

# Electrochemical Migration of ENIG surface finish in $\text{Na}_2\text{SO}_4$ Environment

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**Abstract:** *The electrochemical migration (ECM) behavior of Electroless Nickel Immersion Gold (ENIG) surface finish was studied using  $\text{Na}_2\text{SO}_4$  solutions with various concentrations. The investigations were carried out by water drop (WD) test. During WD test the electrochemical processes were followed by electrical and visual inspections. Based on the mean-time-to-failure (MTTF) data it was shown that MTTF increased at 0.1 mM  $\text{Na}_2\text{SO}_4$  solution, then on higher concentrations MTTF significantly decreased and stabilized over the concentrations.*

## 1. INTRODUCTION

In order to optimize the production processes of printed circuit board (PCB) assemblies, it can be found simulation studies [1, 2]. Even more reliability issues are published related to solder alloys or surface finishes used in PCB assemblies [3-9]. This reliability study focuses on a humidity induced failure mechanism called ECM.

ECM is a possible manifestation of electrochemical corrosion mechanism, which may pose safety risk (electrical short) in the case of operating electronics. According to the literature many ECM models are exist [10] depending on the environmental factors (e.g.: contaminations) or the used surfaces finishes and (lead-free) solder alloys. During the short formation mechanism so called dendrites (See Fig 1) are growing usually from the cathode to the anode side. Many types of surface finishes that are commonly applied in the electronic assemblies have significant susceptibility for ECM, like Ag or Sn [11]. Furthermore, other surface finishes types like organic solderability preservative (OSP) or electroless nickel immersion gold (ENIG) are also investigated in NaCl solutions related to ECM [12].

The types of the tested electrolytes have also a wide range: deionized water, salt solutions and also acidic or alkaline solutions as a simulation of the contamination impacts [10-12].

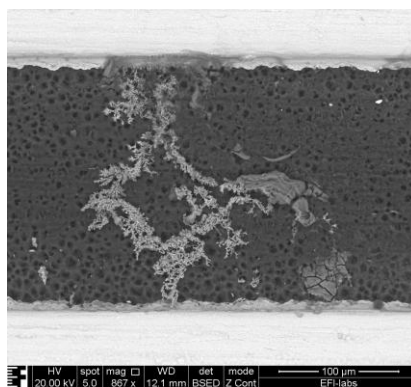


Fig.1. Metallic dendrites formed a short.

For example sulfur as contamination can originate from the circuit assembling steps and also from the environment (the air has some sulfur content). Furthermore, sulfur has an impact on electrochemical migration processes as well. On the one hand, it is theoretical possible, that nickel and gold ions can bond to hydroxides [12] and also can bond to sulfate ions.

On the other hand, the impact of sulfate ions on nickel and on gold is not widely published related to ECM. Furthermore, there are still many contradictory statements and results concerning to nickel and gold migration [12]. Therefore, in this study, various  $\text{Na}_2\text{SO}_4$  solutions with five concentrations were applied as a simulation of the sulfur contamination effect applying ENIG surface finish.

## 2. MATERIALS AND METHODS

Bare copper layer was covered with electroless nickel and immersion gold surface finish on fiberglass-epoxy resin (FR4) substrate. The gap size between the conductor stripes on the test board was 0.2 mm, while the width of the conductor stripes was 0.4 mm (See the structure of the test pattern in Fig. 2).

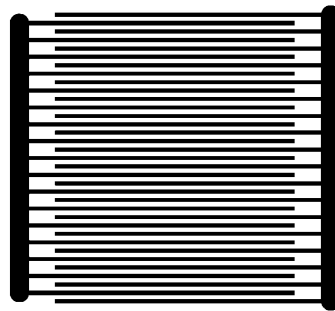


Fig. 2. Comb structure of the ENIG test pattern.

The measuring set up follows the various ECM processes by visually (in-situ) using an USB-microscope and also by a voltage measurement applying a Novus MyPcLab data logger. The real-time voltage measurement indicates the short circuit formation mechanism (e.g. dendrite growth) and help to understand the optical results as well (See Fig. 3).

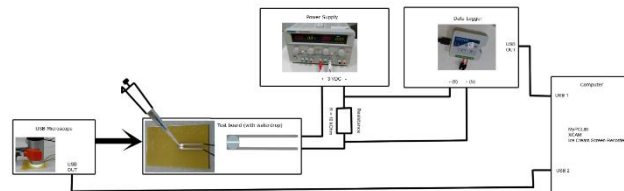


Fig. 3. Arrangement of the test set up for ECM inspection.

Before each investigation, the ENIG surface finishes were washed out with isopropyl alcohol (IPA) water, degreased with deionized water (DI) secondly, and dried in normal conditions. The test solution was  $\text{Na}_2\text{SO}_4$  in aqueous media with five concentration levels (0.1 mM, 1 mM, 10 mM, 500 mM and saturated solution), which was prepared from analytical grade reagents and DI water (18.2 M $\Omega$ cm).

In each WD test a volume of 10  $\mu$ l droplet was placed onto and between the ENIG conductor lines. During the droplet placement it was always tried covering the same active area. Every WD tests were done at least ten times from the reproducibility point of view. Normal distribution was supposed while Mean-Time-To-Failure (MTTF) and deviations ( $1 \sigma$ ) were originated from the electrical measurements. the first significant voltage jump was the main indicator for the failure events caused by ECM (See Fig. 4).

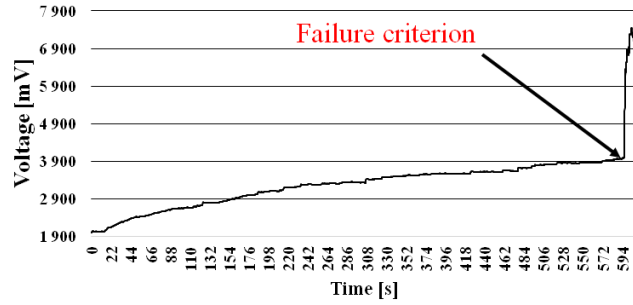


Fig. 4. Example for the failure criterion during WD test.

After the WD tests, the formed dendrites and precipitates were investigated by (FEI Inspect S50) Scanning Electron Microscopy (SEM) and (Bruker Quanta) Energy Dispersive X-ray spectroscopy (EDX) methods.

### 3. RESULTS AND DISCUSSION

#### 3.1 Results of WD test in case of 0.1 mM Na<sub>2</sub>SO<sub>4</sub> solution

In Figure 5, a typical picture from WD test under biased can be seen. In all cases many (H<sub>2</sub>) gas bubbles were observed originated from the cathode side.

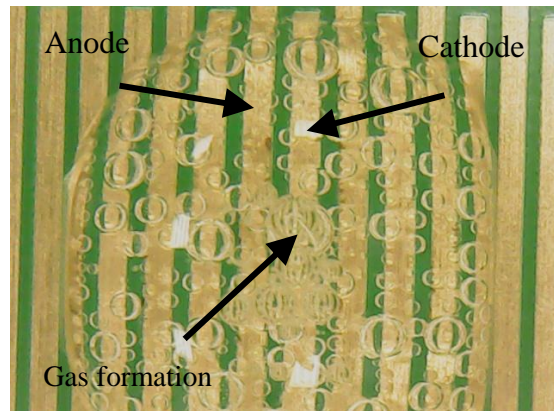


Fig. 5. ENIG surface finish under WD test.

During the real-time electrical measurements the base value was 5.5 VDC and all of the samples were failed due to ECM. The calculated MTTF value was around 1400 sec. This value was 25 times higher comparing to non-solder mask (pure FR4) case. According to the optical microscopy investigations blue-green colored precipitates were detected next to dark dendrites (Fig. 6).

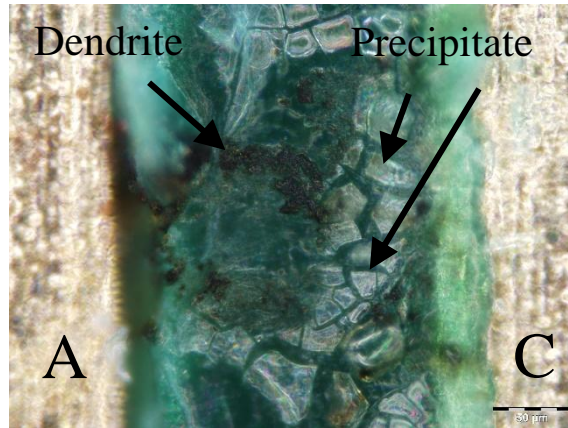


Fig. 6. Dendrites and green-blue colored precipitates were formed during the WD test.

After optical inspection SEM and EDX analysis were carried out to see the structure of the dendrites (See Fig. 7) and collect data from elemental composition point of view. Table 1 contains the EDX data from Fig. 7 and 8.

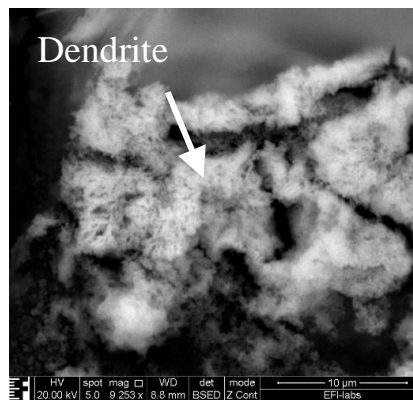


Fig. 7. SEM image of a dendrite and the spot were the data collected during EDX measurement in case of 0.1 mM.

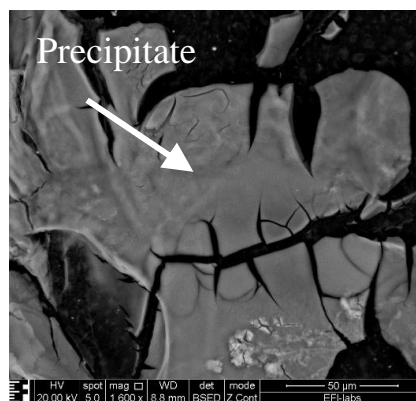


Fig. 8. SEM image of a precipitate and the spot were the data collected during EDX measurement in case of 0.1 mM.

According to the SEM investigations, the dendrites were grown in fibrous form in case of 0.1 mM and Cu was dominated during the ECM processes (Table 1).

Table 1. EDX results from the dendrite (Fig. 7) and precipitate (Fig. 8) in case of 0.1mM Na<sub>2</sub>SO<sub>4</sub> after WD test.

		O	P	S	Ni	Cu	Au
<b>Pre.</b>	at%	54	1.5	1	9.5	34	-
	wt%	24	1	1	15	59	-
<b>Dend-rite</b>	at%	2.5	-	-	3.5	94	-
	wt%	0.6	-	-	3.4	96	-

### 3.2. Results of WD test in case of 1 mM Na<sub>2</sub>SO<sub>4</sub> solution

An intensive gas evolution was also observed during WD test and base voltage value was increased up to 6.3 VDC. Meanwhile, the calculated MTTF value was significantly decreased down to around 90 sec. The shape of the dendrite was changed into ball-like or tuberous-like types, while the green-blue precipitates were similar to the 0.1mM case.

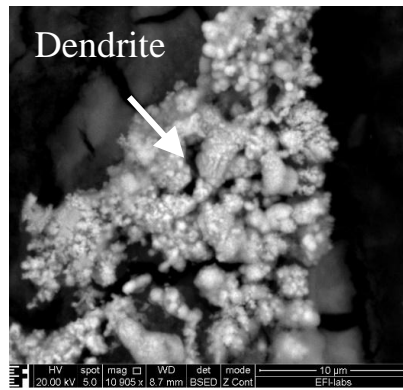


Fig. 9. SEM image of a dendrite and the spot were the data collected during EDX measurement in case of 1 mM.

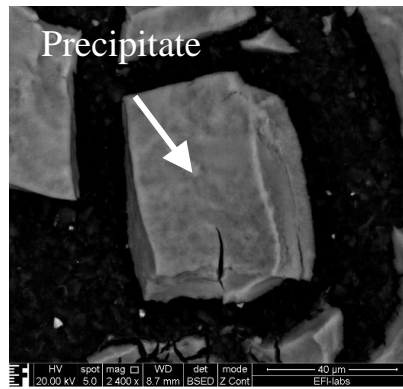


Fig. 10. SEM image of a precipitate and the spot were the data collected during EDX measurement in case of 1 mM.

Table 2. EDX results from the dendrite (Fig 9) and precipitate (Fig 10) in case of 1mM Na<sub>2</sub>SO<sub>4</sub> after WD test.

		O	P	S	Ni	Cu	Au
<b>Pre.</b>	at%	33	1.3	0.70	13	52	-
	wt%	11	1	0.5	16	71.5	-
<b>Dend-rite</b>	at%	12	1	-	1	86	-
	wt%	3.5	0.5	-	1	95	-

### 3.3 Results of WD test in case of 10 mM Na<sub>2</sub>SO<sub>4</sub> solution

In this case, also many gas bubbles were observed during WD test and base voltage value was increased up to 6.6 VDC. Meanwhile, the calculated MTTF value was around 92 sec, so it was not changed significantly. The shape of the dendrite was changed into fibrous types (See Fig. 11), which was very similar to the 0.1 mM case, while the green-blue precipitates remained (Fig. 12).

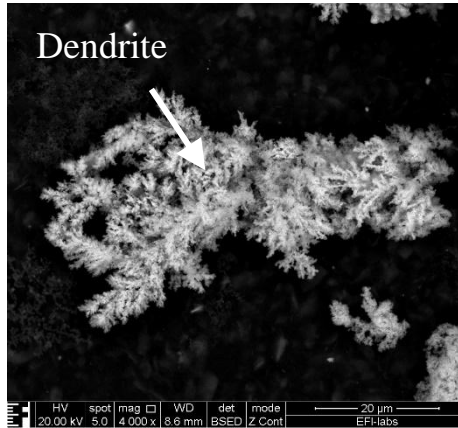


Fig. 11. SEM image of a dendrite and the spot were the data collected during EDX measurement in case of 10 mM.

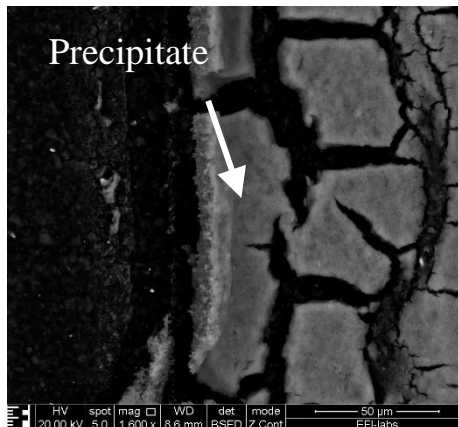


Fig. 12. SEM image of a precipitate and the spot were the data collected during EDX measurement in case of 10 mM.

Table 3 contains the EDX data from Fig. 11 and 12.

Table 3. EDX results from the dendrite (Fig 11) and precipitate (Fig 12) in case of 10 mM Na<sub>2</sub>SO<sub>4</sub> after WD test.

		O	P	S	Ni	Cu	Au
Pre.	at%	73	1.5	1.5	19	5	-
	wt%	45	2.5	1.5	35	15	-
Dend-rite	at%	20	-	-	1	79	-
	wt%	6	-	-	1	93	-

### 3.4 Results of WD test in case of 500 mM Na<sub>2</sub>SO<sub>4</sub> solution

In this case, also many gas bubbles were observed during WD test and base voltage value was increased up to 6.7 VDC. Meanwhile, the calculated MTTF value was around 92 sec, so it was not changed significantly. The shape of the dendrites was not seen due to the thick salt a precipitate layers and the color of the precipitate was change into white one (Fig. 13).

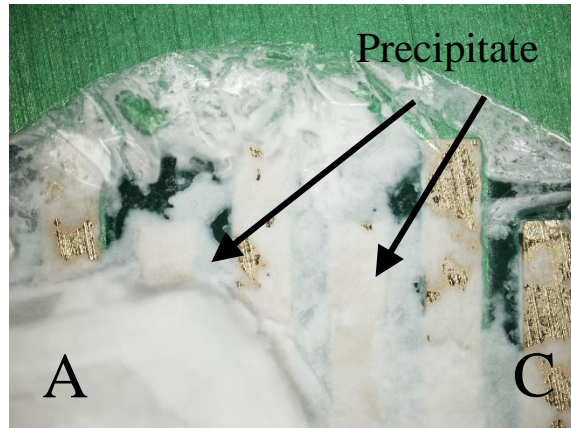


Fig. 13. White colored salt and precipitate after WD test in case 500 mM  $\text{Na}_2\text{SO}_4$

### 3.5 Results of WD test in case of saturated $\text{Na}_2\text{SO}_4$ solution

On the one hand, in case of the saturated solution a massive salt cover layer was formed. On the other hand the MTTF (94 sec) and base voltage (6.7 VDC) values were not significantly changed.

After removing the thick salt layer from the surface (See Fig. 14), SEM-EDX investigations were repeated. Based on the EDX results a relative high Ni content (16 at% and 38 wt%) was detected, meanwhile the Cu content was significantly lower (1 at% and 3 wt%).

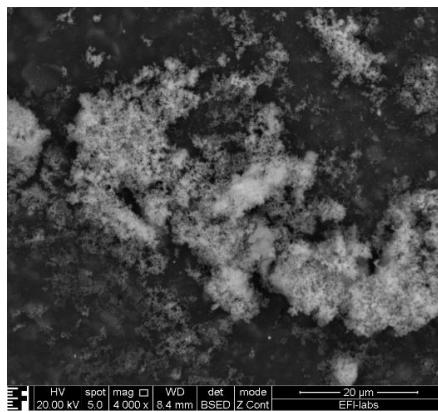


Fig. 14. SEM image from the surface after WD test and removal of the salt layer in case of saturated solution.

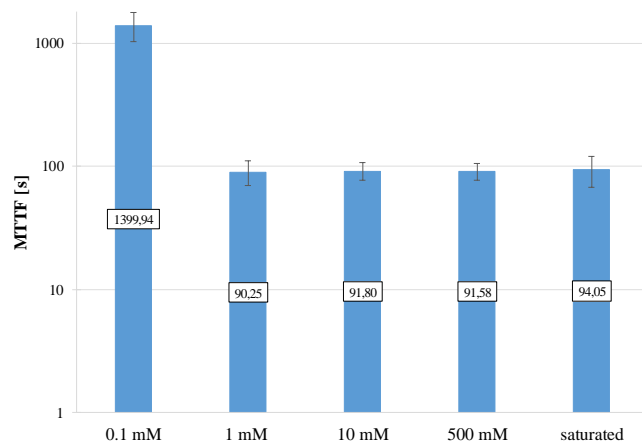


Fig. 15. Comparison of the MTTF values over  $\text{Na}_2\text{SO}_4$  concentrations in case of ENIG surface finish.

## 4. CONCLUSIONS

The ECM behavior of ENIG surface finish was studied using  $\text{Na}_2\text{SO}_4$  solutions with various concentrations. Based on the MTTF data it was shown that ECM susceptibility was decreased at 0.1 mM  $\text{Na}_2\text{SO}_4$  solution, then on higher concentrations ECM ability significantly increased and stabilized over the concentrations (10mM, 500mM and saturated solutions).

## ACKNOWLEDGEMENTS

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