Effect of Nickel-Coated Precipitated Calcium Carbonate on Corrosion Properties of Sn-9Zn Solder

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Abstract. The effect of 0.5 wt. % Nickel (Ni)-coated precipitated calcium carbonate (PCC) additions on the corrosion properties of Sn-9Zn solder was investigated in 3.5% sodium chloride (NaCl) solution employing potentiodynamic polarization. The morphological differences before and after corrosion analysis have been investigated to support the findings. The scan rate used was 1 mVs⁻¹ after stable potential developed. Slight improvement of corrosion potential (Ecorr) with a significant reduction in corrosion current (icorr) was seen for the Sn-9Zn/Ni-coated PCC compared to Sn-9Zn, indicating the kinetics of corrosion reaction was reduced. The current consumed under the passivation stage for the Sn-9Zn/Ni-coated PCC was also smaller, highlighting that further corrosion protection was improved. Microstructural observation also verified that the number and size of blackish spot clusters were reduced for the Sn-9Zn/Ni-coated PCC, revealing that Ni-PCC additions improve the overall corrosion performance of Sn-9Zn solder.

1 Introduction

Since the last two decades, several international legislations have banned the use of tin-lead (Sn-Pb) based solders such as the eutectic Sn-37Pb and near-eutectic Sn-40Pb from electronic packaging due to toxicity issues [1]. Therefore, much research has been conducted to replace conventional Sn-Pb solders with Pb-free solders. Alloys such as tin-silver (Sn-Ag), tin-zinc (Sn-Zn), tin-silver-copper (Sn-Ag-Cu), and tin-copper (Sn-Cu) have been proposed to be used as a drop-in replacement for Sn-Pb solders [2]. With most of the Pb-free solders are Sn-based alloys, their performance in melting temperature, wetting properties, mechanical properties, and thermal conductivity are vastly varied based on the alloying content contained within the alloys. These characteristics should be extensively studied to guarantee that the Pb-free solders work effectively in applications after being manufactured. In recent years, the demand for miniaturization in electronic packaging has forced manufacturers to produce a higher density of solder joints in more restricted space [3]. This posed a new challenge as Pb-

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free solders needed to produce high creep resistance, mechanical properties, microstructure stability and corrosion resistance during application [4].

The use of non-reacting nanoparticles ceramics as reinforcement in composite solder has been seen as one of the promising routes to produce Pb-free solder capable of fulfilling this need. Studies have shown that the additions of ceramics reinforcement can improve properties such as wettability and tensile strength of soldiers. For example, Geranmayeh et al. [5] reported that the uniform distribution of alumina particles in the tin-antimony-silver solder matrix reduced the size of the intermetallic compound (IMC) and improved the shear stress properties. Comparable IMC refinement also was seen in the titanium oxide/Sn-3.0Ag-0.5Cu solder system [6]. One of the well-known fillers used in various industries is precipitated calcium carbonate (PCC). The PCC was usually used due to its low cost, high availability and environmental friendly [7]. However, agglomeration of reinforcement such as PCC in solder is a severe concern. To solve this problem, metal coating, primarily made of nickel (Ni), is seen as a noble path to solve this issue since Ni has a high solubility in Sn [8-10] and would help disseminate PCC uniformly in the solder matrix. In particular, Yang et al. [11] demonstrated that the wettability of SAC solder was improved with the addition of Ni-coated-multi wall carbon nanotube. Billah [12] explained that nickel caused reinforcement particles distributed evenly in the solder. This shows that the Ni coating effect is prominent to distribute an inert filler in ceramic.

The eutectic Sn-9Zn is one of the Pb-free solders with good mechanical properties but severely suffered from low corrosion resistance [13, 14]. The addition of Ni-coated PCC in Sn-9Zn is expected to improve the corrosion problem significantly. However, best to our knowledge, the corrosion performance of Ni-coated PCC/Sn-9Zn has never been reported. As part of the reliability issue, the corrosion performance Ni-coated PCC/Sn-9Zn is worth systematically investigated in this work. Microstructure analysis before and after corrosion analysis will also be investigated to help in understanding the effect of adding Ni-coated PCC on the corrosion properties.

2 Experimental Procedure

1000 ml of distilled water was heated up and maintained at 80 °C and kept there to prepare Ni-coated PCC. After that, 5 wt. % nickel dichloride hexahydrate (NiCl₂•6H₂O) and calcium carbonate (CaCO₃) were added into the distilled water. The mixed solution was stirred at 400 rpm. Next, few drops of sodium hydroxide (NaOH) were added to maintain the solution at pH 8. After that, a reducing agent, sodium hypophosphate (NaH₂PO₂), was added, and the pH was maintained at 8 by adding NaOH. The mixture is heated and stirred for two hours before it is filtered. The remaining residue was dried in the oven at 70 °C for 1 day and then ground in powder. The Sn and Zn were weighted to the desired amount (91 wt. % Sn and 9 wt. % Zn) and co-melted at 550 °C in an inert atmosphere to produce a Sn-9Zn ingot. The air-cooled Sn-9Zn ingot will be re-melted at 300 °C to fabricate composite solder with the additions of 0.5 wt. % Ni-coated PCC. The mixture was stirred to ensure good distribution. The solder was machined into a pellet of 5 mm diameter and 3mm thickness. The samples were then cold mounted and metallographically polished to a mirror-finished surface. For electrochemical analysis, a three-electrode system was used. A mounted sample was immersed in 3.5 wt. % NaCl solution with a platinum plate used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The potentiostat used was Metrohm µStat i-400s, at a potential range of -2.0 to 1.0 V, at the scanning rate of 1 mVs⁻¹. The corrosion test was repeated at least three times to ensure the reproducibility of the results. Microstructure analysis was performed using an optical microscope (Olympus BX50) before and after the electrochemical corrosion test.
3 Result and discussion

The potentiodynamic polarization technique provides rapid information on corrosion behaviour. Figure 1 shows the potentiodynamic curve of pure Sn-9Zn and Ni-coated PCC/Sn-9Zn in 3.5 wt. % NaCl solution, at applied potential ranging from -2.0 to 1.0 V. Generally, the result can be divided into 2 parts, which were cathodic (-1.75 to -1.25 V) and anodic (-1.25 V onwards) regions. The slope formed in the cathodic area (part AB) is generally attributed to the cathodic reaction of hydrogen gas evolution [15]:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (1) \]

Fig. 1. Potentiodynamic polarization curve for Sn-9Zn and Sn-9Zn/Ni-coated PCC in 3.5 wt % NaCl

Anodic polarization started as the cathodic reaction completed, signified by the increase in current density. Anodic polarization can be divided by several parts labelled as BC and CF (for Sn-9Zn) and BD and DE (for Ni-coated/Sn-9Zn system). Starting at point B, the dissolution process of solder started, producing potential known as corrosion potential \( E_{\text{corr}} \), with corresponding current density at \( E_{\text{corr}} \) known as corrosion current density \( i_{\text{corr}} \). This primary dissolution process (BC and BD) is typically associated with the dissolution of Zn as the most electrochemically active element in the Sn-9Zn solder system according to [16]:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad (2) \]

Table 1 gives the result of \( E_{\text{corr}} \) and \( i_{\text{corr}} \) variations with the additions of 0.5 wt. % Ni-coated PCC. The \( E_{\text{corr}} \) was slightly increased from -1.29 to -1.21 V vs SCE with the additions of 0.5 wt. % Ni-coated PCC, indicating that the electrochemical stability of the Sn-9Zn is improved. Meanwhile significant reduction in \( i_{\text{corr}} \) from 2.14 to 1.87 µA/cm\(^2\) revealed that the corrosion reaction kinetic is lowered in Ni-coated/Sn-9Zn, as \( i_{\text{corr}} \) is direct proportionally associated with corrosion reaction kinetics [14]. The DE region correlates to the development of a passivation layer on the solder surface in oxygen saturated NaCl solution since the current densities generated were nearly completely independent of the applied potential rise. Formation of passivation layer can be contributed by [14]:

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (3) \]
It is also worth noting that the passivation potential (E_{pa}) produced by Ni-coated PCC/Sn-9Zn (-0.756 V vs VSE) was higher compared with Sn-9Zn (-0.897 V vs VSE). This shows that the passivation film produced in DE has a higher protection ability against further corrosion. Therefore, it can be concluded that the inclusion of Ni-coated PCC enhanced the passivation ability of the solder alloy.

Table 1: Electrochemical parameter obtained from the potentiodynamic polarization curves of Sn-9Zn and Sn-9Zn + Ni-PCC solder in 3.5 wt %

| Solder         | Ecorr (V Hg/HgO) | icorr (μA) | icc (μA) | Esp (V Hg/HgO) | Epc (V Hg/HgO) | icc (μA) | la (μA) |
|----------------|------------------|------------|----------|----------------|----------------|----------|---------|
| Sn-9Zn         | -1.29            | 0.7677     | 2.14     | -1.091         | -0.897         | 2.07     | 3.71    |
| Sn-9Zn+0.50 Ni-PCC | -1.208          | 0.1086     | 1.87     | -0.897         | -0.756         | 1.78     | 3.4     |

Microstructure observation on the effect of adding Ni-coated PCC to the Sn-9Zn is shown in Figure 2. In general, the microstructure of Sn-9Zn is characterized by a dark-contrast needle-like structure of Zn in the matrix of β-Sn (Fig. 2a). The limited solubility of Zn in Sn allows the formation of the needle-like structure [17]. However, significant refinement of the needle-like structure is seen with the additions of Ni-coated PCC (Fig. 2b). The presence of Ni-coated PCC is believed to serve as heterogeneous nucleation sites that reduce the undercooling temperature during solidification of the solder, as previously explained [6]. This enables the formation of additional nuclei during solidification and the refinement of the microstructure by adding Ni-coated PCC to the system. Besides that, the presence of Ni-coated PCC restricts grain movement through Zener pinning effect, hence also limiting the grain’s size [18].

![Fig. 2. Optical microscope image of (a) Sn-9Zn and (b) Ni-coated PCC/Sn-9Zn before corrosion test](image)

After polarisation in 3.5 wt. % NaCl, a few blackish spots clusters were detected on the surface of Sn-9Zn (Figure 3a). The presence of blackish spot clusters is believed to be contributed by pitting formation due to the aggressive Cl− ions [19]. Interestingly, the number and size of blackish spot clusters were reduced as the Ni-coated PCC was added (Fig. 3b). This observation was following the reduction of icc seen in potentiodynamic polarization, highlighting better protection ability of the corrosion product for the Ni-coated PCC/Sn-9Zn system. The refinement of the needle-like structure of Zn might be attributed to the smaller pitting size that also helps improve the overall corrosion resistance.
Fig. 3. Optical microscope image of (a) Sn-9Zn and (b) Ni-coated PCC/Sn-9Zn after corrosion test.

4 Conclusion

The effect of adding Ni-coated PCC to the corrosion properties of the Sn-9Zn was investigated. The corrosion resistance was significantly improved with the additions of Ni-coated PCC, as witnessed by the increase in $E_{\text{corr}}$, reduction in $i_{\text{corr}}$ and $i_{\text{cc}}$. Meanwhile, microstructure evaluation also shows a significant refinement of needle-like Zn, which helps produce smaller pitting and a better protective corrosion resistance layer on the surface. Therefore, it can be concluded that the reliability of the Sn-9Zn was improved with the addition of Ni-coated PCC.

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References

1. D. Frear, e&i Elektrotechnik und Informationstechnik, 118.2 (2001)
2. M. Abtew and G. Selvaduraj. J Mater. Sci. Eng: R: Reports, 27,5-6, (2000)
3. L. Tsao, J. Corrosion Resistance, 107 (2012)
4. A. Barros, C. Cruz, A. Garcia, and N. Cheung, J. of Mater. Res. Technol, 12 (2021)
5. A. Ganmamayeh, R. Mahmudi, and M. Kangooie, J. Mater. Sci. Eng : A, 528, 12 (2011)
6. I. Ahmad, M.F.M. Nazeri, N.A. Salleh, S. Kheawhom, A.M. Erer, A. Kurt, and A.A. Mohamad, J. Arabian of Chem, 103392 (2021)
7. V.K. Yadav, K.K. Yadav, M. Cabral-Pinto, N. Choudhary, G.Ganamoomothy, V. Tirth, S. Prasad, A.H. Khan, S. Islam, and N.A. Khan, J. Appl. Sci, 11.9 (2021)
8. B. Bostani, N. Parvini Ahmadi, S. Yazdani, and R. Arghavanian, Trans. of Nonferrous Metals Society of China, 28.1(2018)
9. P.-C Huang, K.-H. Hou, J.-J. Hong, M.-H. Lin, and G.-L. Wang, Wear, 477 (2021)
10. S. Mirzamohammadi, H. Khorsand, and M. Aliaofkhazraei, Surface and Coatings Technol, 313 (2017)
11. Z. Yang, W. Zhou, and P. Wu, J. Mater. Sci. Eng: A, 590 (2014)
12. M.M. Billah, Electronic Theses and Dissertations. 5443
13. M.N. Mohamed, N. Aziz, A.A. Mohamad, and M.F.M. Int. J. Electroactive Mater, 3 (2015)
14. M.F.M. Nazeri, and A.A. Mohamad, Int. J. Electroactive Mater, 2 (2014)
15. N. Jumali, N. Mohd Zaini, N.S. Sa’don, A.A. Mohamad, and M.F. Mohd Nazeri. Materials Science Forum. Trans. Tech. Publ. (2020)
16. N. Jumali, A.A. Mohamad, and M.F. Mohd Nazeri. *Materials Science Forum*. Trans. Tech. Publ. (2017)
17. Y. Z. Peng, C.J. Li, J.J. Yang, J.T. Zhang, J.B. Peng, GJ. Zhou, C.J. Pu, and J.H. Yi, J Metals, **11**, 4 (2021)
18. O. Mokhtari, A. Roshanghias, R. Ashayer, H.R. Kotadi, F. Khomamizadeh, A.H. Kokabi, M.P. Clode, M. Miodownik, and S.H. Mannan, *J MRS Online Proceedings Library*, **1424** (2012)
19. R.T. Loto, *J. of Mater. Res. Technol*, **8**, 1 (2019)