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Effect of trace additive on the process of oxidation of Sn–Pb eutectics

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Abstract

The thermal properties of Sn–Pb eutectic alloy doped with Ga, Te or Cu in different particle sizes have been investigated by DTA and XRD methods. It has been shown that SnO was formed on the surface of the eutectic particles doped by Ga at about 475°C. In other cases, SnO_2 was also observed. In larger particles, the oxidation occurred in multiple stages, while simple step occurred only on the smaller sized particles. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sn–Pb eutectic; Ga doped; Oxidation process

1. Introduction

Sn–Pb eutectic alloy is extensively used as a solder in the electronic industry. It is very important to study the progress of oxidation process. Farrell [1] observed the oxide products of SnO and PbO when Sn–Pb eutectic was heated even at temperatures as low as 80°C. Zhang examined the effect of 25 doped elements on the oxidation of liquid Sn–Pb eutectic. The results revealed that trace elements, such as Ga, Ge, As and P, strengthened the protective property against oxidation, while S or Fe group elements had a deteriorative effect [2]. The powder Sn–Pb eutectic alloy has become an increasingly important material in the electronic industry with the development of SMT technology to date. In this paper, the effects of some elements as dopants on the process of oxidation of Sn–Pb eutectic powder with different particle sizes have been investigated in detail.

2. Experimental

2.1. Preparation of samples

Following [2], Ga, Te and Cu were considered to be the doping agents for Sn–Pb eutectics. The purity of Sn, Pb, Ga, Te and Cu were all 99.99%; Ga, Te and Cu were mixed as 0.1 and 0.01%.

Sizes of Sn–Pb eutectic samples were: (a) 0.16–0.14 mm, (b) 0.12–0.10 mm, (c) 0.07–0.05 mm, (d) 0.03–0.01 mm and (e) <0.01 mm obtained by sieving the fillings.

2.2. Differential thermal analysis (DTA)

A CR-G type DTA equipment (Beijing Optical Instrument) was employed and calibrated by standard substances with known melting points. Al_2O_3 was

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used as a reference substance. The heating rate was 20°C min^{-1}. For convenience in comparing samples, the weights used for DTA were standardized at 0.016 g. The error in measuring temperature was ±3°C.

2.3. X-ray powder diffraction analysis

The samples removed during the process of the oxidation were analyzed by Rigaku D/max-1 X-ray diffractometer.

3. Results and discussion

With pure Pb the size of the bead had very little influence on the shape of DTA response. It was expected that the smaller the size of the particles the more oxidation will be observed. Oxidation of pure Pb occurred below 100°C, in agreement with Farrell's result [1]. Ga, Te and Cu, which have a marked effect on pure Sn and Sn alloys, were totally ineffective for pure lead [2,3]. The DTA response of doped lead was identical to that of the original sample.

3.1. Oxidation of Sn–Pb eutectics with different particle sizes

The DTA responses of the pure Sn–Pb eutectics, with the different sizes used, are shown in Fig. 1. The Sn–Pb eutectic melted at 183°C, after which some oxidation was observed, but unexpectedly at about 580°C oxidation occurred within the larger particle

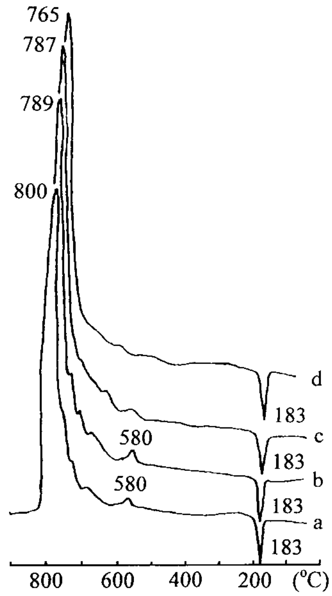

Fig. 1. DTA curves of Sn–Pb eutectic with different sizes.

samples and not the smaller ones. The oxidation only occurred on the surface of the particles, as confirmed by the XRD pattern (see Fig. 2a, sample of size b was quenched at 600°C). An absorption band, characteristic of SnO_2, Sn and Pb, appeared in the XRD pattern simultaneously.

At about 765–800°C, all the particles oxidized to SnO_2 and Pb_2SnO_4, no metal, and no PbO remained (see Fig. 2b, sample b was quenched at 850°C). From Fig. 1, it is apparent that the smaller sized particles

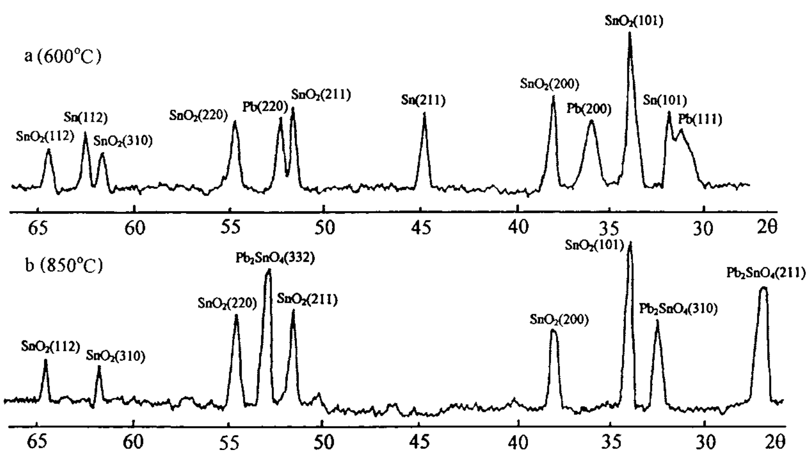

Fig. 2. XRD patterns of Sn–Pb eutectic (sample of size b) oxidized in air.

appeared to oxidize but in a single step; however, the larger particles oxidized in multiple stages with many exotherms on the DTA response (see Fig. 1a–c, between 580–800°C). This is a new chemical phenomenon since no new oxide was observed.

3.2. Oxidation of Sn–Pb eutectics doped by Ga with different particle sizes

The DTA analysis of the Sn–Pb eutectics doped with Ga is presented in Fig. 3.

As the content of doped Ga increased to 0.1 wt.%, a new exotherm developed at about 475°C in all the DTA analysis (see Fig. 3a–d). XRD measurement at 500°C indicated that SnO was formed on the surface of the particles. As the temperature increased to 627–648°C, SnO_2 also was formed, but on the surface. All particles totally oxidized above 787–805°C. Below 475°C, there was no evidence of any oxide in the XRD patterns, even so, it is believed, in this case, if any trace oxide could exist on the surface of the particles, the oxide could only be SnO.

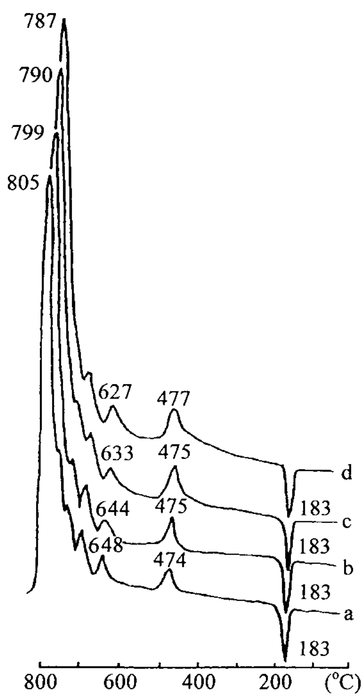

Fig. 3. DTA curves of Sn–Pb eutectics doped by 0.1 wt.% Ga having different sizes.

From the experiment on doped Ga sample, it is considered that the Sn–Pn eutectic powder could be somewhat stabilized against oxidation at a higher temperature. At least, the temperature at which SnO_2 formed was elevated to 627–648°C — much higher than that of the eutectic material. Zhang [2] reported that traces of Ga which were not >10 ppm in the liquid matrix Sn–Pb eutectic, were enriched on the surface by over 2000 times that of the matrix. Ga_2O_3 forms a complex with SnO and PbO in a very thin, compact and tenacious film and this protects the surface from further oxidation. In the powder condition, especially for the pulverized ones, perhaps it will have the same mechanism. In this way, a lower content of oxide in powder eutectic would be obtained.

3.3. Oxidation of Sn–Pb eutectics doped by Te or Cu with different particle sizes

Te sensitizes Sn–Pb eutectic to oxidation, and produces serious deterioration. Cu has little influence on the eutectic in oxidation [2]. In these systems, the DTA responses of doped eutectics were similar to those of the undoped samples.

4. Conclusion

1. At about 580°C, the surface of Sn–Pb eutectic particles is directly oxidized to SnO_2 but no SnO or PbO is formed.
2. At about 710–800°C, Pb_2SnO_4 and SnO_2 are formed as the final products.
3. Ga additive influences the surface of Sn–Pb eutectic. SnO is formed on the surface of the particles at about 475°C and the formation of SnO_2 is elevated to 627–648°C.

Acknowledgements

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