Influence of Grain Refinement via ECAP to the Corrosion Behaviour of SAC 305 Solder

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Abstract. Equal Channel Angular Pressing or ECAP has been generating interest due to the ability to form bulk ultra-fine grains (UFG) or nanostructured materials. This formation of ultra-fine grains leads to a favorable combination of strength and ductility. Solder materials, which function as the mechanical bridge joining chip to substrate, or package to mother board, could very well benefit from this combination. High strength would offer better joint, and enhanced ductility would enable solder to have better fracture toughness and drop-impact resistance as solder joint regularly being subjected to vibration and impact. This paper reports about corrosion behaviour of ECAPed SAC 305 alloy formed via route Bc up to four passes. The focus is on the effect of grain refinement on corrosion behaviour of bulk solder in 3.5 wt.% NaCl solution. The resulting microstructure was observed by Scanning Electron Microscope (SEM). The grains formed after different passes of ECAP were observed, along with the distribution of intermetallic compound or IMC within the bulk solder. Finer grains were formed with increasing number of ECAP passes leading to reduction of corrosion rate and increased strength of SAC305. The high fraction of grain boundaries in the microstructure with increased of ECAP passes reduced the corrosion rates by accelerating the passivation process.

1. Introduction

Solder is widely used to connect chips to their packaging substrates in flip chip technology as well as in surface mount technology [1]. Among the alternative lead-free solders, Sn-Ag-Cu (SAC) alloy is seen as the most likely candidate due to their low melting temperature (~217°C), better solderability, good mechanical properties and slower growth of the intermetallic at the interface compared with Sn-Pb and Sn-Ag solder alloys [2]. As solder joint serves as mechanical and electrical connection, reliability of the joint is critical for the performance of the device. Exposure to corrosive environment is one of the risk to reliability especially if the device or electrical component is used in aggressive environment such as high humidity or in coastal atmosphere [3]. Mohanty and Lin (2008) studied corrosion behaviour of Pb-free Sn-8.5Zn-0.05Al, Sn-8.5Zn-0.05Al-0.02Ga, Sn-8.5Zn-0.05Al-0.05Ga, Sn-8.5Zn-0.05Al-0.2Ga and Sn-3Ag-0.5Cu alloys in 3.5 wt.% NaCl solution. From this research, the corrosion potential (E_{corr}) value for Sn-8.5Zn-0.05Al-xGa alloy is shifted toward more negative values with increasing of Ga content. While, the E_{corr} value for Sn-3Ag-0.5Cu alloy is shift towards more noble values. The corrosion rate increase with increasing in Ga content from 0.02 to 0.2 wt.%. But, a significant increase in the corrosion rate is found for Sn-3Ag-0.5Cu alloy [4].
Equal-Channel Angular Pressing (ECAP) is one of the modern techniques utilizing severe plastic deformation (SPD) to fabricate bulk ultrafine-grained (UFG) and nanostructured materials that will enhance their physical, mechanical and corrosion properties [5]. This process will also alter the microstructure of Sn-Ag-Cu alloy by reducing the large dendrites into fine and equiaxed grains. Although the refined grains provide improvement in mechanical properties, the effect to corrosion behaviour of SAC may not be as positive. This is added with the possible influence of increased dislocation density and fragmentation of intermetallic particles due to ECAP process. For Sn-Ag-Cu lead-free solder, it has been found that Ag3Sn precipitates are also present within the Sn matrix. Gong et al. (2010) have reported that during ECAP process, Ag3Sn could be broken into small fragments and more uniformly distributed within Sn matrix which resulted in better corrosion resistance in 3.5 wt.% NaCl solution compared to SAC solder with large Ag3Sn structure [6]. However, there was limited explanation of Sn-Ag-Cu lead-free solder on why ECAP process was able to improve the corrosion resistance. Sadawy and Ghanem, (2016) have reported the increase of ECAP number of passes increases the corrosion resistance of the bronze alloy [7]. Therefore, the present work focused on the effect of ECAP as a grain refinement technique on the microstructure evolution and corrosion behaviour of the Sn-Ag-Cu alloy attempting to study the correlation between grain refinement, fragmentation of IMC particles, dislocation density and the corrosion resistance.

2. Experimental study

This experiment was carried out using commercial SAC305 solder bar. The solder bar was cut by using horizontal band saw into smaller pieces and melted at 350°C using lab crucible furnace. The molten solder alloy was then casted in steel mold with shape and size following the ECAP mold cavity. An ECAP die with a channel intersection angle (φ) and an angle at the arc of curvature (ѱ) where the two parts of the channel intersect 120° and 20° respectively was used in the ECAP process, which was estimated to yield a shear strain of approximately 1.83 for each pass. ECAP process was carried out up to 4 passes at room temperature by route Bc. During the ECAP process a layer of lubricant was applied to reduce the friction between the die and the sample. The solder alloys were cut to smaller pieces using horizontal band saw after ECAP were ground with SiC abrasive paper grit 100 until 2000 before polished using 1 μm alumina powder. Once mirror-like surface was obtained, the samples were chemically etched with 5 % HNO3-2 % HCl-93 % CH3O etching solution to reveal the microstructure before observed using Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray(EDX).

For the electrochemical behavior, the as-cast and ECAPed SAC305 samples were tested by using potentiostat (AUTOLAB PGSTAT). A three-electrode cell composed of the sample as working electrode, Pt as counter electrode, and saturated calomel electrode (SCE) as reference electrode was used for the tests. The as-cast and ECAPed SAC305 discs with exposed surface area of 1.0 cm² were used as the working electrodes. The solder materials were soldered to copper wires with a plastic insulating layer. Then the samples were mounted with epoxy. Surface of samples were prepared via grinding using SiC papers from 600 to 2000 grit. Potentiodynamic polarization tests were carried out at a scan rate of 1.0 mV/min at room temperature (25 ± 0.1°C). Potentiodynamic polarization curves were recorded in the potential range -1000 to +1000 mV vs. SCE. The corrosion experiment was carried out in 3.5 wt.% NaCl solution as electrolyte. The surface morphology and phase analysis of samples after polarization was observed by SEM and XRD respectively.

3. Results and discussion

3.1 Microstructural observation

The microstructure of the as-cast and ECAPed SAC305 of 2 and 4 passes are shown in Figure 1. In Figure 1(a), the as-cast microstructure consists of light areas identified as large β-Sn dendrites and
surrounded by thin, gray network of the eutectic region consisting of Cu$_6$Sn$_5$ and Ag$_3$Sn IMCs within Sn matrix. In the microstructure of as-cast SAC305, the needle or rod like Ag$_3$Sn and irregular but slightly equiaxied shaped Cu$_6$Sn$_5$ can also be found in the β-Sn dendrites. The average grain size of as-cast is 16.8 μm. While the average grain size of β-Sn structure in Figure 1(b) and Figure 1(c) were 6.61 μm and 5.51 μm respectively. The β-Sn structure has been reduced to smaller grains with thinner and more evenly distributed eutectic network following ECAP process. Besides that, Ag$_3$Sn needles were observed to be broken into small fragments and distributed more uniformly within the Sn matrix. Ag$_3$Sn refinement along with finer Sn grains are expected to lead to higher strength of ECAPed solder than the as-cast SAC305 alloy.

![Bulk microstructure of SAC305 solder alloy](image)

**Figure 1.** Bulk microstructure of SAC305 solder alloy (a)(b) as-cast, (c)(d) 2 passes ECAP and (e)(f) 4 passes ECAP.

### 3.2 Potentiodynamic polarization

Potentiodynamic polarization curves of the as-cast and ECAP processed samples were shown in Figure 2. There are no significant differences in polarization curves. For as-cast condition SAC305 there was a passive process beginning at -0.749 V/SCE and extended to -0.415 V/SCE. The passivation process is due to the formation of Sn oxides on the surface [8,9]. The passive behaviour after ECAP condition process of 2 passes occurred at -0.757 V/SCE until -0.397 V/SCE. Further ECAP up to 4 passes seems to enhance the passivation process of SAC305 alloy as the passive behaviour occurs at lower value of -0.743 V/SCE and extended to -0.438 V/SCE. Then, the passivation disappears when a sharp increase of anodic current density occurs due to the breakdown of passive film. As can be observe in Figure 2, the pseudopassivation range value of as-cast SAC 305 solder extends from -0.188 to +0.062 V vs. SCE. In contrast, 2 and 4 passes SAC 305 solder exhibits a pseudopassivation range extending from +0.149 to +0.199 V vs. SCE and +0.095 to +0.241 V vs. SCE respectively when surface film begins to break down in the solution and the anodic current density rises again. Due to a larger pseudopassivation range, the corrosion resistance of 4 passes SAC 305 solder is better than that 2 passes and as-cast condition. The improved passivation behaviour of ECAP processed SAC305 alloy could be due to the small grain size which promotes uniform distribution of the elements and facilitating rapid formation of the passive film [10,11]. The anodic polarization curves show that the corrosion potential ($E_{corr}$) shifts to more noble potential and the corrosion rate decreased from 0.047 mpy to 0.026 mpy with increasing ECAP number of passes up to 4 passes, and
this is shown in Table 1. It can be observed that further grain refinement due to the increased of ECAP number of passes resulted in increased amount of grain boundaries. Therefore, the difference between the rate of anodic and cathodic reactions are expected to alter significantly which leads to more uniform attack and lower corrosion rate [12].

Table 1. Results obtained from potentiodynamic polarization measurements for the as-cast and ECAPed SAC305 solder alloy in 3.5 wt.% NaCl solution

| Samples    | Tafel slope anodic process (Ba) (V/dec) | Tafel slope cathodic process (Bc) (V/dec) | Ecorr (V/SCE) | Icorr (A) | Corrosion rate (mpy) | Polarization resistance (Ω) | jcorr (A/cm) |
|------------|----------------------------------------|------------------------------------------|--------------|-----------|----------------------|----------------------------|--------------|
| As cast    | 0.189                                  | 0.244                                    | -0.749       | 5.71E-06  | 0.047                | 8124.9                     | 5.71E-06     |
| 2 passes   | 0.206                                  | 0.254                                    | -0.757       | 4.16E-06  | 0.033                | 9649.2                     | 4.16E-06     |
| 4 passes   | 0.109                                  | 0.352                                    | -0.743       | 3.32E-06  | 0.026                | 10867                      | 3.32E-06     |

Figure 2. Tafel polarization curves of the as-cast SAC305 solder alloy and deformed by ECAP in 3.5 wt.% NaCl solution

Since all corrosion tests were performed in aerated NaCl solution, the cathodic branch of polarization curves maybe ascribed to the oxygen reduction reaction.

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

From the microstructure shown in Figure 3, it can be observed that the corrosion product on surface of SAC305 samples has needle-like shape. Pits were found on as-cast SAC305 surface as shown in Figure 3(a)(b). EDX analysis at the pit confirmed the presence of corrosion product constituted by tin oxychloride. The corrosion product film for sample with ECAP 2 passes contains many agglomerates and the ones on surface of sample with 4 ECAP passes is uniform and relatively smoother. The corrosion product on the ECAPed 4 passes SAC305 surface was observed to be more compact and better adhered thus providing better corrosion resistance. Both samples of 2 and 4 passes shown in Figure 3(c)(d) and 3(e)(f) respectively seems to have uniform corrosion product covering the surface compared to pitting on surface of SAC305 sample. This could be due to the grain refinement via ECAP process and better distribution of IMC particles that encouraged more uniform attack on the surface.
Figure 3: Microstructure of the corrosion product and EDX spectrum of solder alloy (a)(b) as-cast, (c)(d) 2 passes and (e)(f) 4 passes after the completion of polarization

Figure 4 shows the XRD pattern for as-cast and ECAPed SAC305 solder alloy after electrochemical corrosion tests. Several phases are detected at the exposed surface which are Sn₃O(OH)₂Cl₂, SnO₂, SnCl₂, Cu₆Sn₅, Ag₃Sn and β-Sn. The surface is fully covered with corrosion products of which Sn₃O(OH)₂Cl₂ could be the dominant ones. The formation of oxides of tin may take place through the following reaction [13].

Sn + 2OH⁻ → Sn(OH)₂ + 2e⁻

Sn(OH)₂ → SnO + H₂O

From the XRD pattern, the corroded product on SAC305 is confirmed to be Sn₃O(OH)₂Cl₂ that formed according to following reaction [14].

3Sn + 4OH⁻ + 2Cl⁻ + 6e⁻ → Sn₃O(OH)₂Cl₂ + H₂O

The formation of oxides at the sample surface enhanced passivation and thereby lead to reduction of the corrosion rate. Electrochemically, Ag₃Sn is nobler than Sn. Therefore, if there is an electrochemical coupling between the large Ag₃Sn and Sn phases, large Ag₃Sn plates could acts as a cathode to drive corrosion on Sn phase. For as-cast SAC305, enhanced localized corrosion could occur because of the low area ratio of anode (Sn phase) to cathode (Ag₃Sn phase) in localized regions [15].
Figure 4. XRD pattern of the corrosion products on as-cast and ECAPed SAC305 solder alloys after polarization test in 3.5 wt.% NaCl solution

4. Conclusion

The ECAP process resulted in grain refinement in the SAC305 solder. After anodic polarization in 3.5 wt.% NaCl solution, the ECAPed SAC305 solder had a more adherent and compact surface film of corrosion products than the as-cast solder. 4 passes ECAPed SAC305 solder with Ag$_3$Sn needles break into small fragments exhibited better corrosion resistance than as-cast commercial SAC305. This could be due to the more compact and continuous oxide film containing SnO(OH)$_2$Cl$_2$ and SnO$_2$ formed on the surface of solder preventing further oxidation. The increase of ECAP number of passes increases the corrosion resistance of the SAC305 alloy. The corrosion potential of SAC305 alloy shifts to more noble position with increasing ECAP number of passes from 2 to 4 passes.

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