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Effect of sample perimeter and temperature on Sn–Zn based lead-free solders

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Abstract

This paper presents studies conducted on Sn–40Pb, Sn–9Zn and Sn–8Zn–3Bi lead-free solders for electronic applications. Differential Scanning Calorimeter (DSC) profile and the microstructure of the solders were discussed. The wettability between different copper perimeter and molten solders with the presence of flux at 250 °C was investigated. The withdrawal force divided by the sample perimeter was used to calculate the surface tension of the molten solders. The wetting properties of the solders were tested at different temperatures using two types of fluxes. The surface tension of Sn–40Pb, Sn–9Zn and Sn–8Zn–3Bi solders was 0.357, 0.481 and 0.4523 N/m, respectively, and these values showed good agreement with reported data. The Cu_6Sn_5 IMC phase was formed between Sn–40Pb solder and Cu substrate. The Sn–9Zn solder exhibits Cu_6Sn_5 and γ-Cu_5Zn_8 phases with Cu substrate while Sn–8Zn–3Bi solder forms a mixture of Cu–Sn + Cu–Zn phase as a first layer from the solder and γ-Cu_5Zn_8 phase as a second layer next to the Cu substrate. For Sn–8Zn–3Bi solder the MHS flux improves the wetting force and contact angle at higher temperatures. Increase in sample perimeter has no effect on contact angle but the addition of Bi to the Sn–Zn system reduces the surface tension and contact angle.

Keywords: Lead-free solders; Wettability; Surface tension; Contact angle; Intermetallic

1. Introduction

Sn–Pb solders have been the most important material for the interconnection in electronic components. It is used because it is cheap and has good material properties. However, due to environmental and health concerns alternative solder alloys are needed. So, the development of a good Pb-free solder which is environmentally friendly materials is a great challenge.

There are many candidates' alloys being considered as replacements for Sn–Pb solders. Binary alloys investigated include Sn–Cu [1], Sn–Ag [1,2], Sn–Bi [3] and many others. Ternary alloys of Sn–Ag–Cu [4,5], Sn–Zn–Ag [6] and Sn–Zn–RE [7] also have been reported. Of these, the Sn–Zn system has been expected to be one of the best alternative choices for Sn–Pb replacement because of its melting temperature close to that of Sn–Pb (183 °C) eutectic alloy, so that existing production lines and electronics components do not require major modifications [8,9]. Apart from its favourable melting temperature, its mechanical properties, e.g. tensile strength, are better than that of the Sn–Pb [7]. But the Sn–Zn alloys are susceptible to oxidation and corrosion. Therefore, alloying Bi to Sn–Zn near eutectic alloy could improve the soldering properties by lowering the melting temperature [10]. Although the Sn–Zn system appears to be an attractive one, the wetting on Cu substrate is poor when utilized with fluxes used for Sn–Pb solders [11,12]. The used of a stronger flux in Sn–Zn alloy soldering may become a potential problem in the application of those alloys due to the removal of flux after soldering. So, a flux specially designed for Sn–Zn system is indeed needed.

The selection of the flux plays a critical role in determining the manufacturing yield and product reliability of electronic assemblies. Fluxes are used to remove oxides and other contaminants from the surfaces to be soldered. They inhibit the reoxidation of these surfaces while assisting in the transfer of heat. Fluxes enhance the flow of solder and help wet the solid

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surface by lowering the surface tension between the molten solder and the metal surface [13].

Pb-free solder materials require a low melting point, mechanical reliability, and a good wetting property. In wettability evaluation that determines whether a Pb-free solder alloy can be used as a solder, results and rates of the wetting are obtained using various methods such as area of spread method, edge dip method, rotary dip method, globule method, and wetting balance method. Among these methods, wetting balance is the most versatile solderability method, which is suited to the quantitative investigation of the solderability of specimens in any shape [14]. Most of the studies about Pb-free solders are based on the results of wetting balance test which give rise to maximum wetting force, withdrawal force and wetting time for wetting property evaluation. However, it is difficult to compare among studies directly because each study has its own standard, different test conditions and analysis.

Many studies have been performed to determine meaningful values of the force–time curve which evaluated almost every aspect of wetting balance test. However, the withdrawal force curve from the force–time curve has not been fully analyzed yet. The mechanism of withdrawal force as well as the time and force indices were described and reported for Sn–37Pb and Sn–3.5Ag solder alloys [15]. In that paper, the author varies the sample perimeter and used the wetting force equation to calculate the surface tension of the solders. Lin and Chen [16] applied the wetting balance method to investigate the effect of different fluxes on the wetting of Ni–Cu–P deposit by the In–Sn solders. Vianco and Rejent [17] used it to study the wettability of Sn–Ag–Bi solder alloys. In our previous work [18,19] we used the wetting balance to study the influence of fluxes and time on wetting force for Sn–Zn–Bi system solders.

Since lead-free solders are Sn based, the common intermetallic compound layers formed when they are soldered with Cu are Cu_3Sn and Cu_6Sn_5. According to Suganuma et al. [9], for Sn–Zn based solder, the reaction with Cu produces three sub-layers. From the solder side, they are γ-Cu_5Zn_8/β'Cu–Zn/ a thin unknown Cu–Zn phase, respectively. In another study [20], the transformation from Cu–Zn IMC to Cu–Sn has been reported. Chang et al. [6] shows the XRD pattern of the IMCs formed at the interface between Cu substrate and the Sn–9Zn solder as γ-Cu_5Zn_8 and η-Cu_6Sn_5 which are the same as reported by Yu et al. [21]. Although the Gibbs free energy of γ-Cu_5Zn_8 is lower than that of η-Cu_6Sn_5, the planar γ-Cu_5Zn_8 IMC formed close to the Sn–9Zn solder while the isolate-shaped η-Cu_6Sn_5 IMC formed close to the Cu substrate after aging at 150 °C for 600 h [21].

In this work DSC was used to study the melting temperature of the solders. Wetting balance was used to study the effect of sample perimeter on the withdrawal force and contact angles at 250 °C. It was also discussed if it is possible to calculate the surface tension of the solders based on these results and some literature values of the surface tension were produced as comparison. The formation of IMCs between the solders and the Cu substrate were discussed. The effect of different solder temperatures and fluxes on wetting force and contact angle was studied. Sn–9Zn and Sn–8Zn–3Bi solder alloys were used and Sn–40Pb was used as a reference.

2. Wetting balance theory

The dipping test using wetting balance measures the forces imposed by the molten solder on the test specimen as the specimen is dipped into and held in the solder bath. The wetting force is measured as a function of time and is plotted. Three of the most commonly applied wetting indices are the wetting time (t_o), the maximum wetting force (F_{max}) and the withdrawal force (F_w). A typical wetting curve is shown in Fig. 1 [22]. The wetting time, t_o, is the moment when the wetting force is equal to buoyancy force and at this moment the measured wetting force is zero. The wetting force (F_{max}) achieved after a specific time has the most practical significant because this specific times are comparable to the soldering times applicable to automated soldering [15].

When the substrate was dipped into the molten solder, the maximum wetting force (F_{max}) is achieved after a stable state. In a static equilibrium conditions, the wetting force, F, can be expressed as follows:

$$F = P\gamma\cos\theta - \rho g V \quad (1)$$

where P is the perimeter of the specimen, γ is the surface tension of the solder in contact with the flux, θ is the contact angle, ρ the density of the solder, g the gravity acceleration constant and V an immersed volume.

The steep rise to the withdrawal force curve means increase of buoyancy force by withdrawal process, and the top point shows that sliding solder along the side of the sample meets the bottom corner, and contact angle falls down to zero. After this, interface between the solder and the sample changes from side edge to the bottom edge of the sample, and test ends when necking of the solder, leads to the detachment between the solder and substrate. By applying the above theory and using Eq. (1), the force at the

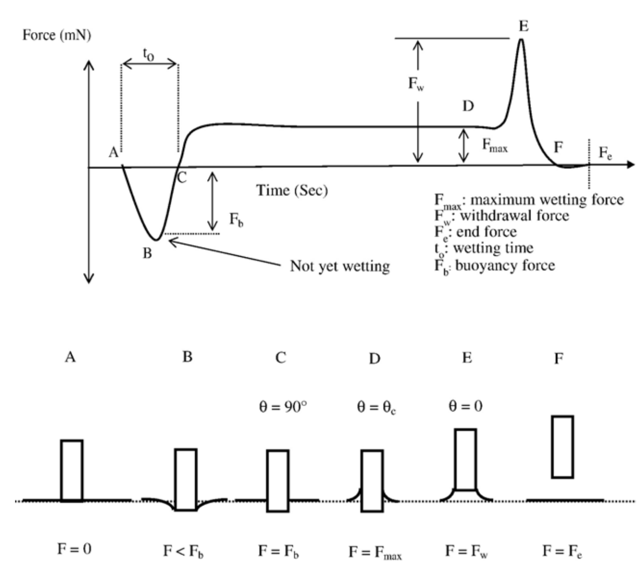

Fig. 1. A typical wetting curve and wettability indices.