

## Temperature dependence of anelastic properties in Sn–Ag–Cu system and Sn-3.5Ag alloys of lead-free solders

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The environment of solders used in welds is becoming more severe because of the increases in temperature associated with the miniaturization and increasing density of electronic apparatuses. Damage to soldered spots is a source of major problems in electronic apparatuses, and so it is important to obtain solders with reliable strength. The tin–lead system alloy has been used for soldering. However, the noxiousness of lead dissolved from the waste of electronic apparatuses has become a global environmental problem and laws regulating its use have been enacted. Therefore, in recent years, many lead-free solders have been developed and several solders including Sn-3.5Ag have come into practical use. The ternary alloy of Sn–Ag–Cu with addition of Cu to Sn–Ag alloy has been developed to improve wettability and reduce corrosion, and is now becoming the global standard lead-free solder. This system includes solders of various compositions and each country recommends different compositions. Although it is presumed that the eutectic composition is Sn-3.5Ag-0.7Cu in this system, the Sn-3.0Ag-0.5Cu composition is recommended in Japan. The differences in mechanical properties between them are of great interest, but few data are available for comparison. It is desirable for solders to show only small reductions in Young's modulus with increasing temperature without relaxation phenomena accompanying discontinuous reductions. In this experiment, the temperature dependence of Young's modulus and internal friction was measured for Sn-3.5Ag-0.7Cu, Sn-3.0Ag-0.5Cu, and Sn-3.5Ag solders using flexural vibration with no effect of creep, and the difference between them and the effects of addition of Cu were investigated. Furthermore, the cause of internal friction peaks appearing in the temperature characteristic by flexural vibration was investigated by examining longitudinal vibration at low frequencies.

The samples examined were three kinds of solder: Sn-3.5Ag-0.7Cu (Ag: 3.58%, Cu: 0.72%), Sn-3.0Ag-0.5Cu (Ag: 3.07%, Cu: 0.52%), and Sn-3.5Ag (3.43%) (Nihon Handa Co. Ltd., Tokyo, Japan). The Sn–Ag–Cu system solder and Sn-3.5Ag solder have melting points ( $T_m$ ) of 217 °C and 221 °C, respectively. These samples were melted at  $T_m + 100$  °C and test specimens were made by pouring the melts into a mold. The sizes of specimens used for flexural vibration and longitudinal vibration measurements were 3 ( $t$ ) × 5

( $w$ ) × 80 ( $l$ ) mm and 2 ( $t$ ) × 5 ( $w$ ) × 40 ( $l$ ) mm, respectively. In the former, bending rigidity was increased by making the specimens thicker to give resistance to high temperature and the increases in eigenfrequency were reduced by making the specimens longer. Six specimens were examined for each vibration method. The densities of the specimens were measured by the Archimedean method and were 7.34–7.37 g/cm<sup>3</sup> for Sn-3.5Ag-0.7Cu, 7.32–7.35 g/cm<sup>3</sup> for Sn-3.0Ag-0.5Cu, and 7.29–7.36 g/cm<sup>3</sup> for Sn-3.5Ag, which were 98.8–99.2%, 98.8–99.2%, and 98.4–99.3% of the theoretical densities, respectively.

The flexural vibration experiments were performed in an electric-drying oven. A free–free specimen was excited in fundamental mode by an electromagnetic transducer set facing it in the center and the vibration sound guided out of the oven by a glass pipe was detected with a condenser microphone. In general, Young's modulus,  $E$ , in flexural vibration is obtained from the equation  $E = 48\pi^2 \rho l^4 f_0^2 m^{-4} h^{-2}$  ( $\rho$ , density;  $l$ , length;  $f_0$ , eigenfrequency;  $h$ , thickness;  $m$ , constant). However, it is very difficult to accurately determine the values of  $l$ ,  $h$ , and  $\rho$  under conditions of high temperature. In contrast,  $f_0$  can be determined with a high degree of accuracy of 0.1%. Thus, in this experiment  $f_0^2$  was used instead of  $E$ . The values of  $f_0$  and internal friction  $Q^{-1}$  were obtained from the peak and half-value width of a resonance curve, respectively. The measurement frequency range was about 1400–1100 Hz. The temperature was increased close to the melting point at a rate of 1 °C/min. After measuring at intervals of 5–10 °C, the same experiment was performed again to investigate the effects of heat history. The indicating temperature of the digital thermometer, which was set closely by the specimens, was calibrated with a standard thermometer. Furthermore,  $E$  and loss tangent,  $\tan \delta (= Q^{-1})$ , were measured by forced longitudinal vibration at frequencies of 1, 10, and 100 Hz using a dynamic mechanical analyzer (DMA) (TA Instruments Co., Crawley, UK). Briefly, the specimens were fixed at a span of 13 mm with chucks and vibration was applied under the action of a static tensile force of 0.005 N. The measurement temperature was the same as that in flexural vibration.

Examples of measurements obtained for each solder by flexural vibration are shown in Figs 1–3. Young's

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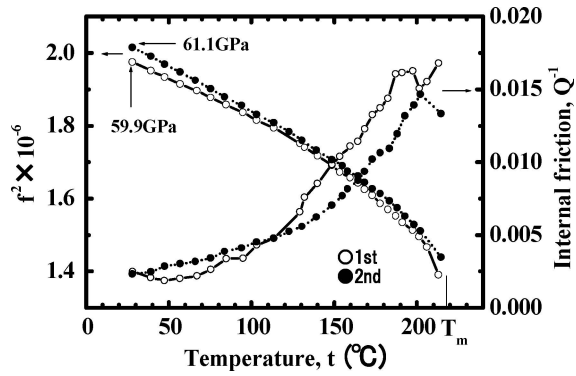


Figure 1 Temperature dependence of the square of resonant frequency  $f^2$  and internal friction  $Q^{-1}$  for Sn-3.5Ag-0.7Cu solder by flexural vibration.

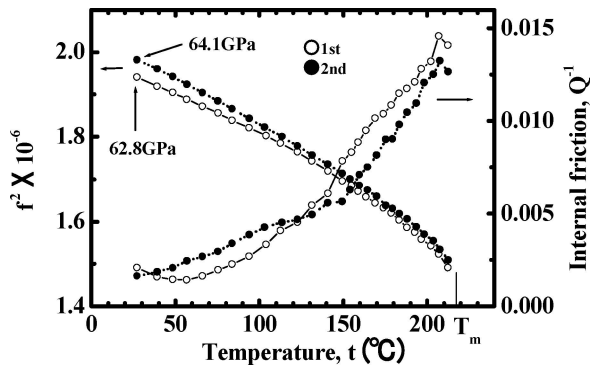


Figure 2 Temperature dependence of the square of resonant frequency  $f^2$  and internal friction  $Q^{-1}$  for Sn-3.0Ag-0.5Cu solder by flexural vibration.

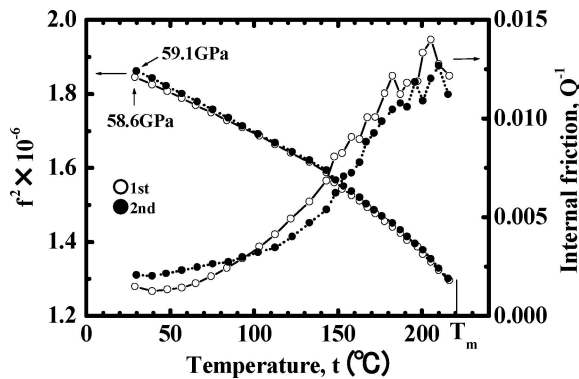


Figure 3 Temperature dependence of the square of resonant frequency  $f^2$  and internal friction  $Q^{-1}$  for Sn-3.5Ag solder by flexural vibration.

modulus at room temperature is shown in the figures. In all the solders,  $f^2$  decreased and  $Q^{-1}$  increased with increasing temperature, and a  $Q^{-1}$  peak appeared near the melting point. However, in Sn-3.5Ag solder a  $Q^{-1}$  peak also appeared at around 180 °C. The  $f^2$  at the second measurement was slightly higher than that at the first measurement, and the  $Q^{-1}$  at the second measurement was lower in the range of high temperature where  $Q^{-1}$  was large. This is because the first measurement functioned as the heat treatment effect. The effect on Young's modulus was 0.3–3.1% at room temperature. The comparison between solders at the first measurement is shown in Fig. 4. The Young's modulus at room temperature shown in the figure is the average. The

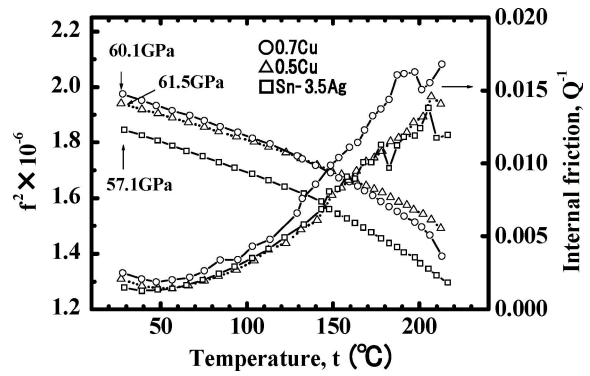


Figure 4 Comparison between Sn-3.5Ag-0.7Cu, Sn-3.0Ag-0.5Cu, and Sn-3.5Ag solders at first flexural measurement.

rate of  $f^2$  decreased between 30 °C and 210 °C, with Sn-3.5Ag solder showing the greatest decrease, 29%, followed by Sn-3.5Ag-0.7Cu solder with a decrease of 27%, and Sn-3.0Ag-0.5Cu solder showed the smallest decrease of 24%. There was little difference in the increase in internal friction between Sn-3.0Ag-0.5Cu solder and Sn-3.5Ag solder, and that of Sn-3.5Ag-0.7Cu solder increased at temperatures above 130 °C corresponding to the change in  $f^2$ . The Sn–Ag–Cu system showed greater elastic modulus than Sn-3.5Ag solder. This was because the Cu metal added had greater elastic modulus than Sn and Ag metals. In the Sn–Ag–Cu system, there was no  $Q^{-1}$  peak at around 180 °C in Sn-3.5Ag solder and there was only a single  $Q^{-1}$  peak near the melting point. Consequently, Sn-3.0Ag-0.5Cu solder was better than Sn-3.5Ag-0.7Cu solder with regard to temperature dependence of elastic modulus, and the temperature characteristics of Sn–Ag alloy can be improved by adding an appropriate amount of Cu.

To confirm whether the  $Q^{-1}$  peaks appearing in flexural vibration were relaxation phenomena obeying the Arrhenius equation, measurement was carried by longitudinal vibration at low frequencies of 1, 10, and 100 Hz. The results for each solder are shown in Figs 5–7. With increasing temperature, the Young's modulus decreased and the internal friction increased in the same manner as flexural vibration. In Sn–Ag–Cu system, no  $Q^{-1}$  peak was observed. However, in Sn-3.5Ag solder a small  $Q^{-1}$  peak that appeared at lower temperature with decreasing frequency was observed as expected. In addition, the disagreements of each curve

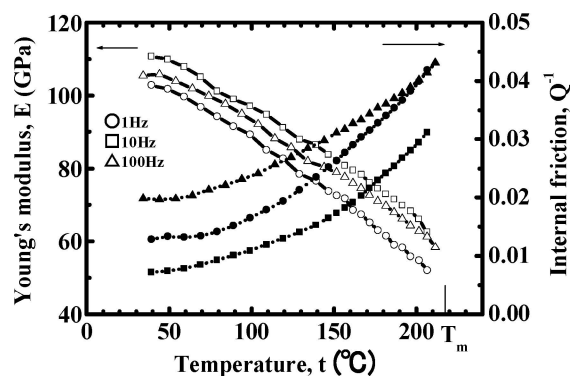


Figure 5 Temperature dependence of Young's modulus  $E$  and internal friction  $Q^{-1}$  for Sn-3.5Ag-0.7Cu solder by longitudinal vibration.

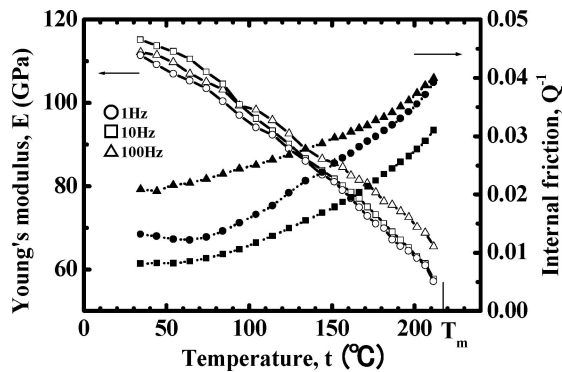


Figure 6 Temperature dependence of Young's modulus  $E$  and internal friction  $Q^{-1}$  for Sn-3.0Ag-0.5Cu solder by longitudinal vibration.

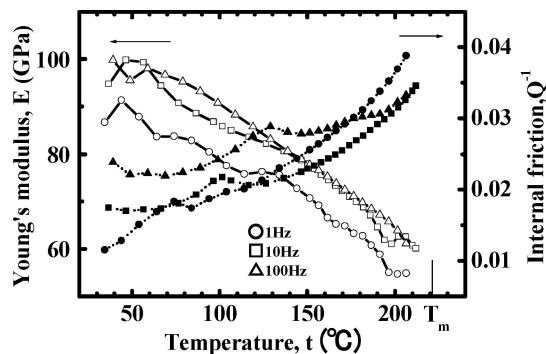


Figure 7 Temperature dependence of Young's modulus  $E$  and internal friction  $Q^{-1}$  for Sn-3.5Ag solder by longitudinal vibration.

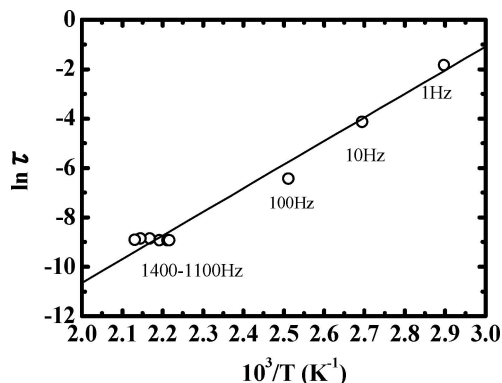


Figure 8 Arrhenius plots for the low-temperature peak of internal friction  $Q^{-1}$  of Sn-3.5Ag solder.

are due to the frequency dependence of  $E$  and  $Q^{-1}$  [1]. In Sn-3.5Ag solder, Arrhenius plots were made for the low-temperature peak in flexural vibration and the peak in longitudinal vibration, and the results are shown in

Fig. 8. A strong linear relation was observed between measured points. Therefore, the relaxation mechanisms of each peak were the same, and the activation energy was determined to be 79 kJ/mol from the slope of the straight line. Our value agreed well with those reported previously as the activation energies of the grain boundary relaxation in Sn metal [2–4]. In Sn-3.5Ag solder, the eutectic structure consisting of  $\beta$ -Sn, which hardly forms a solid solution with Ag, and the fibrous stable compound  $Ag_3Sn$  dispersed microscopically is formed as a belt surrounding the primary phase  $\beta$ -Sn grains with the dendritic structure. Therefore, it was estimated that the origin of the low-temperature peak in Sn-3.5Ag solder was related to the grain boundary and that the grain boundary is more coherent by mixing  $Cu_6Sn_5$  compounds, formed by addition of Cu and crystallized microscopically, in the eutectic structure and the peak disappears.

Drapkin *et al.* [2] observed internal friction peaks at  $0.94$ – $0.99T_m$  for four metals, including Sn, by flexural vibration of 600–800 Hz and introduced studies by other researchers explaining the anomaly near  $T_m$  by energy scattering due to elastic vibration and fluctuations of thermodynamic potential and estimated that similar factors were responsible for their peaks. Our high-temperature peaks were observed at almost the same temperatures, i.e.,  $0.92$ – $0.95T_m$ , and factors similar to those described above may be involved in our peaks.

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