Dependence of frequency on Young's modulus and internal friction in Sn–9Zn and Sn–3.5Ag eutectic lead-free solders

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The tin-lead eutectic solder Sn–37Pb has been an essential material for micro soldering in electronic assemblies because of the excellent properties such as low melting point, wettability, etc. However, an environmental problem has been pointed out on the danger of dissolved lead from industrial waste. Therefore, it is urgent to develop lead-free solders having high performance, and many studies have been made on various alloy-system solders based on tin, e.g., Sn–9Zn, Sn–3.5Ag, Sn–3.0Ag–0.5Cu, etc. as likely substitutes [1, 2].

An elastic modulus which is influenced considerably by microstructure is important as a basic physical constant also for solders. Since a solder is a soft alloy, in static measurement methods, generally the elastic strain is large and creep occurs easily. In contrary to this, in the vibrational measurement methods, generally the strain is small and no creep occurs; furthermore, the internal friction can also be measured and it is useful for the discussion on the microstructures of a material. These are the merits of vibrational measurement methods. However, in vibrational measurements of elastic modulus and internal friction, it is necessary to investigate frequency effects, because a solder is an anelastic body. Thus studies on lead-free solders have scarcely been carried out [3, 4].

In this study, the dependence of frequency over a range of 0–3 kHz on Young's modulus and internal friction in Sn–9Zn and Sn–3.5Ag, typical eutectic lead-free solders, was investigated at room temperature, and as a comparison, in Sn–37Pb old eutectic solders was also investigated.

Samples were extruded eutectic solders of Sn–9Zn (8.8%Zn), Sn–3.5Ag (3.43%Ag) and Sn–37Pb (36.5%Pb) with dimensions of 2.0 mm in thickness (t), 16 mm in width (w) and 250 mm in length (l). Specimens for flexural vibration were 250–50 mm in length. Rectangular bars with 5 (w) × 80 (l) mm and 5 (w) × 40 (l) mm were cut off from the sample solders and polished. The former and the latter were specimens for three point bending and longitudinal vibration, respectively. Furthermore, in order to consider the frequency behavior of Sn–9Zn and Sn–37Pb eutectic solders, specimens of Sn, Zn and Pb metals were made in the same manner as the solders. All the samples were made by Tanaka Electric Industry Co.

A stress-deformation curve was measured by three-point bend testing and static Young's modulus was calculated from the slope of a straight line in the range of strain less than 10^{-4}. The span was 30 mm, and the head speed 0.5 mm/min.

Dynamic Young's modulus, E, and loss tangent, $\tan\delta(= Q^{-1}$: internal friction), in the frequency range of 1–150 Hz were measured by longitudinal forced vibration using DMA (Dynamic Mechanical Analyzer) of TA Instruments Co. A specimen was fixed by chucks at both ends and vibration was given to it under the action of a static tensile force. The span was 16 mm, the amplitude 0.5 μm, the static tensile force 5 N and the strain less than 10^{-5}. The value of Young's modulus was calibrated using the standard specimen attached to DMA.

Dynamic Young's modulus and internal friction in the frequency range of about 50–3000 Hz were measured by free-free flexural vibration at the first mode.

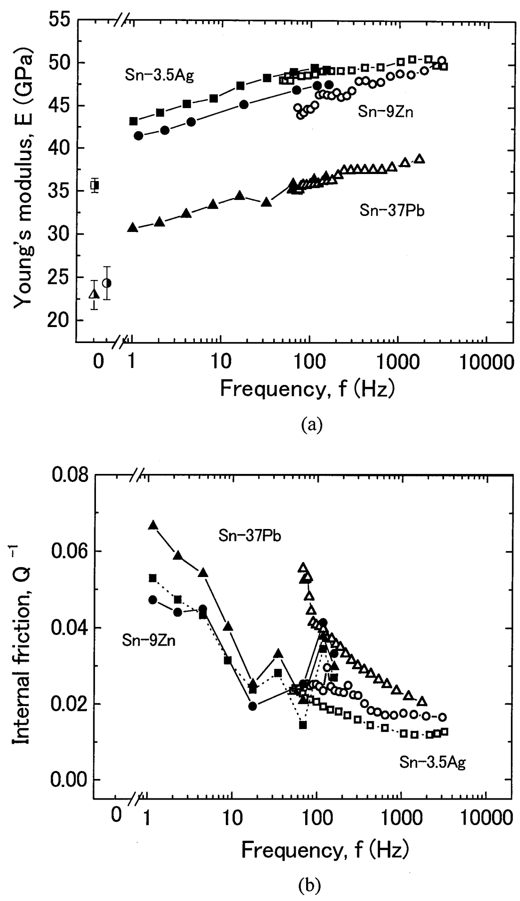

Figure 1 Frequency dependence of Young's modulus and internal friction in Sn–3.5Ag, Sn–9Zn and Sn–37Pb solders. Open: Flexural, Close: Longitudinal, Half close: three point bending.

The frequency was varied by cutting the specimen length by degrees. The dynamic Young's modulus and the internal friction were calculated from the peak frequency, f_0, and the half width, $\Delta f'$, and f_0 of a resonance curve, respectively. The vibration amplitude in the end of a specimen, h, was measured using a laser displacement meter, and the maximum strain amplitude, $\varepsilon_{\max}$, was calculated from the following equation [5]:

$$\varepsilon_{\max} = \frac{\pi^3 hd}{4l^2}, \tag{1}$$

where l and d are the length and the thickness of specimens, respectively. From the experimental results, the $\varepsilon_{\max}$ was less than 10^{-5}.

The frequency dependence of Young's modulus and internal friction in three kinds of solders was measured at room temperature and the results are shown in Fig. 1. The measured values of static Young's modulus are shown on the left hand-side of Fig. 1a with the standard deviation. With the increase of frequency, the Young's modulus and the internal friction of all the solders increased and decreased, respectively, though at around 100 Hz, where two values measured by longitudinal vibration and flexural vibration overlapped, they agreed in Young's modulus and disagreed in internal friction. However, it is estimated that the peak of internal friction exists at around 100 Hz, where the increased slope of Young's modulus changes.

When the effect of frequency (0–2 kHz) on Young's modulus was shown by the ratio of Young's modulus at 2 kHz, E_{2k}, to that at 0 Hz, E_0, the ratio of E_{2k}/E_0 was 1.4 in Sn–3.5Ag solder, 2.1 in Sn–9Zn solder and 1.7 in Sn–37Pb solder, so Sn–3.5Ag solder is the smallest. The frequency behaviors of Young's modulus and internal friction may be explained as follows: From the thermodynamic point of view, a value measured statically is an isothermal modulus and a value measured vibrationally is an adiabatic modulus, and the latter is larger than the former; furthermore, in a relaxation process, elastic modulus shifts from relaxed elastic modulus to unrelaxed elastic modulus with the increase of frequency, moreover, at the inflection point of elastic modulus, the peak of internal friction occurs, therefore our frequency range is in the latter stage of the relaxation process.

Secondly, in order to consider the frequency behavior of Sn–9Zn and Sn–37Pb solders, their part metals were also measured in the same manner as the solders. The results of Sn–9Zn, Sn and Zn are shown in Fig. 2, and those of Sn–37Pb, Sn and Pb in Fig. 3. In all the metals, the Young's modulus increased and the internal friction decreased, with increase of frequency in the same manner as the solders. The values of Young's modulus at 1 Hz and 2 kHz in solder alloys which followed a mixture law were calculated from those in metals and a straight line connecting both values is shown in the figures (a). In Sn–9Zn solder, all the measured values lay under the straight line, $\Delta E = -6.1 - -6.5\%$. In Sn–37Pb solder, the measured values were slightly higher

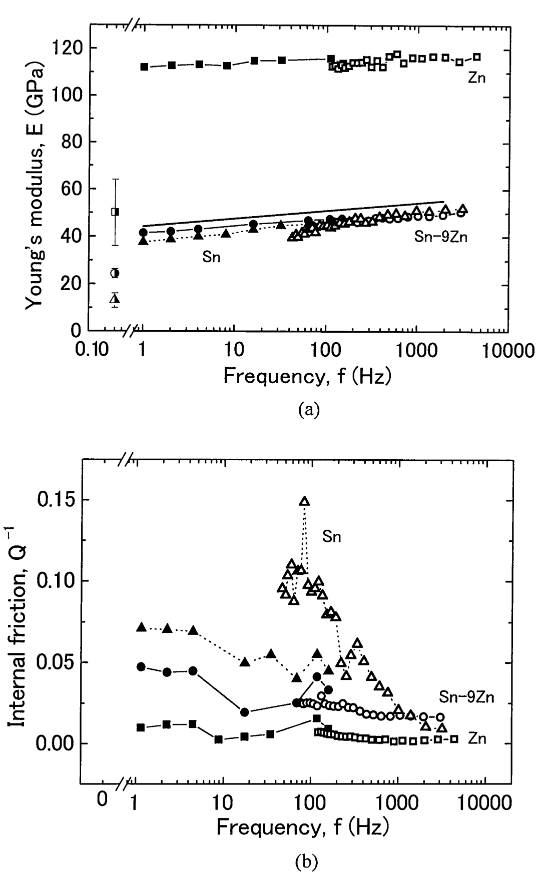

Figure 2 Frequency dependence of Young's modulus and internal friction in Sn–9Zn solder and Zn and Sn metals. Straight line in (a): value calculated by mixture law. Open: flexural, Close: longitudinal, Half close: three point bending.

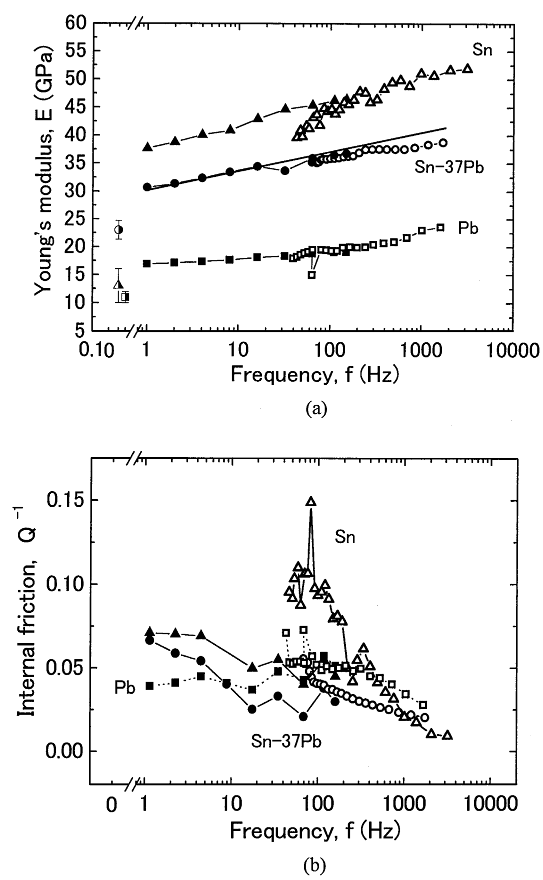

Figure 3 Frequency dependence of Young's modulus and internal friction in Sn–37Pb solder and Sn and Pb metals. Straight line in (a): value calculated by mixture law. Open: flexural, Close: longitudinal, Half close: three point bending.

than the calculated ones in the low frequency range, $\Delta E = 2.0\%$ at 1 Hz, and lower in the high frequency range, $\Delta E = -6.3\%$ at 2 kHz. Sn and Zn hardly form solid solutions in each other; however, Sn and Pb form solid solutions with each other. Therefore, this difference in ΔE between two solders may be due to the difference in microstructure. On the other hand, from the figure (b), the difference between longitudinal and flexural values measured at around 100 Hz was large in all the metals and particularly large in Sn, and clear information on the peak of internal friction could not be obtained. Frequencies around 100 Hz were in upper limit in our longitudinal vibration and lower limit in our flexural vibration. This peak of solder alloys is the subject for a future study.

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