

Influence of Flux on Wetting Behavior of Lead-Free Solder Balls during the Infrared-Reflow Process

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The effects of two different fluxes (A6 and B6) on the wetting performance of Sn-3.5Ag-0.5Cu lead-free solder balls were investigated during the reflow process. Solder ball wetting behavior in real time via an optical microscope coupled with a video recorder during the reflow process was studied. The lead-free solder balls started to melt and wet at 210°C by using A6, which is 8°C lower than the melting point (218°C) of the solder material used. The wetting performance of the lead-free solder ball was dramatically enhanced by using A6. The wettability test indicated that the height of the solder ball after the reflow process with flux A6 was significantly lower than that with B6. It was found that strong fluxing capability caused these phenomena.

Key words: Temperature cycle test, flux, lead-free solder (Sn-3.5Ag-0.5Cu)

INTRODUCTION

In recent years, environmental issues have had an ever-increasing influence on the selection of green materials and processes in surface mount technology. Many studies have been carried out on lead-free solders,^{1–4} to replace the lead-bearing solder. Along this trend, it has been predicted that the current lead-containing soldering interconnection technology in the advance integrated circuit (IC) assembly will be gradually replaced by lead-free soldering technology. The Sn/Ag/Cu alloy is one of the materials with the greatest potential being used in the future solder joint.

Soldering with fluxes has been practiced for thousands of years by artisans and metal workers, but only began developing as a technology with the industry revolution.^{5,6} A flux is considered as a catalyst that lowers the surface tension between the molten solder and a metal surface.⁷

There are three basic flux formulations: (1) no-clean, (2) rosin, mildly activated (RMA), and (3) water-washable. The “no-clean” formulations are mild activity fluxes that produce postsoldering residue, which is both nonconductive and noncorrosive. Therefore, the residue can be safely left on the assembly with no corrosion concern, and cleaning is not required. No-clean

flux residues can be removed after soldering if desired. Cleaning procedures are generally similar to RMA flux residue removal. The RMA formulations were the precursor to no-clean formulations. However, the RMA flux residues may be conductive or corrosive after soldering. Removal of the flux residue is recommended. The RMA flux residues, being rosin based and organic in nature, are generally removed with a solvent/saponifier. The “water-washable (soluble)” fluxes are higher activity fluxes designed for removal after soldering. The flux residue is cleanable using water. The water is typically heated and used in a pressurized spray. Water-washable flux residues are corrosive and conductive after soldering; therefore, removal is mandatory.

In reality, the chemistry of flux interactions at oxide surfaces is complicated and involves acid-base, oxidation-reduction, and coordination-type and adsorption-type reactions.^{8–10} Most fluxes react as Bronsted–Lowry acids with metallic oxides to form their respective salts and water, and the salts serve as surfactants that promote solder wetting.⁸

Some research has reported the flux influence on lead-free solder wetting behavior on different surface roughness Cu plating¹¹ and flux residue on ionic migration.¹² The cleaning flux residue of lead-free solder pastes is more challenging than that of Sn/Pb systems. This is primarily due to (1) higher reflow

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Wetability test on Cu plate

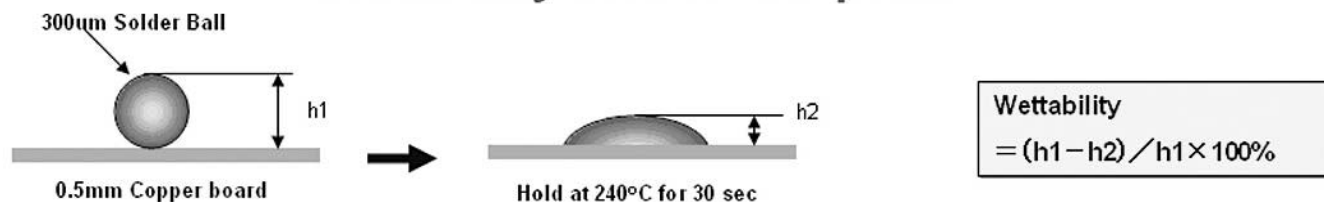


Fig. 1. Schematic illustration of the wettability test method.

temperature, (2) higher flux capacity (therefore higher flux-induced side reactions), and (3) more tin-salt formation in lead-free solder ball placement.¹³

In this paper, the effect of two different types of fluxes on lead-free solder wetting was investigated. Wetting behavior of the solder ball with the flux during the IR reflow process was examined. The phase transition of metal lead-free solder ball, the thermal behavior, and the fluxing capability of fluxes during the reflow process for understanding the lead-free solder ball wetting mechanism were discussed.

EXPERIMENTAL PROCEDURE

Sn-3.5Ag-0.5Cu solder balls (0.30 mm in diameter) and two fluxes (A6 and B6) were used as the lead-free solder ball and flux, respectively. The eutectic temperature of the lead-free solder was measured as $217^{\circ}\text{C} \pm 1^{\circ}\text{C}$ by a differential scanning calorimeter (DSC, Perkin Elmer) at a heating rate of $10^{\circ}\text{C}/\text{min}$. The physical and chemical properties of the two fluxes donated by two different vendors are shown in Table I. Flux A6 has a lower viscosity and tackiness than Flux B6 and both the fluxes are water soluble. Gas chromatography-mass spectrometry (GCMS, Perkin Elmer) was used to characterize the chemicals of the fluxes. The bismaleimide triazine substrate with a ball pad opening 0.25 mm in diameter was used to observe the solder ball placement mechanism during the infrared (IR)-reflow process.

The typical lead-free reflow profile (TLFRP) was used to study the flux decomposition and lead-free solder ball phase transition, which is shown in Fig. 2. In order to investigate the evolution of solder wetting during the heating and cooling processes under the TLFRP condition, an optical microscope combined with a heating stage and a video-recording unit was used.

After the reflow process, the specimens were washed by 50°C deionized (DI) water for 5 min, and

they were then inspected by scanning electron microscopy (SEM). A thermal-gravimetry analyzer (TGA) was used to obtain weight loss for the fluxes. Differential scanning calorimetry was also used to analyze the melting peak of one lead-free solder ball with two kinds of fluxes.

Wettability of the solder balls was determined by measuring the height of a solder ball before and after the reflow process, as shown in Fig. 1. A Cu plate was used as a wetting substrate, which was aged by water steam for 2 h, followed by heating at 240°C for 30 sec, and then cooled to room temperature. After the wettability test, the substrate was washed by 50°C DI water for 10 min.

Electron spectroscopy for chemical analysis (ESCA) was used to analyze the depth profile of oxidation layers on the surface of the as-received solder ball and the solder ball with the two fluxes after the reflow process.

RESULTS AND DISCUSSION

Wetting of Lead-Free Solder Balls with Fluxes

Figure 2 shows the DSC profiles of the lead-free solder ball under the TLFRP. It can be seen that the melting range of the lead-free solder ball was from 221°C to 228°C and solidification ranged from 188°C to 194°C . From this result, it was found that the reflow peak temperature design should be higher than 228°C . A higher peak temperature easily induces higher possibility for package warpage and lesser flux residual. This would be more critical in the lead-free solder process than in the tin-lead solder process, due to the higher reflow peak temperature in the reflow process. Thus, the DSC results can be a reference to determine the lowest reflow peak temperature design for the lead-free solder process.

The size of grains in solder materials can be controlled by the cooling rate; a faster cooling rate induces a finer structure, resulting in higher initial solder ball shear strength and temperature cycle reliability performance. However, too fast cooling brings serious residual stress that causes the solder masking chipping on a substrate during the following wafer singulation process. Using the above principle and concept, the solder ball microstructure and the initial ball shear strength should be controlled by designing the cooling rate properly. In summary, the upper limit of the solder melting temperature and the solidified temperature range are very

Table I. Properties of Fluxes Used

| Properties | Flux A6 | Flux B6 |
|------------------|------------------------|-----------------------------|
| Appearance | Deep amber or deep red | Slightly light yellow paste |
| Viscosity (Pa·s) | 6 | 22 |
| Halogen | 20 or less | 20 or less |
| pH | 3.5 | 4.5 |
| Tackiness (gr) | 15 | 130 |

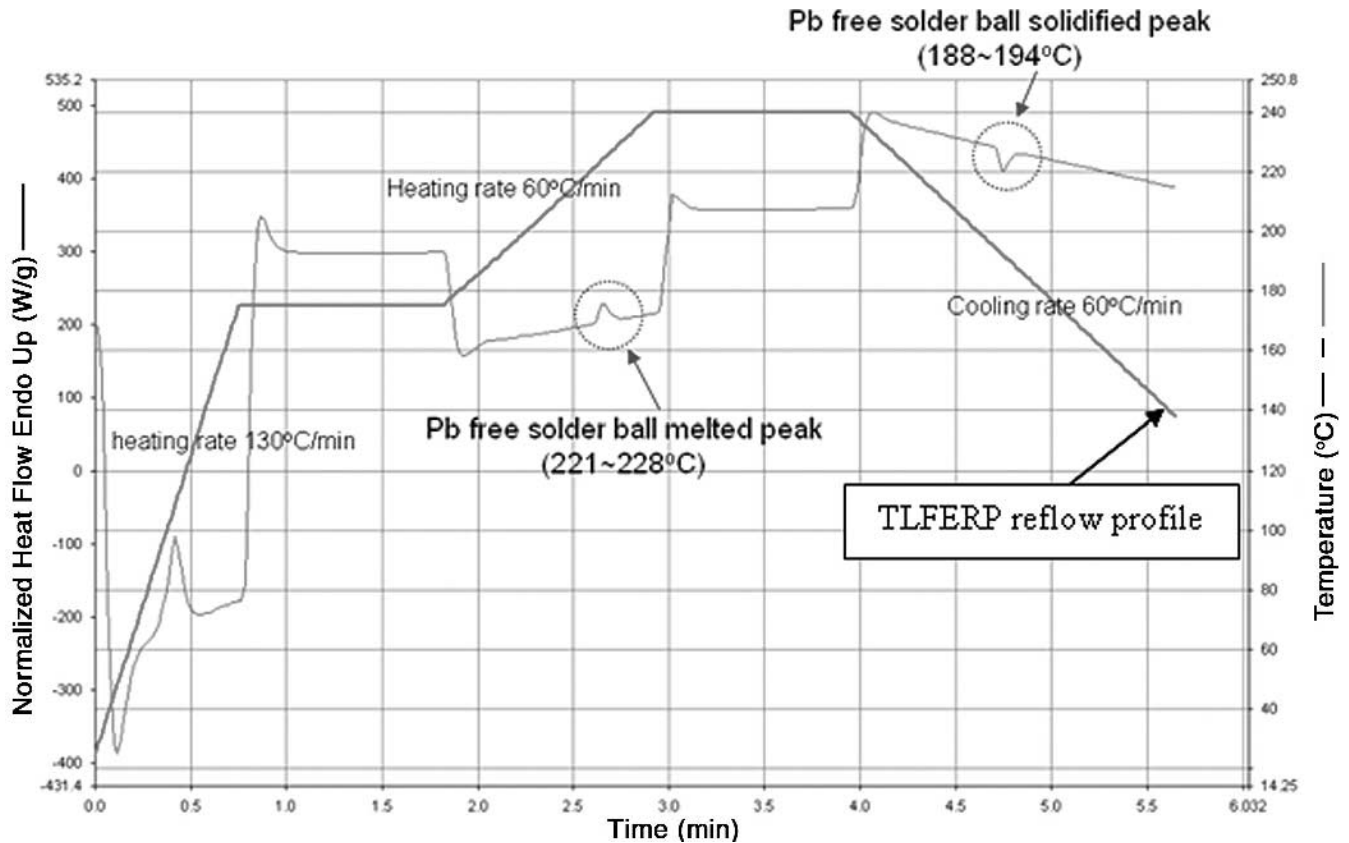


Fig. 2. DSC profiles for the lead-free solder ball under TLFERP. The solid line is the TLFERP reflow profile.

important to control the wetting and solder ball strength during the reflow process.

Figure 3 shows the top views of the solder ball with the two fluxes, A6 (Fig. 3a–c) and B6 (Fig. 3d–f), during the wetting test under the reflow condition. It can be seen that the spherical solder ball was melted and wetted on the ball pad, with increasing temperature. Two dotted circles are added on the photo (Fig. 3a) to clearly indicate the boundary of the solder and the bond pad area on the top views. In the case of A6, there is still a gap between the solder ball and the bond pad areas at 210.1°C. As the temperature reached 210.8°C, the gap became filled with the solder due to the occurrence of solder partial melting and wetting (Fig. 3b). Figure 3c shows the solder regime fully occupied by wetting. Interestingly, the solder ball, which has a melting point of 217°C, with the flux A6 started to partial melt and wet below 211°C.

Unlike flux A6, B6 did not show improved wettability. Although the temperature increased, the gap between the solder ball and the pad area still remained (222.7°C, 239.5°C, and 240°C), as shown in Fig. 3d–f. It can be seen that the solder ball wetted well on the pad surface at 240°C.

The fluxes used were characterized by using GCMS, and their possible chemicals are shown in Fig. 4a and b. Flux A6 is believed to contain over three different chemicals with alcohol and carboxylic functional groups, while B6 possesses mainly one

type of chemical with alcohol groups. Flux A6 is likely stronger acid and provides higher etching capability than B6. This is in agreement with pH values data, as shown in Table I. Thus, it is postulated that A6 could more actively etch the oxide layer than B6 below the lead-free solder ball melt point during the reflow process.

Figure 5a shows a SEM photo of the as-received solder ball, and Fig. 5b and c a bird's-eye views of the solder balls with two fluxes after the reflow process. It can be seen that more solder materials wetted on the pad surface with A6 than with B6, shown as Fig. 5b and c, respectively. This is in good agreement with the top view test during the reflow process, as shown in the Fig. 3.

It can also be seen that B6 had more flux residues than A6; after the reflow process, the residues were supposed to be removed during the rinsing process. However, it was found that after rinsing, the Flux B6 system exhibited much more residual flux than the Flux A6 system (Fig. 5c and b). Flux A6 showed better wetting than B6. This may be associated with the surface morphology of the lead-free solder ball after the reflow process. The lead-free solder ball surface with dendrite texture is oxidized during the reflow process; if the flux cannot protect the solder surface from oxidation and remove the thickened oxidized surface layer, then the dendrite texture will remain after the reflow process. As shown in Fig. 3c and d, the dendrite on the solder surface had been

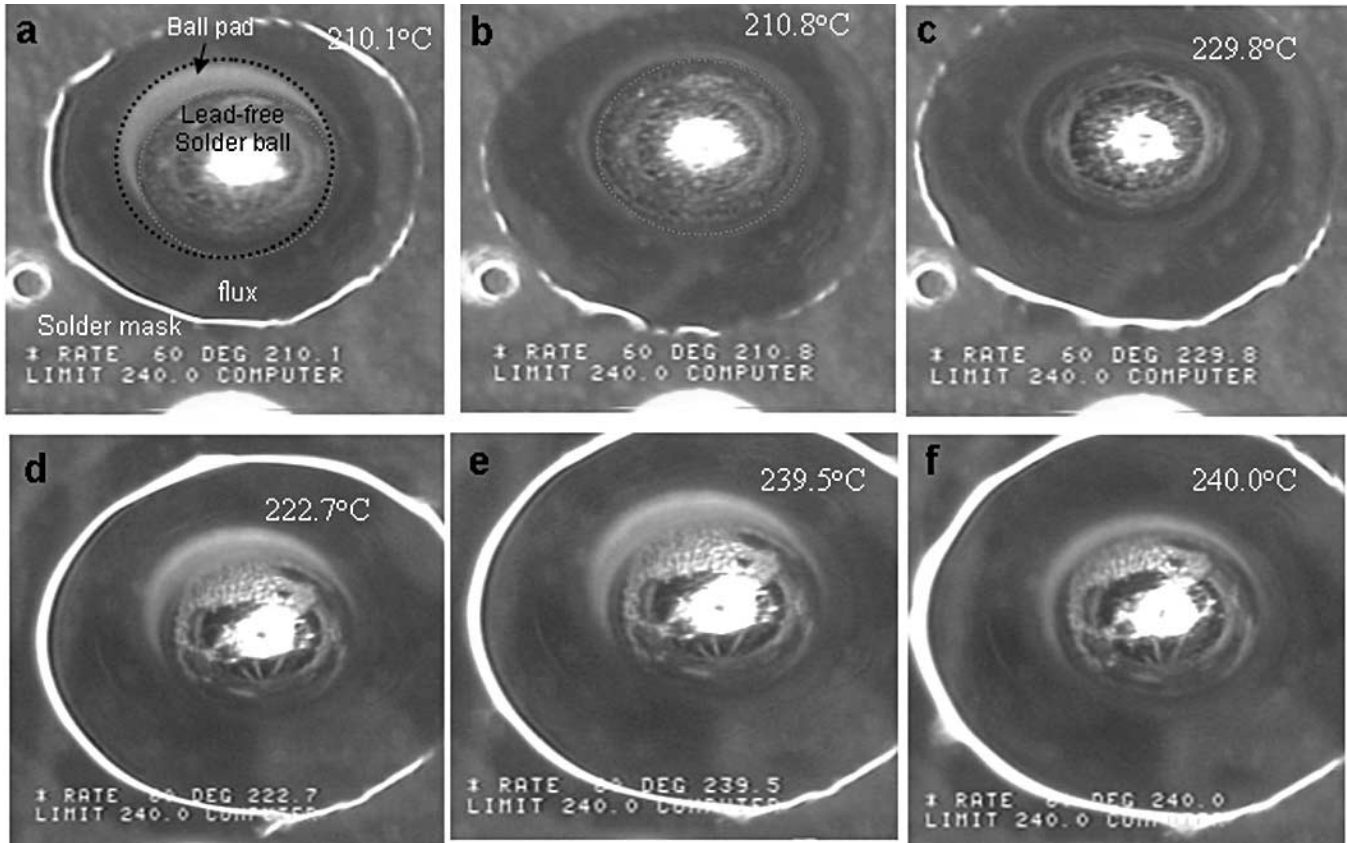


Fig. 3. The solder ball melting evaluation in the (a)–(c) Flux A6 and (d)–(f) Flux B6 system during the reflow process; the ramping rate was 60°C/min. The temperatures at (a)–(f) were 210.1°C, 210.8°C, 229.8°C, 222.7°C, 239.5°C, and 240.0°C, respectively.

removed in the Flux A6 system, but dendrite still remained in the Flux B6 system.

Figure 6 shows the wettability test result for three types of solder ball/flux combinations (Flux A6 + 63Sn/37Pb solder ball, Flux B6 + lead-free solder

ball, and Flux A6 + lead-free solder ball) on an aged copper plate. Wettability of those systems was determined as 83%, 40%, and 55%, respectively. The Flux A6 + 63Sn/37Pb solder ball system exhibited the best wettability among these systems. The Flux B6 + lead-free solder ball showed the worse wettability, with organic residual on the solder ball surface after rinsing. In general, Sn/Pb solder has better wettability than Sn/Ag/Cu. It was clear that A6 provided better wetting performance than B6.

Thermal Resistance

Figure 7 shows the weight loss profiles of the fluxes under a ramping schedule simulated to the TLFRP. The melting range of lead-free solder was shifted to 221–228°C. At 228°C, A6 showed more residues (73.5 wt.%) than B6 (64 wt.%). For A6, a greater amount of remaining flux covered on the solder ball surface can protect the solder ball from oxygen attaching and provide a lower surface tension environment as the solder melts to liquid. The lower surface tension environment provided from the flux can render the liquid of solder to form a better spherical shape and a smooth surface during the followed cooling process.

Thermal Profile in DSC

Figure 8 shows the DSC thermal profiles for the solder balls with A6 and B6. One solder ball was

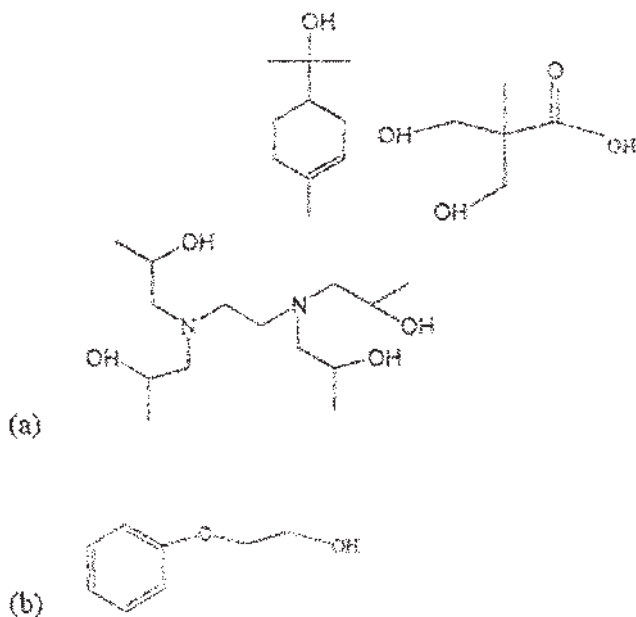


Fig. 4. Possible chemical structures of (a) Flux A6 and (b) Flux B6 analyzed by GCMS.

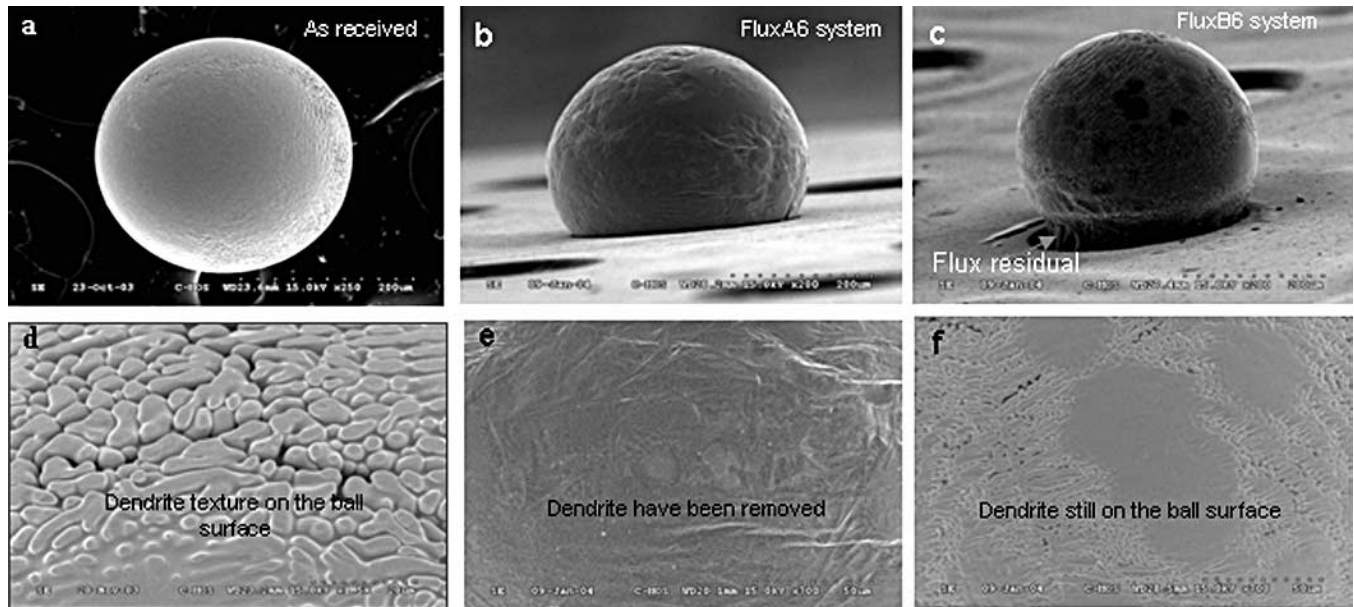


Fig. 5. SEM pictures of the (a)–(c) side view and (d)–(f) lead-free solder ball. (a) and (d) are as-received solder ball, (b) and (e) are in Flux A6, and (c) and (f) are in Flux B6 going through the TLFRRnofile.

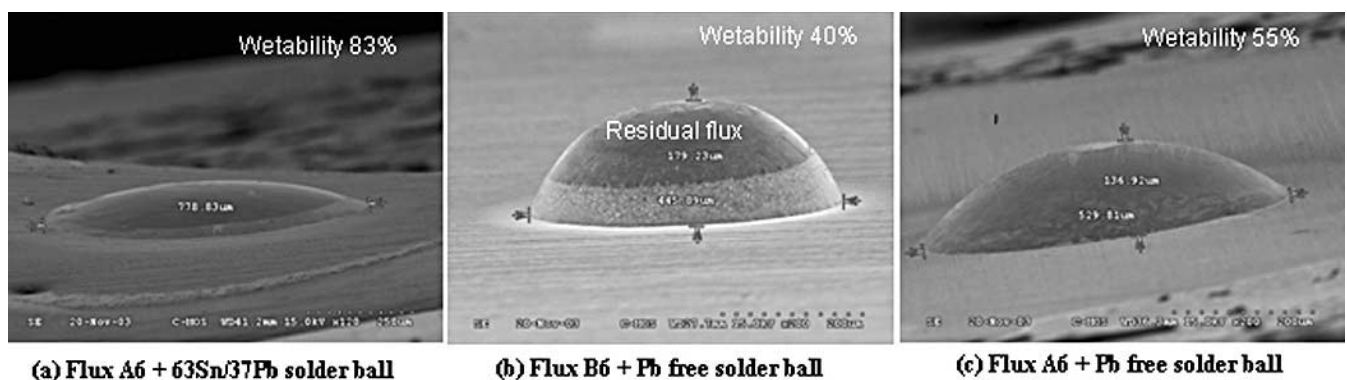


Fig. 6. The wettability test and the corresponding sideview observation by SEM. The wettability test put the solder ball and flux on the copper plate at 240°C for 30 sec and then cooled to room temperature, followed by washing in 50°C DI water for 10 min. The remaining solder ball height was measured to estimate the wettability.

used for each test. Both thermograms showed identical primary melt peaks at approximately 217°C. Interestingly, the flux A6 system showed an extra small endothermic peak at 205°C, which was 12°C lower than the lead-free solder melting point. This endothermic peak was not found in the B6 system. Figure 9 shows the first and second runs of the Flux A6 system in DSC. It can be seen that the extra endothermic peak at 205°C disappeared in the second run profile and the primary melting peak at the second run was shifted down by 1°C. It may be because the poor thermally conductive flux led to superheating during the first heating process before the solder ball fully contacted the DSC aluminum pan surface. It is postulated that the extra endopeak at 205°C was the reaction peak between the Flux A6 and the Sn oxide layer on the solder ball surface. Some lower melting point slags may be formed in the Flux A6 system before primary solder melting, and solder early wetting phenomena also occur below the primary lead-free solder melt point (see Fig. 3b).

The ESCA depth profiles for the as-received lead-free solder ball, the lead-free solder ball with Flux A6, and the lead-free solder ball with Flux B6 are shown in Fig. 10. It can be seen that the depth of the oxidation layer on a fresh solder ball, in Flux A6 system, and in Flux B6 system were approximately 70 Å, 70 Å, and 350 Å, respectively. These results can explain the wetting behavior in Fig. 5b and c. The dendrite textures on the lead-free solder ball surface have been almost removed in the Flux A6 system (see Fig. 5e) after the reflow process, and the Flux A6 system revealed a thinner oxidation layer than the Flux B6 system on the lead-free solder ball surface (Fig. 10b and c). It was found that A6 can remove the oxidation layer on the solder ball surface more efficiently than B6 and then create a fresh metal surface during the reflow process. The Flux A6 system may have a better etching capability for the oxidation layer of the solder ball. This is a very important material property of flux for ball placement of lead-free solder. Generally, the

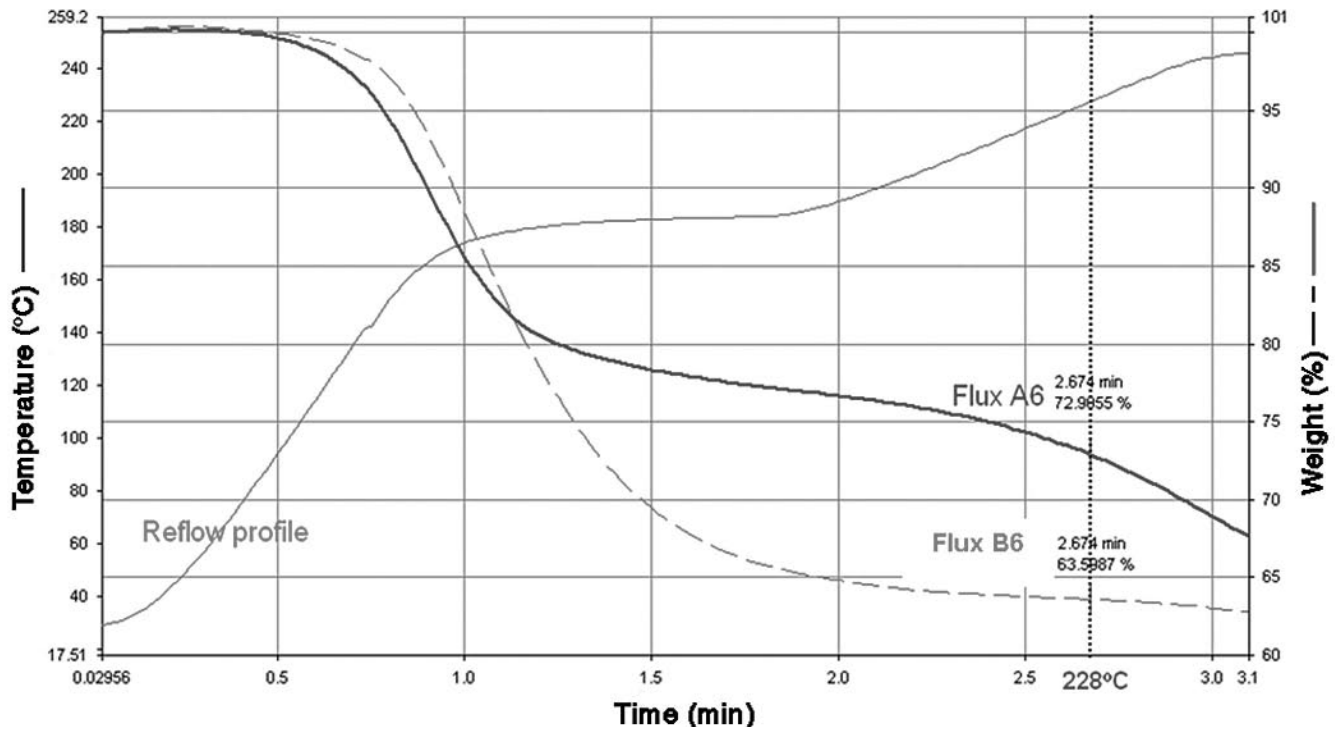


Fig. 7. The TGA curves simulated the TLERP reflow profile for two kinds of flux system, Flux A6 and Flux B6. At the lead-free solder ball melt point, 228°C, the remaining weight percents of Flux A6 and Flux B6 were 73 wt.% and 64 wt.%, respectively.

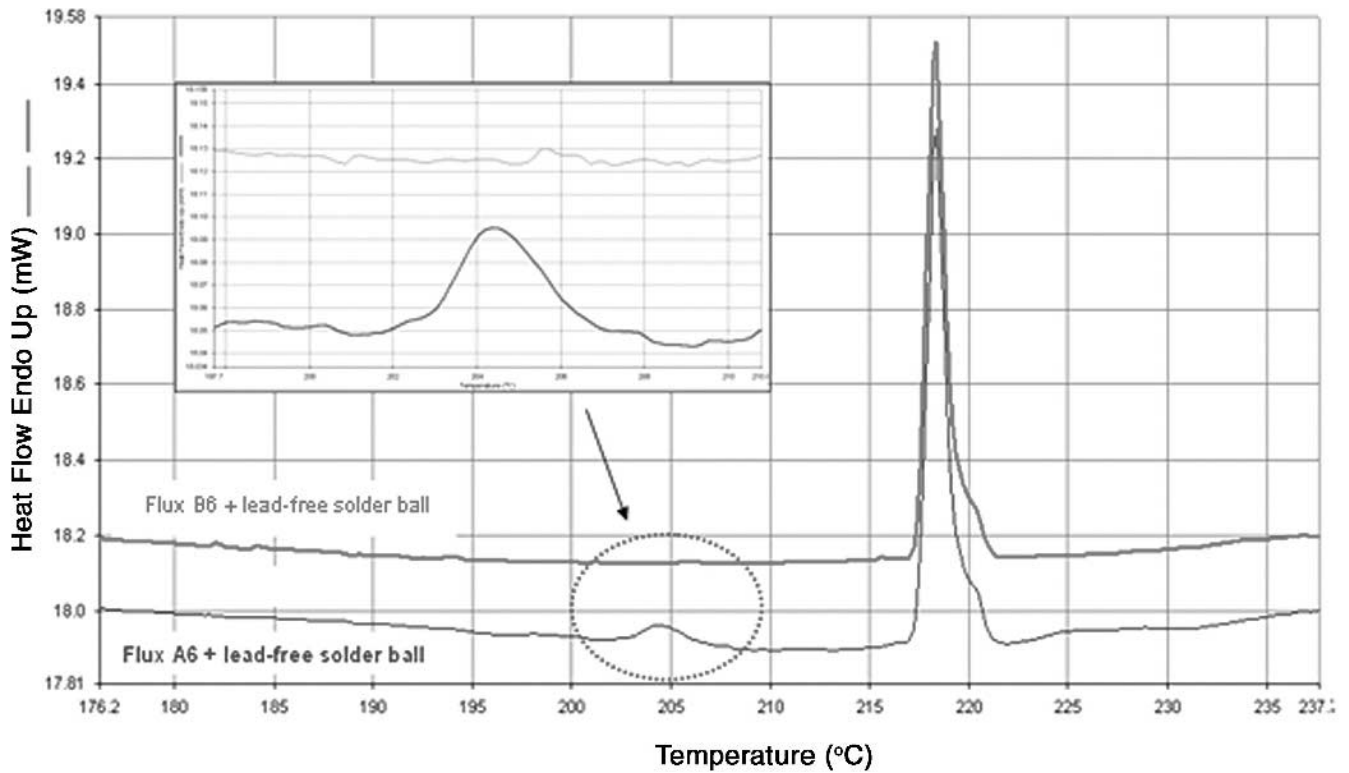


Fig. 8. DSC normal scanning curves at heat rate 10°C/min for only one pill of lead-free solder ball with two kinds of fluxes (Flux A6 and Flux B6). Both thermograms exhibit one main melting peak at 218°C. The Flux A6 system showed an extra small endothermic peak at 205°C.

lead-free solders have serious problems in oxidation due to the higher reflow temperature, which results in poor wettability and ball shape.

CONCLUSIONS

The effect of two types of fluxes on the wetting performance of lead-free solder was investigated.

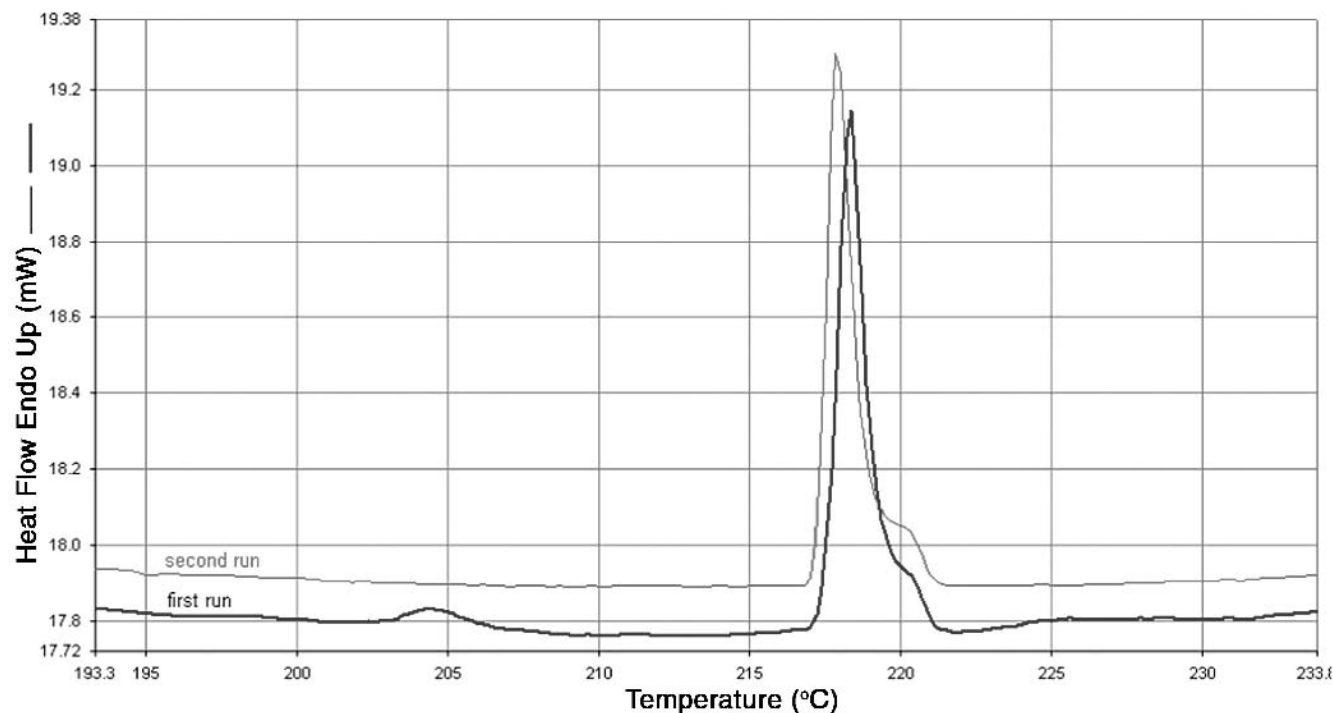


Fig. 9. First and second run of DSC normal scanning at heating rate 10°C/min for one pill of lead-free solder ball with Flux A6. Only the first running exhibited an extra endothermal small peak.

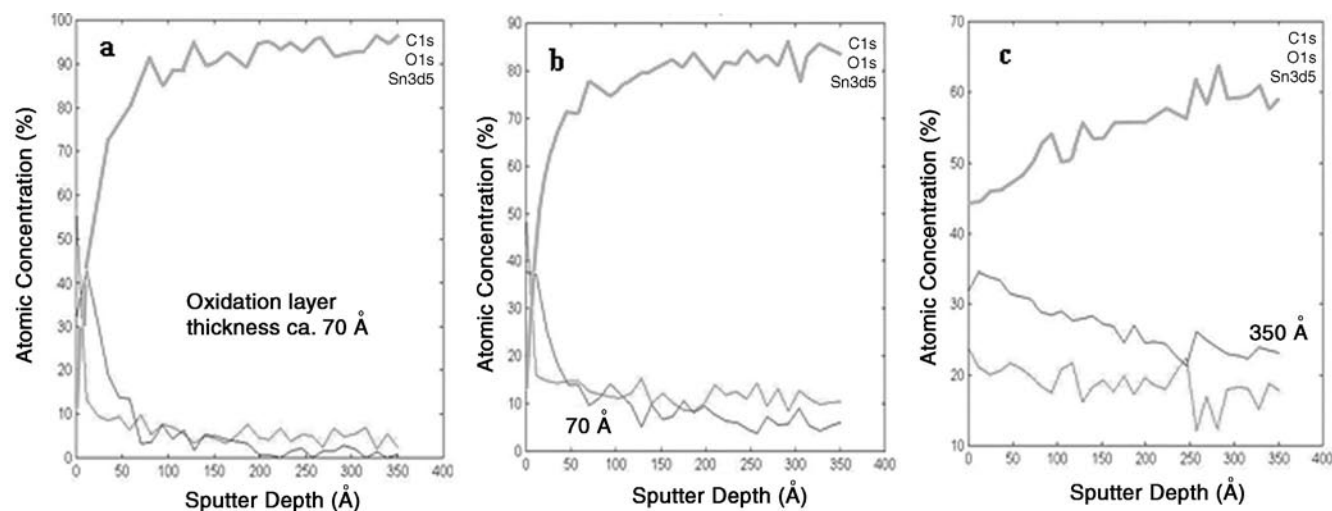


Fig. 10. ESCA depth profile results of (a) as-received lead-free solder ball and (b) lead-free solder ball with Flux A6 and (c) with Flux B6 after reflow profile and then washing by 50°C DI water for 10 min. The thicknesses of the oxidation layer of as-received solder ball and with Flux A6 and Flux B6 after reflow profile were about 70 Å, 70 Å, and 350 Å, respectively.

The lead-free solder balls started to melt and wet at 210°C by using Flux A6, which is 7–8°C lower than the melting point (218°C) of the solder material used. From GCMS analysis, A6 contains chemicals with alcohol groups as well as carboxylic groups, while B6 has mainly alcohol groups. Thus, A6 was believed to more actively remove the oxidation layer of the solder ball at high temperatures than was B6.

The DSC profiles of the lead-free solder ball with Flux A6 indicated a small extra endothermic peak at 205°C and the bulk melting point at 217°C. This endothermic reaction at 205°C may be related to the

early melting and wetting phenomena. By using A6, not only temperature was beneficial, but also the wetting performance was better than by using B6. The wettability test indicated that the height of the solder ball after the reflow process with Flux A6 was significantly lower than that with Flux B6. In addition, ESCA analysis indicated that the Flux A6 system may have a better etching capability for the oxidation layer of the solder ball. The low surface tension environment on the solder ball surface by using A6 could also provide better solder ball shape after the reflow process.

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