Electrochemical Migration of Lead-free Solder Alloys in Na_2SO_4 Environment

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***Abstract**: The effect of sulphate ion concentration on electrochemical migration of lead-free solder alloys was investigated with the use of water drop tests, by applying an in-situ optical and electrical inspection system. According to the Mean-Time-To-Failure (MTTF) values it was found that in the case of 0.1 and 1 mM Na_2SO_4 solutions X alloy (composition in wt%: Sn=90,95%, Ag=3,8%, Cu=0,7%, Bi=3%, Sb=1,4%, Ni=0,15%) has higher migration susceptibility than SAC305 alloy (composition in wt%: Sn=96,5%, Ag=3%, Cu=0,5%). However on higher concentration levels, MTTF decreased and the failures usually happened in the same time on each solder alloy type. Failures were not happened in the case of X covered boards in case of 10 mM concentration.*

1. INTRODUCTION

Electrochemical migration (ECM) is a failure phenomenon which may cause high reliability risk in electronics applications [1]. The failure mechanism starts with dissolution of the anode, which produces metal ions. Due to the applied voltage between the anodic and cathodic site, metal ions are driven by the electric field towards the cathode (migration), where they are able to electrochemically deposit in the form of dendrites (metal filaments) (See Fig 1.) [2]. It could result in the reduction of surface insulation resistance and short circuit formation between the electrodes. Printed circuit boards (PCB) with smaller distance between the biased points have higher susceptibility to the ECM failure.

ECM is mainly studied with water drop (WD) tests or thermal humidity bias tests (THB) in climatic chambers, besides these thin electrolyte layer tests (TEL) are also useful [3]. The significance of TEL tests is rising because the thickness of the water layer also has effect on the failure mechanism [4]. Other methods such as cyclic voltammetry, are based on electroanalytical methods.

Nowadays the Surface Mount Technology (SMT) and the Pin in Paste (PiP) technology are probably the most widespread in the electronics assembly. In both case there are recent studies which investigate the optimization of the technological processes [5-9], and the behavior of the used materials [8-10]. From the reliability point of view, many studies focus on ECM and whisker growth [10-11] mechanisms.

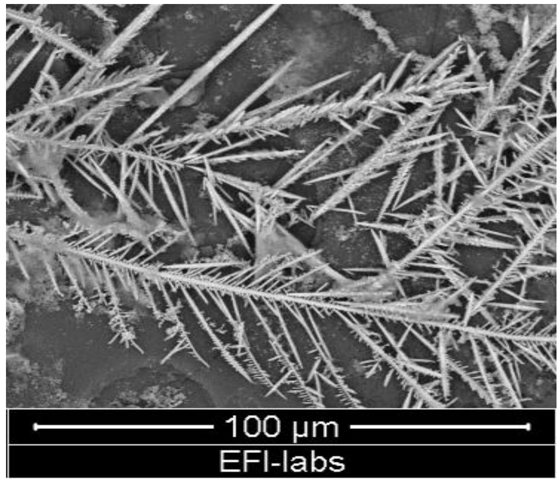

Fig. 1. Dendrites on a PCB.

It was proven that the metals which primarily compose lead-free solder alloys (Sn, Ag, Cu) have considerable susceptibility for ECM failure [2]. Other components of solder paste such as flux activators could also change the ECM susceptibility [12]. Investigations of solder flux residues from no-clean flux systems containing weak organic acid (WOA) activators with higher deliquescence point have positive effect on the reliability of electronics under high humidity [12] compared to halide containing flux systems. The ECM phenomenon is highly influenced by the presence of contaminations. Sources of these impurities are often the applied technological processes of electronics, which can result in various residual ionic contaminations. Sulphate is very common residue, therefore its effect on ECM is widely investigated. The impact of chloride ion contaminations on ECM is also studied frequently [13]. The migration of lead-free solder alloys in sulphate environment is not deeply addressed in the literature, for that reason different concentrations of Na_2SO_4 solutions were investigated in this study, in order to analyze the effect of sulphate ion concentration on ECM in terms of SAC305 and X solder alloys ((composition in wt%: Sn=90,95%, Ag=3,8%, Cu=0,7%, Bi=3%, Sb=1,4%, Ni=0,15%).

2. Experimental

The test sample used in this study consists of FR4 substrates with copper wiring coated with SAC305 or X lead-free solder alloys using stencil printing and reflow methods. The width of the conductor traces on the test board was 0.3 mm, while the gap size was 0.3 mm. The applied reflow soldering profile was for conventional lead-free solder alloys (See Fig. 2).

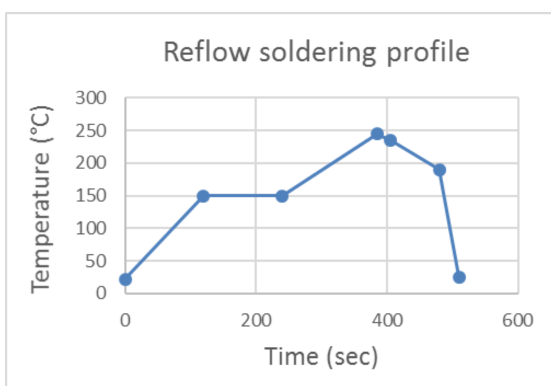

Fig. 2. The applied reflow profile.

The measuring platform (See Fig. 3.) was able to in-situ observe the ECM formation with the use of optical inspection system, while recording real-time voltage data. According to the voltage data, dendrite-growth was followed, and time-to-failure was determined.

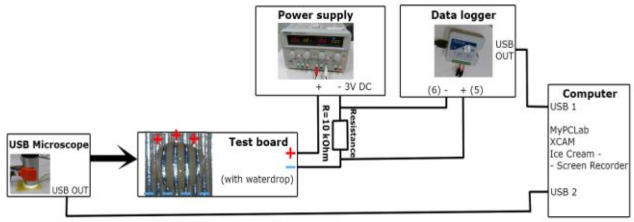

Fig. 3. Schematic of the measuring platform for ECM WD tests.

The electrolytes used for the water drop tests were Na_2SO_4 solutions with five different concentrations (0.1mM, 1mM, 10mM, 500mM and saturated). They were made by deionized water (18.2 MΩcm) and from analytical grade reagents. Before each test, the surface of the test board were rinsed with deionized (DI) water, and cleaned with isopropyl alcohol. In each experiment a droplet of 13 μl was placed onto the surface, by that the droplet crossed six adjacent conductor lines. Between the electrodes, 3 VDC bias was applied. Time-to-failure measurement from voltage diagrams was done on the basis of first-jump principle. Failure criterion in this case was the first observation of significant jump in voltage (see Fig. 4). All ECM tests were repeated more than five times to reach adequate reproducibility. To summarize the results, MTTF was calculated at each concentration and with respect to different solder alloys.

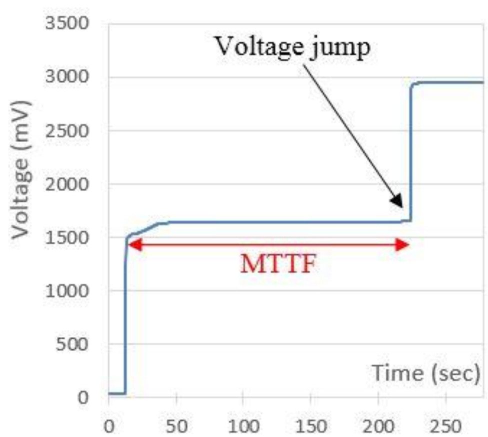

Fig. 4. Example of time-to-failure value determination with voltage jump, as failure criterion.

After the tests photographs were taken about the printed circuit boards using optical microscopy. Scanning Electronmicroscopy and Energy Dispersive Spectroscopy (SEM-EDS) methods were also applied to analyze the composition of dendrites, and residues on the boards.

3. Results and Discussion

3.1. ECM results of SAC305 solder alloy in Na_2SO_4

In case of 0.1 mM Na_2SO_4 solution, right after the 3 VDC bias was applied the voltage at the resistor decreased slowly, and H_2 outgassing was observable at the cathode. At the same time white colored residue showed up near the cathode. The growth of gray colored dendrites from the cathode to the anode was also detectable and the MTTF was about 10 minutes.

In case of 1 mM Na_2SO_4 solution, the process was similar to the 0.1 mM. Differences were that outgassing was more intense, and the highest amount of residue was observed (See Fig 5.). Residue was first inspected close to the cathode and then it bridged over the anode. The biggest difference was that MTTF was significantly longer than in the previous case. Failures happened on average after 33.5 minutes.

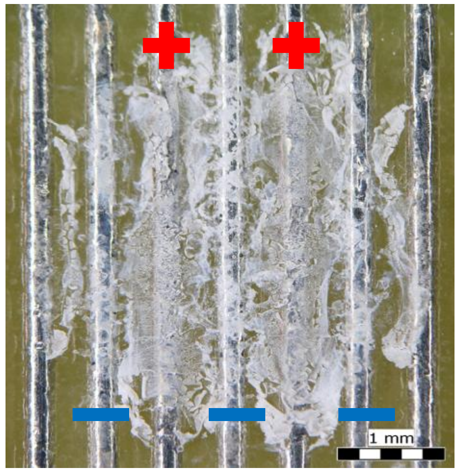

Fig. 5. High amount of white residue were formed during WD test with 1 mM Na2SO4 solution.

Experiments with 10 mM Na_2SO_4 solution showed changes in the failure mechanism. In contrast with the previous concentrations, after the DC bias was applied the voltage at the resistor was stagnated through 6.5 minutes. Outgassing and the formation of white residue was not as intense as it was in case of 1 mM. After 6.5 minutes the voltage decreased gradually. Similarly to the 10 mM case the white residue bridged over the anode (See Fig 6.), and gray dendrites were grown from the cathode to the anode. MTTF decreased to 13 minutes.

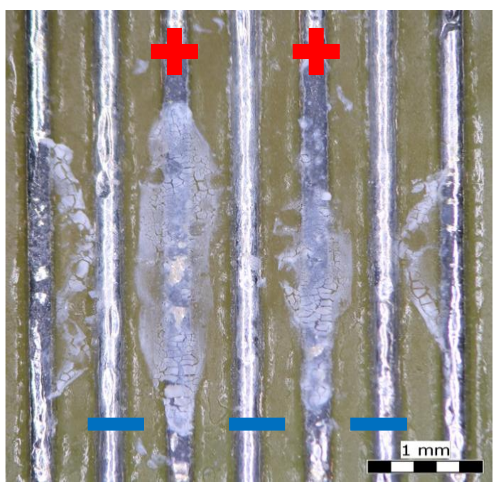

Fig. 6. Lower amount of white residue were formed during WD test with 10 mM Na2SO4 solution.

At the 500 mM level of Na_2SO_4 concentration the measured voltage was not changed considerably until the occurrence of the failure. Gray dendrites were observed (See Fig. 7.) The volume of white residue was bigger than it was at the 10 mM case, although the outgassing at the cathode was the most intense from all concentrations. Furthermore, the failure process was faster, and MTTF was decreased highly to 3.3 minutes.

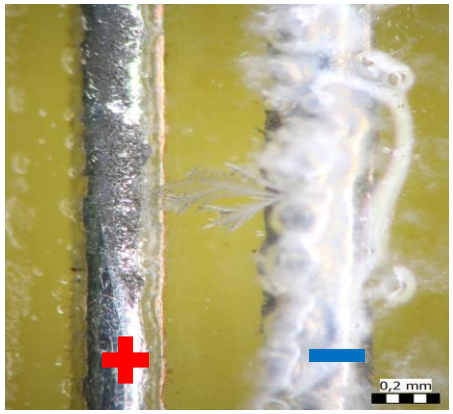

Fig. 7. Gray colored dendrite and traces of outgassing at WD test with 500 mM Na2SO4 solution.

In the saturated case, the only difference compared to the 500 mM was the residue formation, and outgassing was not as intense. Failure usually occurred after 2.6 minutes. At saturated level and even at 500 mM concentration, after the droplet dried Na_2SO_4 salt crystals were appeared (See Fig. 8.).

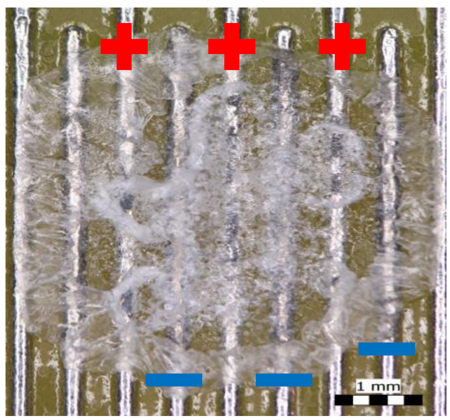

Fig. 8. Na_2SO_4 salt crystals in the case of saturated solution.

SEM-EDS analysis proved that dendrites mainly consist of tin, and residues primarily contain tin and oxide. Presumably in some cases residues are composed by $Sn(OH)_2$ (See Fig. 9.).

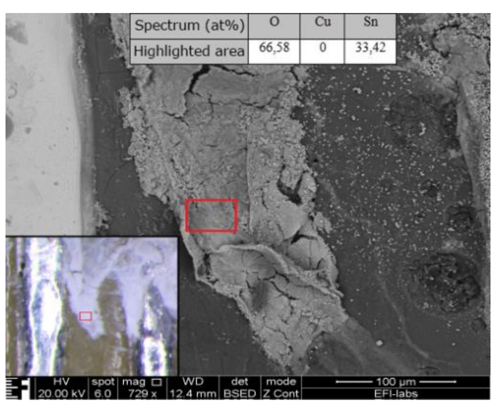

Fig. 9. SEM-EDS analysis of white residue shows that it is dominantly composed by tin and oxide. Maybe it is tin-hydroxide.

3.2. ECM results of X solder alloy in Na_2SO_4

In case of 0.1 mM Na_2SO_4 solution, no change was detected in the measured voltage until the failure occurred. Negligible amount of residue was detectable and the intensity of outgassing was low. Dendrites were grey and they were grown from the cathode to the anode. Failure usually happened after about 1 minute.

Experiments with 1 mM Na_2SO_4 solution showed that after the 3 V DC bias was applied the voltage at the resistor decreased constantly. Gray dendrites were grown with the direction of cathode to the anode (See Fig. 10.). High amount of residue was appeared (See Fig. 11.), and the outgassing was very intense. Residue was first observed by the cathode, but soon it started to deposit over the conductor traces of the anode, close to the edge of the droplet. MTTF increased significantly to about 8.3 minutes.

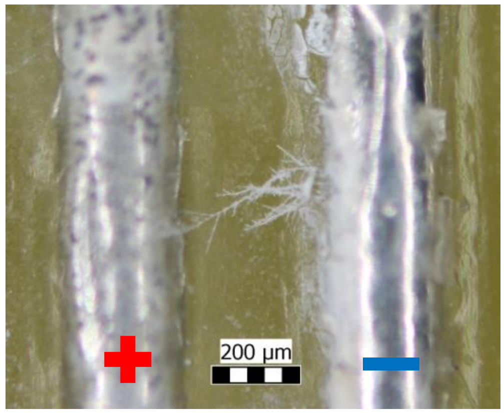

Fig. 10. Gray colored dendrite in the case of 1 mM Na_2SO_4 solution.

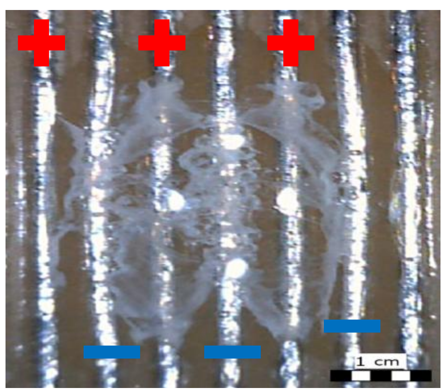

Fig. 11. High amount of white residue was observable in experiments with 1 mM Na_2SO_4 solution.

At the 10 mM level of Na_2SO_4 concentration failures were not happened. The measured voltage wasn't changed until the droplet was dried. The amount of residue was similar to the previous case.

In case of 500 mM Na_2SO_4 solution, after the 3 V DC bias was applied until the failure happened, the measured voltage at the resistor was increased with 0.5 V. Outgassing and residue formation was the most intense compared to the other concentrations. It was unexpected that beside the white residue, small amount of pale blue residue was detected as well (See Fig. 12.). Dendrite growth direction, and color was similar to the 0.1 and 1 mM cases. MTTF decreased to 3.2 minutes.

In the saturated case, differences compared to the 500 mM was that residue formation, and outgassing was not as intense, the measured voltage was close to constant until the failure happened, and only white colored residue was observable. Failure on average occurred after 2.4 minutes. At saturated level and even at 500 mM concentration, after the droplet dried Na_2SO_4 salt crystals were detected.

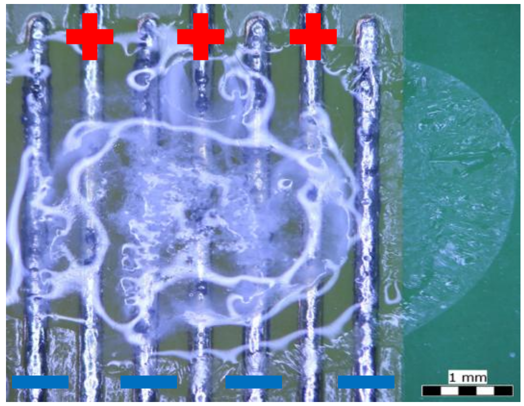

Fig. 12. White and also pale blue residue was observable in the case of 500 mM Na_2SO_4 solution.

The SEM-EDS analysis proved that the dendrites (See Fig 13.) on the examined boards contained tin, and the residues were composed by tin (probably tin hydroxide). Micro-alloys (Bi, Sb, Ni) from X solder were not detected in the composition of dendrites or residues, which mean that they probably did not took part in the process of electrochemical migration.

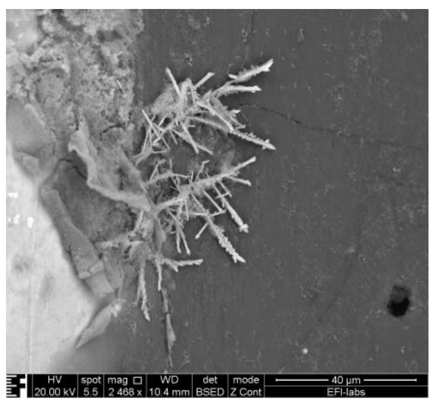

Fig. 13. Dendrites mainly composed by tin.

3.3. Comparison of SAC305 and X solder alloys from the aspect of MTTF

According to the MTTF data (See Fig. 14.) it was shown that in the case of 0.1 and 1 mM solutions X alloy has higher migration susceptibility than SAC305 alloy. However, on concentration levels over 10 mM the failures usually happened in the same time on each solder alloy type. Failures were not happened in the case of X covered boards in case of 10 mM concentration.

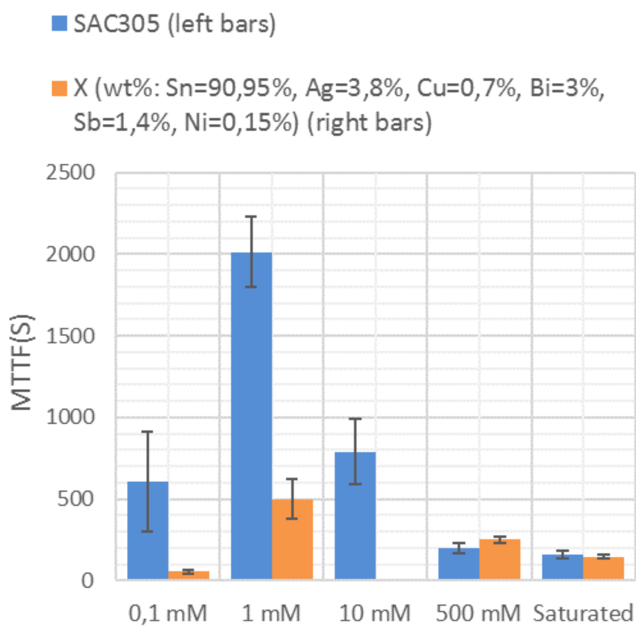

Fig. 14. Comparison of the MTTF values of SAC305 and X solder alloys, by concentration (with 1σ deviation).

4. Conclusions

The effect of sulphate ion concentration on electrochemical migration of lead-free solder alloys was investigated with the use of water drop tests, by applying an in-situ optical and electrical inspection system. Observation of the ECM formation was carried out using an optical system, while recording voltage data. According to the voltage data, dendrite-growth was followed, and time-to-failure was determined, then MTTF was calculated. According to the MTTF data, in the case of 0.1 and 1 mM solutions X alloy has higher migration susceptibility than SAC305 alloy. In the case of 10 mM concentration no failures occurred in the case of X alloy, while the ECM susceptibility of SAC305 alloy was increased. However, on concentration levels over 10 mM MTTF values were similar by both solder alloys.

The results of SEM-EDS analysis showed, that the examined boards mostly consisted of tin, and the residues were primarily composed by tin and oxide. Micro-alloys (Bi, Sb, Ni) from X solder probably did not took part in the process of electrochemical migration.

Further investigations are needed to explain the MTTF results.

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