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Thermal Analysis of Lead-free Solder

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1. Introduction

As the switch from tin-lead solders continues, various tin-based alloys are being adopted as lead-free solders based on a balance of various properties. While melting temperature, oxidization, mechanical characteristics, costs and other elements are part of the evaluation, investigating thermal characteristics is important when setting the actual process conditions.

In this brief, various thermal analysis methods are used to measure lead-free solders¹⁾.

2. Measurements

Four lead-free solders were used as measurement samples. Their alloy composition by weight is as follows.

- a. Sn 97% - Cu 3%
- b. Sn 97% - Bi 3%
- c. Sn 97% - Ag 3%
- d. Sn 89% - Zn 8% - Bi 3%

The following instruments were used for measurements.

- DSC6200 Differential Scanning Calorimeter
- DSC6100 High Sensitivity Differential Scanning Calorimeter
- TG/DTA6200 Thermogravimetry / Differential Thermal Analyzer
- TMA/SS6100 Thermomechanical Analyzer

3. Result

Figure 1 shows the DSC results for the three samples with 3% of Cu, Ag or Bi added to Sn and the Sn 89% - Zn 8% - Bi 3% sample. Comparing the two-component samples shows that the 3% Ag sample had the lowest melting temperature peak. Furthermore, all samples were nearly eutectic compositionally and no shoulder peaks were observed in this measurement condition.

Figure 2 shows the results for the Sn 97% - Ag 3% sample measured at the low heating rates. Lower heating rates improve DSC curve resolution and shoulder peaks were observed here that were not seen in the 10°C/min condition. The eutectic composition of Sn-Ag alloys is an Ag content of 3.5%. Since this measurement sample is close to eutectic, it is difficult to observe shoulder peaks. The final temperature of a shoulder peak is the temperature at which the solder completely melts. These results show that the work temperature of near-eutectic samples can be investigated by measuring at low heating rates.

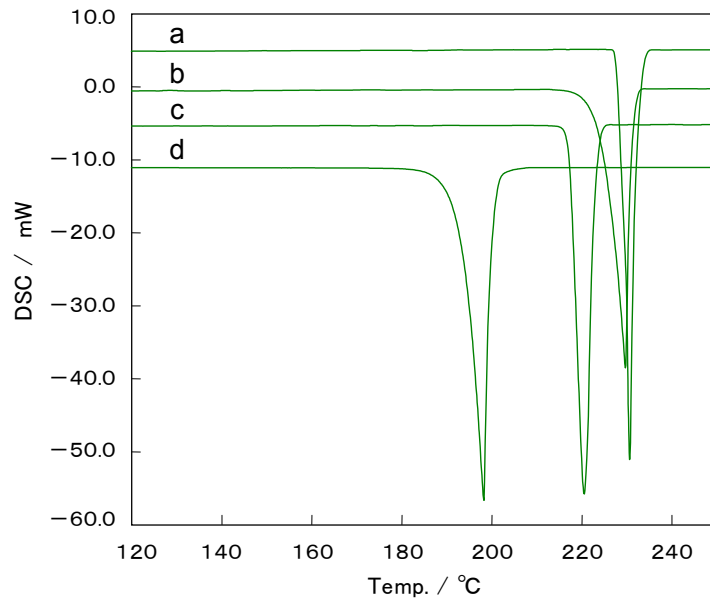


Figure 1 DSC Results for Lead-Free Solders
 a. Sn97%-Cu3%, b. Sn97%-Bi3%
 c. Sn97%-Ag3%, d. Sn89%-Zn8%-Bi3%
 Unit : DSC6200
 Sample weight : 20mg
 Heating rate : 10°C/ min

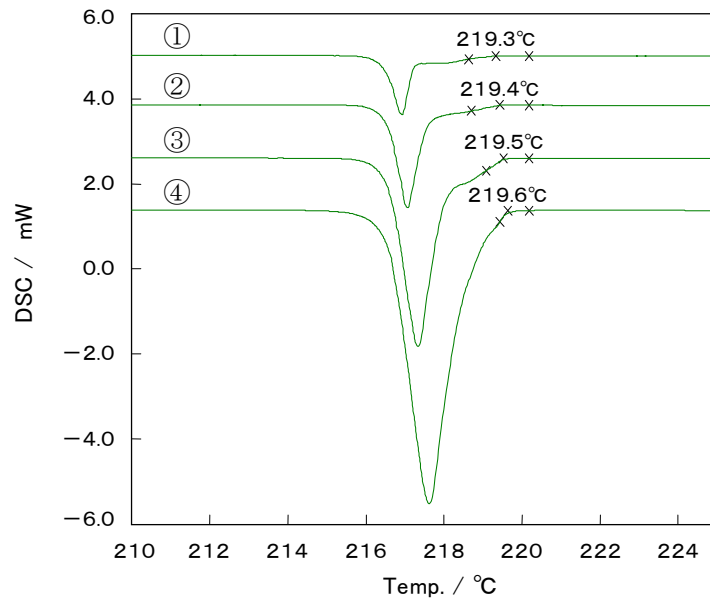


Figure 2 DSC Results for S 97%-Ag3% at Low Heating Rates
 ① 0.1°C/min, ② 0.2°C/min
 ③ 0.5°C/min, ④ 1.0°C/min
 Unit : DSC6100
 Sample weight : 20mg

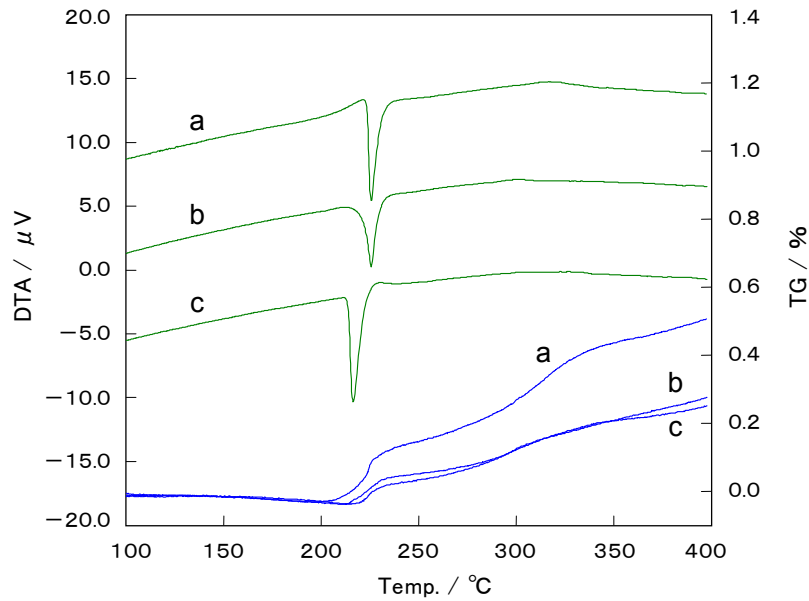


Figure 3 TG/DTA Results for Lead-Free Solders
 a. Sn97%-Cu3%, b. Sn97%-Bi3%
 c. Sn97%-Ag3%
 Sample weight : 10mg
 Heating rate : 5°C/ min

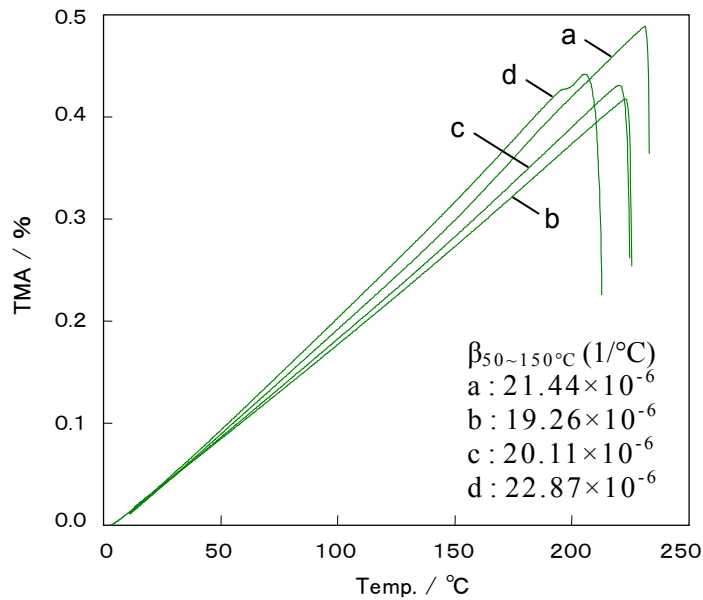


Figure 4 TMA Results for Lead-Free Solders
 a. Sn97%-Cu3%, b. Sn97%-Bi3%
 c. Sn97%-Ag3%, d. Sn89%-Zn8%-Bi3%
 Sample length : 20mm
 Heating rate : 5°C/ min

Figure 3 shows the TG/DTA results for the three samples of Sn alloys with 3% of Cu, Ag or Bi. In this condition, powder samples were heated in air. All DTA curves showed endothermic peaks caused by melting and the TG curves showed weight increases starting from near the melting temperatures. In particular, the DTA curve for the Sn 97% - Cu 3% sample showed endothermic peak before melting and this sample had the largest weight increase, indicating that it oxidizes more easily than other samples. These results show that TG/DTA is effective in investigating the relation of work temperatures and oxidization reactions.

Figure 4 shows the TMA results for the lead-free solders. All samples showed thermal expansion as the temperature increased. The average linear expansion coefficient β ($1/^\circ\text{C}$) was calculated for the 50°C to 150°C range for all samples. The results show that the Zn-Bi sample had the highest expansion rate. It is important to be aware of variations in the thermal expansion rate of solders and joint material, as this may cause stress when temperatures change. These results show that TMA can accurately evaluate the thermal expansion of solders.

4. Summary

This brief introduced examples of the thermal analysis of four lead-free solders.

The thermal analysis methods introduced here can evaluate various thermal characteristics of solders, including liquid phase temperatures, oxidization reactions and thermal expansion rates, which are important in the research, development, and quality management of lead-free solders.

Reference

- 1) T. Nakamura, Y. Ichimura, K. Oshiro and R. Kinoshita, The 37th Japanese Conference on Calorimetry and Thermal Analysis, p98 (2001)