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Surface Properties of the Sn-9Zn Alloy with the Trace Addition of Lanthanum

Zuoan Li[1], **Adolf Mikula**[2], and **Zhiyu Qiao**[1,*]

[1] Dept. of Physical Chemistry, University of Science & Technology Beijing, Beijing 100083, China
[2] Institute of Material Chemistry, University of Vienna, Vienna, Austria

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Summary. The surface properties of solders play an important role in its wettability. The poor wettability of the Sn-9Zn alloy has prohibited its commercial application. In this paper, the solid surface properties of the Sn-9Zn alloy were studied by using X-ray photoelectron spectroscopy (XPS). It was shown from the XPS analysis that zinc is highly enriched on the surface of the Sn-9Zn alloy. Although the zinc concentration on the surface is greater than 9%, lanthanum is accumulated on the surface of the Sn-9Zn-1La alloy. In addition, the analysis of the valence of tin and lanthanum indicated that tin and lanthanum could form complex oxygen-containing salts so that the anti-oxidation of the solder was enhanced, and the wettability of the solder was improved accordingly.

Keywords. Sn-9Zn lead-free solder; Surface property; XPS; Lanthanum.

Introduction

In recent years, the development of lead-free solders for electronic interconnection materials used in electronic devices has been an urgent task for material scientists because of the health and environmental safety problems caused by conventional Sn-37Pb (weight percent is used in this paper) solder, although such solder has a unique combination of electrical, chemical, physical, and mechanical properties, especially its wettability. New lead-free solders, which will be used as the alternative of Sn-37Pb solder, must meet some requirements, such as low melting temperature near 183°C (Sn-37Pb eutectic temperature), melting range within 20°C, good wettability, and excellent mechanical properties [1]. Numerous investigations have been carried out on lead-free solder alloys, such as Sn–Ag, Sn–Cu, and Sn–Ag–Cu. Although these solders have many merits and have been regarded as the drop-in lead-free solders, their melting temperatures (216–227°C) are much higher than 183°C. Soldering at these temperatures may do more harm than good to other electronic components [2–4].

* Corresponding author. E-mail: zyqiao@metall.ustb.edu.cn

The eutectic temperature of the Sn-9Zn alloy is 199°C, which is the closest to 183°C among all Sn-based binary alloys. Furthermore, the tensile strength and creep resistance of such alloy are far better than those of the Sn-37Pb alloy. Hence, the Sn-9Zn alloy may be a promising alternative for the Sn-37Pb solder. However, Zn is chemically active so that Sn–Zn binary alloy is susceptible to oxidation and corrosion, which leads to poor wettablity and reduces the reliability of solder joints [1, 9]. In order to improve the wettability of the solder, trace amounts of rare earth elements were added to some solders in recent investigations. For example, with the trace addition of rare earth to Sn-9Zn, the wettability and mechanical properties were improved to a large extent [5, 6]. But several issues still need to be further investigated. The mechanism why the rare earth elements could improve wettability is still not clear. Although rare earth elements in solders were studied in the past, in-depth studies on the mechanism of pure rare earth element, mainly La and Ce, should be conducted. Because of their different electronic structures they have different properties. Lanthanum was regarded as more suitable element to improve the properties of lead free solders. As we know, the surface properties of the alloy play an important role in the wettability, which is crucial to the reliability of solder joints [7]. It is, therefore, worthwhile conducting further in-depth studies on the lanthanum's mechanism and the effect on the surface properties of the Sn-9Zn solder alloy. In this investigation, 1% La was added to the Sn-9Zn solder alloy. XPS was applied to study the surface properties of these alloys, such as the element concentration, and the valence state. In addition, a thermodynamic approach was used to analyze the XPS results.

Results and Discussions

In Fig. 1 the whole XPS spectra of the Sn-9Zn and Sn-9Zn-1La alloys are shown. From the spectra, it is evident that the surface of the solders contains tin, zinc, lanthanum, oxygen, and carbon. Of course, La only exists on the surface of

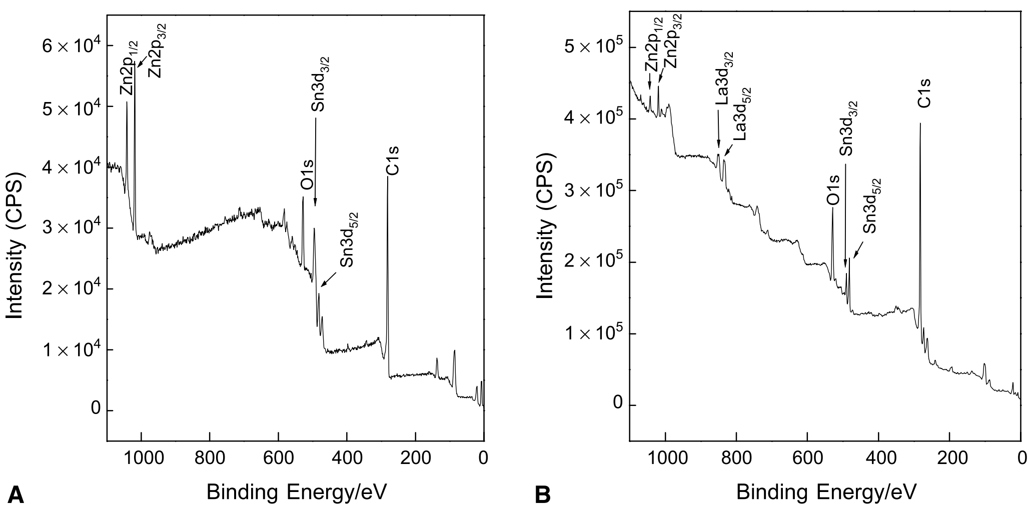

Fig. 1. Survey scan of XPS spectrum of (A) Sn-9Zn and (B) Sn-9Zn-1La

Table 1. XPS analysis results of the Sn-9Zn alloy

Peak	Position BE / eV	FWHM / eV	Raw area (CPS)	RSF	Atomic mass	at%	mass%
Zn $2p_{3/2}$	1021.2	2.798	99768.2	3.726	65.387	79.9	68.6
Sn $3d_{5/2}$	484.0	3.675	25386.9	4.725	118.744	20.1	31.4

Table 2. XPS analysis results of the Sn-9Zn-1La alloy

Peak	Position BE / eV	FWHM / eV	Raw area (CPS)	RSF	Atomic mass	at%	mass%
Zn $2p_{3/2}$	1022.2	2.358	53402.5	3.207	65.387	28.3	16.7
La $3d_{5/2}$	835.6	6.484	91960.2	5.222	138.898	36.1	45.2
Sn $3d_{5/2}$	485.2	1.347	71239	4.946	118.744	35.6	38.1

Sn-9Zn-1La. The signal of carbon results from the XPS instrument. Table 1 and 2 present the concentration of each element on the surface of the Sn-9Zn and Sn-9Zn-1La solders, respectively. The analysis results indicate that the zinc concentration on the surface of Sn-9Zn solder is 68.6% (59.6% higher than its original concentration of 9%) and this indicates that zinc highly aggregates in the surface phase. Zinc is chemically active so that a zinc oxidation state rather than pure zinc exists on the surface. Many investigations have pointed out that the first intermetallic compound formed between solder and the copper substrate has a great effect on the reliability of solder joint. The intermetallic compound γ-CuZn is formed instead of Cu_6Sn_5 when Sn-9Zn solder reacts with the copper substrate [8]. In the past investigations, various fluxes were developed in order to improve the wettability of Sn-9Zn solder [9], but this could also lead to new environmental problems. Therefore, the zinc properties in the surface phase play an important part in the reliability of solder joints. According to our results, it is obvious that zinc oxide accumulates on the surface so that the reaction between Sn-9Zn solder and copper substrate can be depressed. As a result, the wettablility of Sn-9Zn solder is poor. Hence, decreasing zinc concentration on the surface may be the key to improve the wettability of Sn-9Zn solder, which is our new approach to develop Sn–Zn based lead free solders.

The surface concentrations are deduced from the corresponding XPS peak area with the help of additional parameters, such as RSF and FWHM. The above abbreviations, BE, FWHM, RSF, and CPS stand for binding energy, full width at half maxima, relative sensitivity factors, and counts per second, respectively.

Comparing Table 2 with Table 1 it can be seen that with 1% La added in the Sn-9Zn alloy the zinc concentration on the surface decreases dramatically. With the decrease of the zinc concentration, the concentration of added lanthanum is far higher than its original concentration of 1%, which means that lanthanum is highly inclined to accumulate on the surface. Lanthanum is a surface-active element and can improve the activation of the surface. Our results are in good agreement with previous experiments and are able to explain why rare earth elements (mainly Ce and La) could improve the wettability of the Sn-9Zn solder [5, 6].

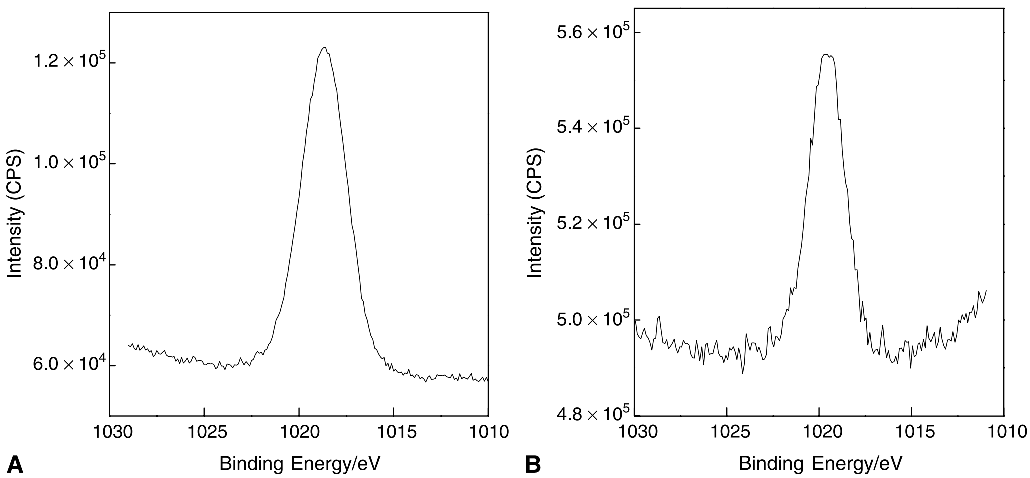

Fig. 2. Narrow scan of $Zn2p_{3/2}$ XPS spectrum of (A) Sn-9Zn and (B) Sn-9Zn-1La

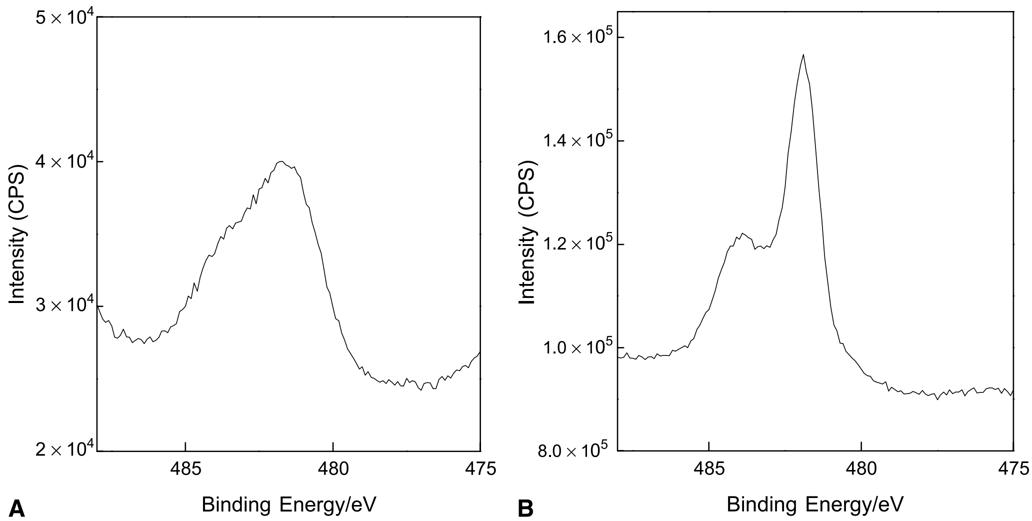

Fig. 3. Narrow scan of $Sn3d_{5/2}$ XPS spectrum of (A) Sn-9Zn and (B) Sn-9Zn-1La

Table 3. XPS analysis of tin valences obtained from the $Sn3d_{5/2}$ XPS-peak

	Energy	FWHM	Area	at%
Sn-9Zn				
Simple Substance	485.0	2.242	9137.6	59.4
Oxidation State	487.0	2.503	6251.3	40.6
Sn-9Zn-1La				
Simple Substance	485.2	1.141	23795.1	56.9
Oxidation State	487.1	2.035	18007.2	43.1

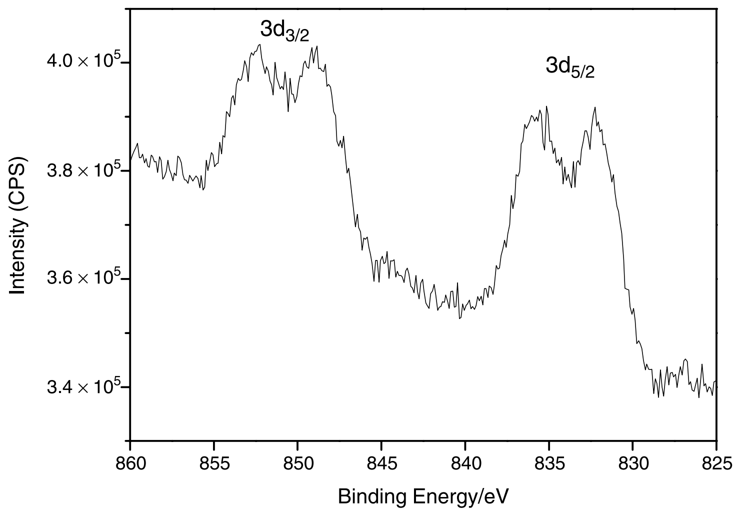

Fig. 4. Narrow scan of La3$d_{5/2}$ (right) and La3$d_{3/2}$ (left) XPS spectrum of Sn-9Zn-1La

Table 4. Enthalpy of formation for some metal oxides

Metal oxide	La_2O_3	ZnO	SnO
ΔH/kJ/mol	−1793.7	−350.5	−285.8

After lanthanum is added into Sn-9Zn solder, it has an effect on not only zinc but also tin, which can be seen from Fig. 3 and Table 3. Although there is not much difference in the ratio of Sn3$d_{5/2}$ simple substance to oxidation state on the surface of Sn-9Zn and Sn-9Zn-1La solders, its FWHM values in Sn-9Zn-1La solder become much smaller than in Sn-9Zn, which makes it easy to identify these 2 valences.

Figure 4 shows the features of the oxidized state of La with a spin-orbit splitting of La3d into La3$d_{3/2}$ and La3$d_{5/2}$ which involves a main peak and a satellite peak caused by shake-up.

It is obvious that lanthanum only exists in the form of the oxidized state. Therefore, lanthanum and tin are more likely to form complex oxygen-containing acid salts on the surface as a protective film to prevent the further oxidation of zinc, and the anti-oxidation of the solder has been enhanced [7]. As a result, the wettability of the solder could be improved accordingly.

So far as the XPS results are concerned, it can also be explained from the viewpoint of thermodynamics. Table 4 shows the enthalpy of formation for each metal oxide. The enthalpy of zinc oxide is more negative than that of tin oxide, which means zinc forms an oxide on the surface of Sn-9Zn solder more easily than tin. Because the enthalpy of lanthanum oxide is more negative than that of zinc oxide, the lanthanum oxide will be formed first on the surface of Sn-9Zn solder, and the formation of zinc oxide will be depressed.

Conclusions

The solid surface properties of Sn-9Zn solder with the addition of 1% lanthanum were studied by using XPS measurements. From the XPS results it is obviously indicated that Zn is highly enriched on the surface of Sn-9Zn, that La is accumulated on the surface of Sn-9Zn-1La, and that both Sn and La exist in oxidized form. Accordingly, a reasonable explanation for the mechanism of the improved wettability of Sn-9Zn solder due to the trace addition of La was given. In addition, our approach to study the surface properties of Sn-9Zn solder provides a new way to develop Sn–Zn based lead free solders.

Experimental

The compositions of Sn-9Zn and Sn-9Zn-1La were used as the sample alloys in this paper. These alloys were prepared from high purity metals (5N tin and zinc, and 99.5% lanthanum). The metals were weighed in the dry box and sealed in quartz tubes under vacuum. Alloys of Sn-9Zn and Sn-9Zn-1La were melted at 600 and 1000°C, respectively, for several days. After that the alloys were quenched in ice water. In order to prevent the pollution of the alloy surface, the quartz tubes were broken immediately before the XPS measurements.

The XPS measurements were made on the solid phase and were performed with an Axis Ultra spectrometer (Kratos, UK) using Mg $K\alpha_{1,2}$ (1253.6 eV) radiation at a power of 225 W (15 mA, 15 kV). To compensate for surface charging effects, binding energies were calibrated using the hydrocarbon C1s peak at 284.8 eV. A piece of free surface for each alloy was cut out for the XPS measurement in order to eliminate the effect of the quartz tube.

Acknowledgements

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