Final Report of PD120898

During my first research period I have carried out Thermal-Humidity-Bias (THB) test using VDC bias on different surfaces finishes in terms of electronics (in good Agreement with my research plan). The different humidity induced failure phenomena have even growing importance because of the high integration and miniaturization trends in the electronics. One of these failure phenomena is called electrochemical migration (ECM). The first theoretical explanation of the ECM was given in connection with the silver migration. In this classical migration model, dendrites are grown on the cathode by the deposition of anodically dissolved ionic constituents that are present in the conductive strips. The migrated resistive shorts occur at practically random locations, and emerge mainly under extreme conditions (i.e. elevated temperature and humidity). However, a number of electrical field governed failure types are correlated with migration. A device can operate for many hundreds of hours under normal operating conditions, and then, after a short exposure to special environmental conditions, it may fail suddenly. Later it was proven in numerous further studies that several other metals also show dendrite growth caused by ECM, i.e. Cu, Pb, Sn, Ni, Au and solder alloys as well. Usually, the investigations are carried out in two different scenarios: one of them is done under laboratory circumstances (at room temperature and humidity), while the other one is carried out in extreme climatic conditions. The latter one is carried out by environmental tests, which provide high temperature and humidity levels, while the patterns are followed by some kinds of electrical parameters, such as surface insulation resistance, leakage current or voltage changing. However, the environmental tests provide data mainly about the ECM processes (fault detection) and give very little useful information about the antecedent processes such as water condensation mechanism. Although environmental tests can also simulate the mechanism of water condensation, there is little information available about the physical aspects of condensation which can lead to ECM and dendrite growth. During the investigations the water condensation process and ECM behavior of Nickel (Ni), Electroless Nickel Immersion Gold (ENIG) and pure copper were investigated using Thermal Humidity and Bias (THB) test in NaCl environment. The THB results show that Cu has higher ECM resistance than Ni and ENIG surface finishes, which was an unexpected result. The main influencing factors of the water condensation (e.g.:

surface roughness, thermal parameters) and the ECM processes (precipitates and dendrites) were investigated and discussed in details. According to the results a qualitative ECM model affected by NaCl can be summarized as follows in case of Ni and ENIG during THB test:

1. Water condensation process starts (more intense) on the metal and NaCl crystals played as condensation cores.
2. Formation of “water-bridges” between the conductor lines (start of ECM).
3. Precipitate (probably CuCl) and dendrite (Cu and Ni) formations that resulted in short.

The above-mentioned work (Title: Electrochemical migration of Ni and ENIG surface finish during Environmental test contaminated by NaCl) was published in the Journal of Materials Science: Materials in Electronics (Q2, IF = 2.019) (http://real.mtak.hu/63107/).

Next to this work I have written with Chinese colleges (Leader: Prof. Xiankang Zhong) a critical review paper about ECM of the Sn-based lead-free solder alloys. Sn and Sn solder alloys in microelectronics are the most susceptible to suffer from ECM which significantly compromises the reliability of electronics. This topic has attracted more and more attention from researchers since the miniaturization of electronics and the explosive increase in their usage have largely increased the risk of ECM. This article first presents an introductory overview of the ECM basic processes including electrolyte layer formation, dissolution of metal, ion transport and deposition of metal ions. Then, the article provides the major development in the field of ECM of Sn and Sn solder alloys in recent decades, including the recent advances and discoveries, current debates and significant gaps. The reactions at the anode and cathode, the mechanisms of precipitates formation and dendrites growth are summarized. The influencing factors including alloy elements (Pb, Ag, Cu, Zn, *etc.*), contaminants (chlorides, sulfates, flux residues, *etc.*) and electric field (bias voltage and spacing) on the ECM of Sn and Sn alloys are highlighted. In addition, the possible strategies such as alloy elements, inhibitor and pulsed or AC voltage for the inhibition of the ECM of Sn and Sn solder alloys have also been reviewed. The review paper was published in RSC Advances (Q1, IF = 3.108) (http://real.mtak.hu/63112/).

Furthermore, I have made collaboration with Professor Rajan Ambat at the Technical University of Denmark (DTU), Materials and Surface Engineering, Department of Mechanical Engineering. As a first milestone, we have published an IEEE conference papers related to ECM and electrochemical corrosion reliability on lead-free solder alloys using different environmental tests (Published: http://real.mtak.hu/70294/). In the work potentiostatic pitting technique has been employed in order to avoid the disadvantage of equilibrium potential scattering during polarization tests, and it can provide the possibility to clarify the influence of intermetallic compounds (IMCs) to corrosion reliability by controlling applied voltage, the time of applying voltage as well as the concentration of electrolyte. During the potentiostatic tests, the cathodically active Bi phase in InnoLot alloy introduced pitting in the Sn phase nearby, whereas Ag_3Sn phase prompted pitting on the adjacent to β-Sn phase in SAC 305, SACX Plus 0307, SACX 0807 and SACX Plus 0807 solder alloys.

In my second research period I have carried out Water Drop (WD) tests using VDC bias on different surfaces finishes and many types of lead-free solder alloys (in good Agreement with my research plan). During the investigations ECM and corrosion mechanism were studied. In case of ECM, the results were published on 2018 IEEE 24th International Symposium for Design and Technology in Electronic Packaging, titled: Electrochemical Migration of SAC305 Solders and Tin Surface Finish in NaCl Environment. In that research work the impact of chloride ion contamination on ECM of SAC305 lead-free solder alloys, and galvanic tin surface finish was studied using water drop tests and by using an in-situ electrical and optical measuring set up as well. Tests were performed with the use of 3.5 wt NaCl solution. The “A” type SAC305 alloy had a rosin&acid/flux paste ratio of 12.5 wt%, however by the “B” type SAC305 alloy it was only 9.3 wt%. According to the mean-time-to-failure (MTTF) data it was shown that “A” and “B” type solder alloys have approximately the same ECM susceptibility, but in the case of tin surface finish failures happened typically after shorter period of time (Published: https://ieeexplore.ieee.org/document/8599244/authors#authors).

Furthermore, the corrosion reliability was also investigated with the Cellcore research group (https://www.celcorr.com/) from the DTU. Five Sn-Ag-Cu (SAC) based lead-free solder alloys. The first focus was placed on microstructural analysis of the

IMCs formation in the ingots of SAC alloys and their influence on micro galvanic corrosion performance. The microstructural and phase analysis of solder alloys has been carried out using the scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and Xray diffraction (XRD) methods. Results were published in 2018 IMAPS Nordic Conference on Microelectronics Packaging (https://ieeexplore.ieee.org/document/8423855) REAL: http://real.mtak.hu/88468/.

During my third research period I have investigated with Professor Xiankang Zhong (and his group) the silver ECM behaviors in case of SAC305 lead-free solder alloy. The motivation was that Ag participating the ECM of Sn-Ag based alloys is still controversial. In this work Ag^+ concentration in electrolyte layer and Ag distribution in dendrites formed during the ECM of 96.5Sn-3Ag-0.5Cu (SAC305) alloy were investigated using Inductively Coupled Plasma Source Mass Spectrometer and ScanningTransmission Electron Microscopy, respectively. Results show that Ag^+ can only be detected when Ag can re-lease from Ag3Sn during the anodic polarization of 96.5Sn-3Ag-0.5Cu alloy. Under such a condition, Ag could also be found in dendrites. Therefore, it can be concluded that Ag participates the ECM of 96.5Sn-3Ag-0.5Cu alloy, but it is potential-dependent. The presence or absence of Ag^+ in the electrolyte layer during ECM strongly depends upon the anodic polarization potential. E.g., Ag^+ could not be detected at the -0.12 V vs. SCE and 0.38 V vs. SCE, but it can be found at 2.38 V vs. SCE. Moreover, Ag could also be found in dendrites formed at 2.38 V vs. SCE. The distribution of Ag in dendrite is not occasional, but widely co-existed with Sn and Cu. The results were published in Corrosion Science (D1 Journal IF* = 6.355) (Real: http://real.mtak.hu/104634/, https://www.sciencedirect.com/science/article/pii/S0010938X19301738?via%3Dihub).

Furthermore, the possibility of manganese micro-alloying in case of SAC lead-free alloys and conducted various reliability tests were investigated. Our aim was to investigate the impact of manganese content on low-silver micro-alloyed lead-free SAC alloys, considering both mechanical properties and economical aspects as well. The results of the hardness tests showed that the addition of manganese to the SAC solder alloy could reduce the hardness. The tensile strength test results showed that the addition of Mn to the lead-free SAC alloy results in a slight decrease. After reflow soldering, it was found that the alloys we made did not reach the mechanical strength than that of the SAC305 alloy. However, examination of the post-aging state of the soldered joints was good agreement with earlier literature. Namely, over a longer aging period, the mechanical strength of Mn-containing solder joints is greater compare to SAC305 alloys. Although the mechanical properties of manganese alloyed SAC alloys were generally worse than those of SAC305, the minimum soldering requirement was exceeded. Taking into account both economic and mechanical properties, we recommend the industrial application of SAC0307 solder alloy with manganese micro-alloying in case of commercial electronics without any high reliability requirements. (Real: http://real.mtak.hu/104635/) The corrosion and ECM investigations related to Mn-containing SAC solder joints are ongoing.

Among the conferences, one of the biggest corrosion related conference is the EUROCORR (https://eurocorr.org/). The European Corrosion Congress – EUROCORR, the European Federation of Corrosion (EFC's) annual conference, is the flagship event of the international corrosion calendar. Attracting upwards of a thousand delegates, it is held every year in September in a different European country. EUROCORR is famous for its high technical standard and its popular social programme. I have been elected and my elections were approved as a member in the Board of Administration (BoA) and in the Scientific and Technology Administration Committee (STAC) for three years in EUROCORR (The membership will start from 1st of January in 2020).

Last, but not least I would like to write some metrics from the scientific point of view over the three years. According to the MTMT2 database my $IF_{3\ years\ ago} = 17.934$ and $\boldsymbol{IF_{now} = 37.632}$ (summarized), number of **independent citations** 3 years ago = *52* and **now** = ***234***, ***H-index (now): 10.***

Budapest, 2019.12.23. Dr. Bálint Medgyes