

NaCl hatása az elektrokémiai migrációra különböző Sn-Sb forrasztótvözetek esetén

Kutatási jelentés

I. Introduction

Many reliability problems of electronics have to be answered nowadays [1-4]. One of the most dangerous ones is the electrochemical migration (ECM) failure phenomenon. ECM may pose a relative huge reliability risk related to applications of electronics [5]. This failure phenomenon appears at moisture presence in the case of operating electronics: the dissolution of conductors starts at the anode side and results metal ions that are governed by the applied voltage (electric field) and migrate towards cathode, where they can reduce as pure metals – dendrites (See Fig. 1). Dendrite growth can lead to short. Many types of the metals, which are widely used in the electronics industry, have relevant susceptibility for ECM, such as Sn, Ag or Cu [6]. Sn and Sn-alloys are also widely investigated related to ECM [6-11]. Usually, migration tests were carried out by three main methods [12]; water drop (WD) test [13], environmental tests under elevated thermal-humidity conditions [14] and by various electroanalytical methods, like voltammetry or polarization tests [15]. On the one hand the electrochemical corrosion and migration investigations of Sn-alloys were usually tested in bulk solution. On the other hand, migration tests in thin electrolyte layers (TEL) is also important, since ECM ability depends on the thickness of water layer as well [16]. Furthermore, the concentrations of the used electrolytes had a wide spectrum as well: deionized water [6], acidic or alkaline electrolytes [8, 17] and also salt electrolytes [18], which usually simulate the possible contamination effects. One of the most common contaminant is the Cl, which can strongly influences the electrochemical corrosion mechanism and therefore, the migration ability of tin and tin-based solder alloys. According our previous research work [19], it was firstly shown that next to the common used component of the solder alloy (Sn, Ag, Cu), antimony can also take part in the ECM processes using lead-free micro-alloyed solder alloy in NaCl environment. In this work we have produced different Sn-Sb alloys to check the migration ability of antimony in NaCl environment.



Fig. 1. SEM picture from Sn dendrites.

2. Experimental

2.1. Sample preparation

The following metal and alloys were prepared and investigated:

- Pure Sn,
- Sn99.9Sb0.1 wt%,
- Sn99Sb1 wt%,
- Sn97Sb3 wt%,
- Sn95Sb5 wt%.

The pure Sn sample was prepared according to the conventional PCB technology using electroplating and chemical etching techniques. For the solder alloy samples immersion silver (iAg) was used as a surface finish with the same dimension of the pure Sn sample (See Fig 2.).

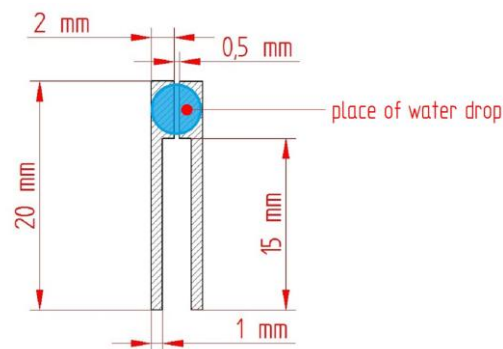


Fig. 2. Dimension of the test structure for WD test.

The preparation of the Sn-Sb solder alloy samples contained many steps. Firstly, we have received solder alloy ingots from a Metal Foundry (See Fig 3).



Fig. 3. Sn-Sn solder alloy ingots.

In the next step the ingots were rolled to flat layer with 0.5 mm thickness (Fig. 4). Afterwards a special tool was design and prepared (Fig. 5.) to rich adequate preforms in a phisical way (Fig. 6) for the test board. Finally, the preforms were melted on the layout using hand soldering methods (Fig 7.). After the soldering the samples were cleaned by iso-propil-alcohol and rinsed with deionised water (Fig. 8).



Fig. 4. Sn-Sn solder alloy plate after rolling.

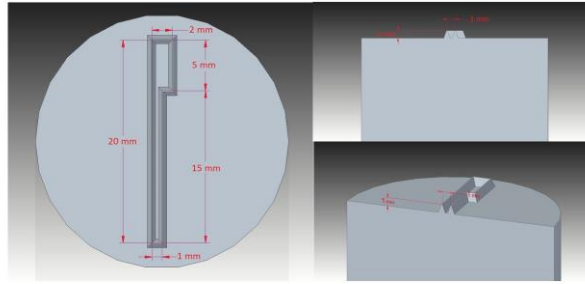


Fig. 5. Design of the cutting tool for preform preparation.



Fig. 6. Preform (right) after using the cutting tool on the rolled solder alloy plate (left).

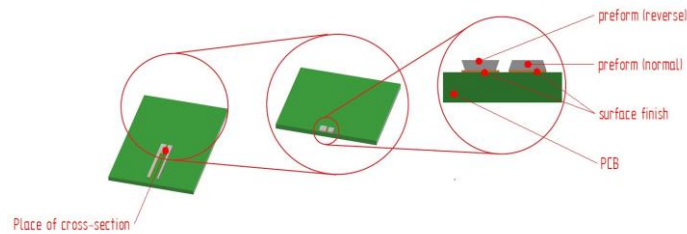


Fig. 7. Schematic draw about the preform placement on the iAg surface finish before soldering.

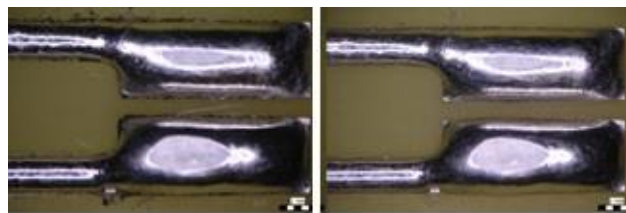


Fig. 8. Two examples for test structure of Sn-Sb solder alloy after hand soldering and before WD test.

2.2. Platform of WD test

The susceptibility of migration was checked by WD test. Furthermore, the morphology and elemental composition of the dendrites were also investigated using SEM-EDS methods. During the WD test a 15 μl drop of 3.5 wt% NaCl was placed onto surface of the samples and then 3 VDC was applied. The formation of dendrite growth was visually monitored during the WD test, but it can be observed the velocity of dendrite growth and time dependence of leakage current as well. The schematic of the WD test platform can be seen in Figure 9. During the WD tests real-time optical inspection (video record) was carried out and Mean-Time-To-Failure (MTTF) was measured and calculated with the failure criterion of the first significant voltage jump. In case of every sample type 10-10 measurements were carried out during the WD test.

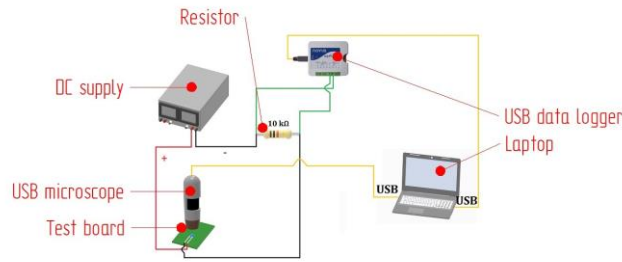


Fig. 9. Schematic draw about the WD test.

3. Results and Discussion

3.1. Results of the WD test

Figure 10 presents the MTTF results of the WD test in case of Sn-Sb solder alloys and pure Sn samples. According to the MTTF data, there were no significant differences, only a decreasing trend was observed with the increasing antimony content (See Fig. 10). In order to find out the potential effect of Sb on the ECM behavior, SEM-EDS investigation was introduced.

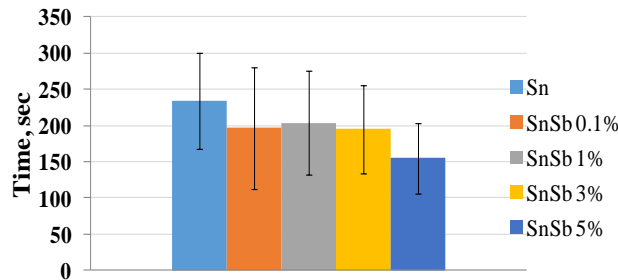


Fig. 10. MTTF data of WD test.

3.2. Results of the SEM-EDS investigations

During the SEM-EDS investigations, rather dendrites were in the focus to get information about their morphology and chemical composition as well. It was found that two types of dendrites were formed: fishbone and tree-like formation. Furthermore, in all cases Sn was dominated the composition of dendrites. However, in case of Sn-Sb5% a small amount of antimony was detected in the dendrite. Figure 11 presents the SEM picture in case of a Sn-Sb5% dendrite and the area of the EDS measurement. Table 1 shows the EDS results according to Figure 11.

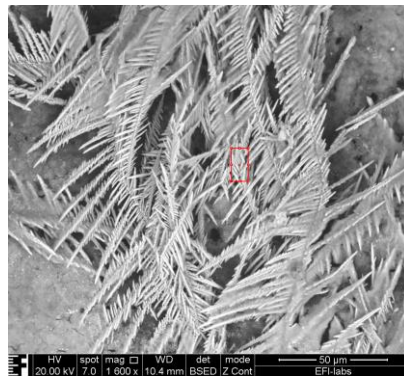


Fig. 11. SEM picture of a dendrite grown from SnSb 5% solder alloy sample (red rectangle: place of the EDS measurement).

Table 1. EDS results according to Figure 11.

Dendrite	O	Na	Cl	Sn	Sb
at%	49	28	9	13,5	0,5
wt%	24	19	10	45	2

Conclusions

WD test and SEM-EDS methods were used to investigate the ECM behavior of different Sn-Sb alloys and pure Sn surface finish used in electronics. The results show that all of the Sn-Sb solder alloy types have similar ECM risk comparing to the pure Sn. However, an increasing ECM tendency was found with increasing antimony content. Furthermore, in case of Sn95-Sb5 solder alloy antimony was found in the dendrites. It means that Sb was taken part during the ECM processes in case of Sn95Sb5 solder alloy. Furthermore, the Sn-Sb wt % ratio of the dendrite was similar compare to the original Sn95Sb5 alloy content.

Acknowledgement

The work reported in this paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The authors would like to thank to the Pro Progressio Foundation (Hungary) for the financial support as well.

References

- [1] V. Verdingovas, M. S. Jellesen, R. Ambat, "Impact of NaCl Contamination and Climatic Conditions on the Reliability of Printed Circuit Board Assemblies", *IEEE Transactions on Device and Materials Reliability*, Vol. 14, No. 1, pp. 42-51, 2014.
- [2] O Krammer, B Gyarmati, A Szilágyi, R Storcz, L Jakab, B Illés, A Géczy, K Dušek, "Investigating the thixotropic behaviour of Type 4 solder paste during stencil printing", *Soldering & Surface Mount Technology* 29(1) pp. [10-14, 2017](#).
- [3] B. Illés, B. Horváth, "Tin Whisker Growth from Micro-alloyed SAC Solders in Corrosive Climate", *Journal of Alloys and Compounds*, Vol. [616](#), pp. [116](#)–121, 2014.
- [4] C-A. Tămaş, N. D. Codreanu, M. Pantazică, "Investigations on modern power supplies development based on custom PCB structures", *38th International Spring Seminar on Electronics Technology (ISSE)*, pp. 436 - 439, 2015.
- [5] X. Zhong, G. Zhang, Y. Qiu, Z. Chen, W. Zou, X. Guo, "In situ study the dependence of electrochemical migration of tin on chloride", *Electrochemistry Communications*, Vol. 27, pp. 63–68, 2013.
- [6] B. Medgyes, B. Illés, G. Harsányi, "Electrochemical migration behaviour of Cu, Sn, Ag and Sn63/Pb37. ", *Journal of Materials Science: Materials in Electronics*, Vol. 23, pp. 551-556, 2012.
- [7] J-Y. Jung, S-B. Lee, H-Y. Lee, Y-C. Joo, Y-B. Park, "Effect of Ionization Characteristics on electrochemical Migration Lifetimes of Sn-3.0Ag-0.5Cu Solder in NaCl and Na2SO4 Solutions", *Journal of Electronic Materials*, Vol. 37, No. 8, pp. 1111-1118, 2008.
- [8] V. Verdingovas, M.S. Jellesen, R. Ambat, Influence of sodium chloride and weak organic acids (flux residues) on electrochemical migration of tin on surface mount chip components. *Corros. Eng. Sci. Technol.* Vol. 48, pp. 426, 2013.
- [9] X. Zhong, X. Guo, Y. Qiu, Z. Chen, G. Zhang, In situ study the electrochemical migration of tin under unipolar square wave electric field. *J. Electrochem. Soc.*, Vol. 160, pp. D495, 2013.
- [10] S.B. Lee, H.Y. Lee, M.S. Jung, Y.B. Park, Y.C. Joo, Effect of the composition of Sn–Pb alloys on the microstructure of filaments and the electrochemical migration characteristics. *Met. Mater. Int.*, Vol. 17, pp. 617, 2011.
- [11] L. Hua, C. Yang, "Corrosion behavior, whisker growth, and electrochemical migration of Sn–3.0Ag–0.5Cu solder doping with In and Zn in NaCl solution", *Microelectronics Reliability*, 51, pp. 2274, 2011.
- [12] X. Zhong, S. Yu, L. Chen, J. Hu, Z. Zhang, "Test methods for electrochemical migration: a review", *Journal of Materials Science: Materials in Electronics*, Vol. 28, pp. 2279-2289, 2017.
- [13] B. I. Noh, J. W. Yoon, W.S. Hong, S.B. Jung, "Evaluation of Electrochemical Migration on Flexible Printed Circuit Boards with Different Surface Finishes", *Journal of Electronic Materials*, Vol. 38, No. 6, pp. 902-907, 2009.

- [14] B. Medgyes, B. Illés, Richárd Berényi and G. Harsányi, "In situ optical inspection of electrochemical migration during THB tests", *Journal of Materials Science: Materials in Electronics*, Vol. 22, pp. 694-700, 2011.
- [15] G. Harsányi, G. Inzelt, "Comparing migratory resistive short formation abilities of conductor systems applied in advanced interconnection system", *Microelectronics Reliability*, Vol. 41, pp. 229-237, 2001.
- [16] X. Zhong, G. Zhang, X. Guo, "The effect of electrolyte layer thickness on electrochemical migration of tin", *Corrosion Science*, Vol. 96, pp. 1-5, 2015.
- [17] O. Devos, C. Gabrielli, L. Beitone, C. Mace, E. Ostermann, H. Perrot, "Growth of electrolytic copper dendrites. II: Oxalic acid medium", *Journal of Electroanalytical Chemistry*, Vol. 606, pp. 85-94, 2007.
- [18] B. Medgyes, L. Gál, D. Szivós, "The effect of NaCl on water condensation and electrochemical migration", In: *IEEE, 20th International Symposium for Design and Technology in Electronic Packaging (SIITME)*. Bucarest, Romania, pp. 259-262, 2014.
- [19] B. Medgyes, B. Horváth, B. Illés, T. Shinohara, A. Tahara, G. Harsányi, O. Krammer, "Microstructure and elemental composition of electrochemically formed dendrites on lead-free micro-alloyed low Ag solder alloys used in electronics", *Corrosion Science*, Vol. 92, pp. 43-47, 2015.

A fent közölt kutatási eredmények publikálásra kerültek:

Bálint Medgyes, Róbert Kiss, Szabolcs Szurdán, Dániel Rigler, László Gál, Richárd Berényi and Gábor Harsányi
Electrochemical migration investigations on Sn-Sb solder alloys using 3.5 wt% NaCl solution
In: *Proceedings of the 40th IEEE International Spring Seminar on Electronics Technology*. Konferencia helye, ideje: Szófia, Bulgária, 2017.05.10-2017.05.14. Seattle: IEEE, 2017. pp. 1-4.

DOL, **IEEE Xplore**, **Scopus**

Készítette: Dr. Harsányi Gábor

Budapest, 2018. január 31.