Solder Joint Structure of Sn-58Bi Solder Paste with Epoxy-based Flux

Qingyang Li, Xiaojun Yang and Chengfei Li
College of Material Science and Engineering, Beijing University of Technology, Beijing, China
E-mail: yangxj@bjut.edu.cn

Abstract. Non-clean soldering technology and low temperature bonding will be of great significance for applications in electronic industry. A curable solder paste containing epoxy-based flux and Sn-58Bi solder powder was developed. The solder joint covered by cured epoxy shell can be obtained by soldering process. The thermal-curing process of the curable flux was monitored by DSC to ensure the wetting and metallurgical connection between Sn-58Bi and Cu substrate. The microstructure characteristics of the solder joints were analyzed by metallurgical analysis and SEM observation. The factors influencing the structure of the solder joints were analyzed and discussed.

1. Introduction

In conventional soldering process, flux is generally used to reduce the oxidation of the solder and the substrates to assist the wetting. However, the unavoidable post-processing residuals of flux should be cleaned to eliminate the unfavorable effects on the reliability of electronic devices. And the cleaning process makes the soldering technology more complicated, and the cost correspondingly increased. In the SMT process, the cleaning process of flux residue is getting difficult due to the decrease of interconnection pitch. Thus, a non-clean soldering technology will significantly provide a great impact to the industry.[1-2]

Sn–Bi alloys were studied for its promising application to realize low temperature bonding in electronic industry. Sn-58Bi eutectic alloy has a relatively low melting point of 138.9 °C, making it more suitable for the temperature-sensitive substrates.3-4 But due to their low mechanical properties, the applications were limited to the fields that did not require much mechanical or thermal performance. In addition to the additive alloying elements such as Ag, Cu and In, used to improve mechanical properties and thermal aging resistance through a combination of solid-solution strengthening, precipitate hardening, grain or microstructure refinement and diffusion modifiers, the use of curable resin flux instead of rosin was also considered to be helpful to the thermal cycling reliability and the reinforcement of the shear strength of the solder joints.[2-3,5-8]

In this study, a curable solder paste containing epoxy-based flux and Sn-58Bi solder powder was developed, the cross-section microstructure of the solder joints on Cu substrate were observed by optical microscope and SEM (scan electron microscope). The microstructure characteristics of the solder joints were analyzed in connection with the reflow temperature, which might be the most important factor that have significant impact on the thermal-curing process of the curable flux, as well as on the wettability of the solder alloy and its metallurgical bonding with the Cu substrate.
2. Experimental

2.1. Materials
The solder paste is prepared by the mechanical blending of the curable flux and solder alloy. The curable flux consists of bisphenol A epoxy resin, the curing agent and catalyst, carboxylic acids as reducing agent to remove the oxide layer on solder and Cu substrate, and other additives to improve the processability of the solder paste. The epoxy resin and the curing agent were mixed at the stoichiometric ratio. The weight ratio of carboxylic acids in the curable flux was adjusted according to the wettability of the solder paste on Cu substrate. The solder alloy used is Sn/58Bi powder with an average diameter of 20 μm. The solder pastes with different weight ratios of Sn/58Bi powder and curable flux were prepared. The chemical and metal components were purchased from commercial sources and used as received.

2.2. Experiment
The thermal-curing process of the curable flux was monitored by differential scanning calorimetry (DSC, NETZSCH 200PC) at a heating rate of 20 °C/min under argon atmosphere. The melting point of the solder alloy Sn/58Bi powder was monitored by DSC at the same heating rate under argon atmosphere. The preheating temperature and heating rate of the hot plate for soldering process on Cu substrate was determined according to the DSC curves of the curable flux and solder alloy. The microstructure of the solder joint was analyzed by metallurgical analysis of the cross-section structure of the samples mounted in cold-mount epoxy. The cross-sectional structure was obtained by mechanical grinding and diamond polishing of the mounted sample.

3. Results and Discussion

3.1. Macroscopic Morphology of the Solder Joints on Cu Substrate
Figure 1(a) shows the schematic structure diagram of the solder joints formulated by reflow process of the curable solder paste containing epoxy-based flux and Sn-58Bi solder powder. The epoxy-based flux has more advantages than the conventional rosin-based flux. First, no more volatile organic solvent is needed for epoxy-based flux, because of the proper viscosity and processability of the uncured epoxy resin at room temperature. Second, the cured epoxy shell acts as a dense protective layer for oxidation of solder joint, thermal reliability of the solder joints could be improved due to the inert character of crosslinked structure of cured epoxy resin. At the same time, cleaning process is also unnecessary.[8]

Figure 1(b) is the photograph of the solder joint. It shows that the solder alloy is covered by the film of cured epoxy, and the outer fringe of the joint is surrounded by cured epoxy resin, which provides additional bonding strength for solder joint connection.

![Figure 1. Schematic structure diagram (a) and photograph (b) of the solder joints.](image_url)

3.2. Thermal Curing Behavior of the Curable Flux
The DSC curves of the epoxy-based fluxes are shown in Figure 2. Three kinds of epoxy-based fluxes with different composition are expressed as EP-FLUX-1, EP-FLUX-2 and EP-FLUX-3, respectively.
The initial curing temperature can be obtained from the curve, which corresponds to the beginning of the crosslinking reaction of epoxy resin. The initial curing temperature and peak temperature of the three epoxy-based fluxes are listed in Table 1.

![DSC curves of the epoxy-based fluxes and solder paste](image)

**Figure 2.** DSC curves of the epoxy-based fluxes and solder paste

As shown in Figure 2(a), the curing temperature of EP-FLUX-1 is above 200 °C, which means that the soldering piece should be kept above 200 °C for a period of time to ensure the curing of the epoxy resin. It is obviously not suitable for use in curable solder paste. Compared with EP-FLUX-1, the initial curing temperature of EP-FLUX-2 decreased by nearly 50 °C. However, it is still more than 15 °C higher than the melting point of Sn-58Bi solder alloy. In addition, with the increase of heating rate from 10 to 20 °C/min, the initial curing temperature of EP-FLUX-2 increased by more than 10 °C, as shown in Figure 2(a) and 2(b). As indicated by the arrow in Figure 2(b), there is a small exothermic peak at about 140 °C, which is attributed to the curing reaction between the acid and the epoxy resin in the flux. The initial curing temperature of EP-FLUX-3 decreased by 8 °C, as shown in Figure 2(b). It can be explained by the higher acid content in EP-FLUX-3. DSC test for the solder paste prepared by EP-FLUX-2 and Sn-58Bi with the weight ratio of 1/9 was conducted. The solid curve in Figure 2(c) showed that the melting peak of Sn-58Bi in solder paste shifts slightly toward high temperature, and the peak value is a few degrees higher. It can be considered that the liquid organic component provides a thermal barrier between Sn-58Bi particles. According to the DSC results, as shown in Figure 2(d), the initial curing temperature of EP-FLUX should be higher than 150 °C, so as to ensure that Sn-58Bi can be melted completely before the curing of epoxy resin, to avoid the obstruction of crosslinked epoxy resin to the spreading of molten solder on Cu substrate.
Table 1. Composition and initial curing temperature of the epoxy-based fluxes

| Composition of EP-FLUX (phr) | Thermal curing behavior (°C) |
|-----------------------------|-----------------------------|
| Epoxy          | Curing agent | Catalyst | Carboxylic acid | Initial temperature | Peak temperature |
| EP-FLUX-1     | 1            | 0.8      | 0      | 0.08      | 213               | 251               |
| EP-FLUX-2     | 1            | 0.8      | 0.001  | 0.08      | 164(178)          | 185(202)          |
| EP-FLUX-3     | 1            | 0.8      | 0.001  | 0.16      | 170               | 205               |
| Solder paste  | EP-FLUX-2/Sn-58Bi (1/9) | | | | 147 | |

3.3. Microstructure of the Solder Joints on Cu Substrate

![Cross-section structure of the solder joints](image)

The cross-section microstructure of the solder joints of the curable solder paste EP-FLUX/Sn-58Bi was analyzed by metallurgical analysis and SEM observation, as shown in Figure 3 and Figure 4. Several typical solder joint structures of the EP-FLUX/Sn-58Bi solder paste on Cu substrate are shown in Figure 3(a)-(f), which are closely related to the solder process parameters, such as preheating temperature and heating rate of the hot plate for soldering process. The evaluation of solder joints includes porosity, wetting angle on Cu substrate, and the amount of dispersed solder particles in epoxy resin shell. The solder paste used in the experiment is composed of EP-FLUX-2 or EP-FLUX-3 and Sn-58Bi powder. The weight ratio is 1:9, which is expressed as EP-FLUX-2/Sn-58Bi(1/9) or EP-FLUX-3/Sn-58Bi(1/9).

Table 2. Solder paste and solder process parameters corresponding to the solder joints in Figure 3.

| Solder paste | Range of temperature(°C) | Heating rate(°C/min) | Solder joint in Fig. 3 |
|--------------|--------------------------|----------------------|-----------------------|
| EP-FLUX-2/Sn-58Bi(1/9) | 30-130 | 50 | (a) |
|               | 130-190                  | 20                   | (b) |
|               | 130-150                  | 20                   | (c) |
|               | 150-190                  | 10                   | (d) |
|               | 130-190                  | 10                   | (e) |
|               | 140-180                  | 20                   | (f) |
| EP-FLUX-3/Sn-58Bi(1/9) | 180 | 1 min(constant) | (e) |

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Figure 4. SEM images of the solder joints.

It is supposed that the porosity could be reduced by increasing the preheating temperature to above 140°C under the experimental condition, as shown in Figure 3(e) and 3(f). This kind of influence can be analyzed from two aspects. On the one hand, with the increase of the temperature (below the melting point of the solder), the viscosity of the flux decreases, the solder particles are deposited on the copper substrate to separate the organic components from the solder paste. It can be observed that the top layer becomes transparent. On the other hand, the thermal curing reaction of epoxy resin is also carried out at the same time, which reduces the fluidity. The higher the temperature, the faster the curing reaction and the more obvious the effect. The thoroughly separation of solder and organic components is expected to obtain defect free solder joint. Therefore, the initial curing temperature of the epoxy-based flux should be at least higher than 150 °C, so as to ensure the direct contact between Sn-58Bi and Cu substrate, to realize metallurgical connection. For the heating rate of hot plate in the experiment, 20°C/min is better than 10 °C/min. It is also to reduce the adverse effect of the curing reaction of epoxy resin.

The microstructure of the solder joints in Figure 3(c) and 3(e) was also observed by SEM, as shown in Figure 4. It can be observed that the solder joint is completely covered by the cured epoxy, and at the border of the solder joint, epoxy is bonded to Cu substrate. It is also found that the solder particles dispersed in the epoxy shell have an adverse effect on the strength of the shell. The typical metallurgical structure of Sn-58Bi alloy is observed in Figure 4(A2) and 4(B2). No obvious pores and other defects were observed in the interface structure.

4. Conclusions
A curable resin flux instead of rosin was used to develop the curable solder paste, which is composed of epoxy-based flux and Sn-58Bi solder powder. The microstructure of the solder joint was analyzed, and the influence of soldering parameters was discussed. The solder joint covered by cured epoxy is inert to the environment and need not to be cleaned. The cured epoxy is bonded to Cu substrate at the border of the solder joint, which provides additional bonding strength for solder joint connection. It is expected to have better thermal reliability and higher shear strength than the conventional solder joints.
5. References

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