A Review: The Wettability and Oxidation Resistance of Sn-Zn-X Lead-Free Solder Joints

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Abstract-**With the development of lead-free solders, Sn-Zn solder was attracted increasing attention due to its low melting point, cost saving and excellent mechanical properties. However, there are many problems need to resolved, such as poor wettability and oxidation resistance. In order to overcome these shortcomings, more recent studies on Sn-Zn solder have proposed strategies aimed at obtaining a good wettability and solderability by adding a third or fourth elements, such as In, Ga, P, Bi, Ni, Cr, Ag, Cu, Al and rare earth. This work summarizes the effects of alloying elements to the wettability and oxidation resistance of Sn-Zn lead-free solders.**

Keywords-lead-free solders; alloying elements; wettability; oxidation resistance

I. INTRODUCTION

For a long time, the traditional Sn-Pb solder has been widely used in the electronic devices. Due to the increasing environment and toxic concerns, governments of many countries have established laws to prohibit the use of Pb from electronic packaging [1-3]. Today, studies on the lead-free solder have made breakthrough progress, Sn-Ag, Sn-Cu, Sn-Zn and Sn-Ag-Cu solders have been developed. Among series of lead-free solders, Sn-Zn solder was highly recommended as the promising lead-free solder of the next generation, owing to its favorable melt temperature, low cost and excellent mechanical properties [4,5]. However, because the high activity of Zn, the wettability and oxidation resistance of the Sn-Zn alloys are poor, which is a major obstacle to its application [6]. In order to overcome these drawbacks, two methods are taken. One is to develop a new kind of flux which is suited to lead-free solder and the other is to add alloying elements into the Sn-Zn solder.

In this paper, we summarize the development of Sn-Zn solders, and analyze the effects of alloying elements on wettability and oxidation resistance.

II. WETTABILITY

Wettability of solder can be defined as the ability of the molten solder to spread over on a substrate during the reflow process [7]. The better wettability is to evaluate the performance of important indicator. For Sn-Pb solder, due to the existence of Pb, the solder alloy owns better wettability. But for lead-free solders, the wettability may be dropped obviously due to the replacement of Pb. Hence, adding alloying elements is an effective method to improve the wettability of Sn-Zn solder alloy.

The addition of alloying elements can be classified as follows:

(i) Add surface-active elements, which can easily accumulate at the solder interface in the molten state.

(ii) Add a large amount of low-active elements to reduce the activity of Zn.

(iii) Add more reactive than Zn elements, using oxide film that is preferentially formed on the surface of Zn, which can improve the wettability.

The addition of 5%~10% In into Sn-9Zn solder can improve the wettability [8]. The researcher has attributed to solder flux. Yu et al. [9] has also confirmed it. Fima et al. [10] has reported the effect of 0.5%~1.5% In on Sn-Zn solder under Ar protective atmosphere and found that the Ar atmosphere can better decrease the surface tension and improve the wettability. Ga was incorporated into Sn-9Zn solder, which can significantly change the wettability and optimal content was about 0.5% [11]. Due to the surface-active, Ga would accumulate at solder interface in the melting state then the surface tension of the liquid solder was decreased [12]. The similar phenomenon can be found for P addition into Sn-Zn solders [13]. Zhou et al. [14] confirmed that the addition of Bi to the Sn-Zn solder decreases surface tension of the liquid solder, and suppose it is effective to enhance the wettability. The effect of Ni addition to Sn-9Zn lead-free solder on the wettability of aluminum and copper base metal was studied by Huang et al. [15]. It is found that the wettability of Sn-9Zn-xNi solders on Al substrate was much better than on copper substrate. In addition, with increasing of Ni content, the wettability on copper substrate was slightly enhanced but became worse on Al substrate. Due to the high mutual solubility Al and Zn, Al atoms can dissolve from the substrate into Sn-Zn based solders during reflow, to form Al-Zn solid solution during solidification. Chen et al. [16] studied the effect of Cr on the wettability of Sn-9Zn solder compared with Sn-37Pb and Sn-3.5Ag-0.75Cu. It is indicated that the wettability of Sn-9Zn-xCr solder is poorer than both solders. However, adding Cr element can slightly improve the wettability of Sn-9Zn solder alloy. The addition of trace amount of Ag into Sn-9Zn solder can't obviously change the wettability [17]. With the 0.5% and 1.0% addition, the wetting angle is slightly lower. With the Ag addition concentration increasing, the wetting angle increases. The reason could attributed to Sn-Zn-xAg solder has better oxidation resistance

than Sn-Zn solder, but when the Ag content exceed a certain, the liquidus temperature increased [18], and the fluidity of the solder decreases with the same soldering temperature. So the wetting angle increases slightly. Yu et al. [19] found that the addition of Cu can alter the wettability of Sn-9Zn solder. Results show that the wetting angle of Sn-9Zn is120° while that of Sn-9Zn-10Cu is about 54°. Fima et al. [20] has also investigated the effect of Cu on Sn-8.8Zn solder, the soldering temperature was250°Cand ALU33®flux was used. It is found that the wetting angle of Sn-8.8Zn is about 42°, with 0.5%Cu addition, the wetting angle was decreased to about 32°. Some researchers have proposed the ideas that through adding more active Al to inhibit oxidation of Zn then improve the wettability of Sn-Zn lead-free solder. But according to the existing literature, we find that researchers have different views on improvement the wettability of Sn-Zn solder with the addition of Al. Chen et al. [21] has found that adding Al may deteriorate the wettability of the solder. Huang et al. [22] proposed that adding Al can no signification change the wettability of Sn-Zn solder on copper substrate. However, Chen et al. studied the effect of Al under N2 protective atmosphere and ZnCl2 + NH4Cl fluxas well asno-cleaningflux were used, the wettability of solder was extremely improved [23]. Comprehensive results of the study, we can find that only a small amount of Al can show this enhancement effect. When the addition is excessive, the negative effect can be found obviously.

Trace amount of RE elements (Ce and La), can reduce the surface tension of Sn-9Zn. When the RE content is 0.05 and 0.1%, the wettability is greatly improved with the RA flux[24]. The addition of Er into Sn-Zn was investigated by Zhang et al. [25]. When the addition of Er was 0.08%, the spreading area gave an 19.1% increase (Fig.1). Ce [26], La [27], Nd [28] and Pr [29] can also improve the wettability of Sn-Zn solders because of the lower surface tension caused by rare earth. Adding a proper amount of rare earth Pr and Nd to the Sn-9Zn-0.5Ga solders were studies by Xue et al. [30, 31]. With the addition of 0.08%Pr or 0.1%Nd can significantly improve the wettability of the solder. It is concluded that the rare earth elements can improve the wettability of Sn-Zn solder, only the optimal contents are different for different elements.

III. OXIDATION RESISTANCE

The poor oxidation resistance of the Sn-Zn solder is one of the most factors to hinder its development. Due to the existence of mass Zn element, the Sn-Zn solder is easily oxidized (Table 1), worsened the wettability of solder during soldering. Therefore, it is no doubt that the key issue is improving oxidation resistance of Sn-Zn solder.

TABLE I. THE PARTIAL PRESSURE'S DATA OF COMMON SOLDER'S OXIDE[32].

	Bi_2O_3	In_2O_3	SnO_2	PbO	ZnO	CuO
298K	9.0×10^{-39}	5.2×10^{-39}	6.9×10^{-92}	7.0×10^{-67}	2.3×10^{-112}	4.7×10^{-46}
400K	1.4×10^{-41}	4.4×10^{-50}	6.5×10^{-66}	2.2×10^{-47}	2.3×10^{-82}	6.5×10^{-32}
500K	1.5×10^{-31}	2.1×10^{-38}	8.9×10^{-57}	5.9×10^{-38}	4.6×10^{-63}	6.8×10^{-24}
600K	8.6×10^{-35}	1.4×10^{-35}	1.5×10^{-40}	1.8×10^{-28}	5.4×10^{-51}	2.0×10^{-18}

Oxidation resistance of Sn-9Zn-xGa solder was tested by means of thermal gravimetric analysis (TGA) method by Chen et al. [11]. Fig. 2 shows that the oxidation resistance is enhanced with the addition of 0.5%Ga. The addition of Ag can improve the oxidation of the solder, and Sn-9Zn-0.3Ag solder exhibits much lower mass grain than Sn-9Zn in the liquid state at 245°C[33]. Lee et al. [34] reported the oxidation behavior of Sn-9Zn-xAg and Sn-9Zn-xCu solders during 85°C/85% relative humidity (RH) exposure. It is found that the addition of Ag or Cu can effectively improve the oxidation resistance, as compared with the Sn-Zn and Sn-Zn-Bi solders. Chang et al. [35] studied the effect of Ag and In addition on the oxidation resistance of Sn-9Zn solders and found that both Sn-9Zn-0.5Ag and Sn-9Zn-0.5Ag-1In solders have a higher oxidation resistance than that of Sn-9Zn solder. Chen et al. [16] demonstrated that the oxidation resistance of Sn-Zn solders can be improved with the addition of Cr, which can be attributed to segregation Cr in the sub-surface layer of Sn-Zn-xCr solder to prevent further oxidation. Adding Al element can obviously improve the oxidation resistance, however, an excessive amount of Al addition will form thick film and deteriorate the wettability of Sn-Zn solder [36].

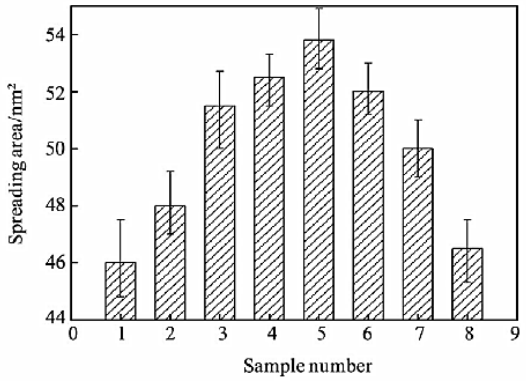

FIGURE I. SPREADING AREA OF SN-9ZN-XER [25].

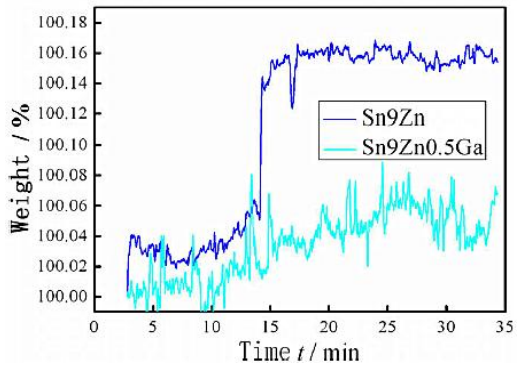

FIGURE II. TGA RESULTS OF SN-9ZN-0.5GA SOLDER COMPARED WITH THAT OF SN-9ZN SOLDER AT 235°C [11].

IV. CONCLUSIONS

To conclude this review, we can find that the addition of surface-active elements (Ga, P, Bi, Ni, and Cr) can improve the wettability of Sn-Zn solder. But when the additives are more than optimal content, the wettability of solder becomes stable, so it is difficult to improve the wettability greatly. The addition of In element can decrease the melting point of the Sn-Zn-In solder and enhances the wettability of the lead-free solder, but the In is very expensive, the addition of In can increase the cost

of lead-free solders.Adding Ag can enhance the wettability. The addition of Al element can effectively enhance the oxidation resistance, but just only a small amount of Al addition can improve the wettability. Moreover, the addition of rare earth elements show the most obvious improvement of wettability, however, rare earth elements may worsen the oxidation resistance, because rare earth is more reactive than Zn.

In a word, adding alloy elements are difficult to significantly improve the wettability and oxidation resistance of Sn-Zn solders. However, we find a great enhancement effect on the wettability of the flux, so the development of flux for Sn-Zn solder may be the main aspect of future research.

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