Method to Measure Intermetallic Layer Thickness and Its Application to Develop a New Equation to Predict Its Growth

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Abstract

Lead Free Technology has brought new materials and different quality concerns to the Electronics Industry. For that, the creation of new methods to determine the quality of materials is needed and preferred. Intermetallic compounds for example can grow faster in lead-free metallization and decrease the possibility to form good joints. For that, a new method to measure IMC layer thickness is presented. This new method uses a combination of X-Ray Fluorescence Method (XRFM) and Coulometric Stripping Method (CSM). XRFM is capable to measure percentage of elements and correlate the values to their layer thickness. This procedure makes XRFM not so suitable to measure intermetallic thickness when it is growing because the elements only combine each other and are not removed; therefore XRFM gives similar values in thin metallization layers of tin-copper with thick or thin IMC layer, for example. On the other hand, CSM removes pure element layer using an electrochemical depletion. The combination of both methods allows evaluating the IMC layer thickness in a more precise form. For validation of the method, SEM/EDX and Auger microanalyses were made to compare values. Besides, several experiments were carried over in several temperatures and reflow profiles to measure IMC growth in Chemical Tin PCB's. The results were used to develop a more precise equation to predict the IMC growing. The new equation uses the Activation Energy depending on the IMC thickness.

Introduction

The change into a new technology implies new challenges in order to meet quality goals; and this has happened with the arrival of lead-free in electronics. The elimination of lead from solder and metallizations has had several consequences in manufacturability because the new solders have increased the temperature to solder and reduced processes windows; as consequence, quality variability in materials has become more critical since then.

One of the main technologies for lead-free in Printed Circuit Board (PCB) is Immersion Tin[1, 2] as metallization to protect pads from oxidation. This has become popular because it allows more complex products with small size. The process to deposit Immersion Tin is carried over in different way from electroplating or electroless plating; this process is in fact a chemical replacement reaction between Tin and Cu, and it is not catalyzed or auto-catalyzed. Consequently, its thicknesses are very thin and their averages are from 0.8 to 1.2 um typically, but it can go from 0.1 to 1.5 um at most because the reaction is self-limiting. It is necessary to control temperature, pH, and chemical ingredients to get consistent and uniform surfaces. The role of Sn is to give wettability as a layer that prevents corrosion or oxidation from happening too fast. The surface looks shiny and white[3]. The cost is competitive but it is not wire boundable and not good as switch material.

Nevertheless, the Intermetallic Compounds (IMC) between the copper and the tin surface has to be monitored because its presence can determine if the joint between PCB and solder paste alloy can be formed[3,4] because its excessive growth in components or pads before soldering implies possible wetting issues. IMC can form more stable oxides, such as copper oxides which are harder to remove by solder paste fluxes[5]. When the oxides are not removed adequately, the diffusion between solder and pad material or pad metallization is prevented from happening and open joints and malfunction of the electronic module are the results consequently. Therefore, predicting the IMC growth layer is fundamental to prevent quality issues[6] and foresee the probability of good and bad joints. Several formulas to determine the IMC thickness growth have been proposed before[1, 4].

Intermetallic Thickness Measurement

The technique used to determine IMC layer thickness in Tin surfaces, such as Immersion Tin, consists of a combination of X-Ray Fluorescence (XRF) and Coulometric Stripping (CM) methods[9]. This method is new, however, uses two very known techniques for Immersion Tin Measurements[10]. A brief description of its three steeps is done next.

The first step is to measure the total thickness of IMC and tin layers. For that, XRF Method is used. This method measures elemental composition of materials and its principle is that a primary x-ray from an x-ray tube or radioactive source hits the sample and because of the photoelectric effect some electrons are expulsed from inner shells creating vacancies or holes; while the atom returns to its basal condition, electrons from outer shells jump to inner shells. A x-ray whose energy is the representative between the two binding energies of the corresponding shells is emitted[12-14]. The x-ray energies is related to the element from which was generated, and their number can be correlated to element concentrations. They can also be correlated to thickness of material if the equipment is calibrated adequately using known standards. Nevertheless, the XRF method wouldn't see difference among pure material and IMC thickness when the IMC layer is growing because IMC layer is formed of the same materials as the metallization and the base. XRF cannot distinguish between atoms from pure element and atoms forming IMC. In other words, when the equipment is initially calibrated with known layer thicknesses, the reference of atom concentration is therefore correlated to the thickness. When a sample with similar thickness is measured but it already have half atoms diffused forming IMC, the amount of X-ray emitted is similar to the one without diffused atoms (The atoms don't disappear). Therefore, the thickness value given by XRF is really representative of the initial thickness with a small bias due to an effect of shield due to base material atoms[10]. This bias is very small when thickness is small also, and in our previous studies[9] with Immersion Tin Printed Circuit Boards (PCB), it was found a maximum variation of 0.02 um which can be neglected for this study.

In the second step, using CS method[15], we apply a stable electrical current to the pads in order to strip tin. The controlled flow of electrons can be used to know the amount of tin that is stripped. During the process, voltages changes represent when the material passes from tin to copper or intermetallic layers. The amount of stripped material is proportional to the time between voltages and therefore, to its thickness according to Faraday's Law. However, there is an electrochemical commercial equipment based on electrical controlled dissolution of the metallization compound, which claims its capability to evaluate intermetallics[21]; however, Scheuerlein[16] et al has evaluated a similar technique and concluded that is not able to measure intermetallics as expected. In our case, only tin is depleted according to reference 10 and we can obtain how much tin was removed and use it to calculate the tin layer thickness.

As a result, **we measure the total layer (Sn + IMC) with XRF Method as a first step. Later in the second step, we strip tin layer using CS Method to obtain tin layer thickness and the difference between their values is approximately the IMC layer thickness, as a third step,** see Figure 1. We will reference to it as XRF/CS Method; the advantage of this method is we can get a value that is the mean of a determine area better than a series of points coming from microsections as SEM/EDX measurements are done. This improves the measurement repeatability and the time spending to make measurements.

Third step

  C = A - B

Where

  C = Intermetallic Layer Thickness

Figure. 1 The combination of both techniques can determine IMC layer thickness with a better precision.

To prove the correlation between the data given by this new method with the intermetallic layer, it was compare with data from microsections analyzed by SEM and diffusion data obtained from Auger depth profiling of PCB under several condition [9]. The results are shown next; please see Figures 2 and 3.

Two-Sample T-Test and CI: SEM, XRF/CSM
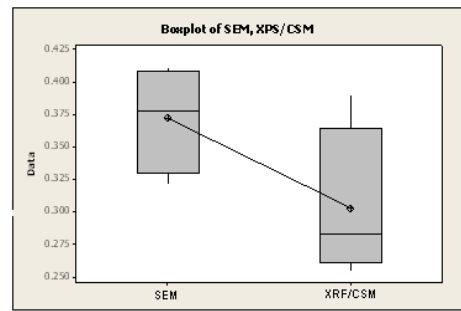
Two-sample T for SEM vs XPS/CSM

	N	Mean	StDev	SE Mean
SEM	4	0.3715	0.0417	0.021
XRF/CSM	4	0.3025	0.0598	0.030

Difference = mu (SEM) - mu (XPS/CSM)
Estimate for difference: 0.068950
95% CI for difference: (-0.024781, 0.162681)
T-Test of difference = 0 (vs not =): T-Value = 1.89 **P-Value = 0.117** DF = 5

Figure 2. Statistical test to compare results from SEM/EDX measurements and XRF/CS Method

The results for SEM/EDX analysis were obtained from several microsections and these were measured at least in 30 points at each and are compared with the results of XRF/CS Method using a statistical analysis (t-student). In Figure 2, the statistical analysis of the results is shown. The comparison was made using Immersion Tin pads of the same PCB. This is because both tests are destructive: Microsections for SEM, and the tin depletion of XRF/CSM. The statistical conclusion is there is no significant difference between both set of values (P-value > 0.05).
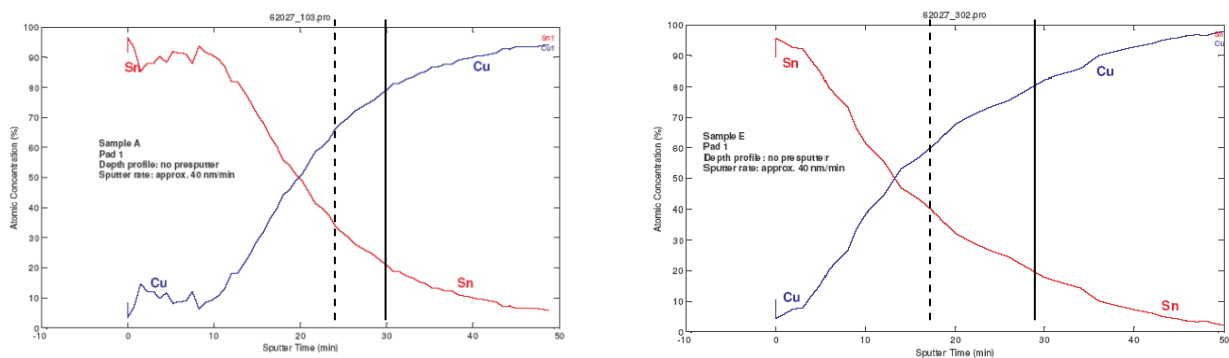
Figure 3. (a) Auger Depth profile of a Immersion Tin PCB as received (b) after 110 min at 150°C. The solid lines represent the value given by XRF, and the dashed lines represent the value obtained by the new method.

In Figure 3(a) and 3(b), we can observe the concentration vs time obtained by Auger depth profiling. In the Figures, there are two set of lines, solid and dashed ones. The first ones represent to the value obtained by the XRF. It is interesting to observe that the percentages of tin and copper are very similar (approximate 70% Cu and 30% of tin) even though the second graph is the diffusion after a thermal treatment and the expected value would have been different to a lower percentage. Besides, it is observed that the intermetallic layer is not complete form or it is partially formed because the percentage of tin is not constant at 45.5% as expected when intermetallic is present, see Figure 2(b). The dashed lines are the values obtained using the method mentioned before. The values are closed at 50% of tin that is closed to the intermetallic percentage (45.5% for Sn_5Cu_6). The principle of Coulometric Stripping is very similar to the chemical process of titration in which a chemical changes one of its properties (i.e color) with a small change of a compound concentration. In this case, the coulometric method shows a change when the concentration between copper and tin turns 50% approximately that is very similar to the intermetallic concentration and useful to our purpose.

Intermetallic thickness predicting formulas (Semi-Empirical)

Fick's law is a very used equation to predict diffusion of a component(s) into a solution[7]. It is also highly used in semiconductor's design to predict the diffusion of dopants (Ga, Ge) into Si matrix, see Equation 1.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial t^2} \qquad (1)$$

The equation can be solved in different ways according to initial conditions. In the case of a plane with constant composition, the diffusion shifts proportionally to the square root of the time, which also means that the thickness of the diffusion zone (or its average) is also $\propto t^{0.5}$, see Equation 2, where D_o can be substituted by Equation 3. In this Equation, the dependence of the D_o to temperature is shown with the Arrhenius Equation and Q is called Activation Energy (AE). Although, in principle the phenomenon of intermetallic diffusion and formation has more conditions, this formula has been highly used to model the intermetallic growth. Therefore it turns semi-empirical.

$$h = D_o t^{0.5} \qquad (2)$$

$$D_o = A_o e^{\left(\frac{-Q}{RT}\right)} \qquad (3)$$

In order to improve the exactitude of the predictions, when Equation 2 is applied to IMC layer thickness prediction, it has to be adjusted with an exponent different from 0.5. For example, J. Kang and C. Hans[8] described the total growth of the total ($Cu_3Sn + Cu_6Sn$) IMC layer in Cu60Sn40Pb solder joints during static annealing at 50 °C to 150 °C using the Equation 4 where p can goes from 0.38 to 0.70.

$$h = h_o + A_o e^{\left(\frac{-Q}{RT}\right)} t^p \qquad (4)$$

The conclusion of their report was the derivation of the values of the time exponent p from the ideal of 0.5 for diffusion growth may be due to inaccuracies of errors pertaining to the measured thickness (specially h_0) and the complex nature of the diffusion process. However, many other investigations[1, 4, 8], including others done by the author, have had used this approach of modifying the exponent to get better correlations of the physical data to the equations. This discards the fact of possible errors during measurements and points out the physical phenomenon behaves differently from the parabolic ideal (p = 0.5).

New Equation

Based on empirical observations, a new equation is proposed for Immersion Tin Intermetallic Compound Thickness, see Equation 5 and 6.

$$h = (D_o t^{0.5}) e^{\frac{-Q'}{RT}} \qquad (5)$$

$$where$$

$$Q' = mh + Q_o \qquad (6)$$

In this formula, the activation energy is replaced by a linear equation in which a linear dependency between the activation energy and diffused layer thickness exist (although other correlations would be used).

The equations 5 and 6 form a set that has to be solved all together using a numeric method. The principal of the Equation is more energy will be needed for the atoms to form similar distances of IMC thickness. This energy will be growing as the thickness average grows, see Figure 4. The possible physical explanation of this increasing of energy would be two: (1) in the case of Immersion Tin, the layer is thin, and after some thickness, the copper diffused atoms reaches the surface, and this would delay the diffusion because the concentration will increase; (2) the formation of intermetallic layer would modify the diffusion phenomenon between Cu and Sn would "need" more energy to follow the diffusion as before. Both explanations are hypotheses and we are working to prove or disprove one of them. However, the new equation has shown good correlation to the data in range of temperatures and with some considerations as shown below.
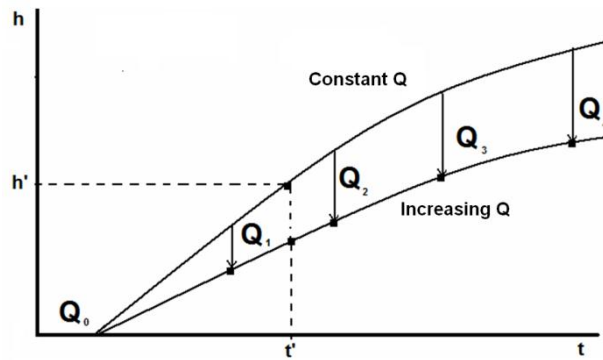
Figure 4. Activation Energy is growing as thickness is growing, $Q_0 < Q_1 < Q_2 < Q...$

Experiments

Two experiments were proposed to measure IMC layer growth or copper diffusion into tin: the first was in steady-state temperature conditions and the second was in dynamic-state ones. The material was Immersion Tin Printed Circuit Board pads, and the IMC layer was Tin-Copper. The method to measure the IMC thicknesses was XRF/CS.

- **Experiment 1.** Three sets of five Immersion Tin PCBs were aged or thermal treated in the next conditions:

  - 150 °C during 360 minutes
  - 120 °C during 480 minutes
  - 80°C during 2880 minutes

During several intervals, the IMC layer was measured using XRF/CS method in several similar pads to minimize error method since the measurement is destructive.

- **Experiment 2.** Several temperature profiles (dynamic-state) with different reflow time (over 221°C) and peak temperatures was set. Table 1 shows the number of thermal profiles and their main characteristics[21] for the experiment (Peak Temperature and Reflow time over 221°C). The Figure 5 shows a typical profile form used in this experiment and 5 PCBs were passed though every profile to reduce the variability error.

Table 1. Thermal profiles for the dynamic-state experiment

Profile Number	Peak Temperature	Reflow time over 221°C
1	230	13.45
2	230	38.84
3	245	41.33
4	245	38.85
5	245	65.49
6	260	85.41
7	260	50.05
8	260	115.54
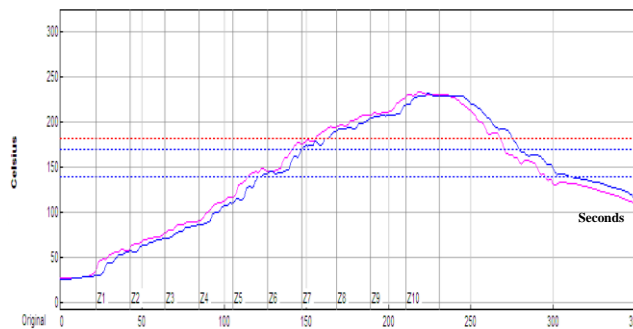
Before and after every profile, the IMC layer was measured using XRF/CS method. The pads were selected close each other to minimize the error of testing different pads.

Results

The results of the first experiment are in Figures 6(a-c) showing the confidence intervals of the results. Figure 4(a) corresponds to the values at 80°C, Figure 4(b) at 120°C, and Figure 4(c) at 150°C. In the same graphs is the regression of the Equation 7 ("H(t^0.5)" in Figures 4(a-c)) that was taken from IPC 4554[10] and it represents the Equations 2 and 3. It is used to compare to the new proposed equation.

$$h^2[m] = (3.0 \times 10^{-9} \left[\frac{m^2}{seg}\right] * (t[seg]) e^{\frac{-70000\left[\frac{J}{mol}\right]}{8.1314\,[J/mol°K]*T[°K]}} \qquad (7)$$

The Equations 5 and 6 are represented by 8 and 9 with the constant values obtained by a numeric methods. They represent the Equations 5 and 6. Its graphs are in Figures 4(a-c) marked as "New Equation (Q dependant)".

$$h^2[m] = (1.7919 \times 10^{-9} \left[\frac{m^2}{seg}\right] * (t[seg]) e^{\frac{-Q'}{8.1314\,[J/mol°K]*T[°K]}} \qquad (8)$$

$$Q' = 1 \times 10^9 \left[\frac{J}{mol*m}\right] * h[m] + 67680.24 \left[\frac{J}{mol}\right] \qquad (9)$$

As we can see Equation 7 and the set formed by Equations 8 and 9 have good correlations to the real data. In the case of the graph at 150°C, both equations follow similar tendencies. The selection of the slope for the Equation 9 was selected to give the least error in the regressions of the three temperatures. It is interesting to see the Activation Energy value of Equation 7 (70000 J/mol) is quite similar to the constant of the Equation 9 (67680 J/mol).

In the case of the experiment 2, the application of either Equation 7, or 8 and 9 didn't predict the final IMC layer thickness correctly and the difference between the real value and the predicted had an error bigger than 100%. For that, a temperature at which diffusion speed was accelerated was proposed. Additional experiments were carried out to determine if that temperature existed and which it was. It was found that transition temperature was located between 215°C and 219°C, something that was not expected initially. Figure 7 shows how the final IMC thickness jumped up in that interval versus the peak temperature of the profile.
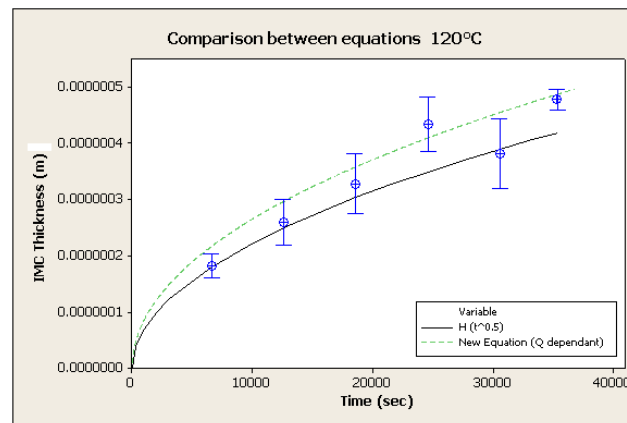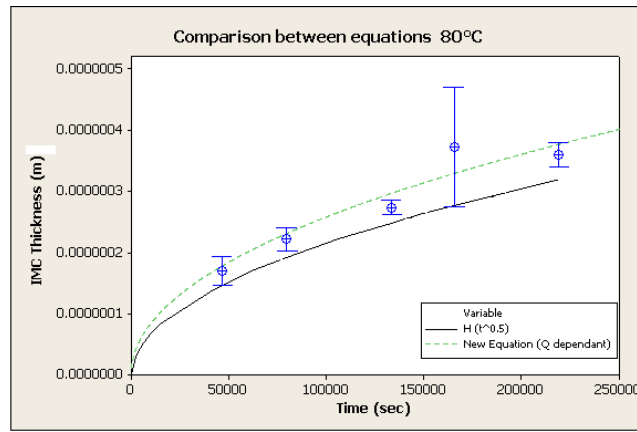
(b)
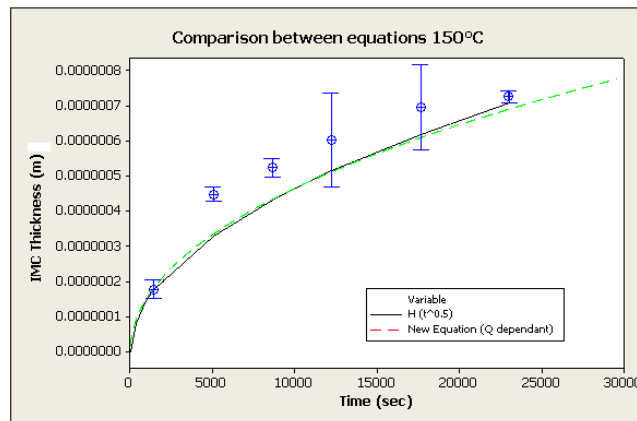
(c)

Figure 6. IMC layer thickness results and their correlations to the new equations and IPC 4554 one (a) at 80°C, (b) 120°C, (c) 150°C
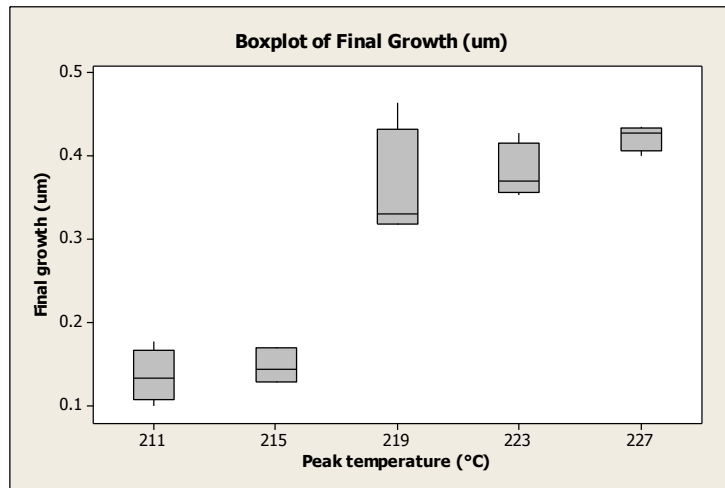
Figure 7. Confirmation that between 215°C and 219°C the diffusion speed is accelerated

The selected temperature was 217°C (The average between 219 and 215°C). An important remark is that temperature is similar to the eutectic point for Sn-Cu-Ag alloy: 215.9 to 216.3°C [17, 22-23], see Figure 8. Under that assumption, we are considering an additional element, Ag that shouldn't be present in the metallization. However, its presence was confirmed by SEM/EDX analysis in the Immersion Tin Surface, see Figure 9. Silver can be justified by the presence of an additive to reduce whisker appearance. In the case of Cu, its presence can be deduced by the diffusion of this element into the Tin layer.
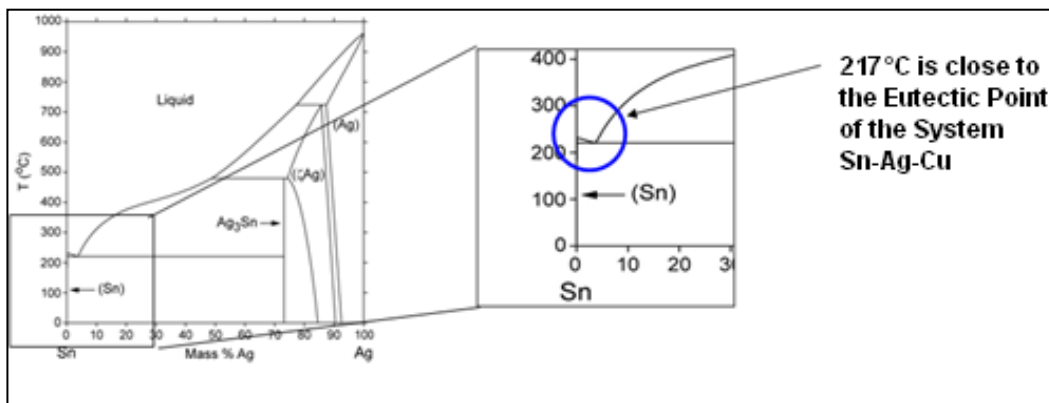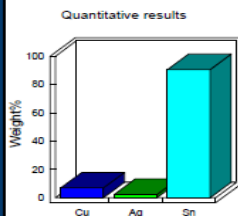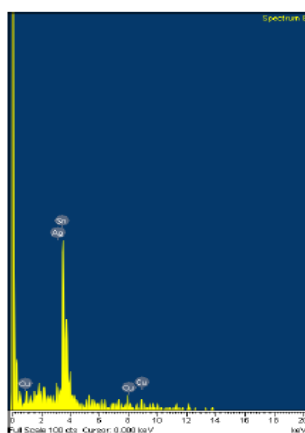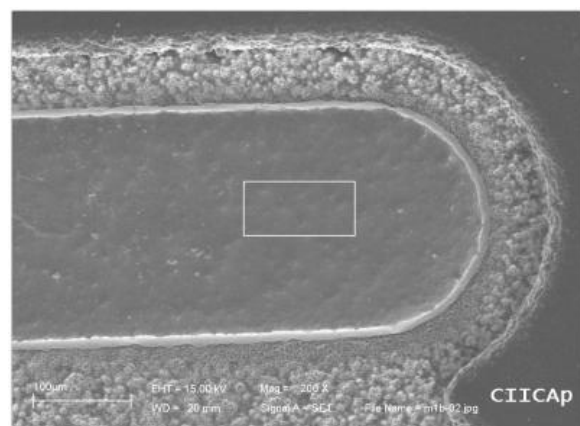

Figure 8. Phase Diagram of Sn-Ag-Cu Alloy



(a)   (b)

Figure 9. (a) EDX results of the Immersion Tin Surface in (b)

One interesting fact is if Equation 4 with a p = 0.5 is used to predict the final thickness by selecting an **AE per every thermal profile**, the AE values give a linear dependency between them and the final IMC thickness (the initial value of most PCBs were quite similar). This means the AE is changing as the thickness is growing. **This is the corroboration to the hypothesis of IMC thickness grows while the AE is growing too,** see Figure 10.
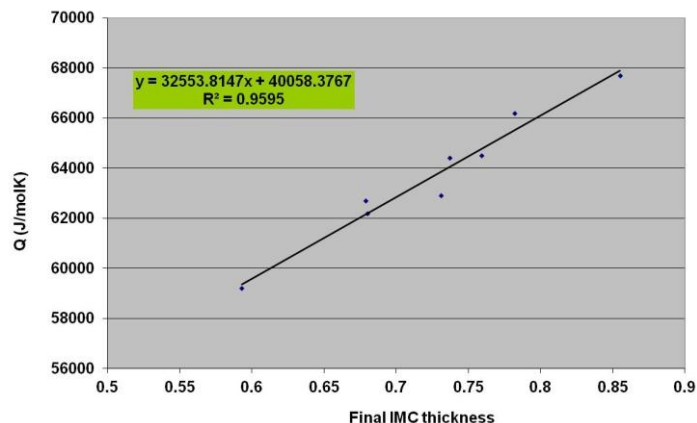
Figure 10. Linear dependency of the Activation Energy and Intermetallic growth

In order to include the new observations, it was finally decided to add a new equation for Energy Activation after 217°C. The new equations are 10 and 11 and use the Equation 8 as a base for both.

The additional equation (Equation 11) had the form of the Equation 6. After finding a good correlation, it is obtained in average approximately of 34.4 x 10^9 J/mol*m for the slope and 32000 J/mol for the constant. The interesting thing to observe is that the slope is much bigger in Equation 11 than Equation 10 and the constant in Equation 11 is half than Equation 10 that is used to temperatures below 217°C. This means less energy is used to diffuse the same thickness after 217°C. This can be justified due to the fact tin, or Ag-Cu-Sn better said is melted on the intermetallic surface and this eases the formation of intermetallic compounds.

$$Q' = 1x10^9 \left[\frac{J}{mol*m} \right] * h[m] + 67680.24 \left[\frac{J}{mol} \right] \quad T < 217°C \qquad (10)$$

$$Q'' = 34.4x10^9 \left[\frac{J}{mol*m} \right] * h[m] + 32000 \left[\frac{J}{mol} \right] \quad T \geq 217°C \qquad (11)$$

Figure 11 shows representative curves of IMC layer growth through a typical thermal profile for the Experiment 2 using the new equation with and without the diffusion acceleration change at 217°C. As seen, if no correction is done, the error is much bigger. All profiles are over 217°C and the growth after that temperature is much bigger than before it.
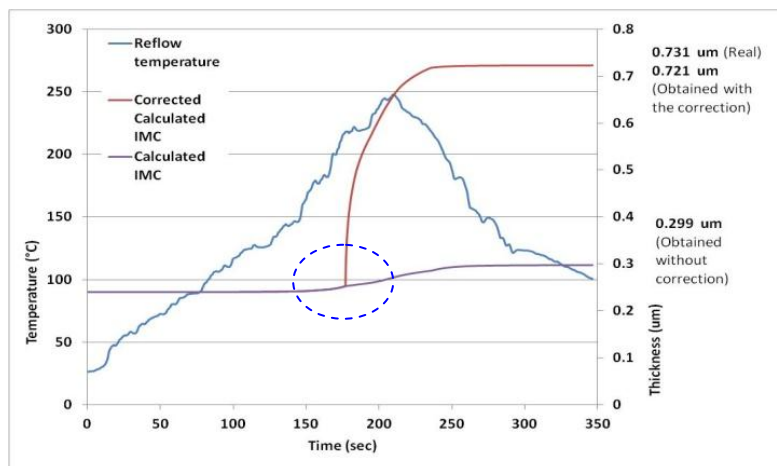
Figure 11. Predicted IMC growth through thermal reflow profile, and the reformulation at 217°C

An important observation is made. In Figure 11, there is a sharp increasing at 217°C (dashed circle line). This type of behavior in diffusion is rare and not expected. This comes from the theoretical assumption mentioned above and not for physical measurement. Therefore, it is necessary to study this part of the diffusion to corroborate it or not in next studies.

Finally, in the Table 2, the initial and final average values of IMC layer per thermal profile are shown and a comparison between using a unique Activation Energy over 217°C ($Q = 9 \times 10^9$ J/mol and $D_o = 6 \times 10^{-14}$ m^2/seg, values given the least errors) and using the Equations 10 and 11 to predict the final value is made. The sum of the error absolute values is 98.62% with the fixed Activation Energy against 7.72% with the new equation. This is a big difference that shows the prediction of the new one is more exact.

Table 2. Values before and after reflow compared to the predicted value using fixed Activation Energy(A) and the new equation (B).

Peak Temperature (°C)	IMC Thickness (µm)		Calculated IMC$^{(A)}$ (µm)	Error (%)	Calculated IMC$^{(B)}$ (µm)	Error (%)
	Before Reflow	After Reflow				
230	0.21	0.593	0.44	25.44%	0.59	0.60%
230	0.17	0.681	0.59	13.16%	0.68	0.46%
245	0.24	0.731	0.70	4.83%	0.72	1.35%
245	0.2	0.679	0.58	13.87%	0.69	1.17%
245	0.19	0.737	0.74	0.07%	0.74	0.64%
260	0.23	0.782	0.84	8.02%	0.80	2.20%
260	0.18	0.759	0.66	13.64%	0.75	1.02%
260	0.25	0.855	1.02	19.59%	0.85	0.28%
			Sum (abs)	**98.62%**	**Sum (abs)**	**7.72%**

Application in field

An important use of this information was done when wetting issue were gotten in double side leaded production with Immersion Tin PCB's. The first side or reflow was good soldered and pads showed good wetting. However, after the second reflow or side, there were important wetting issues in several pads, see Figure 12. A preliminary analysis points at an intermetallic issue although the metallization thickness was inside of specifications. The recommendation was to reduce the peak temperature below 217°C during the first reflow in order to reduce the intermetallic layer growth. An analysis showed possible organic residues were inside of the tin metallization, and these were displaced by the intermetallic layer to the surface during the first reflow. Reducing the intermetallic layer thickness made these organic residues not to move to the surface layer, and allowed to have a better wetting performance in the second reflow. The identification of these residues couldn't be gotten properly. This action reduces the incident of wetting issues more than 90%. After PCB process was better controlled and monitored this problem was eliminated.
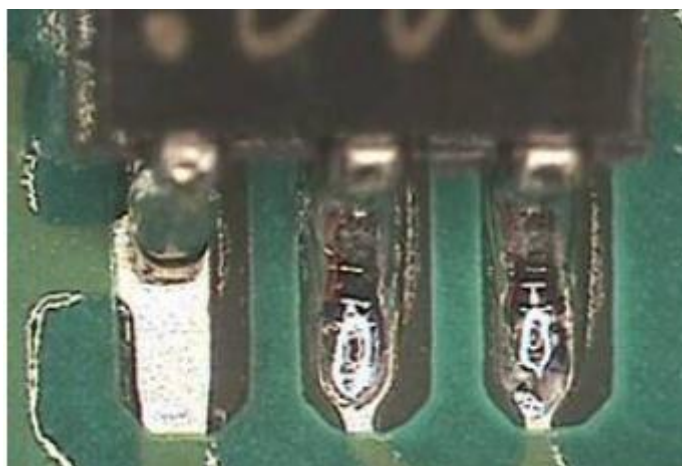
Figure 12. Wetting issues during a double side Immersion Tin PCB.

Conclusions

The application of the XRF/CS Method has been very helpful to determine more acutely IMC layer growth or diffusion in Immersion Tin PCB's. This allows getting an important finding: there is also a linear relationship between the activation energy and the IMC thickness. This was observed especially in temperature dynamic-state experiment with the reflow profiles; although it is also applied to temperature steady-state experiments.

Another important finding is to see clearly the acceleration of the diffusion rate after a determined temperature in Immersion Tin PCB's. It was found the intermetallic formation was accelerated approximately at 217°C, very similar temperature to the eutectic point of the copper-tin-silver. Because of that, the corroboration of Ag presence had to be done with SEM/EDX analysis in the case of Immersion Tin pads. This phenomenon would also justify the fact of using different Activation Energy Equation over 217°C. Applying a relationship between the Activation Energy and IMC Thickness resulted in a linear equation with an approximate constant of 67680 J/mol for temperatures below 217°C and 32000 J/mol for temperatures over 217°C. This indicates the energy is to start the diffusion over 217°C is almost half that of below 217°C.

The linear dependency between Q and IMC is positive; this means we will need more energy as long as the IMC growth. This would be explained with the fact more energy would be needed to diffuse more atoms through a stable IMC layer, this hypothesis needs to be proved. Although with the application of the new method to measure IMC layer and the proposed set of equations is possible to simulate any thermal degradation of Immersion Tin, such as, passing PCB's through baking or several reflows, so quality issues can be prevented.

Acknowledgment

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