A BME ETT-n gyártott NyHL-en kialakított ólommentes forraszötvözetek korróziós vizsgálata NaCl-os környezetben

Kutatási jelentés

I. Introduction

One of the most important reliability challenges of the automotives focuses on the solder joints investigations; such as failure detection, prevention, etc. The various failure types can lead back to the not proper physical-chemical properties of the solder materials and/or the not adequate applied circuit mounting processes (e.g. oven set up during soldering). This challenge was updated in 2006, with the introduction of lead-free solder alloys governed by the RoHS directive of EU [1]. Due to the lead-free restrictions, various solder types such as near-eutectic Sn-based binary, ternary and solders with even more alloying components were occurred as candidates for traditional Sn-Pb solders. So, a high number of lead-free solder alloy types are produced and therefore many studies are reported from different reliability viewpoints. Reliability tests include manufacture modeling [2], thermal cycling [3], vibration tests [4], shock and drop tests [5], shear and pull tests [6], solder voids tests [7], solder printing tests [8], tin whisker tests [9], electrochemical migration [10, 11] and corrosion tests [12, 13] to write a few. However, the corrosion reliability of the novel lead-free solder alloys still has many open questions. This is the reason that the electrochemical corrosion (ECC) investigation of the lead-free solders is a relevant research field. Another aspect of the ECC investigations is the effect of various contaminations on the reliability. Chloride ion is a common contaminant on the surfaces of electronics origins from the various environment sources (just a few remarks):

- salt spraying from marine environments;
- humidity in the atmosphere may contain chloride ions;
- humans fingerprints contain NaCl, etc.

Many studies were published related to the effect of chlorine on the corrosion behavior of PCB surface finishes and components [14, 15]. There are also many reports about ECC on lead-free solders contaminated by NaCl as well [13, 16-18]. However, not all of the solder types were tested in aqueous chlorine media and not all of the concentration levels were investigated yet. Therefore, in this study various NaCl solutions were used to investigate the effect of chloride ion concentration on the ECC behavior on lead-free solder alloys. Moreover, the effect of $MgCl_2$ is also not deeply discussed in the literature. The other motivation to use $MgCl_2$ as an electrolyte was that the sea water also contains $MgCl_2$, which component is the second largest one after NaCl.

II. Experimental

The lead-free solder materials applied during the ECC investigations were the following types:

- Sn96.5/Ag3/Cu0.5 (reference: sample 1)
- Sn98.95/Ag0.3/Cu0.7-Ni0.05 (sample 2),
- Sn98.4/Ag0.8/Cu0.7/Bi0.1 (sample 3),
- Sn98.45/Ag0.8-Cu0.7/Ni0.05 (sample 4),
- Sn90.95/Ag3.8/Cu0.7/Bi3/Sb1.4/Ni0.15 (sample 5).

The sample preparation is described elsewhere [17].

The ECC investigation was a linear sweep voltammetry (LSV) test using an automatic potentiostat system (VoltaLab PGZ301). The electrochemical cell contains the lead-free solder alloy as a working electrode (W) with an active surface of 100 mm^2, a Pt grid counter electrode (C) and a saturated calomel electrode (SCE) as a reference electrode (Ref) (See Fig. 1). A 0.38 wt% $MgCl_2$ aqueous solution (electrolyte) was prepared to simulate the sea water from the average magnesium-chloride content viewpoint. The various NaCl solutions were 0.1mM, 1mM, 10mM, 500mM and saturated one to investigate the impact of chloride ion concentration on ECC mechanism of the above mentioned lead-free solder alloys.

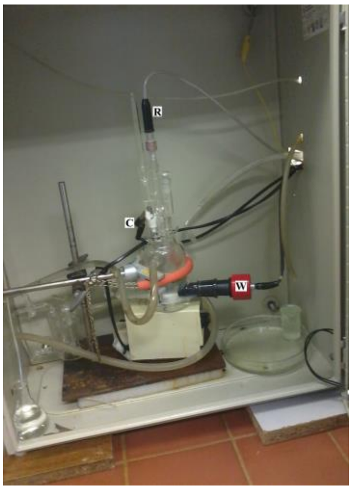

Fig. 1. The electroanalytical measuring platform for LSV test (W-working electrode, C –counter electrode, R-reference electrode).

During LSV measurements, the polarization range was set up between -2000 mV and 2000 mV in case of $MgCl_2$ solution and between -1000 mV and 2500mV in case of NaCl solution to reach the passive state of the solder alloys which was one point of the comparison. All LSV measurement was repeated 10 times to check the reproducibility. From the measured corrosion parameters an average value was calculated with 1 sigma deviation supposing normal distribution. After LSV tests the formed corrosion products were investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) methods.

III. Results and Discussion

A. *Results of $MgCl_2$ investigations.*

In Figure 2, a representation of LSV measurement can be seen, namely three polarization curves show the level of reproducibility. The perfect "curve fitting" is hardly available, mainly due to the inhomogeneous distribution of the different compositions in the solder alloys.

It can be seen (as an example for corrosion parameter determination), that the average value of the critical current density is about 62.58 mA/cm^2 at around 0.27 V critical potential (See Fig. 2). The average passivation current density is about 4.87 mA/cm^2.

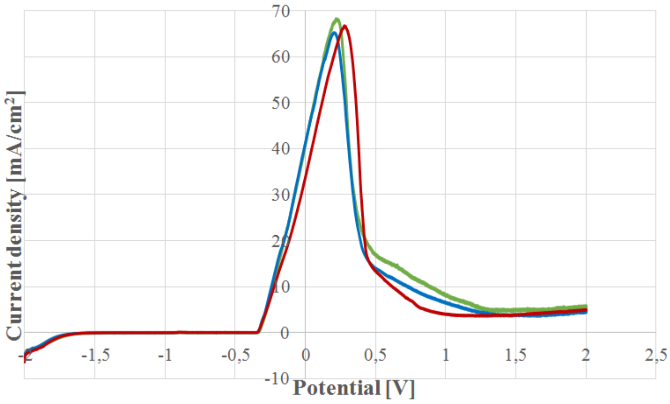

Fig. 2. LSV curves as a reperesentation of the reproducibility.

Based on the LSV investigation method mentioned above, the passivation and critical current density values were obtained and collected in the Table 1.

TABLE I. SUMMARY OF THE CORROSION PARAMETERS AFTER LSV INVESTIGATIONS IN CASE OF $MgCl_2$ SOLUTION.

	J_{crit} [mA/cm^2]	E_{crit} [V]	$J_{pass(min)}$ [mA/cm^2]
1.sample	48.16±3.95	0.28±0.15	3.36±1.46
2.sample	59.21±3.14	0.39±0.09	8.07±1.56
3.sample	52.42±0.87	0.39±0.1	6.07±2.24
4.sample	62.58±4.47	0.27±0.06	4.87±1.43
5.sample	80.78±6.96	0.47±0.16	11.8±2.46

Based on the passivation current density results (see Fig. 3), the following corrosion susceptibility can be established:

SAC305 ≤ Sample 4 ≤ Sample 3 ≤ Sample 2 ≤ Innolot

Based on the critical current density results (see Fig. 4), the following corrosion susceptibility can be established:

SAC305 ≤ Sample 3 ≤ Sample 2 ≤ Sample 4 ≤ Innolot

It can be seen there are no significant differences between the samples, except few cases (See Fig 4). Sample 5 (Innolot) showed the highest ECC susceptibility, while the reference (SAC305) showed the lowest current densities in both cases (See Fig 3-4). Moreover, there are significant differences between Innolot and SAC305 solder alloys (See Fig 3-4).

In order to find out the causes about the above mentioned significant differences SEM-EDX methods were carried out. The same magnification was used during the SEM investigation to compare the morphological differences between the corroded surfaces. Figure 5-9 show the SEM micrographs after LSV investigations in each case.

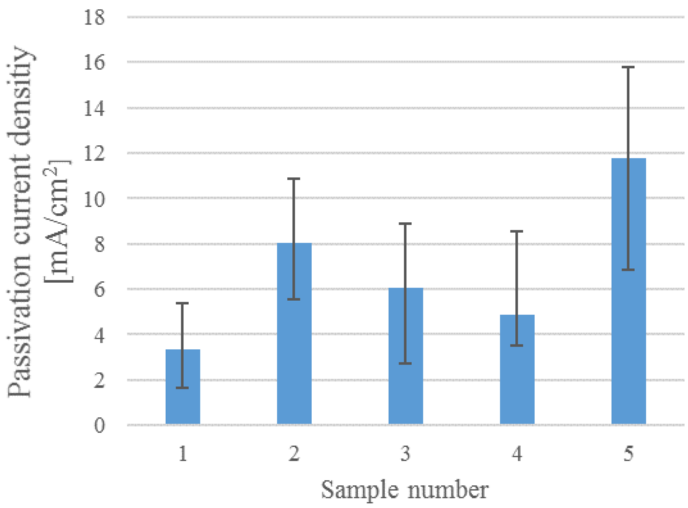

Fig. 3. Average passivation current density values after LSV test in 0.38 wt% $MgCl_2$ solution (1 sigma diviation).

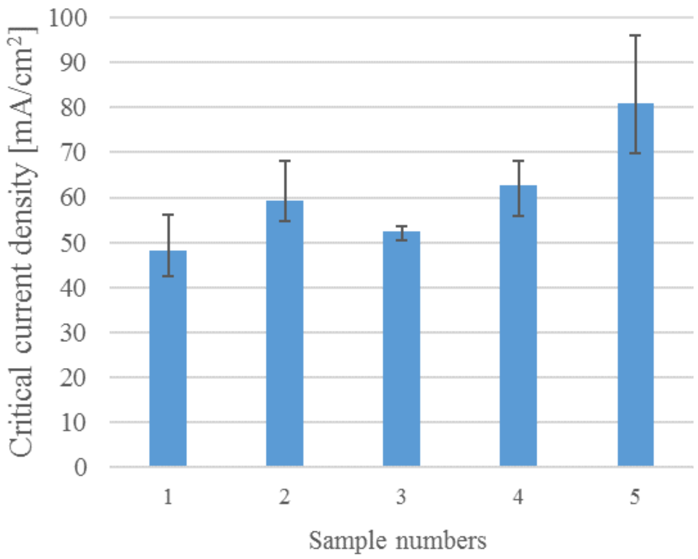

Fig. 4. Average passivation current density values after LSV test in 0.38 wt $MgCl_2$ solution (1 sigma diviation).

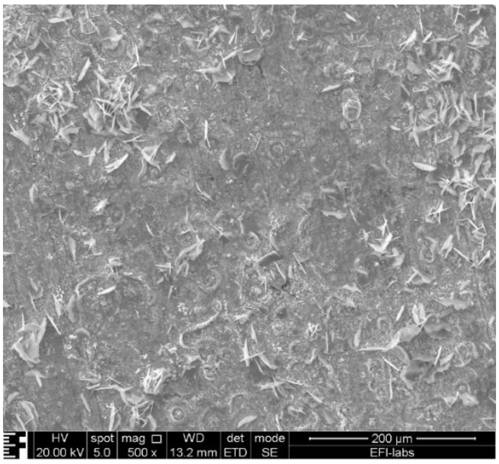

Fig. 5. SEM micrograpgh after LSV in case of sample 1 (SAC305: reference).

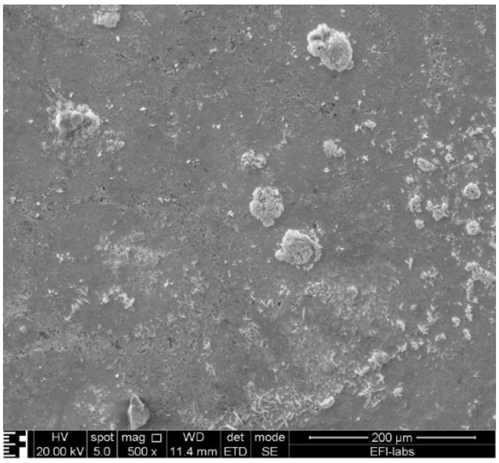

Fig. 6. SEM micrograpgh after LSV in case of sample 2.

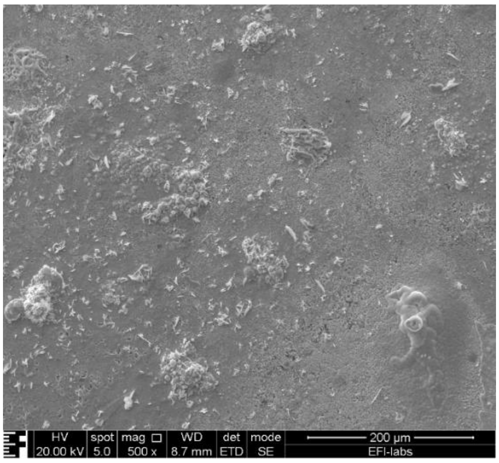

Fig. 7. SEM micrograpgh after LSV in case of sample 3.

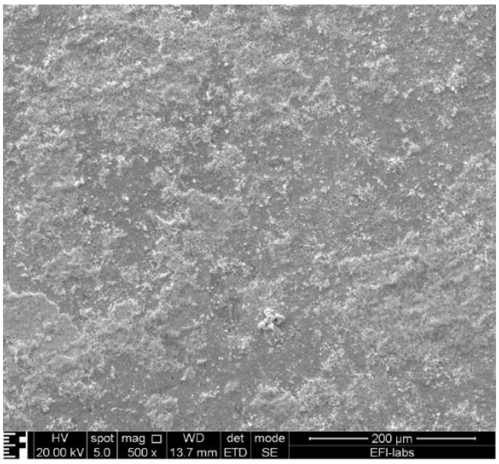

Fig. 8. SEM micrograpgh after LSV in case of sample 4.

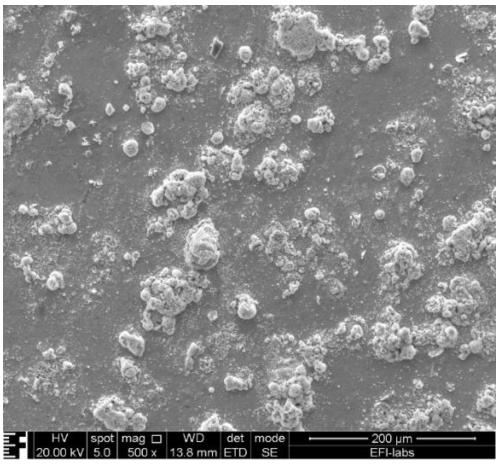

Fig. 9. SEM micrograpgh after LSV in case of sample 5 (Innolot).

Next to the SEM investigations, EDX measurements were also carried out to identify the composition and the concentration of the corrosion products after LSV tests. According to the EDX results oxygen, magnesium, chlorine, silver, copper and tin were detected (See Table 2).

Furthermore, in case of sample 5 (Innolot) antimony and bismuth were also detected (See Table 2). Oxygen always occurring on the surfaces and probably in this case the anodic oxidation process was the dominant mechanism. Magnesium and chloride were originated from the test solution and the metal elements come from the different solder alloys. Interestingly, that in case of Innolot Sb and Bi was also detected. Accordingly, micro-alloying elements such as antimony and/or bismuth can have an impact during ECC processes. It is already known that bismuth can have an impact on the corrosion of the lead-free solder alloys in chloride media [17]. However, the effect of antimony on the ECC behavior of lead-free solder alloys is not so deeply addressed in the literature.

TABLE II. EDX RESULTS (wt %) OF THE DIFFERENT CORRODED SURFACES OF LEAD-FREE SOLDER ALLOYS AFTER LSV TEST.

Samples	O	Mg	Cl	Cu	Ag	Sn	**Sb**	**Bi**
1.	15	2	20	1	2	60	-	-
2.	13	0	15	1	0	69	-	-
3.	13	1	17	1	1	68	-	-
4.	17	1	19	1	1	61	-	-
5.	15	1	16	2	4	58	**2**	**2**

B. *Results of NaCl investigations*

In this case only two lead-free solder alloys were studied: SAC305 and Innolot. Based on the obtained polarization curves after LSV measurements it can be stated that SAC 305 showed lower corrosion susceptibility at low, medium concentrations and at saturated levels (0.1 mM, 1 mM, 10 mM and sat. NaCl). However, the corrosion behaviour of the two solder types was changed at 500 mM NaCl concentration, namely Innolot showed lower ECC susceptibility compared to SAC305. This result of 500 mM NaCl is in good agreement with our former investigations carried out in different laboratories [12, 19]. In Figure 10, the results of LSV tests can be seen in case of 500 mM NaCl concentration level.

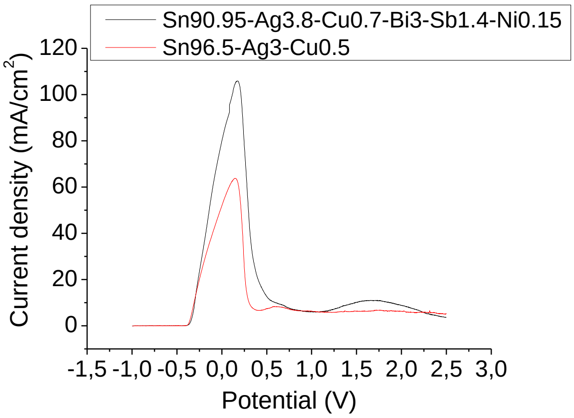

Fig. 10. Dynamic polarization curves of SAC305 (red) and Innolot (black), in case of 500 mM NaCl.

In case of saturated NaCl solution the dissolution (active region) started at relative lower potential and the passivation region began at higher potential compare to the 500 mM NaCl concentration. The passivation current density and the critical current density values were collected in Table 3 in case of 500 mM and saturated NaCl solutions. In this case, the SEM-EDX investigations showed only expected results [12, 19].

TABLE III. CORROSION PARAMETERS AFTER LSV INVESTIGATIONS IN CASE OF 500 mM AND SATURATED NaCl SOLUTIONS.

Concentration	J_{crit} [mA/cm^2]		J_{pass} [mA/cm^2]	
	Innolot	SAC305	Innolot	SAC305
500 mM	106±2.5	63.9±5	7.8±1	6.3±2
Saturated	460.5±54	781±26	148.3±34	63.3±14

IV. Conlusions

Five different lead-free solder alloys were investigated in 0.38 wt% $MgCl_2$ and in five different NaCl concentrations using LSV and SEM-EDX methods. Based on the LSV results, two corrosion susceptibility ranking were established in case of $MgCl_2$ solution, respectively:

SAC305 ≤ Sample 4 ≤ Sample 3 ≤ Sample 2 ≤ Innolot

SAC305 ≤ Sample 3 ≤ Sample 2 ≤ Sample 4 ≤ Innolot

In the above mentioned cases Innolot showed the highest susceptibility for corrosion. According to the SEM-EDX investigation bismuth and antimony was found in the corrosion product of the Innolot. It can be supposed that some type of the micro-alloying elements, such as bismuth and/or antimony can have a significant impact on the corrosion behavior of the lead-free solder alloys.

In case of NaCl investigations two different lead-free solder alloys (SAC305 and Innolot) were investigated in 0.1 mM, 1mM, 10 mM, 500 mM and in saturated NaCl solutions. Innolot sample showed better corrosion parameters in case of 0.1 mM, 1 mM, 10mM and saturated concentrations. However, the corrosion resistance of SAC305 was higher in case of 500 mM NaCl.

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