Electrochemical migration and corrosion behaviours of SAC305 reinforced by NiO, Fe$_2$O$_3$, TiO$_2$ nanoparticles in NaCl solution

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Abstract. Pb-free solders incorporated with nano-sized particles have been identified, as potential Pb-free nanocomposite solders that could provide higher microstructure stability and better mechanical properties than the conventional solders. Nowadays, the miniaturizations of electronic devices increase in their usage have increased the risk of failure due to ion migration and corrosion phenomena. This research investigates the effects the electrochemical migration (ECM) and corrosion behaviour of Sn-3.0Ag-0.5Cu (SAC305) reinforced by NiO, Fe$_2$O$_3$ and TiO$_2$ nanoparticles in 0.1M NaCl solution. The SAC305 solder alloys were doped with different percentages of NiO, Fe$_2$O$_3$ and TiO$_2$ at nominal percentages of 0.01, 0.05 and 0.15 wt% in producing nanocomposite solder paste. Then, the solder paste has flowed in the reflow oven at the temperature of 240°C. After that, the Water Drop Test (WDT) was performed using 0.1 M NaCl solution to investigate the ion migration behaviour and Potentiodynamic Tafel Polarization technique to determine the corrosion behaviour on the solder alloys. In general, the results showed the mean-time-to-failure (MTTF) of SAC305 solder alloy increased when added of the nanoparticles of NiO, Fe$_2$O$_3$ and TiO$_2$. Besides, SAC305-TiO$_2$ has the longest MTTF in 0.1 M NaCl solution followed by SAC305-Fe$_2$O$_3$ and SAC305-NiO nanoparticles. This results is believed due to the presence of nanoparticles as the alloying element in the solder that hinder the process of ECM to suppress the growth of the dendrites accelerating for the short circuit occurs and causes the failure of the IPC-24 test board. The potentiodynamic polarization curve results exhibit the SAC305 with nanoparticles decreased the corrosion rate compared with SAC305 solder alloy only. SAC305 with NiO and TiO$_2$ have slightly lower corrosion rates compared with Fe$_2$O$_3$ nanoparticles. Therefore, SAC305 reinforced by TiO$_2$, Fe$_2$O$_3$ and NiO nanoparticles exhibited excellent ECM and corrosion resistance behaviours in the 0.1 M NaCl solution.

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1 Introduction

Soldering offers important technology on microelectronic packaging industries. It allows electrical current to flow from one point to another and become a supporter of the electrical components. Recently, the lead-free, Sn-Ag-Cu solder alloy has been commercially used as an alternative to Sn-Pb solder due to the vital issue on hazardous effect [1–4]. This Sn-Pb solder is due to poisonous qualities of lead which is harmful to human health and also to the environment [5].

Tin based solder alloy becomes the replacement for lead solder alloy [4]. Tin containing binary and ternary alloying elements has been most directed towards it [6]. Eutectic tin-silver-copper has a melting point around 216°C, which is 30°C little higher than that of eutectic lead-tin (Tm = 183°C). The addition of silver and copper reduces about 16°C of the melting point of tin (232°C). Tin-silver solders are already used with success in high-temperature applications [7].

Others researcher had a focus on some lead-free content solders, which may cause high risk in electronic devices due to electrochemical migration (ECM) failure phenomenon [8]. ECM commonly occurs in all electronic devices in the electronics industry. This phenomenon involves the dendritic growth [11, 12]. It can be led to a short circuit to occur in the electronic device issue is related to the susceptibility of SAC305 to corrosion [11].

The growing of miniaturization of the electronic system causes the use of Pb-free solder materials have led to increase many challenges in electronics installation. These challenges are because of the higher density packaging lead the components event smaller, closer spacing, thinner metallic parts and higher gradient of the electrical field [13]. Furthermore, the devices sometimes have to service in high humidity, salty and polluted environment. Due to the advances in technology, this led to electronic devices are becoming more and more susceptible to corrosion failure, even a small amount of weight loss [14]. Therefore, in this paper, the SAC305 reinforced by NiO, Fe2O3 and TiO2 nanoparticles solder paste toward ECM and corrosion behaviours were investigated by using the Water Drop Test (WDT) and electrochemical polarization technique in 0.1M NaCl solution that simulating seawater environment as a medium.

2 Materials and Methodology

The lead-free SAC305 solder alloy containing 96.5%Sn, 3%Ag and 0.5%Cu were doped in different percentages of NiO, Fe2O3, TiO2 nanoparticles at a nominal percentage at 0.01, 0.05 and 0.15wt% to produce nanocomposite solder paste. Then, all nanoparticles (Aldrich, ≥ 98 per cent trace metal basis, particle size: <25 nm) were mixed with the 96.5Sn–3.0Ag–0.5Cu solder paste (SAC305; Alpha OM-353) using a mechanical stirrer brand Fritsch Planetary Mill PULVERISETTE 5 for approximately 10 min (300 rpm) to achieve homogeneity before the assembly. The methodology of preparing nanocomposites can be referred at [15,16,17]. Then, the nanocomposite solder pastes were then well printed in a standard comb pattern with horizontal lines on the conductor strip is 0.4mm and the gap size about 0.2mm. After the printing with the solder paste, the test board is heated using Desktop free-Lead Reflow Oven TYR108C. The test board was designed according to IPC-B-24 test board, as shown in Fig. 1.

Before the WDT, the test board, voltmeter, resistor in series and power supplier have been connected, as shown in Fig. 2. During WDT, 15µml 0.1M sodium chloride (NaCl) solution was dropped by micropipette onto four comb patterns and 10 Volts DC was applied to each of the samples. During the WDT, short circuit formation is detected by a voltmeter connected with one resistor in series through average Time-To-Fail (MTTF). Par
value failure is 0.1 VDC and resistor value (R) is 1 kOhm. After the WDT, the mean-time-to-failure (MTTF) of each sample should be computed using this formula [1]:

$$MTTF = \frac{y_1 + y_2 + y_3}{n}$$  \hspace{1cm} (1)

where $y$ is time to failure and $n$ the is number of time taken. After the WDT, the test boards were cut to dimension size about 1.0 x 1.0 cm$^2$ in order to investigate its surface morphology and corrosion product by using optical microscopy.

Fig. 1. The IPC-B-24 Standard comb pattern test board.

Fig 2. Schematic diagram of the test platform of Water Drop Test (WDT)

3 Results and Discussion

WDT was performed on SAC305 solder paste alloy and SAC305 reinforced nanoparticles solder alloys that have been printed on the test board by using 0.1M NaCl solution with the power voltage. The droplets volume and the resistance was set constant. The voltage value drops to 0 V and the time-to-failure was recorded. Mean-time-to-failure (MTTF) was the average value of the measured failure times. The test board will be experienced electromigration (ECM) led the short circuit occurs. Average MTTF can be obtained, as listed in Table 1.
Table 1. MTTF data of SAC 305 solder paste reinforced by TiO$_2$, Fe$_2$O$_3$ and NiO nanoparticles.

| Types of Solder Alloy | wt% of nanoparticles | Mean-Time-To-Failure (s) |
|-----------------------|-----------------------|--------------------------|
| SAC305               | 0                     | 857                      |
| SAC305-TiO$_2$       | 0.01                  | 1168                     |
|                      | 0.05                  | 1389                     |
|                      | 0.15                  | 1548                     |
| SAC305-Fe$_2$O$_3$   | 0.01                  | 1130                     |
|                      | 0.05                  | 1345                     |
|                      | 0.15                  | 1526                     |
| SAC305-NiO           | 0.01                  | 1071                     |
|                      | 0.05                  | 1285                     |
|                      | 0.15                  | 1498                     |

In general, the MTTF reveals that the addition of nanoparticles in SAC305 increased the time to failure due to short circuit compared to SAC305 solder alloy in NaCl solution. The MTTF results indicate that SAC305-TiO$_2$ has the most extended values, which is 1548s followed by SAC305-Fe$_2$O$_3$ (1526s) and SAC305-NiO (1498s) in the range of 0.15 wt% of nanoparticles. Meanwhile, SAC305 solder alloy shows faster MTTF valued at 857s. This phenomenon can be attributed due to the chemical reaction of solder paste alloy and NaCl solution with electrical potential as known as ionic migration or electromigration. This effect shows the SAC305 solder is believed to have ECM which metal ions migrate from anode to cathode cause the voltage drops to zero and continue to fail the overall devices. However, by addition of nanoparticles TiO$_2$, Fe$_2$O$_3$ and NiO into SAC305 solder alloy hinder the process of ECM from suppressing the growth of the dendrites for the short circuit occurs and causes the failure of IPC-24 test board. Fig. 3 shows that summarize of MTTF of SAC305 reinforced by nanoparticles in different wt% also exhibits a similar pattern where increasing percentages of nanoparticles until 0.15 wt% increasing the MTTF values.

![Fig 3. Mean Time for Failure of SAC305 reinforced of NiO, Fe$_2$O$_3$ and TiO$_2$ nanoparticles](image-url)
In this study, the morphology and microstructure of SAC305 solder paste with addition of nanoparticles were investigated. Fig. 4 shows the optical micrograph of SAC305 solder paste and SAC305 reinforced nanoparticles after WDT experienced the formation of dendrites growth. As can be seen in Fig. 4a, severe dendrite formation found in SAC305 solder compared to SAC305 with doped nanoparticles which have less severe of dendrites growth (Fig.4b,c,d). It was found than nanoparticles doping increased the MTTF values. This outcome is believed that the dendrites formation have been suppressed by precipitated of nanoparticles in the solder paste.

![SAC305 (a)](image1)
![SAC305-NiO (b)](image2)
![SAC305-Fe2O3 (c)](image3)
![SAC305-TiO2 (d)](image4)

**Fig. 4** Optical micrographs of SAC305 and SAC305 reinforced of nanoparticles solder paste alloy after WDT in 0.1M NaCl solution.

Potentiodynamic polarization curves for SAC305 and SAC305 reinforced nanoparticles for 0.05%wt in a solution containing 0.1M NaCl extrapolates in Fig. 5. The corresponding polarization parameters such as corrosion current ($I_{corr}$), corrosion potential ($E_{corr}$), passivation current ($i_{corr}$) values obtained from the polarization curves listed in Table 2. The Tafel fit using Gamry Echem Analyst Version 7.07 were used to determine the corrosion parameter. At cathode region corresponds to reduction reaction of dissolved O$_2$ to produce hydroxyl ions (OH$^-$). The reaction can be illustrated as follow [13,18]:

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \\
2H_2O + 2e^- & \rightarrow H_2 (g) + 2OH^- 
\end{align*}
\]

The H$_2$(g) will be released at cathode from the reduction reaction. Nevertheless, the oxidation at the anode is rather complicated. The reaction at the anode can be described as follows [13,18,19]:
Sn + 2OH- → Sn(OH)₂ + 2e⁻ \hspace{1cm} (4)
Sn + 4H₂O → Sn(OH)₂ + 4e⁻ + 4H⁻ \hspace{1cm} (5)

Later, Sn(OH)₂ and Sn(OH)₄ will be suffered from dehydration and each of them form SnO and SnO₂ according to the following reactions [13,18, 20]:

Sn(OH)₂ + 2OH⁻ + 2e⁻ → Sn(OH)₄ \hspace{1cm} (6)
Sn(OH)₂ + 2OH⁻ → SnO + 4H₂O \hspace{1cm} (7)
Sn(OH)₄ + SnO₂ + 2H₂O \hspace{1cm} (8)

Due to the dissolution Sn(OH)₂, Sn²⁺ ions released and move to cathode region. Then, these ions arrived at the cathode, ECM deposition occurs. Deposition of this cathode will form a dendrite growth towards the anode led to short circuit after dendritic growth reached to anode [21].

The Eₗcorr values after addition of 0.05%wt nanoparticles shifted towards more negative in from -178 mV to more than -278 mV. As it can be noticed, both cathodic and anodic reactions of SAC305 reinforced nanoparticles of NiO, Fe₂O₃ and TiO have reduced the corrosion rates about 0.189, 0.131 and 0.126 mpy, respectively from 1.431 mpy on SAC305 only. This result indicates that the addition of nanoparticles into SAC305 solder somehow is reduced Eₗcorr, Iₗcorr and corrosion rate values. SAC305-TiO₂ exhibits a lower corrosion rate followed by SAC305-Fe₂O₃ and SAC305-NiO. This influence is most likely due to the presence of nanoparticles as a reinforced tiny precipitate in the solder paste retard the corrosion attack from aggressive ion Cl⁻ [22].

Fig 5. Potentiodynamic polarization curves of SAC305, SAC305-0.05NiO and SAC305-0.05Fe₂O₃ and SAC305-TiO₂ in 0.1M NaCl solution.
Table 2. Potentiodynamic polarization parameters for SAC alloys solder in 0.05wt% nanoparticles in 0.1M NaCl solution

| Solder       | E_{corr} (mV) | I_{corr} (mA/cm²) | Beta a (V/decade) | Beta c (V/decade) | Corrosion rate (mpy) |
|--------------|---------------|-------------------|-------------------|-------------------|----------------------|
| SAC305       | -178          | 12.640 x 10^{-6}  | 297 x 10^{-3}     | 3.317             | 1.432                |
| SAC305-NiO   | -535          | 1.604 x 10^{-6}   | 356 x 10^{-3}     | 563 x 10^{-3}     | 0.189                |
| SAC305-Fe₂O₃| -309          | 1.161 x 10^{-6}   | 243 x 10^{-3}     | 433 x 10^{-3}     | 0.131                |
| SAC305-TiO₂  | -278          | 1.113 x 10^{-6}   | 222 x 10^{-3}     | 700 x 10^{-3}     | 0.126                |

4 Conclusion

The SAC305 reinforced composite nanoparticles by NiO, Fe₂O₃ and TiO₂ were investigated to study the behaviour of electromigration dan corrosion in 0.1M NaCl solution.

1. The results show that the MTTF of SAC305-TiO₂ has slowest the mean-time-to-failure, followed by SAC305-0.15Fe₂O₃ and SAC305-NiO compared to SAC305 attributed to ECM after WDT.

2. The addition of nanoparticles in solder paste suppressed the formation of dendrites to growth from cathode to anode, which can short the circuit, ultimately causing the failure of the test board.

3. Potentiodynamic polarization measurement showed a better corrosion resistance of SAC305-TiO₂ followed by SAC305-0.15Fe₂O₃ and SAC305-NiO compared to SAC305 solder paste. Addition of nanoparticles in solder paste enhanced corrosion resistance due to the nanoparticles act as precipitate to hinder the ion migration.

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