Post-Corrosion Mechanical Analysis of Sn-Zn Alloys: A Short Review

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Abstract. Renewed interest in investigating and improving the corrosion performance of the Sn-Zn based alloys were ignited as this alloy produces excellent mechanical properties but suffered from corrosion attack. To support the electrochemical investigations, mechanical analysis is normally performed. This article focuses on the most common mechanical analysis used, including the basic experimental setups, common parameters and selected case studies that are beneficial in understanding the corrosion process.

1 Introduction

Since the banned of lead (Pb) from electronic industry, large numbers of Pb-free Sn-based alloys have been developed to find the best replacement for Sn-Pb alloys [1]. To ensure the Pb-free alloys perform reliably during application, several key performance characteristics have been established for example comparable melting temperature with Sn-Pb alloys existing assembly lines, good wettability and solderability, adequate physical properties and most importantly, environmental friendly [2].

Corrosion was never viewed as critical design factor in Sn-Pb systems. This is contributed by the presence of the stable oxide layer on the surface. At the same time, minor differences in galvanic potential in between Sn and Pb allows small driving force for galvanic corrosion to take place [3]. However, the perspective is changed for the Pb-free alloy systems as the presence of various elements to replace Pb altered the corrosion dynamic [4]. Worse, the advanced recent technologies require very small interconnections in sub-micrometre, presence of corrosion agent possibly aggravates the damage caused by corrosion. Tin-Zinc (Sn-Zn) alloys, especially at the eutectic composition of Sn-9Zn was one of the Pb-free alloys that shows good attributes to succeed Sn-Pb alloys as the mechanical properties of this solder are considered good [5]. However, the large differences in potential between Sn and Zn seriously affects the corrosion performance. Majority of Zn-

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rich phase was reported to be selectively etched producing deep, elongated grooves on the surface [1]. This significantly affected the appearance and functionality of the solder. As part of reliability of Pb-free soldering, renewed interest in the corrosive have arisen around the globe. At the same time, subsequent characterisation methods have mainly been practised to support the electrochemical evaluation on Sn-Zn solders. Such common techniques include mechanical analysis.

In general, subsequent mechanical analysis on the corroded Sn-Zn is important as it gives information on the changes impart by the corrosion attack on the alloy. When equipped with microstructure and phase characterizations, mechanical analysis offer insight on the cause of failure analysis. This allows correct prevention or corrective actions to be carried out to improve reliability. Therefore, based on this short review undertaken in this study, post-corrosion subsequent mechanical analysis of tensile strength measurement is discussed regarding the capabilities of the equipment and the experimental parameters commonly used. Selected case studies associated with these methods are also discussed.

2 Mechanical analysis

Solder connections are constantly subjected to mechanical stresses and strains during operations. Therefore, preventive action importantly requires the understanding and information on the mechanical properties of the Sn-Zn solders especially in harsh conditions such as a corrosive environment and so forth. Currently, data on the mechanical properties of the Sn-Zn solder joint after exposure to corrosion are limited, such as the ultimate tensile strength (UTS) and shear strength. The UTS is one of the most crucial properties for solders. During application, tensile loading through mechanical handling causes bending to the solder joint [2]. In this case, to determine the UTS for bulk Sn-Zn solders, strain rates used are different, for example 0.9 mm/min [6], 3.33 x 10^{-4} to 3.33 x 10^{-3} [7], and 10^{-4} to 10^{-2} s^{-1} [8]. The size and shape of the specimen also varied. For instance, Chen et al. [9] used a rod-shaped sample with 16 mm gauge length and 4 mm diameter. Meanwhile, Kim et al. [10] prepared a dumbbell-shaped sample of 25 mm gauge length, 8 mm width and 1 mm thickness. In forming the joint, Cu and Al are among the substrate choices used [11-13]. A butt joint for determining the UTS can be prepared with the Sn–9Zn solder positioned between the Cu plates [14](Fig. 1a). The clamped sample, in this case, is heated at 250 °C for 10 s along with the application of ZnCl-based flux, producing the bond for the end Cu/solder/Cu joint product (Fig. 1b). A crosshead speed of 2 mm/min is then preferably applied to evaluate the tensile strength of the joint [14]. In determining the shear strength, the lap joint is used, adding spacers and a reflow oven for reheating (Fig. 1c), as compared to the butt joint formation [15]. For the measurement of shear strength, the shear speed of 0.3 mm/min or equivalent to a shear rate of 10-2 s^{-1} was reported to be used [12].
Fig. 1. Schematic diagram of (a) Cu/Sn-9Zn/Cu butt joint arrangement. Reprinted with permission from Ref. [14] and (b) example of Cu/Sn-9Zn/Cu butt joint.

As an example, for the Cu/Sn-9Zn/Cu butt joint, UTS of 45.9 MPa was reported. These values were in the common UTS range for the Sn-9Zn joint (30-80 MPa) [6, 9, 10]. The UTS dropped to 36.4 and 29.5 MPa (Fig. 2) after polarisation in 6 M KOH. The corroded joint also undergoes lesser elongation thereby reflecting a reduction on the ductility. Such reduction in the UTS coop well with the severity of crack initiation points due to the dissolution of Zn and cracks propagations throughout the joint, which explain the failure mechanisms (Fig. 3) [14]. Changes in the ratio of galvanic coupling (between the Sn and Zn) in the solder is a further factor that contributes to the corrosion tendencies of the solder joint [15].

Fig. 2. Stress-strain curve of the Cu/Sn-9Zn/Cu joint before and after polarisation Reprinted with permission from Ref. [14].
In a separate report, elastic regions from the stress-strain curve for Cu/Sn-9Zn/Cu joints were significantly influenced by the duration of exposure (1, 7, 14, 21 and 18 days) in 3.5 wt. % NaCl (Fig. 4a) [16]. In this case, the length of the flow hardening regions significantly decreased as the immersion time increased and the reduction in the shear strength values correlate well to the severity of the corrosion attack (Fig. 4b).

With the aid of the micrographs and images, changes on the fracture behaviour before (ductile) and after (brittle) corrosion attack are easily explained (Fig. 4c-d). In another case, the higher shear strength of 128.5 MPa was reported for the as-prepared Cu/Sn-9Zn/Cu lap joint [17]. After exposed to 3.5 wt. % NaCl, the shear strength significantly reduced to 70.97 MPa. Again, with the aid of using a micrograph and images, pit formation is noticeable which signals weakening on the structural integrity of the joint. Such selective attack (causing pits) were mainly associated with the dissolution of Zn, which upon shearing caused multiple dimples to occur thereby indicating ductile fracture behaviour [12].

**Fig. 3.** SEM micrographs of polarised Cu/Sn–9Zn/Cu joints. Reprinted with permission from Ref. [14]
Fig. 4. The (a) stress-strain curve of the Sn-9Zn lap joint, (b) the ultimate shear strength of the Sn-9Zn lap joint, (c) the fracture micrographs of the Sn-9Zn lap joint before corrosion and (d) the fracture micrographs of the Sn-9Zn lap joint after corrosion. Reprinted with permission from Ref. [16].

3 Conclusion

As a subsequent testing to support electrochemical investigation, mechanical analysis required relatively simple set-up. Removal of active material (zinc) during corrosion process was found to significantly affect the mechanical integrity by allowing crack propagations in the solder and reduces the ductility. Furthermore, the duration of exposure also affects the flow hardening region in shear strength. This leads to brittle fracture. For consideration in future research work in post-corrosion study, the effect of solidification time on the grain size and corrosion resistance and modelling/simulations on predicting the corrosion performance should provide insightful discussion.

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