

Influence of Cr alloying on the oxidation resistance of Sn–8Zn–3Bi solders

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Abstract Influence of Cr alloying on the oxidation behavior of Sn–8Zn–3Bi– x Cr (SZB x Cr) ($x = 0, 0.1, 0.3, 0.5$) solders under 250 °C has been investigated. It was found that the poor oxidation resistance of the solders is attributed to the oxidation of Zn-rich phase and other Zn atoms which diffused to the β -Sn matrix grain boundaries which form ZnO. With Cr addition, two types of Sn–Zn–Cr phases, along the grain boundaries of β -Sn matrix and across the Zn-rich phase, were detected in Cr-bearing solder alloys, which prevent the oxygen from diffusing into the bulk of the solder, and the SZB0.3Cr alloy had the best oxidation resistance.

1 Introduction

Due to the increasing concerns about the environmental, health and economic shortcomings of the toxic element lead in the traditional solder, many studies have been carried out to investigate new lead-free solders as substitute in electrical packaging industry [1, 2]. Even though Sn–3.0Ag–0.5Cu solder has now been regarded as the industry standard solders [3], there are still strong requirements for further improvement due to some of its limitation. One major problem is that its melting point (217 °C) is much higher than that of traditional Sn–37Pb solder (183 °C). That means many modifications in existing manufacturing lines and electronic components have to be made. Compared with

Sn–3.0Ag–0.5Cu solder, the Sn–9Zn solder has attracted great attention in recent years because of its low melting temperature (198 °C) [4, 5]. Furthermore, it possesses many advantages of high strength, good creep resistance, high thermal fatigue resistance and low cost [6, 7].

In spite of these excellent features of Sn–9Zn alloys, many problems such as poor oxidation resistance under high temperature and low wettability with Cu substrate have to be resolved before practical use [8]. Thus a great deal of effort has been devoted to choosing appropriate alloying elements and flux to enhance its poor wettability and oxidation resistance [9–11]. Adding a small amount of alloying Bi was found to provide better wetting behavior and a slight reduction of the melting temperature [12–14]. The eutectic composition, ternary Sn–8Zn–3Bi (SZB) solder has emerged as one of the most promising candidates. However Bi was found to be rather susceptible to oxidation and corrosion [15, 16].

The oxidation resistance, an important part of reliability, has been one of crucial issues in packaging industry, and it should be investigated under harsh environment, like high temperature, for alloys easily to be oxidized. Therefore many researches focused on using micro alloying method to improve the oxidation resistance of the SZB solder. Chen et al. [17] studied many different alloying elements such as La, Cr, Ti and Al in SZB based solder and Cr was proved to be the best choice in improving the oxidation resistance [18]. T. Bellezze et al. reported the corrosion resistance of pure zinc coatings can be improved by immersing the zinc coated particles in acid solution of Cr VI salts [19]. Recently, S.W. Park et al. [20] have researched enhanced ductility and oxidation resistance of Zn through the addition of minor elements for use in wide-gap semiconductor die-bonding materials and pointed out that the addition of Cr is superior to that with all other elements.

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However, reports about oxidation behavior of SZBxCr solder under high temperature are few and there are no sufficient studies to evaluate the surface evolution of the solder.

Thus this work investigates the oxidation behavior of SZBxCr solders under 250 °C after long time aging process, clarifies their oxidation mechanism, and furthermore determines the effect of Cr addition on promoting the oxidation resistance of SZB alloys.

2 Experimental procedure

A series of SZBxCr solder alloys with $x = 0, 0.1, 0.3$ and $0.5(\text{wt}\%)$ were prepared from pure ($>99.9 \text{ wt}\%$) metals. Because of conflict between high melting temperature of Cr (1863 °C) and relevant low boiling temperature of Zn (907 °C), we firstly prepared SnCr master alloy using medium frequency induction furnace. SnCr master alloy was melted by pure Sn and Cr fragment, and preserved for 30 min at 1300 °C in low vacuum condition. Then it was melted with pure Sn, Zn and Bi within quartz tubes under nitrogen atmosphere, by homogenizing and repeatedly shaking at 650 °C over 1 h. During homogenizing process, KCl/LiCl eutectic mixture served as a barrier layer for oxidation. The compositions of alloys were investigated by inductively-coupled plasma emission spectrometry (ICP-AES) and the chemical compositions of solder alloys are listed in Table 1.

Oxidation resistance was investigated by thermal gravimetric analysis (TGA, TGA2050, TA Co.,Ltd USA). The samples 30 mm × 30 mm in size and 2.5 mm in thickness were sliced then polished with SiC paper of grit 600, 800, 1,000 and 1,200. After that the samples were sequentially degreased in acetone and cleaned by de-ionized water, then exposed under 250 °C for 5, 10 and 25 h at 36 %RH (SH-240, ESPEC Co., Ltd.).

The surface morphology and the chemical composition of the solder were examined by back-scattered electron detector (BSE, FEI SIRION 200) and energy-dispersive X-ray spectroscopy (EDX). The cross-section microstructure of the solders under 250 °C aging was also examined by BSE. X-Ray diffraction (XRD) measurements were performed on a D/MAX-III A (Rigaku, Japan) diffractometer

Table 1 The chemical compositions of solder alloys(wt%)

Alloys	Zn	Bi	Cr	Sn
Sn–8Zn–3Bi	8.21	2.95	0	Bal.
Sn–8Zn–3Bi–0.1Cr	8.13	2.99	0.11	Bal.
Sn–8Zn–3Bi–0.3Cr	8.43	3.01	0.33	Bal.
Sn–8Zn–3Bi–0.5Cr	8.37	2.98	0.54	Bal.

equipped with a scintillation detector, and a rotating Cu anode, operating at 20 kV with a measurement range of $2\theta = 25^\circ\text{--}75^\circ$, a scan speed of $4.5^\circ/\text{min}$ and a sampling step of 0.02° .

3 Results and discussion

3.1 TGA, XRD and EDX analysis

In order to find out the relationship between the oxidation resistance ability and the Cr content, TGA test is used and the results are listed in Fig. 1. As the weight less means the solders have better oxidation resistance, it was found that Cr content improves the oxidation resistance in the order of 0, 0.1, 0.5 and 0.3 wt%.

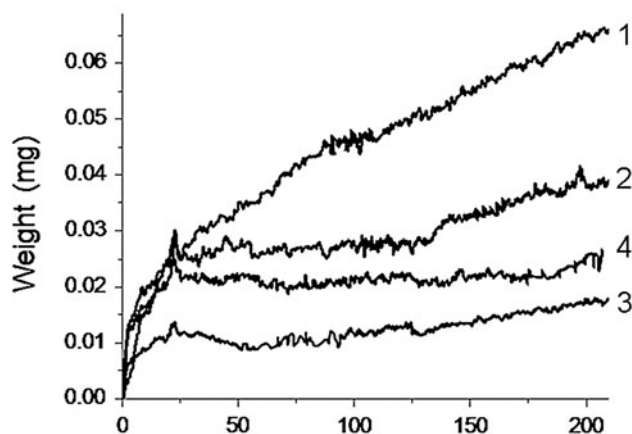


Fig. 1 TGA results of SZBxCr alloys (1) SZB, (2) SZB0.1Cr, (3) SZB0.3Cr, (4) SZB0.5Cr

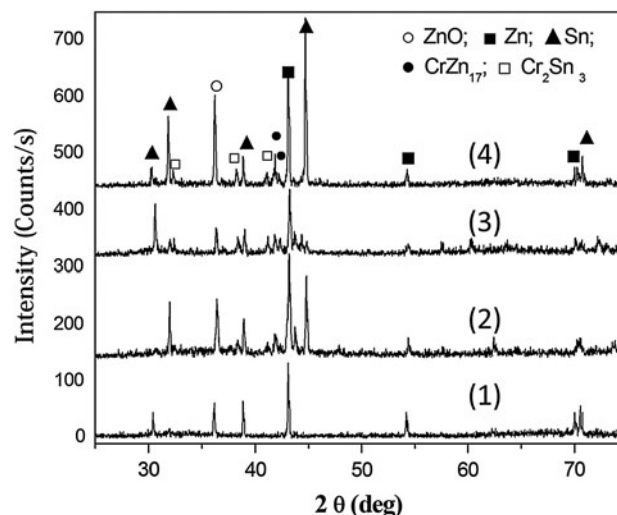


Fig. 2 XRD patterns of SZBxCr alloys surface after 5 h exposure. (1) SZB, (2) SZB0.1Cr, (3) SZB0.3Cr and (4) SZB0.5Cr

Table 2 EDX analysis of solder alloys after 5, 25 h aged

	O wt%	Zn wt%	Bi wt%	Sn wt%	Cr wt%
SZB					
(5 h)	6.81	23.87	3.26	66.07	
(25 h)	32.37	21.36	3.09	43.18	
SZB0.1Cr	6.63	24.02	3.11	66.99	0.25
SZB0.3Cr					
(5 h)	3.07	25.37	3.24	66.98	1.33
(25 h)	19.75	12.01	3.75	63.72	0.76
SZB0.5Cr	6.29	23.23	3.37	66.62	0.49

XRD patterns of SZBxCr alloys surface shown in Fig. 2. The ZnO peak is observed in all Cr content solders, but when the Cr content reaches 0.3 wt%, the ZnO decreased greatly. These mean that the SZB0.3Cr alloy had the best oxidation resistance, and these results are in accordance with TGA results.

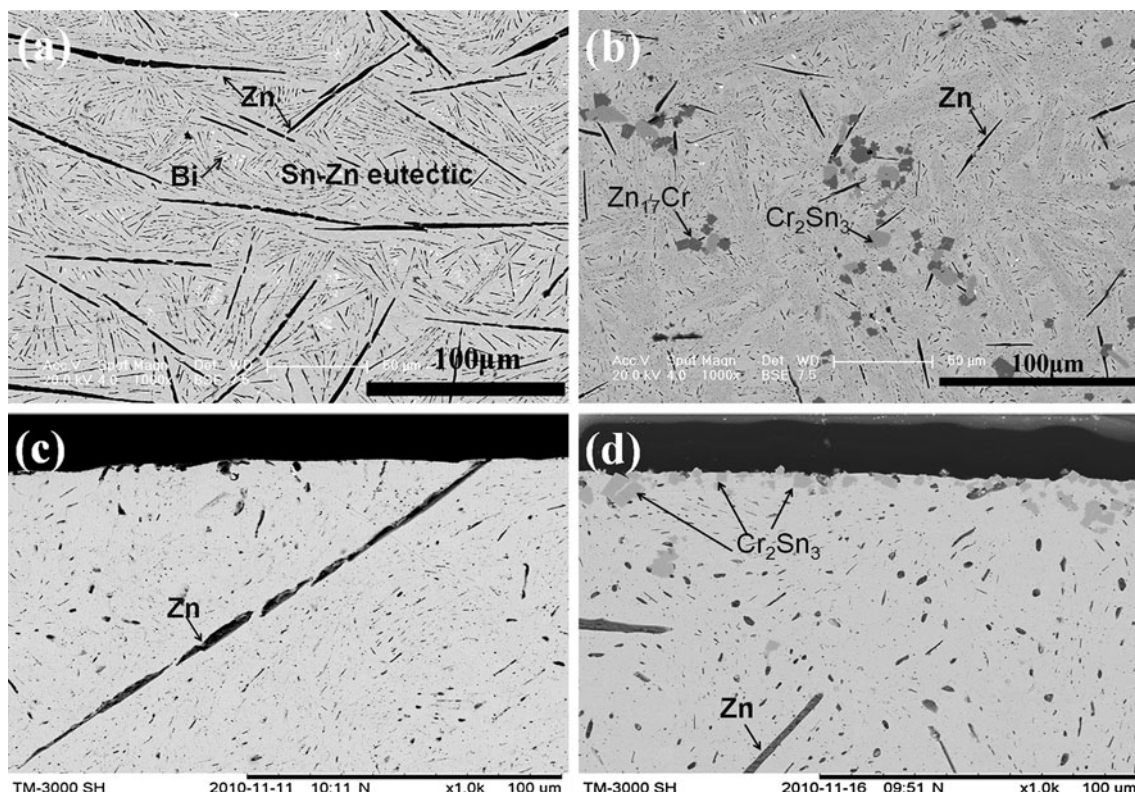
The chemical composition of the surface after 5 h aging was examined by EDX analysis and the results are listed in Table 2. The oxygen content of the SZB0Cr solder is the highest (6.81 wt%) while the SZB0.3Cr solder is the lowest (3.07 wt%). Except for the SZB0.3Cr alloy, the oxygen content of the solders is very close to each other. The oxygen content of the SZB0.3Cr solder is only around half

of that of others. The content of Sn and Bi in each of the solder is almost the same. After 25 h of aging, the chemical composition of SZB0.3Cr solder is 19.75 wt% O, 63.72 wt% Sn, 12.01 wt% Zn, 3.75 wt% Bi and 0.76 wt% Cr. Comparing with 5 h aging, it shows that the Sn and Bi content is almost the same as those that aged for 5 h while the Zn content drops dramatically. These results indicate that as the chemical activity of Zn is stronger than that of Sn and Bi, the Zn-rich phase is more easily to be oxidized, while the Sn matrix and Bi phase was difficult to oxidize in SZB alloying. The poor oxidation resistance of the solders is attributed to the oxidation of Zn.

3.2 Evolution of the morphology

The microstructures of the cross-section and the surface of the SZB and SZB0.3Cr alloys before aged are shown in Fig. 3a–d. The solder consists of two types of Zn morphologies, coarse needle-shaped primary Zn-rich phase and eutectic Zn in β -Sn matrix [21]. A small amount of Bi-rich phase precipitates (white color in Fig. 3a) in the β -Sn matrix. For the Cr-bearing solders, the primary Zn-rich phase and eutectic Zn phase all became finer and smaller (Fig. 3b).

In SZB solder, the Zn-rich phase can reach the surface of the solder (Fig. 3c). As Zn-rich phase is more easily to be oxidized, the solder may have poor oxidation resistance.

**Fig. 3** The microstructures of the alloys **a** SZB, **b** SZB0.3Cr, **c** surface of SZB and **d** surface of SZB0.3Cr

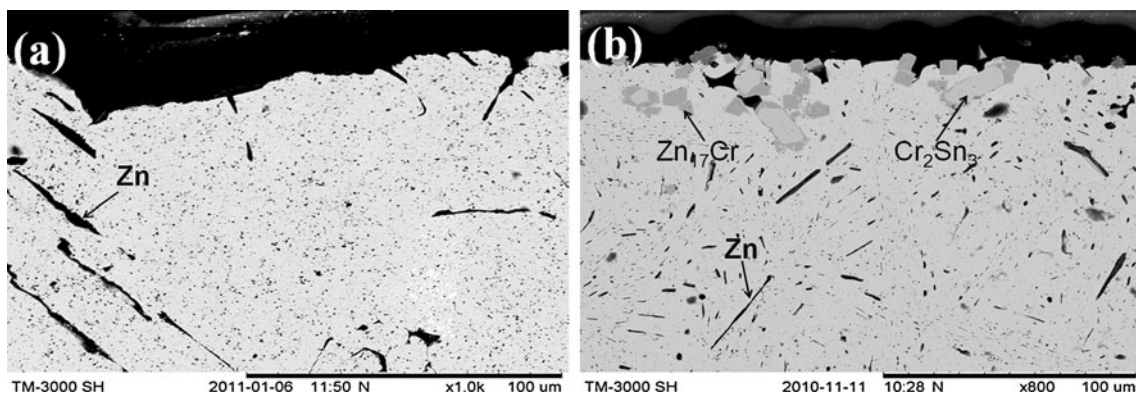


Fig. 4 SEM micrographs of cross-section surface of SZBxCr solders after 5 h aging a SZB and b SZB0.3Cr

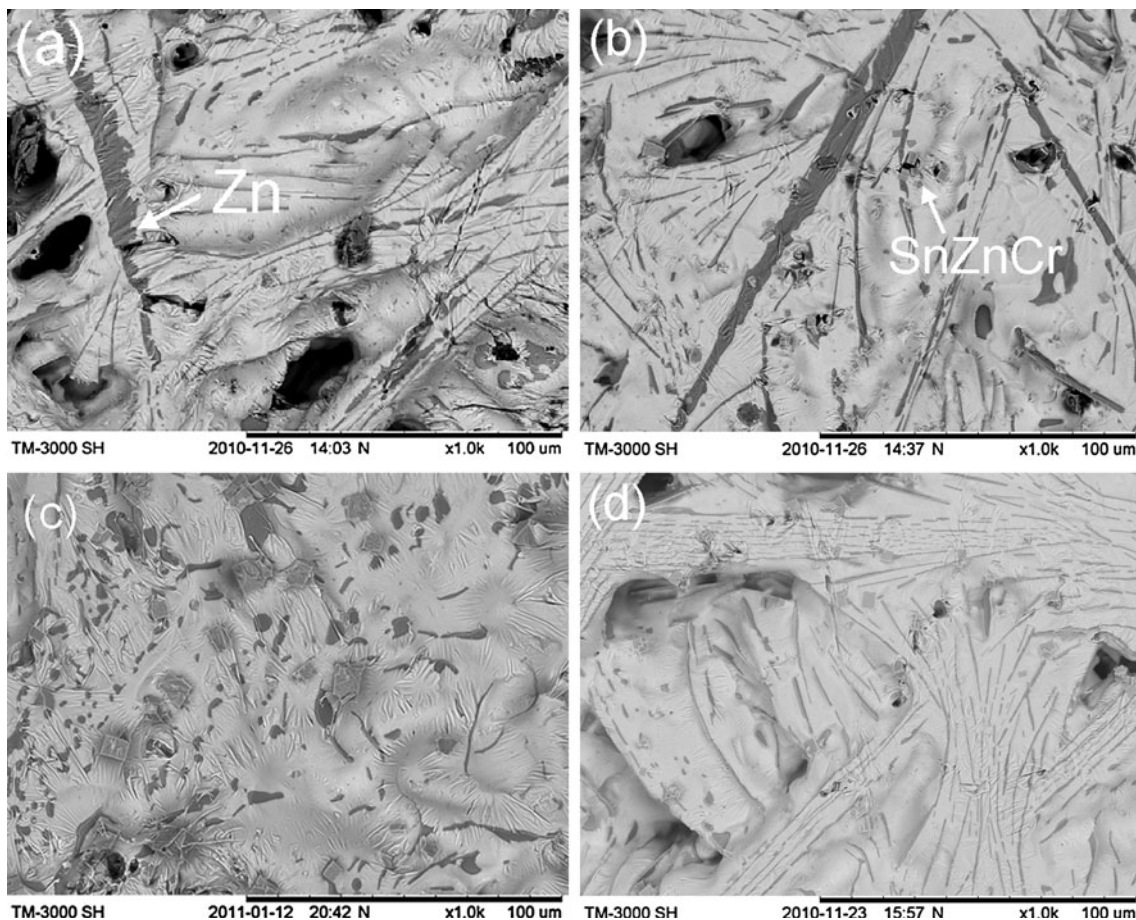


Fig. 5 SEM micrographs of the solders surface (top view) after 5 h aging a SZB, b SZB0.1Cr, c SZB0.3Cr and d SZB0.5Cr

While in SZB0.3Cr solder (Fig. 3d), the Cr-rich phase gathers mainly near the subsurface of the solder. Some of the Cr-rich phase exists across the needle-shaped Zn-rich phase or the grain boundaries of the β-Sn matrix. In all kinds of the Cr-bearing solder, some cubic phases present on the surface, one is darker and the other is brighter. EDS analysis shows that the two phases are all composed of Sn,

Zn, Cr, the light-color particles have a composition of 71Sn–13Zn–16Cr (at. %), the dark-color particles have a composition of 18Sn–71Zn–11Cr (at. %), the dark-colored phase consumed more Zn element. It is known that Zn-Cr binary system can form Zn₁₃Cr and Zn₁₇Cr IMCs [22], Sn-Cr binary system can form Cr₂Sn₃. XRD analysis shown Cr₂Sn₃ and Zn₁₇Cr were all appeared (Fig. 3).

Therefore, the light-color particles might be Cr_2Sn_3 and the dark-color particles might be Zn_{17}Cr [23, 24].

As the oxidation happens from the top of the Zn-rich phase which exposure in the surface into the bulk of the solder. Then oxidation happens along the Zn-rich phase or along the grain boundaries of Sn matrix and Zn diffuses to these boundaries, forming ZnO [25]. In SZB0.3Cr solder, the Cr-rich phase cut off the Zn-rich phase thus can't reach the surface. The oxygen diffusion access through the grain boundaries of β -Sn matrix is also blocked. This morphology of the solders surface makes the Cr-bearing solders have better oxidation resistance.

Figure 4 shows the microstructures of the cross-section of the SZB and SZB0.3Cr alloys after 5 h aged. It can see that in SZB solder the Zn-rich phases have been oxidized, while in SZB0.3Cr solder, as protected by the Cr-rich phase, the Zn-rich phases also can be observed. In SZB0.5Cr solder, the Cr-rich phases Segregate and grow which decrease the oxidation resistance.

Figure 5a–d show the surface morphology evolution (top view) of Sn–8Zn–3Bi–xCr solder after aging at 250 °C for 5 h. The coarse needle-like Zn-rich phases also appear on the surface of SZB (Fig. 5a) solder and SZB0.1Cr (Fig. 5b) solder, besides this it can see that some oxide holes in the surface. While for the SZB0.3Cr (Fig. 5c) and SZB0.5Cr (Fig. 5d) solder, the coarse needle-like Zn-rich phases and the hole are very little. As the Zn-rich phases are easy to be oxidizing, after the coarse needle-like Zn-rich phase in the surface oxidized, some oxide holes appears in the solders surface. This means that the SZB0.3Cr and SZB0.5Cr solder have better oxidation resistance.

4 Conclusions

The addition of Cr makes SZB_xCr alloy form finer microstructure than SZB alloy. Segregation of Cr-rich in the subsurface layer of Cr-bearing alloy can prevent the solder from further oxidation, and SZB0.3Cr solder has the best oxidation resistance. The Cr-rich phase blocked the oxygen diffusion access that contributes to the oxidation resistance of the solder.

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