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Electrochemical migration of lead-free solders and Ag-based electrically conductive adhesives in NaCl solution

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Annotation:
In this article, the electrochemical migration of lead-free solders and electrically conductive adhesives with an Ag content of more than 70% was studied by using a water drop test in NaCl solution. The results of solder pastes were compared with the results of electrically conductive adhesives. It was found that some solder pastes with a low Ag content have a lower susceptibility to electrochemical migration than, for example, solder paste Sn42Bi58. The highest resistance to corrosion has a conductive adhesive CRM-1033B with an Ag content of 75%. Resistance and voltage during the water drop test. From the measured values, it was determined that the values of resistance and voltage decrease with dendrite growing. X-ray spectroscopy was also performed to determine the chemical elemental composition of dendrites. It was found that the dominant element of the dendrite of solder pastes was Sn. In the case of electrically conductive adhesives, Ag was the main element of the dendrite.

INTRODUCTION

The devices may be exposed to effects of extreme temperature and humidity, which may lead to moisture getting on unprotected parts of printed circuit boards (either by leakage or by condensation effect). This may lead to device failures during operation. Researches have established that the failures can be caused by the processes of electrochemical migration [1-5].
Electrochemical migration (ECM) can occur in any area of the printing circuit board (PCB) in the presence of electrical voltage and contaminants remaining after the soldering process or due to poor washing and improper handling of the PCB. The standard algorithm is as follows:

- Anodic dissolution of metal ($Me \rightarrow Me^{n+}$+ ne-);
- Migration of metal ions;
- Cathodic deposition of metal ions ($Me^{n+} \rightarrow Me$).

Under the influence of electric voltage, the conductor-anode dissolves, giving positively charged metal ions to the electrolyte. These ions are directed to the conductor-cathode and reduced on it to a metallic state, forming conductive bridges in the form of a dendritic loose metal structure [6].
Many research works have been done on the topic of the ECM of Pb and Pb-free solders. Works [7-10] have concluded that with increasing Pb content in solder, resistance to electrochemical corrosion increases. But nowadays, solders containing Pb are not used much, they are increasingly being replaced by Sn-Ag and Sn-Ag-Bi solders. In work [8], the ECM of the Sn-Pb solders and Sn-Ag-Bi solders were compared; according to their results, solder of Sn-Ag-Bi has a greater resistance to ECM than Sn-Pb.
The work [11] states that Ag increased the time of the ECM and the main element of the grown dendrite was Sn. Also, works [12] and [13] concluded that SAC solders are less susceptible to ECM than SnPb solders. These works additionally show that Ag does not migrate during ECM and is not contained in dendrite. But in the case of electrically conductive adhesives, which contain from 70% silver, the main element involved in the ECM is silver [13].
This research is aimed at studying and comparing the ECM of lead-free solders and electrically conductive adhesives and also studying the changes in electric values during the water drop (WD) test.

MATERIALS AND METHODS

For the experiment, solders SAC305 (Sn96,5%, Ag3%, Cu0,5%), REL61(Sn, Bi, Ag, Cu), Sn42Bi58 and electrically conductive adhesives AX70MN (Ag70%) and CRM-1033B (Ag75%) were used. Solder pastes SAC305 and REL61 used the same no-clean flux M8, so that it should not have any influence on the whole process.
The solder pastes and adhesives were stencil printed on PCB at 4x4 mm pads with a gap of 2 mm between them. The tested printed circuit board was from FR-4 substrate. Then thermal reflow was used for solder pastes, and in the case of electrically conductive adhesives oven was used. Adhesives were cured in an oven at a temperature of 180C for 10 min (AX70MN adhesive) and 60 min (CRM-1033B adhesive).
The WD test scheme is shown in Figure 1. At first, a suspension of distilled water with 0.002% NaCl was prepared for the test, then a droplet 20 µl was placed by a pipette onto the pads, which were covered with

solder and adhesives and then 1,2uA DC was applied (at higher current values, bubbles are generated, which are not desirable, because they form an air barrier or they can break the dendrite).

During the WD test, while the dendrite was growing, the values of resistance and voltage between the pads were measured by the device Agilent B2911A, which was connected to the computer and to the program created in the LabView software. The full process of dendrite growing was also observed using a microscope for each sample.

X-ray microanalysis of dendritic microstructure was carried by SEM microscope on each sample of solders and adhesives to determine the chemical elemental composition.

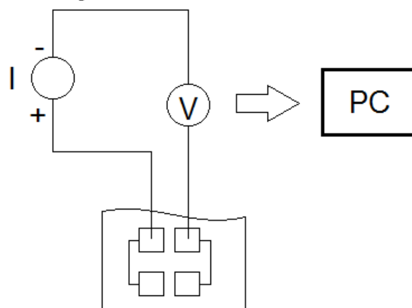

Fig. 1. Scheme of WD test

RESULTS AND DISCUSSIONS

Dendrite growth

The growing time of dendrite of different solder alloys and electrically conductive adhesives can be observed in Figure 2.

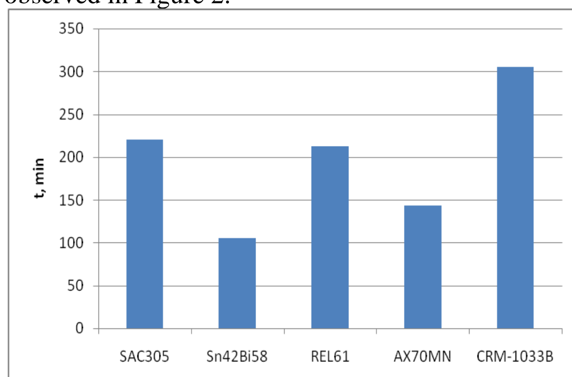

Fig.2. Time of growing dendrite of different solder alloys and adhesives in 2mM NaCl solution

The bar chart shows that the solder paste Sn42Bi58 required the least time for the dendrite growth. Further, two solder pastes SAC305 and REL61, which have similar composition and it differs only that the REL61 solder contains Bi element can be compared. The dendrite growth time for these solder pastes, as Figure 2 shows, differs only in a few minutes.

The dendrite growth time of the electrically conductive adhesives AX70MN and CRM-1033B is very different. The dendrite between pads covered by adhesive AX70MN grew twice faster than of adhesive CRM-1033B. By the way, it should be noted that the adhesive CRM-1033B had the greatest resistance to the dendrite occurrence and its growth. Several WD tests of adhesive CRM-1033B were carried out during which no dendrite was detected.

Grown dendrites of solder pastes Sn42Bi58 and SAC305 are shown below (see Fig.3, Fig.4). Figures show that, for example, the dendrites of the solder paste Sn42Bi58 grow from several points of the surface and have a branching structure. On the contrary, dendrites of solder paste SAC305 do not have such branching shape, but also originate from several points of the surface.

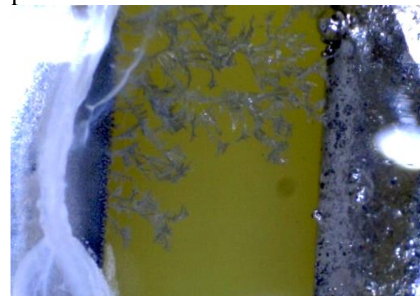

Fig.3. Dendrite growth from Sn42Bi58 during WD test

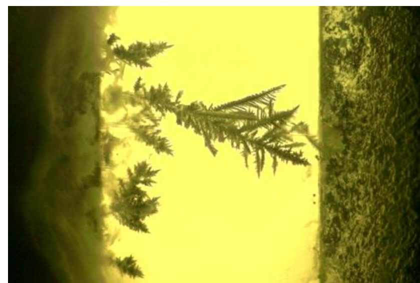

Fig. 4. Dendrite growth from SAC305 during WD test

Figure 5 shows the growing dendrite of adhesive AX70MN. The structure of this dendrite has a completely different shape, unlike the previous ones. The figure shows that it grows from one point, from which it then expands and grows further.

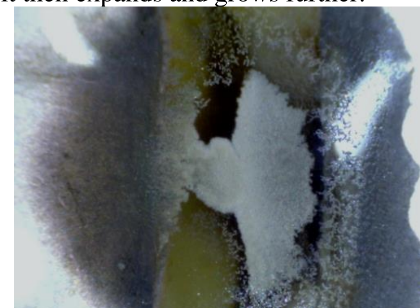

Fig. 5. Dendrite growth from AX70MN during WD test

In situ observation and measurement of resistance and voltage

During the dendrite growing resistance and voltage between pads covered by solder paste and electrically conductive adhesives were measured. The changes of resistance and voltage of solder paste Sn42Bi58 and solder paste REL61 are similar to the changes in

resistance and voltage of solder paste SAC305. The graph of resistance changes during dendrite growth of solder paste SAC305 is shown in Figure 6. The graph shows that during the WD test, while the dendrite grew, the resistance gradually decreased. As soon as the dendrite reached the anode and connected the two pads with solder, the resistance sharply dropped. The same can be seen in the voltage change graph (see Fig. 7).

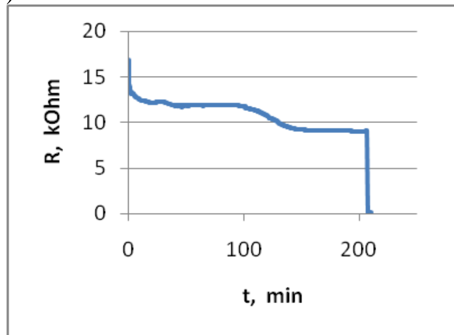

Fig 6. Resistance change during dendrite growth of solder paste SAC305 in 2mM NaCl solution

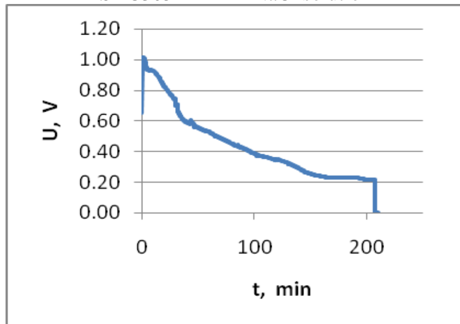

Fig. 7. Change of the voltage during dendrite growth of solder paste SAC305 in 2mM NaCl solution

The resistance change of adhesive AX70MN is different from solder pastes. At the beginning of the graph (see Fig.8), the resistance increases, possibly it is due to the appearance of a corrosion surface or the presence of impurities that impede the flow of current. Having reached a peak of 135 kOhm (see Fig. 8), the resistance begins to decrease gradually, this is due to the dendrite formation. When the dendrite connected the anode with cathode, the resistance dropped sharply, approaching the zero value.

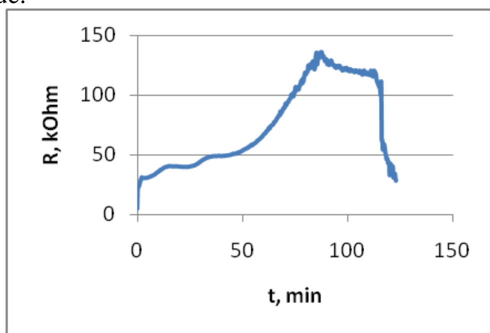

Fig 8. Resistance change during dendrite growth of adhesive AX70MN in 2mM NaCl solution

In the case of a voltage change, a strong increase in the value is not noticeable (see Fig. 9). But it also began to fall gradually with the growth of dendrite and after connecting the two pads with adhesive, it fell sharply.

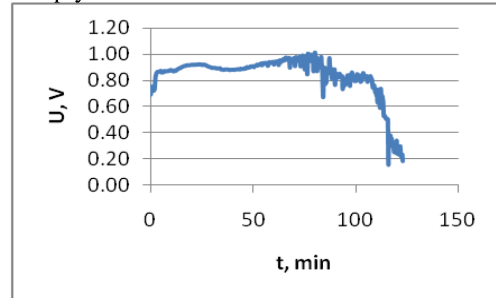

Fig. 9. Change of the voltage during dendrite growth of adhesive AX70MN in 2mM NaCl solution

Figure 10 shows how the resistance of the adhesive CRM-1033B changes. The resistance increases, and the voltage also increases (see Fig. 11). Adhesive CRM-1033B has the greatest resistance to the occurrence of dendrites. Perhaps, this is due to the appearance of a corrosion surface, which increases with the time. Also, unlike other samples, at the same current value bubbles appeared during the WD test. They can also act as an air barrier that prevents the formation of dendrite.

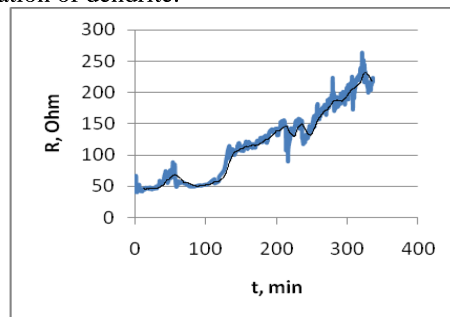

Fig 10. Resistance change during dendrite growth of adhesive CRM-1033B in 2mM NaCl solution

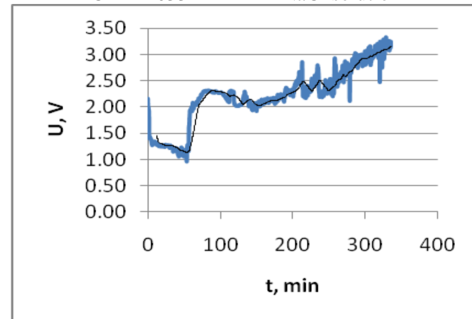

Fig. 11. Change of the voltage during dendrite growth of adhesive CRM-1033B in 2mM NaCl solution

Dendrite characterization

Using SEM microscope and Energy Dispersive Spectroscopy (EDS), the chemical elemental composition of dendrites was defined. Based on X-ray microanalysis, Sn was defined as the main element of the dendrite of the sample with solder paste SAC305, REL61, Sn42Bi58. Oxygen and carbon were also discovered (see Table 1). Most likely, they come from the main material of the PCB -

FR-4, or oxygen can also be a product of the corrosion of dendrite. In the case of electrically conductive adhesives AX70MN and CRM-1033B, Ag was defined as the main element of the dendrite (see Table 1). The dendrite micrograph of SAC305, REL61, AX70MN samples are shown in Figures 12-14.

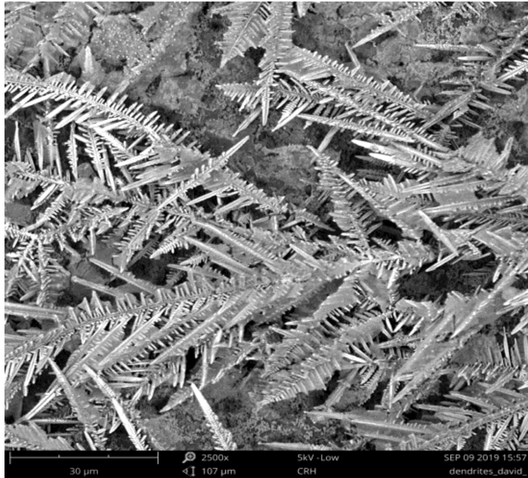

Fig. 12. SEM micrography of the dendrite of solder paste SAC305 in 2mM NaCl solution

Fig. 13. SEM micrography of the dendrite of solder paste REL61 in 2mM NaCl solution

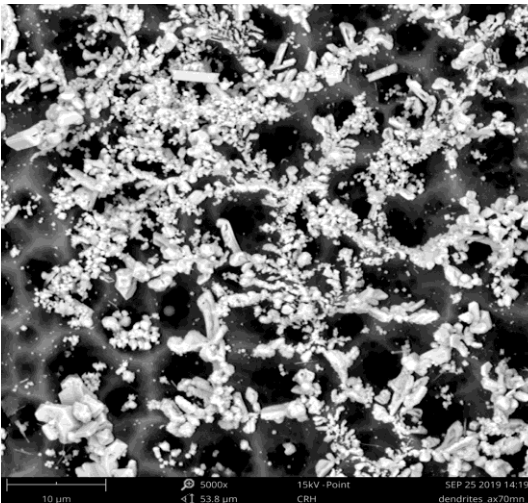

Fig. 14. SEM micrography of the dendrite of adhesive AX70MN in 2mM NaCl solution

Tab. 1 EDS results of solder pastes SAC305, REL61 and adhesive AX70MN dendrite in NaCl solution.

	Weight Concentration, %				
	Sn	***O***	***C***	***Ag***	***Br***
SAC305	85.57	11.78	2.64	-	-
REL61	79.05	14.15	5.70	-	-
AX70MN	-	9.11	14.56	69.46	6.87

CONCLUSION

The ECM of commonly used lead-free solders with a low Ag content SAC305, REL61, Sn42Bi58 and electrically conductive adhesives with a high content of Ag AX70MN, SRM-1033B was investigated and compared. The results of the WD test showed that the sample with the solder paste Sn42Bi58 had the lowest resistance to ECM. Commonly used solder pastes SAC305 and REL61 have similar resistance to ECM, their resistance is higher than the resistance of Sn42Bi58, because they contain Ag. But the highest resistance to ECM has adhesive SRM-1033B, containing 75% Ag. Based on the results of ECM, rating of resistance to ECM can be made:
SRM-1033B>SAC305≥REL6>AX70MN>Sn42Bi58.
According to the EDS microanalysis, in the case of lead-free solders, Sn was the dominant element in the formed dendrite. Ag was the main element of the formed dendrite of electrically conductive adhesives.
The main result is a change in resistance and voltage during the dendrite growing. In according with the resistance and voltage measurements of the common used lead-free solder pastes SAC305, REL61, Sn42Bi58, it follows that resistance and voltage decrease with increasing dendrite. In contrast, the behavior of resistance and voltage of electrically conductive adhesives is significantly different. Most likely, this is due to the appearance of an oxidized silver film, which acts as a barrier, due to which the susceptibility of adhesives to ECM is lower.

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