Influence Of Thermal Aging On Intermetallic Compound Growth In Solder Alloys

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Abstract— **This article will present the influence of thermal aging and the reflow cycle numbers on intermetallic layer growth. Search for the new soldering alloy brings a new and different combination of elements, which behave differently in work conditions. The objects of the experiment are five types of solder alloys, the referential alloy is SAC compared to SnNi based solder alloys combined with germanium, cobalt, phosphor, and copper elements. The results of the experiment will be the thickness of intermetallic layers between the copper pad and solder alloys in different combinations of thermal aging and reflow cycles. Values will be supported by the elemental analysis by the electron microscope using an EDS (Energy-dispersive X-ray spectroscopy) analysis. More details about the solder alloys and settings reflow and aging processes will be presented in the paper.**

Keywords— ***intermetallic compound, intermetallic layers, solder alloy, thermal aging, reflow soldering***

I. Introduction

The issue of intermetallic compound growth is increasingly affecting the sustainability of electronic assemblies. Since the banning of lead solder, there has been a major change in the understanding of the growth of IMC (intermetallic compound) layers [1]. While the use of lead-free solder has reduced the negative environmental impact, it has created other problems. The intermetallic compounds in lead-free solder reach much greater thicknesses. This fact reduces the lifetime of electronic assemblies just due to the unwanted mechanical properties of intermetallic [2]. Intermetallic are formed by the diffusion of the solder alloy element and the contact material. Usually, it is a solder alloy with a high tin content and a copper contact pad. This compound is much harder compared to the solder alloy, but at the same time more brittle, causing long-term mechanical and electrical instability of the joint.

The operating temperature of electronic assemblies may not reach high values, but based on long-term exposure to room temperature, it will cause the growth of intermetallic layers [3]. Long-term thermal stress is unwanted for the electronic assembly overall, not just in terms of solder joints [4]. However, this paper focuses purely on the unwanted growth of IMC under two types of thermal stresses, long-term exposure to higher temperatures and thermal shock stresses. Shock thermal stresses not only affect the growth of intermetallic layers, but also the mechanical strain [5]. Rapid temperature changes cause mechanical expansion and contraction. These effects cause IMC cracking and are one of the reasons for the failure of electronic assemblies [4].

It is possible to limit the growth of IMC by using surface finishes on solder pads or by doping solder alloys with additional elements. In this experiment, I used solder doped with nickel, cobalt, and germanium in varying amounts. The admixture of germanium in the solder alloy is an improvement in wetting properties, which in manufacturing will reduce the possibility of bridges causing short circuits between pins [6]. An additional reason for using germanium is to reduce slag formation in molten solder, which has a positive effect on cost reduction.

Nickel is a common additive in solder alloys, due to its high chemical affinity with tin it can form intermetallic layers (Cu, Ni)6Sn5. As the amount of nickel in the solder increases, the size of the (Cu, Ni)6Sn5 IMC also grows, but on the other hand, it suppresses the growth of the second intermetallic Cu3Sn phase [7]. This has the effect of reducing the diffusion of copper into the intermetallic. Cobalt has a similar ability, and a high affinity with tin and another positive effect is its influence on the internal microstructure of the solder alloy, which increases the shear strength [7].

II. Materials and Procedures

The experiment was designed according to the DOE statistical method (design of experiments). Therefore, the assessment of the results will be performed on the principle of factor analysis. The input parameters are three, namely, solder alloy material, number of remelting, and thermal aging, which is divided into two types (long-term aging and thermal shock stress).

For the experiment, 5 solder alloys were used. The first one is SnNiGe solder alloy. In addition to the core tin element, the solder contains 0.036% nickel and 0.01% germanium. The second solder alloy used in the experiment is SnNiCoP consisting of 0.046% nickel, 0.012% cobalt, and 0.003% phosphorus. The third brazing alloy is the widely used SAC305, composed of 96.5% tin, 3% silver, and 0.5% copper. The last two brazing alloys also contain small amounts of copper. The solder alloy SnCu0,2NiGe is composed of 0,2 % copper, 0,036 % nickel, 0,01 % germanium and the other alloy SnCu0,2NiCo is composed of 0,21 % copper, 0,041 % nickel, 0,006 % cobalt.

Copper was used as the carrier material to which the alloys were brazed using a reflow oven. Actiec 5 Flux was used for

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better wetting and to eliminate oxidation on the copper substrate.

The main factors affecting the growth of intermetallic layers are multiple remelting in the oven and long-term thermal aging. Multiple remelting is used to simulate the manufacturing process, where multiple remelting of the board for soldering other types of components may occur during the mounting and soldering process. This effect will help to show what state the intermetallic layer may be in at the beginning of its product life cycle. This can potentially cause a high rate of complaints at launch.

Parameters from the ČSN EN 60068-2-2 standard were used for thermal stresses. The long-term thermal stress was set at 120°C for 42 days (1000h). As for the shock stress (ČSN EN 60068-2-14 ed. 2), a range of values from -40°C to 120°C was chosen, with 1000 cycles lasting 10 minutes. The test duration was about seven days.

Samples were processed using materialographic cross-sections, which were etched with the solution for better identification of IMC.

An automated layer measurement system was used to process the values, which can measure approximately 100 values after the layer identification. Intermetallic compounds are highly variable in thickness and measuring a few spots can produce an inaccurate result. By using automated measurements, it is possible to obtain statistically more accurate information about the average thickness.

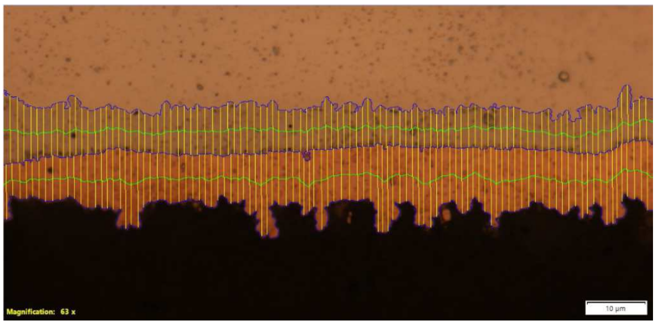

Fig. 1. Example of the automated measurement system (Stream Motion)

The thickness of the copper layer was also included in the results, when IMC is formed, not only the solder alloy diffuses but also the contact area on the other side.

III. Results

A. Solder material

By comparing the solder material factor, you can see the mean value with a 95% confidence interval in Fig. 2. Based on these results, the positive influence of SAC305 solder can be seen, which achieves the lowest IMC thickness values and the lowest variance of values.

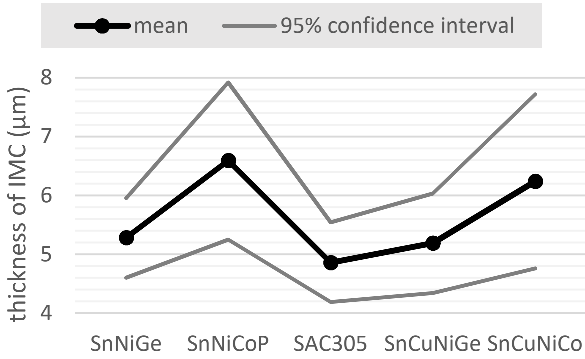

Fig. 2. Factor analysis results of IMC thickness by solder material

SnNiGe and SnCuNiGe solder, which have a common addition of germanium, perform worse. The average IMC thicknesses are similar with slightly more variance compared to SAC305 solder. The values of solder with cobalt admixture came out worst, SnCuNiCo solder is slightly better considering the spread. This difference, however, is very small and therefore cannot be taken into serious consideration.

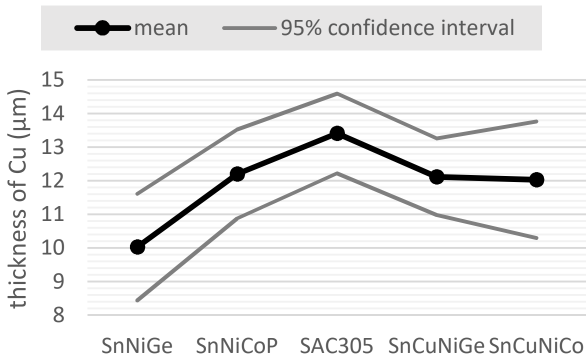

Fig. 3. Factor analysis results of Cu thickness by solder material

The analysis in Fig. 3 shows the changes in copper thickness, specifically its loss due to diffusion into the IMC. Again, the best performing solder is SAC305, which shows the least effect on copper loss. In comparing SnNiGe and SnCuNiGe solder, the main difference between them is the copper content, it can be identified that the increased copper content in the solder has a positive effect on copper diffusion. Comparison of SAC305 solder with a copper content of 0.5% with SnCuNiGe which contains 0.2% copper also confirms that increased copper content reduces diffusion. Cobalt also has a high affinity with tin, hence also causing a reduction in copper diffusion into the IMC.

B. Reflow effect

The effect of remelting was most pronounced on the results of IMC growth and copper depletion. The change in the mean value is larger than its variance, this shows the effect of multiple remelting in the fabrication process has a significant effect on the long-term stability of the electronic assembly.

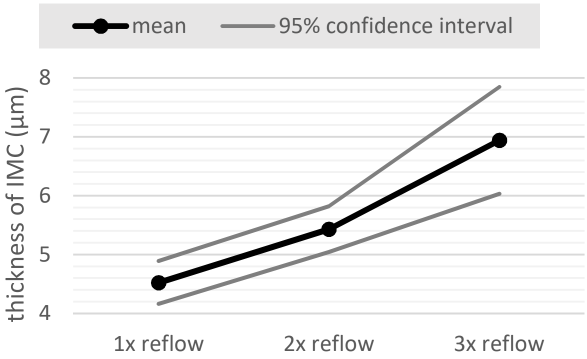

Fig. 4. Factor analysis results of IMC thickness by reflow effect

In Fig. 4 you can see that the second reflow caused a 1 µm increase in IMC thickness. The next reflow caused even more growth, but at the same time, the value has a greater spread, with the minimum value holding a linear growth.

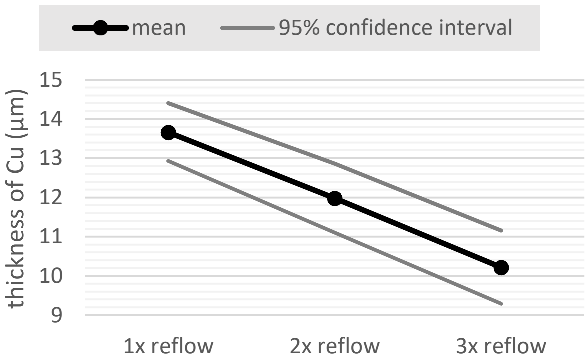

Fig. 5. Factor analysis results of Cu thickness by reflow effect

The copper loss from repeated remelting can be seen in Fig. 5. This shows a practically linear decrease in values compared to the growth of the IMC, both the mean value and the confidence interval range. Accordingly, based on the results, it can be said that the comparison of one and three remelting causes a copper loss of almost one-third, which can cause a large reduction in the mechanical lifetime of solder joints.

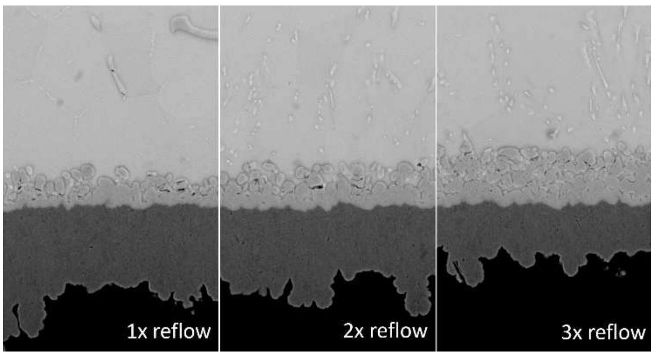

Fig. 6. Preview of IMC grow depending on the number of reflows

The effect on the growth of intermetallic and copper diffusion can be seen in Fig. 6, where the IMC layer increases as a function of the number of remelting. The figure shows a materialographic cross-section of the SnNiGe solder without thermal aging.

C. *Aging effect*

The last observation of factors on the effect of IMC and Cu thickness is thermal stressing, in this case, long-term thermal stressing (120°C for 1000h) and shock stressing (1000 cycles of 10 minutes from -40°C to 120°C) were used.

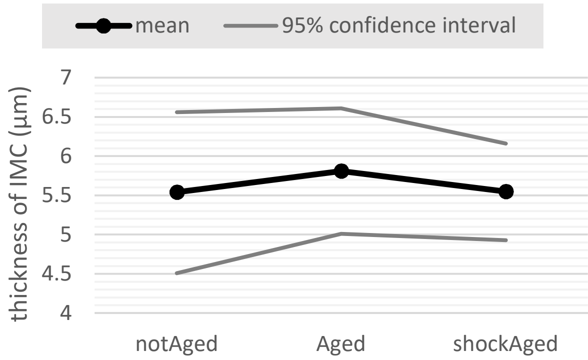

Fig. 7. Factor analysis results of IMC thickness by the aging effect

From the results of the factor analysis in Fig. 7, thermal stress does not have a significant effect on IMC growth. Long-term aging shows a slight increase in values, which can be expected. Shock aging is generally not expected to have such an effect on IMC growth, but rather mechanical stresses caused by thermal expansion of parts of the component involved with different temperature coefficients.

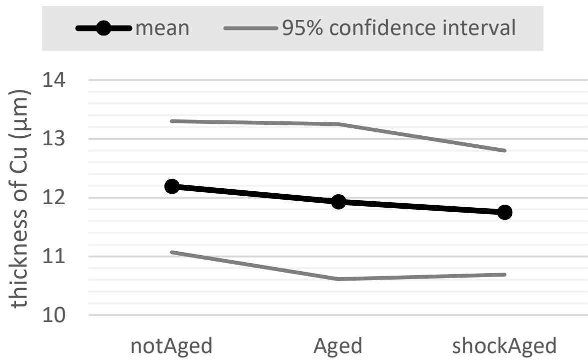

Fig. 8. Factor analysis results of Cu thickness by aging effect

The results of copper loss because of temperature stress are similar. The results in Fig. 8 show a slight decrease in copper thickness after thermal aging. As far as shock stress is concerned, the decrease in the mean value is larger but still at the limit of statistical significance.

D. *SEM images*

The following three figures show electron microscope images to compare the structures of the intermetallic within the solder alloy. The images are of three types of solder alloys namely SAC305, SnNiCuGe, and SnNiCuCo. It is evident from the images that the volume growth of the copper and tin-based IMCs is the smallest in the SAC305 solder (Fig. 9), which has a positive effect on the mechanical resistance of the solder joint. In contrast, silver-based intermetallic are apparent in the whole volume. These results are verified in chapter E.

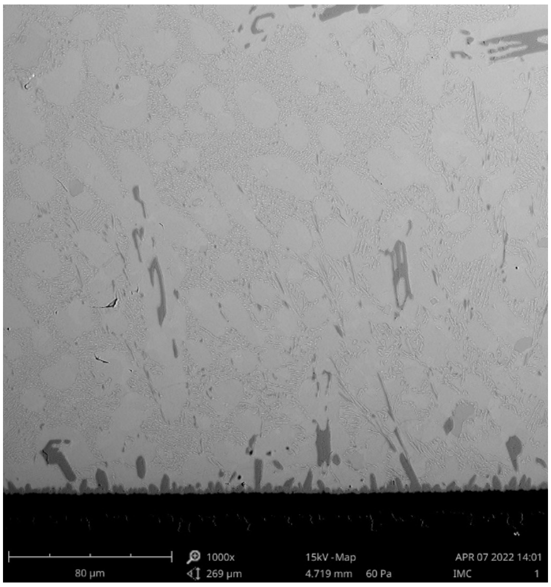

Fig. 9. Solder structure preview of SAC305

Fig. 10. Solder structure preview of SnNiCuGe

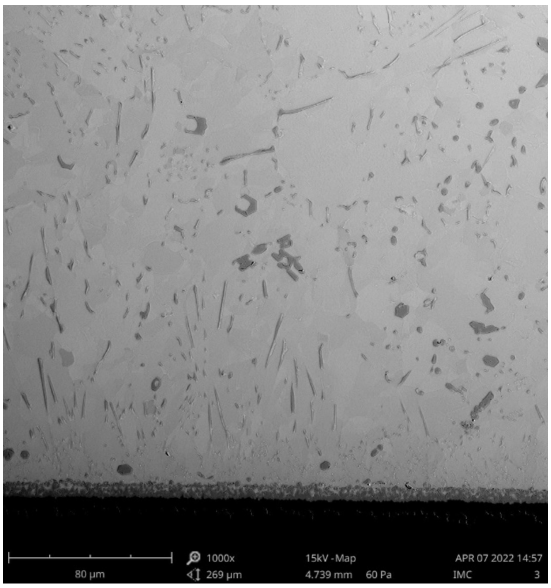

Fig. 11. Solder structure preview of SnNiCuCo

The intermetallic layers in the volume of SnNiCuGe and SnNiCuCo solder grow in very similar concentrations. Fig. 10 shows a smaller number of larger intermetallic structures and Fig. 11 shows a larger number of smaller intermetallic structures. But when observing the layer at the copper contact, the greater thickness is evident, as we have demonstrated in Chapter A.

E. EDS analysis

In the next stage of the results, EDS analysis of the processed samples is performed to verify the material composition of the intermetallic compounds formed at the solder boundary and inside the solder volume.

EDS analysis is used to determine the quantity of individual elements contained in the sample. The software evaluates the reflected electrons from their spectrum and, after comparison with the element database, can tell which elements are present in the sample and what their quantity is.

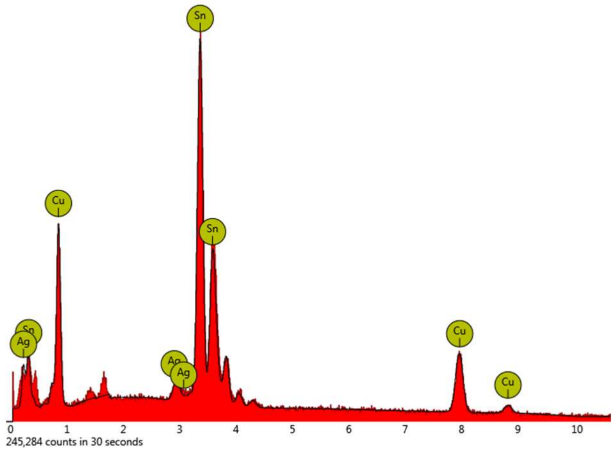

Fig. 12. The spectrum of spot 1 from Fig. 13

In Fig. 12 you can see a spectral plot of the reflected electrons with the KeV unit on the X-axis. In this way, it is possible to determine the quantum representations of the elements according to the size of the peak.

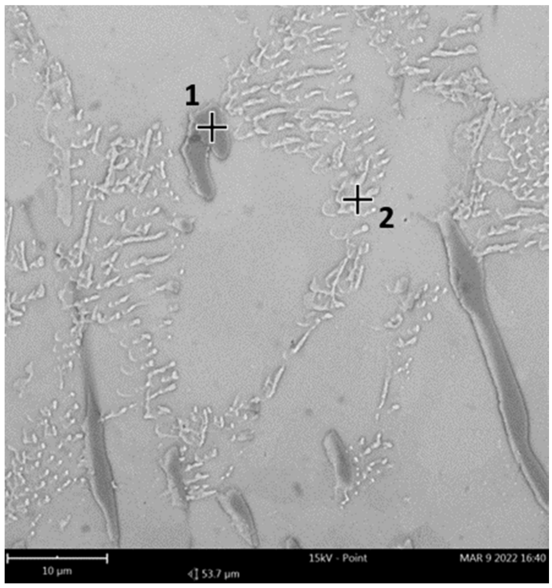

Fig. 13. EDS analysis of inner solder IMC (SAC305)

The two basic intermetallic compounds are Cu6Sn5 and Cu3Sn. The Cu6Sn5 compound is based on atomic concentration composed of 45.5% tin and 54.5% copper. Another compound occurring in Fig. 13 is Ag3Sn which has an atomic concentration of 75% silver and 25% tin. When the results of the EDS analysis were evaluated, the following results were obtained in the indicated locations. **1:** 56% Sn, 42.61% Cu, 1.39% Ag; **2:** 58.07% Sn, 41.93% Ag. This means that point 1 is close to the Cu6Sn5 intermetallic, but because of the small spot, the surrounding area is also included in the results. Point 2 should correspond to Ag3Sn intermetallic, here it is further away from the theoretical chase, also due to an even smaller IMC volume.

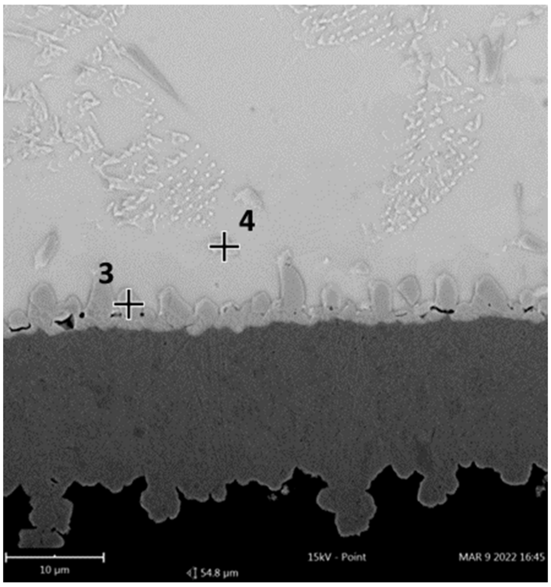

Fig. 14. EDS analysis of IMC (SAC305)

In Fig. 14, an analysis is performed on the intermetallic layer formed at the boundary of the copper and inside the solder. The results of EDS analysis at each location show the growth of IMC Cu6Sn5. 3: 51.77% Sn, 47.26% Cu, 0.97% Ag; 4: 57.49% Sn, 39.8% Cu, 0.71% Ag. Spot 3 is closer to the theoretical atomic concentration, again due to the larger volume of IMC around the investigated spot. The detection of silver confirms its presence in the SAC305 solder.

IV. Conclusion

The goal of the experiment was to investigate the different effects on the growth of intermetallic layers and the loss of copper pad. The experiment involved 3 main factors namely the material composition of the brazing alloy, multiple remelting, and thermal stress. SAC305 solder alloy was used as a reference in the selection of the solder alloy due to its popularity and high applicability. Other solder alloys were mainly related to the added elements germanium and cobalt.

Based on the results looking at the material factor of the solder alloy, it was found that SAC305 solder showed the best results in both intermetallic growth and copper diffusion. The closest solder to SAC305 was the germanium doped solder, which although had a wider confidence interval, performed noticeably better than the cobalt doped solder. In the contrast, when looking at the copper loss, the worst solder was SnNiGe, which showed the highest copper loss. The other three solder alloys came out relatively the same, with SnNiCoGe, which differs from the worst solder mainly in its 0.2% copper content, proving that a larger copper volume in the solder alloy helps to reduce diffusion.

Looking at the remelting effect, the factor analysis shows a virtually linear increase in IMC thickness and a linear decrease in copper pad thickness. This proves that multiple heating of the solder in the manufacturing process determines the size of the intermetallic even at the beginning of the product life cycle. The last factor of thermal stress did not show any definite results.

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