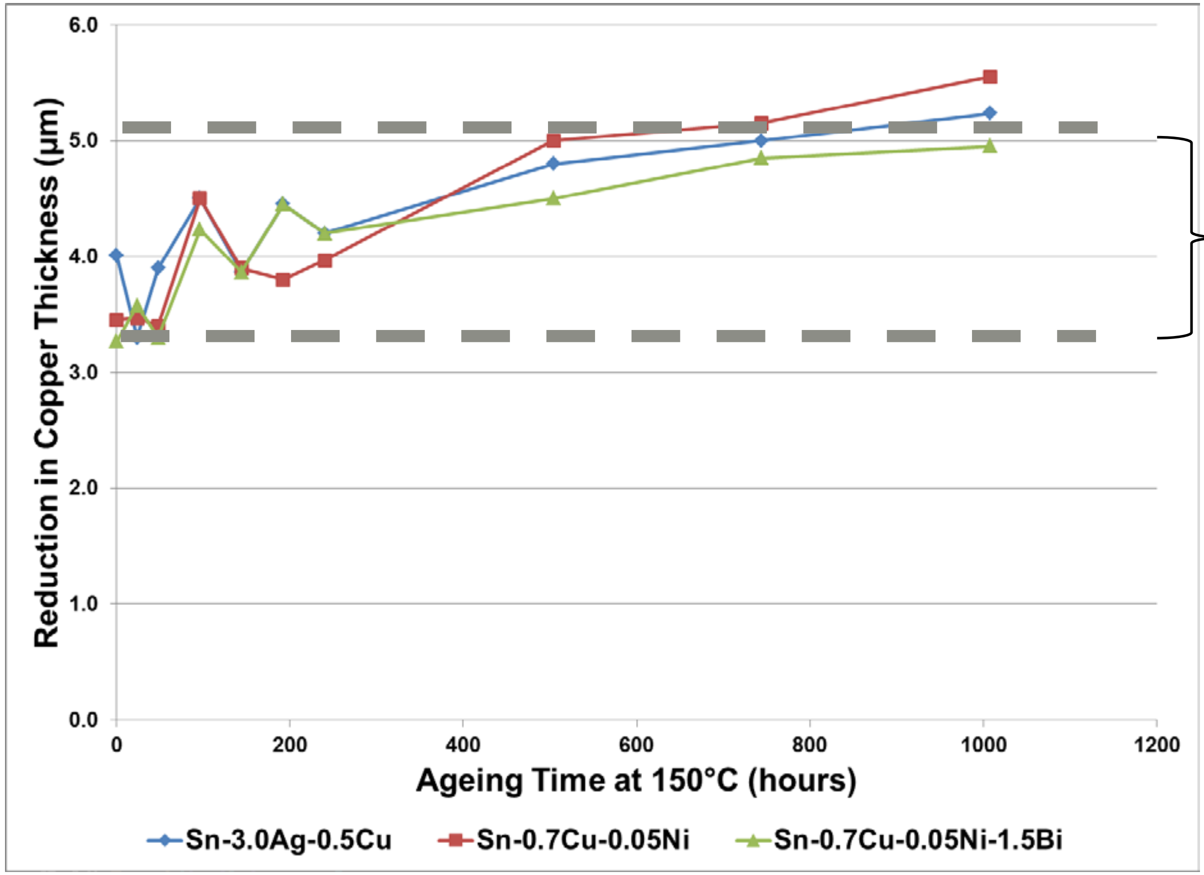
- The ageing temperature: **423.15°K**
- The maximum ageing time: **3,628,800 s**
- The Cu_6Sn_5 layer thickness prior to ageing for Sn-0.7Cu-0.05Ni/Cu: **3.3µm**

This model predicts a Cu_6Sn_5 layer thickness after ageing at 150°C for 1008 hours of: **7.6µm**

i.e. a change of thickness during ageing of 4.3µm (7.6 – 3.3µm).

A Model

Using Eq. 5, the thickness of Cu consumed during ageing is 1.6µm giving a total thickness of Cu consumed of 5.1µm (3.45µm + 1.6µm), which is in reasonable agreement with the experimental results considering the simplicity of this first stage model



1.6µm copper consumption predicted by model

Reasonable fit between model prediction and measured copper consumption

Observations

- The widely recognized effect of Ni in inhibiting Cu dissolution and IMC growth was not detected in the initial <u>area</u> measurements (Slide 17)
  This is probably a reflection of the inaccuracies of the method

- In the second round of more accurate measurement of thickness (Slide 22) the effect of the Ni and Bi on IMC growth are more apparent.
  This suggests Ni and Bi should be having an effect on copper consumption

- In the simple model proposed the two constants that depend on the diffusivity of atomic species through Cu_6Sn_5 are not as strongly affected by the composition of the alloy as indicated in the literature*

- The slower growth of the Cu-rich Cu_3Sn in the alloys containing Ni and Ni+Bi indicates that the supply of Sn from the solder is being limited by diffusion through the Ni-containing Cu_6Sn_5.
  This should mean that the Ni is slowing the consumption of Cu. The separate effect of Bi could not be distinguished.

*JW Yoon, YH Lee, DG Kim, HB Kang, SJ Suh, CW Yang, CB Less, JM Jung, CS Yoo, SB Jung "Intermetallic compound layer growth at the interface between Sn-Cu-Ni solder and Cu substrate", Journal of Alloys and Compounds 381 (2004) 151-157

Conclusions

- As copper substrates get thinner consideration has to be given to the loss of copper thickness that occurs because of
  - Dissolution during the soldering process
  - Diffusion-controlled reaction to form Cu_6Sn_5 and Cu_3Sn during service
- The rate of copper loss can be slowed by a trace additions of Ni
- Bi may have an additional limiting effect on loss of copper substrate thickness.

Future Work

- More accurate measurement of IMC growth and Cu consumption
- Development of the model to take into account more of the factors that affect the rate of Cu consumption. e.g. the growth of Cu_3Sn
- Real time *in situ* observation of wetting and IMC growth in the synchrotron

Thank You

References

[1] ASE Group