Microstructural Evolution During Electromigration in Eutectic Tin-Bismuth BTC Solder Joints

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ABSTRACT
Eutectic tin-bismuth alloy and its variations have been identified as the solders of choice for applications that require low-temperature assembly, even though they pose serious metallurgical challenges. Their high homologous temperature results in the solder microstructure constantly changing and the high electromigration effective valence of bismuth results in a thick, relatively brittle bismuth layer accumulating on the anode side of the solder under current stressing. In addition, as in any tin-based alloy joining to copper surfaces, the intermetallic growth too needs to be considered. Two iNEMI teams have been researching Sn-Bi alloys. One has focused on the assembly process and solder joint mechanical reliability aspects and the other on electromigration. Now, in the next phase, the two are being combined to study the effect of electromigration on the mechanical and electrical properties of the solder joints. We have recently completed and published work on the electrical effects of electromigration over a range of temperature that when plotted on an Arrhenius plot can be used to predict the electromigration life of bottom-terminated-component (BTC) eutectic Sn-Bi solder joints under any application condition. In this paper, we report on the microstructural evolution of BTC eutectic Sn-Bi solder joints during electromigration in terms of bismuth redistribution and accumulation at the anode end, and the intermetallic growth on copper and nickel substrates. These findings will greatly aid in the design of experiments to research the effects of electromigration on the mechanical properties of Sn-Bi solder joints.

Key words: electromigration, microstructure, tin-bismuth solder alloys, bottom-terminated components.

INTRODUCTION
This paper is a follow up of the research presented at the Electronic Component Technology Conference (ECTC) in May 2024 in Denver that reported on the electromigration testing of 60-µm high eutectic Sn-Bi bottom-terminated-component (BTC) solder joints on OSP (organic surface preservative) and ENIG (immersion gold on electroless nickel) surfaces subjected to current densities in the range 1-3 kA/cm2 in ovens set at 60, 80 and 100 ºC **[1]**. Electromigration rates were measured by the rates of changes of solder joint resistances. The results were summarized on Arrhenius plots which can be conveniently used to predict the electromigration life of solder joints under any application condition.

The subject of this follow-up paper is the microstructural evolution of BTC eutectic Sn-Bi solder joints during electromigration. The growth of intermetallic phases at the solder-substrate interfaces and the extent of bismuth electromigration were measured as a function of temperature, current density and time in a bid to complement the electromigration rates measured using the rates of change of solder joint resistance and reported earlier at 2024 ECTC **[1]**. The microstructural changes helped explain the electrical behavior of the solder joints.

EXPERIMENTAL PROCUDURE
The details of the specimen design and preparation and the electromigration stressing and analysis via the rates of change of solder joint resistance were described in the 2024 ECTC paper mentioned above **[1]**. **Figure 1** shows a cross section of a daughter card with four solder joints relevant to the test. The inner two solder joints were tested for electromigration when subjected to high electric currents. The outer two solder joints were there only to measure the voltage drops across the inner two solder joints. Since no electric current flowed through the outer solder joints, they were used for studying microstructural evolution of solder joints with no current flow through them.

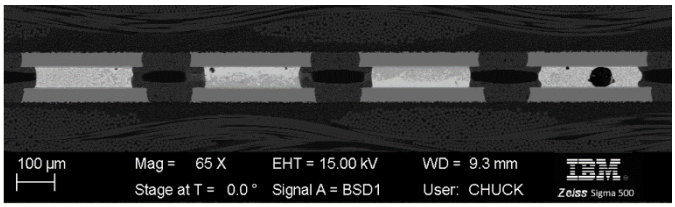


Fig 1. Cross section of solder joints between OSP-OSP metallization that had been subjected to 4.5-A current for 39 days in an oven at 100 ºC. The components are above and the printed circuit board is below the solder joints.

The microstructural evolution of the BTC solder joints were studied using the conventional metallographic means of cross sectioning, grinding and polishing and examining in a scanning electron microscope **[2].**

Two eutectic Sn-Bi solder joint configurations were studied. One termed OSP-OSP was a solder joint between OSP finished copper on the printed circuit board (PCB) and OSP finished copper on the component. The other termed ENIG-OSP was a solder joint between OSP finished copper on the PCB and ENIG finished copper on the component.

RESULTS AND DISCUSSION

Intermetallic growth

Figure 2 shows a cross sectional micrograph of intermetallic growth in an ENIG-OSP solder joint. Near the top is the intermetallic between eutectic Sn-Bi solder and the ENIG finished copper on the component. Near the bottom is the intermetallic between the solder and the OSP finished copper on the PCB. The chemical compositions stated in the figure were inferred from the work of others **[3, 4]**. The Ni_3Sn_4 intermetallic was observed to be nominally about 1-µm thick in all the micrographs. Under the conditions of the testing, there was no noteworthy increase of the Ni_3Sn_4 intermetallic thickness. Therefore, only the combined growth of the Cu_3Sn and Cu_6Sn_5 intermetallic are reported in **Figures 3** for OSP-OSP solder joints and in **Figure 4**.for ENIG-OSP solder joints. Notice that the combined thickness of Cu_3Sn+Cu_6Sn_5 intermetallic is in general lesser on the anode side of the solder joint compared to the cathode side because the accumulated Bi-rich phase on the anode side forms a diffusion barrier between the copper of the PCB and the Sn-rich phase of the solder.

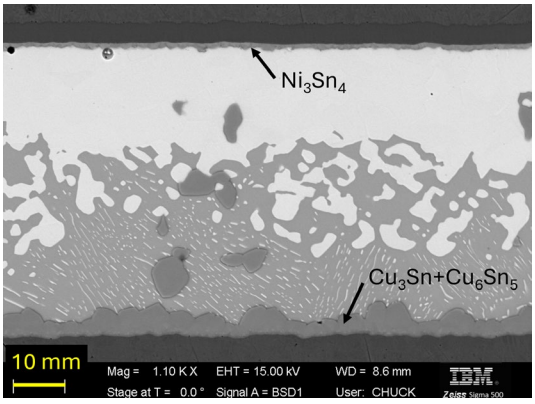
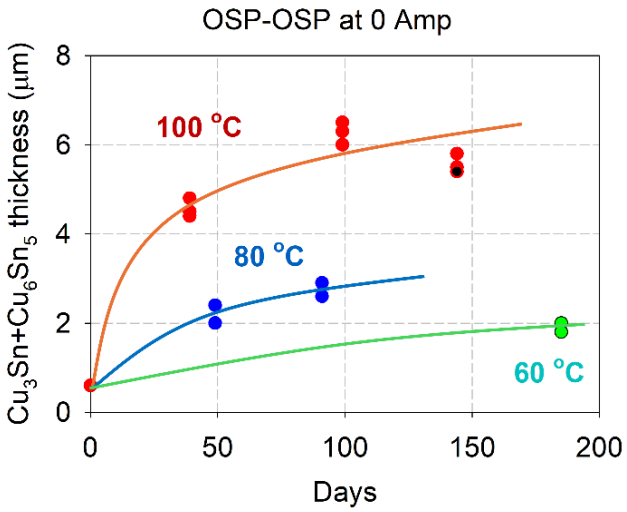
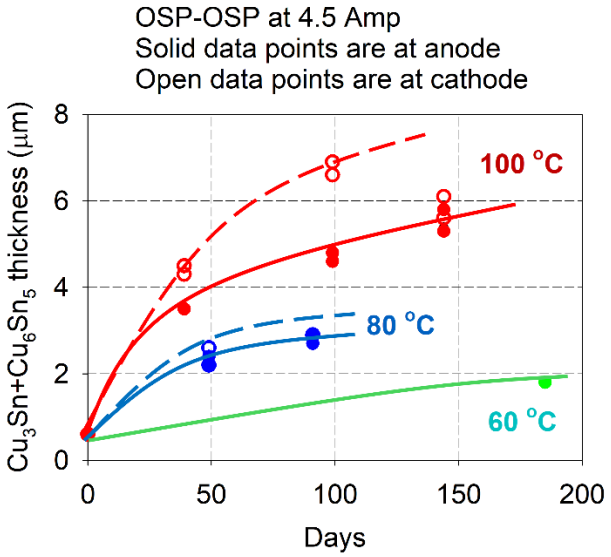


Fig. 2. Intermetallic at the eutectic Sn-Bi solder and the ENIG finished copper interface at top of the solder joint shown and at the eutectic Sn-Bi and OSP finished copper interface at the bottom of the solder joint.

It is customary to plot diffusion-controlled intermetallic growth as a function of the square root of time to obtain a linear plot **[5]**. This custom was not followed here because of excessive scatter in the data. The understanding of the root cause of the excessive scatter in the intermetallic growth rate needs further study.



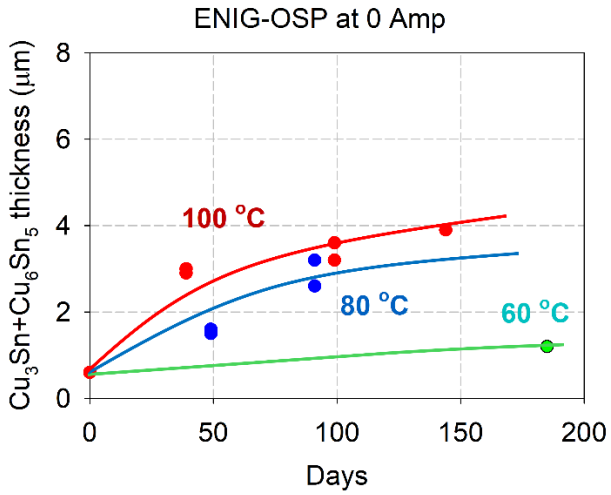
(a) OSP-OSP solder joint with zero Amp current



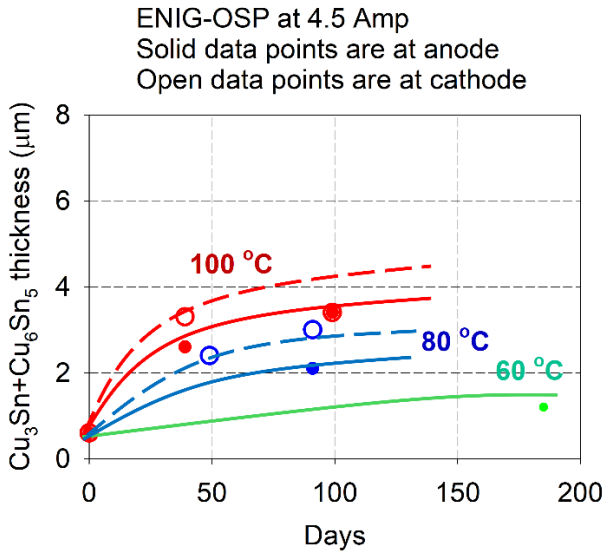
(b) OSP-OSP solder joint with 4.5 Amp current

Fig 3. Intermetallic growth on OSP-OSP solder joints between eutectic Sn-Bi solder and OSP finished copper at (a) Zero Amp current and at (b) 4.5 Amp current.

Comparing **Figures 3 and 4** shows that the combined thickness of the Cu_3Sn and Cu_6Sn_5 intermetallic was somewhat higher in the OSP-OSP solder joints compared to the ENIG-OSP solder joints. The verification and understanding of this difference needs further research.



(a) ENIG-OSP solder joint with zero Amp current

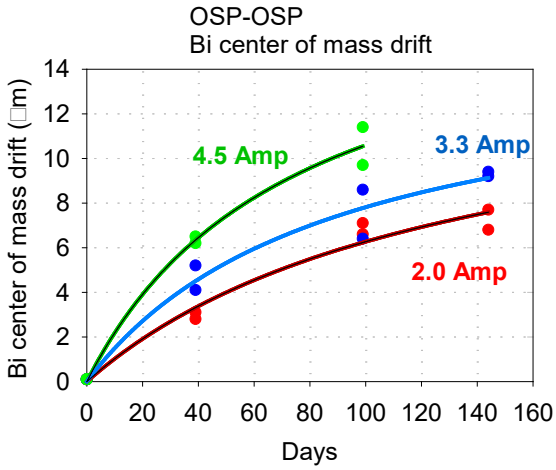


(b) ENIG-OSP solder joint with 4.5 Amp current

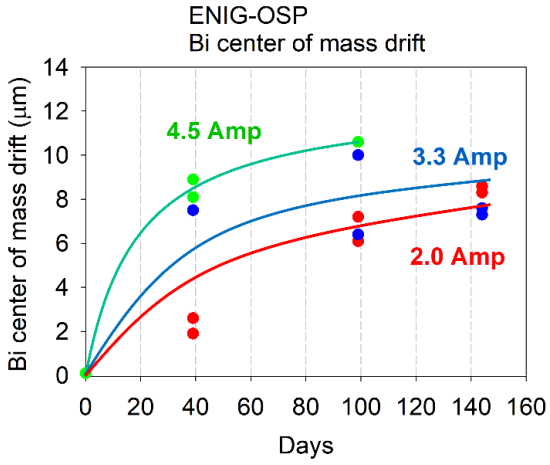
Fig. 4. Intermetallic growth on ENIG-OSP solder joints between eutectic Sn-Bi solder and OSP finished copper at (a) Zero Amp current and at (b) 4.5 Amp current.

Bismuth electromigration

Cross sectional micrographs of BCT solder joints subjected to 2, 3.3 and 4.5 A currents (1-3 kA/cm^2) in ovens held constant at 60, 80 and 100 ºC for various times are shown in **Figures A1-A5** in the appendix. For the purposes of calculating current densities, the typical cross sectional area of the solder joints was 0.25x0.60 mm^2. It is tempting to use the thickness of the accumulated bismuth at the anode as a measure of the bismuth electromigration rate, but for the following reasons the bismuth accumulated thickness is not a true measure of bismuth electromigration rate: Eutectic Sn-Bi alloy consists of Bi-rich phase approximately 50% by volume. In the as-cast solder, the Bi-rich phase is uniformly dispersed, including in the anode region of the solder joint where the bismuth accumulates. So, less than one-half of the Bi-rich phase that is accumulated at the anode got there by electromigration; the other half was already there in the as-cast solder. The second issue to address is that besides the Bi accumulation on the



(a) OSP-OSP solder joints



(b) ENIG-OSP solder joints

Fig. 5. Center of mass of the Bi-rich phase in the solder joints in oven at a constant 100 ºC.

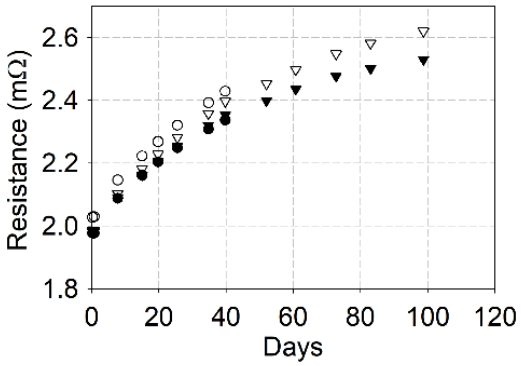
anode end, on the cathode side, too, the Bi-rich phase is drifting as a result of electromigration and must be included in the determination of the rate of electromigration. A third issue complicating the rate of Bi electromigration calculation is that the solder joint is finite in length. The Bi atoms that have accumulated at the anode can electromigrate no further.

The extent and the rate of bismuth electromigration can be obtained from the cross sectional micrographs of **Figures A1-A5** (shown in the appendix) by determining the center of mass of the Bi-rich phase, which is the lighter phase in the micrographs, using an image processing freeware, such as the ImageJ program, a Java-based image processing program, developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation **[6]**. The shift of the center of mass of the Bi-rich phase towards the anode is the sum total of the extent to which the Bi atoms have electromigrated. **Figure 5** shows plots of the shift of the center of mass of the Bi atoms in OSP-OSP and ENIG-OSP solder joints held in 100 ºC oven when subjected to 2, 3.3 and 4.5 A currents. Notice that the rate of shift of the Bi center of mass decreases with time. This is because of the finite length of the solder joint. With time the Bi atoms drift towards the anode leaving lesser concentration of Bi atoms on

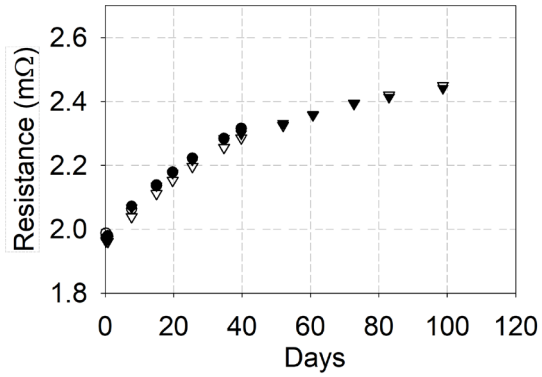
the cathode side to supply the Bi accumulation l on the anode side. An infinitely long solder joint would not suffer from such limitation and its Bi center of mass would have the Bi drift velocity staying constant with time.

Before the solder specimens of **Figure 5** were cross sectioned, their resistance versus days data had been collected, plotted and published in **Reference 1**. Examples are shown in **Figure 6**. Notice that both the center of mass drift (**Figure 5**) and the resistance plots (**Figure 6**) have a parabolic nature arising from the diminishing concentration of bismuth in the middle and the cathode side of the joints. With time, with decreasing concentration of bismuth available in these regions to feed the bismuth accumulation at the anode, the rate of bismuth drift decreases over time in a parabolic fashion.

From a scientific perspective, the most accurate way to measure the Bi atom electromigration drift velocity in a eutectic Sn-Bi alloy, unimpeded by any boundaries, is to the plot the center of mass of the Bi atoms versus electromigration time, as shown in **Figures 5** and determine the slope of the plot at time zero. This slope is equal to the drift velocity of the Bi atoms in an infinitely long eutectic Sn-Bi solder in which the Bi atom electromigration is unimpeded by the finite size of the solder specimen.



(a) OSP-OSP solder joints



(b) ENIG-OSP solder joints

Fig. 6. Resistance versus day plots at 4.5-A current in an oven at 100 ºC showing linear behavior in the second stage up to about 20 days followed by parabolic behavior in the third stage beyond 20 about days. At this high current, the first stage of dipping resistance is too short to be observed on these long-term plots **[1].**

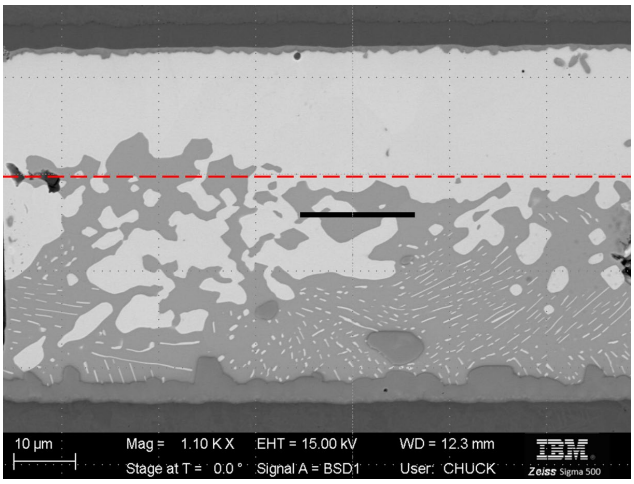


Fig. 7. The dotted line is the Bi-rich phase center of mass. The short solid line is in the center of the solder joint. The wide scatter in the Bi electromigration with the Bi-rich phase motion towards the anode being slower in some regions than others maybe because of the Sn-rich phase orientation affecting the Bi electromigration.

The time zero slopes of the plots of **Figures 5** could be used as a measure of the electromigration rates unimpeded by solder size, if not for the widely scattered and limited data. The number of specimens can be increased to obtain readings at shorter time intervals in the early stages of electromigration stressing, but the scatter resulting from the anisotropy of the Sn-rich body centered tetragonal (BCT) phase cannot be avoided **[7, 8]**. One result of the anisotropy is that in regions where the Sn-rich phase grains are not optimally oriented (that is with the c-axis of the Sn BCT grains not parallel to electron flow), the Bi electromigration may be slower than in adjacent grains that are more favorably oriented (that is with the c-axis of the Sn BCT grains parallel to electron flow). **Figure 7** shows the unpredictable nature of Bi-rich phase electromigration. In some areas the Bi-rich phase is left behind, probably because of the
anisotropic nature of the Sn-rich body centered tetragonal phase [**6, 7**]. From an engineering perspective, it is important to know the thickness of the accumulated bismuth layer at the anode (**Figures A1-A5**) as a function of current density, temperature and time and to know at what critical thickness the solder joint becomes prone to cracking during drop testing. The life of the
solder joint then is the time it takes for the accumulated Bi-rich phase thickness to grow to the critical thickness at which the joint becomes prone to cracking in drop test.

CONCLUSION

The growth rate of Ni_3Sn_4 intermetallic, between the solder and the ENIG finished component did not grow much with time even at temperatures as high as 100 ºC. The thickness of the Ni_3Sn_4 intermetallic remained about 1 µm for the duration of the test. The growth rate of the combined thickness of Cu_3Sn and Cu_6Sn_5 intermetallic decreased in a near parabolic fashion. Its rate of growth was slower on the anode side compared to the cathode side as a result of bismuth accumulation on the anode side acting as a diffusion barrier between the solder and the PCB copper. Electromigration did

not have a noticeable effect on the combined Cu_3Sn and Cu_6Sn_5 intermetallic growth rate. The scatter in the data did not result in a linear plot when plotted with the abscissa as the square root of time.

The bismuth electromigration measured in terms of the drift of the center of mass of the bismuth atoms had a near parabolic behavior with time as did the solder joint resistance data reported in an earlier work by the same authors **[1].** The scatter is the data was high, most probably due to the anisotropic behavior of the Sn-rich body centered tetragonal phase.

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APPENDIX

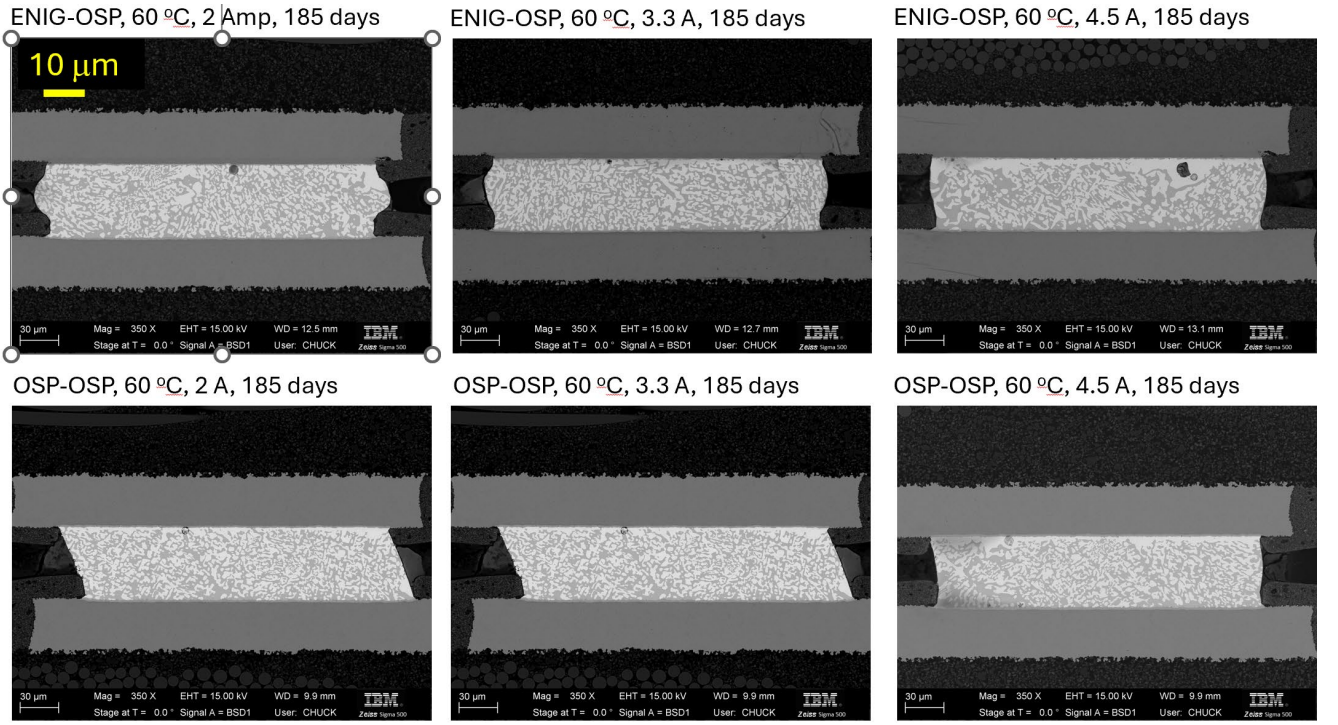

Fig. A1. Cross sectional micrographs of BTC Sn-Bi eutectic solder joints in an oven at 60 ºC subjected to 2. 3.3 and 4.5 A current for 185 days.

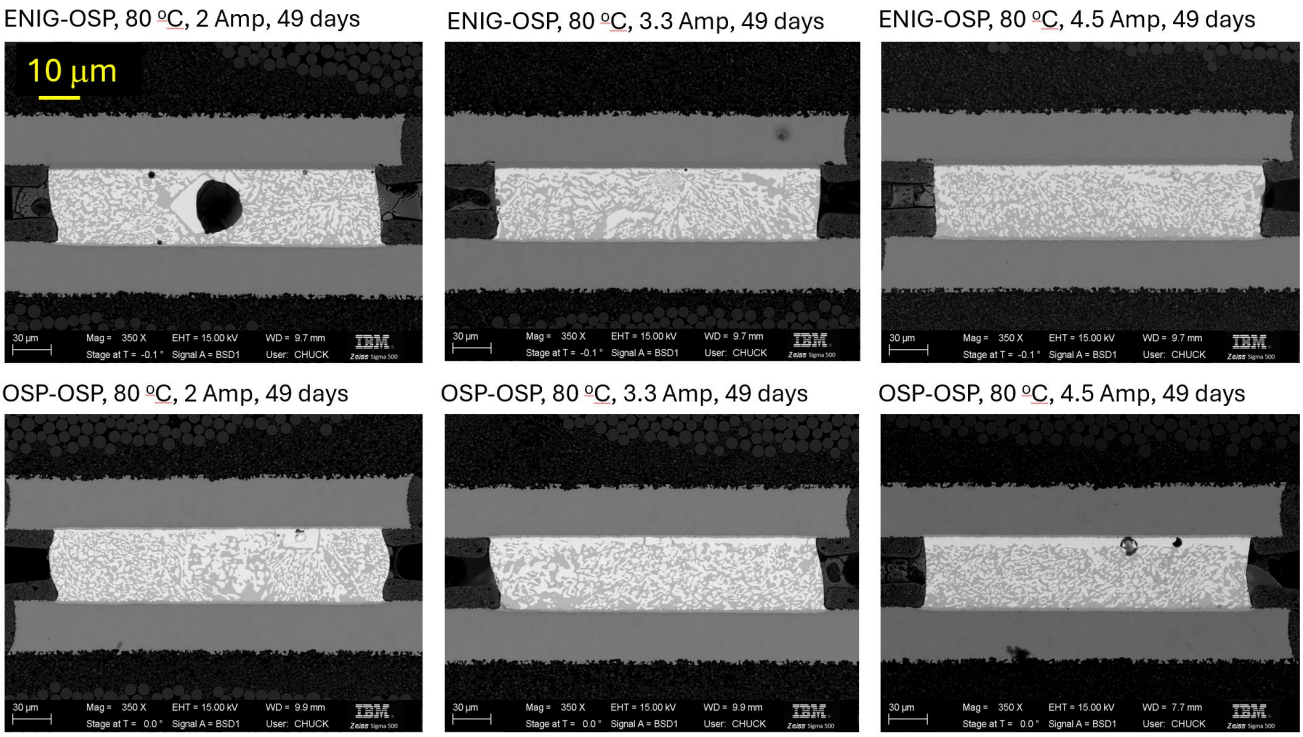

Fig. A2. Cross sectional micrographs of BTC Sn-Bi eutectic solder joints in an oven at 80 ºC subjected to 2. 3.3 and 4.5 A current for 49 days.

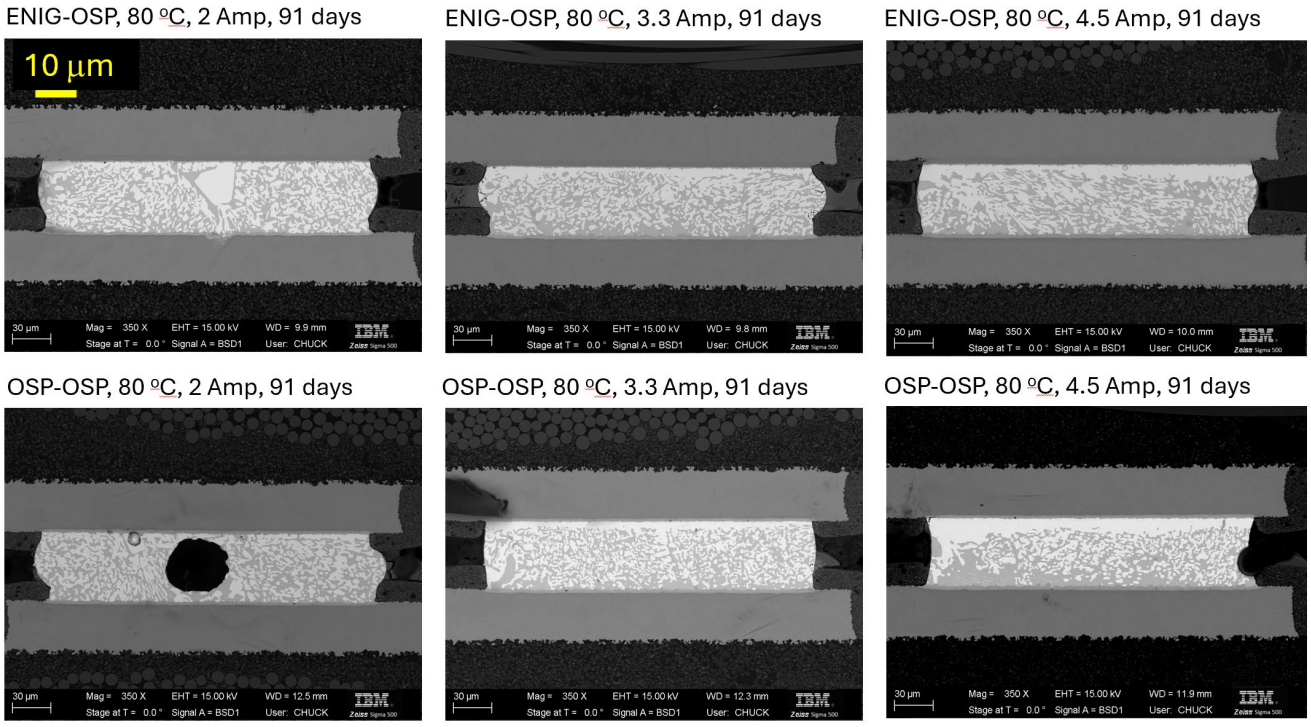

Fig. A3. Cross sectional micrographs of BTC Sn-Bi eutectic solder joints in an oven at 80 ºC subjected to 2. 3.3 and 4.5 A current for 91 days.

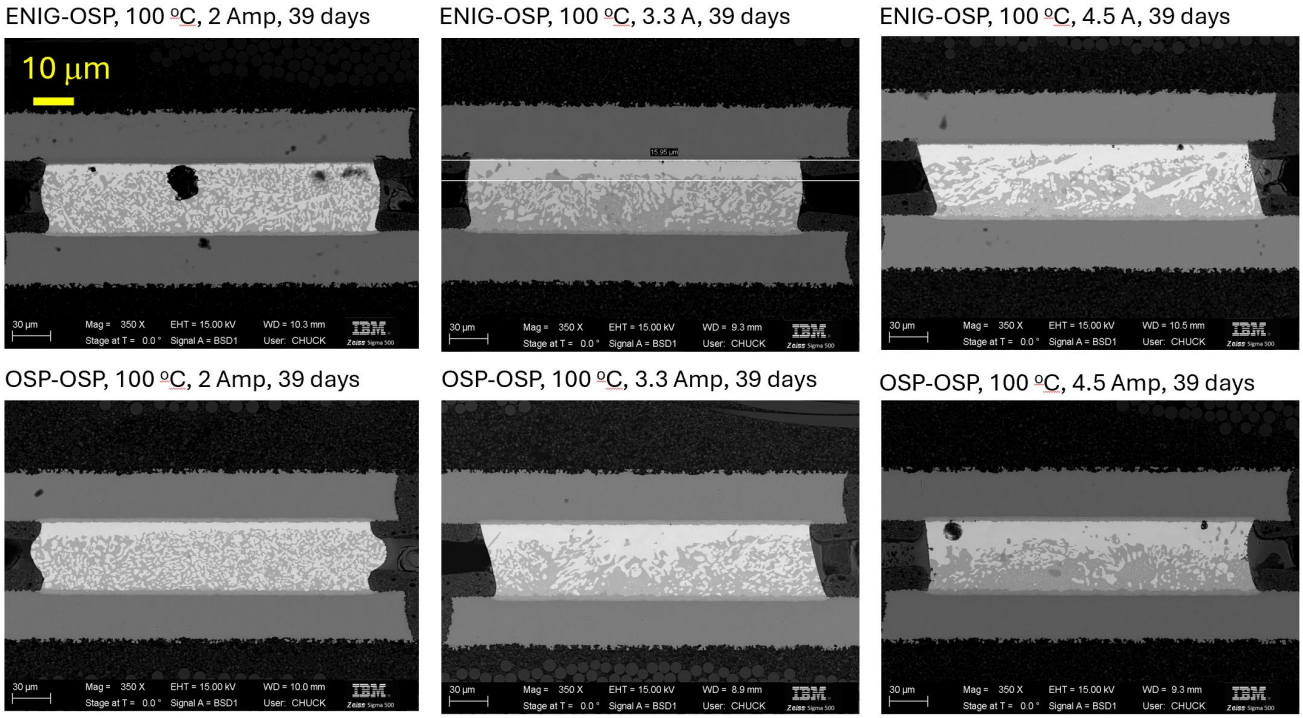

Fig. A4. Cross sectional micrographs of BTC Sn-Bi eutectic solder joints in an oven at 100 ºC subjected to 2. 3.3 and 4.5 A current for 39 days.

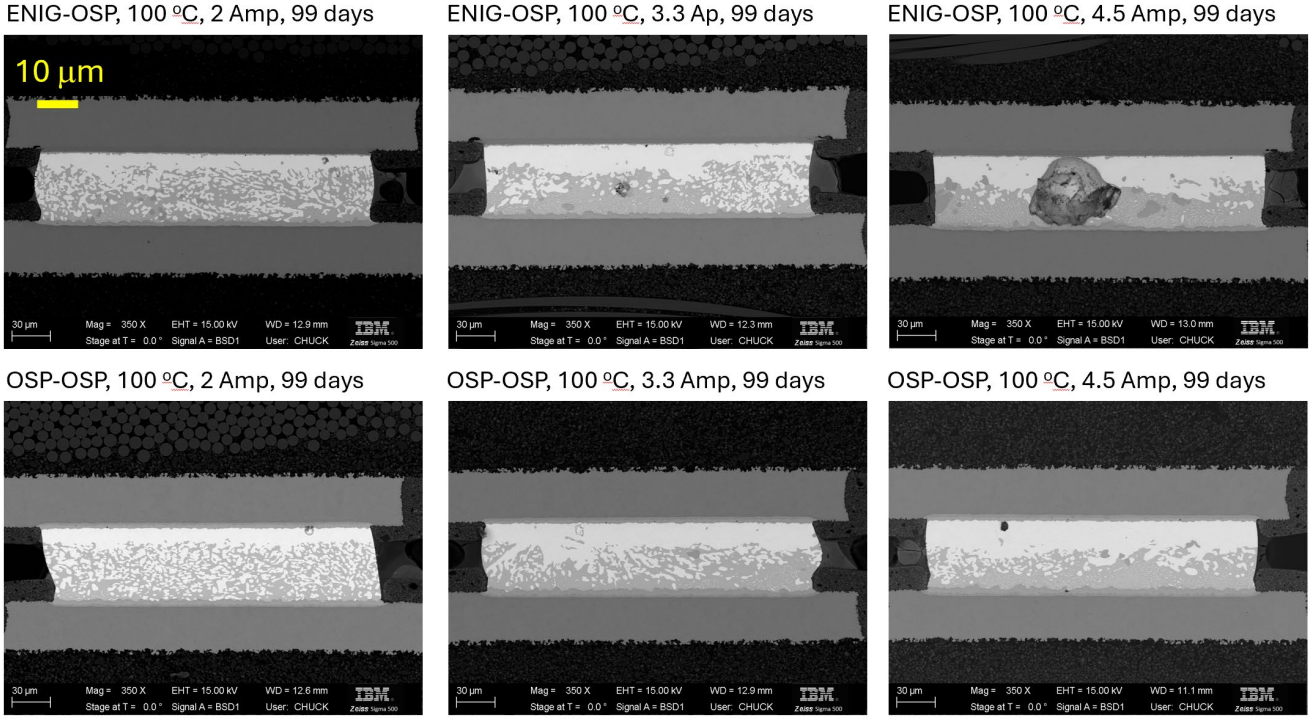

Fig. A5. Cross sectional micrographs of BTC Sn-Bi eutectic solder joints in an oven at 100 ºC subjected to 2. 3.3 and 4.5 A current for 99 days.