

Low-frequency damping properties of eutectic Sn–Bi and In–Sn solders

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Eutectic Sn–Bi and In–Sn solders possess much higher damping capacities than Sn–Ag–Cu solders at temperatures above room temperature. The strain amplitude dependence of damping capacities in Sn–Bi solder determined at room temperature is comparable to that of Mg alloys measured at the same temperature. Sn–Bi and In–Sn solders both exhibit conspicuous high-temperature damping backgrounds, with activation energies of 0.77 and 0.27 eV, respectively.

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Lead-containing solders have been widely used as low-temperature joining alloys for microelectronic packaging in electronic components due to their ease of use and low cost. However, the use of lead-containing solders is now forbidden because of the potential risk of lead toxicity. In 2000, the National Electronic Manufacturing Initiative recommended replacing traditional Sn–37Pb solder with Sn–3.9Ag–0.6Cu for reflow and low-cost Sn–0.7Cu for wave soldering [1]. Although Sn–Ag–Cu and Sn–Cu solders are promising replacements for lead-containing solders, their higher melting temperatures and the formation of undesirable large brittle intermetallics limit their applicability in micro-electronic packaging [2]. Electronic equipments are usually subjected to many different forms of vibration over wide frequency ranges and various acceleration levels, which may damage the interconnected solders and cause failure of electronic components [3]. Consequently, the ability of solders to dissipate energy during vibration, termed damping capacity or internal friction, should be considered. Recently, the damping properties of solders have become more significant because the size of interconnecting solders is decreasing with the manufacture of smaller electronic devices. Unfortunately, lead-free Sn–3Ag–0.5Cu solder exhibits a much lower damping capacity than lead-containing Sn–37Pb solder

since the formation of Cu₆Sn₅ and Ag₃Sn intermetallics in the eutectic network band inhibits dislocation motions [4]. Eutectic Sn–Bi and In–Sn solders are also potential alternative lead-free solders because they possess lower melting temperatures ($T_m = 139^\circ\text{C}$ for Sn–Bi solder and $T_m = 120^\circ\text{C}$ for In–Sn solder) and do not form brittle intermetallics as Sn–Ag–Cu solders do [5]. Lakes and Quackenbush [6] have reported the viscoelastic behavior in In–Sn alloys. However, the damping characteristics of eutectic Sn–Bi and In–Sn solders have not been studied in detail before. The aim of this study is therefore to investigate the low-frequency damping characteristics of eutectic Sn–Bi and In–Sn lead-free solders, focusing especially on their damping properties above room temperature.

The eutectic Sn–Bi and In–Sn specimens used in this study were fabricated from commercial Sn–57.0 wt.% Bi and In–49.1 wt.% Sn solders. Both Sn–Bi and In–Sn solders were purchased from Yeh-Chiang Technology Corp., Taiwan, and had a high purity of >99.7%. The Sn–Bi and In–Sn solders were melted at 800 °C for 10 h in evacuated quartz tubes to form bulk ingots. Each ingot was cut into 30.0 × 6.0 × 1.5 mm³ blocks for further damping measurements. The low-frequency damping properties of the specimens were tested by a TA 2980 dynamic mechanical analyzer (DMA) configured with a single/dual cantilever and a liquid nitrogen cooling apparatus. The upper temperature limit for the DMA experiments was set as 60 °C for Sn–Bi solders

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and 40 °C for In–Sn solders, respectively, which were about 0.8 for their homologous temperatures (T/T_m).

Figure 1a and b plots the strain amplitude (ε) dependence of damping capacities (Q^{-1}) in eutectic Sn–Bi and In–Sn solders, respectively, measured at constant frequency $f = 1$ Hz and various constant temperatures. Figure 1a shows that the Q^{-1} values for Sn–Bi measured at -67 °C ($0.50T_m$) is extremely low (below $Q^{-1} = 0.01$) throughout the applied strain amplitude range. Figure 1a also reveals that the Q^{-1} values for Sn–Bi solder measured at 25 °C ($0.73T_m$) remain almost constant when the applied ε is below 3.2×10^{-5} , then gradually increase with further increasing ε . Thus, the damping capacities for Sn–Bi solder measured at that temperature can be divided into two components [7,8],

$$Q^{-1}(\varepsilon) = Q_0^{-1} + Q_H^{-1}(\varepsilon) \quad (1)$$

where Q_0^{-1} and $Q_H^{-1}(\varepsilon)$ represent the damping capacities independent of, or only weakly dependent on, the strain amplitude and the increase in the damping capacities with the strain amplitude, respectively. Accordingly, the Q_0^{-1} value of Sn–Bi solder measured at room temperature is about 3×10^{-2} , which is similar to that of pure Mg with 99.96 wt.% purity (about 2.5×10^{-2}) [8] but much higher than that of LZ100 alloy (about 6×10^{-3}) [9] measured at the same temperature. The critical strain, which is defined as the transition strain from the strain amplitude independent region to the dependent region, for Sn–Bi solder (3.2×10^{-5}) is also comparable to that of pure Mg (2×10^{-5}) [8] and LZ100 alloy (3×10^{-5}) [9] measured at room temperature.

Figure 1b plots the strain amplitude dependence of damping capacities for In–Sn solder measured at temperatures of -125 °C ($0.37T_m$), -80 °C ($0.50T_m$) and 25 °C ($0.75T_m$). As shown in Figure 1b, the Q^{-1} values for In–Sn solder measured at -125 °C are also extremely low throughout the applied strain amplitude range. The strain amplitude dependence of damping capacities for In–Sn solder measured at -80 °C is similar to that of Sn–Bi solder measured at room temperature and the determined critical strain and Q_0^{-1} values for In–Sn solder are 3.2×10^{-5} and 3×10^{-2} , respectively. However, when In–Sn solder was measured at 25 °C, the Q^{-1} value increases from 0.15 to 0.30 without a conspicuous Q_0^{-1} . This feature indicates that the $Q^{-1}(\varepsilon)$ for In–Sn solder is primarily dominated by $Q_H^{-1}(\varepsilon)$ rather than Q_0^{-1} at room temperature.

Figure 2a and b shows the internal friction curves vs. temperature, $Q^{-1}(T)$, for eutectic Sn–Bi and In–Sn solders, respectively, measured at constant applied strain

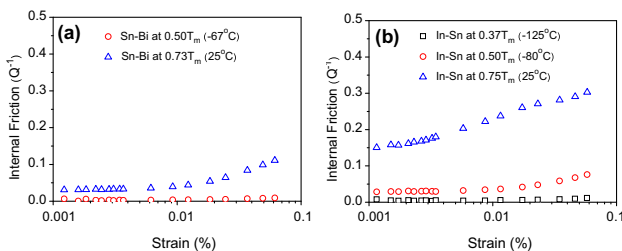


Figure 1. Strain amplitude dependence of damping capacities (Q^{-1}) in eutectic (a) Sn–Bi and (b) In–Sn solders measured at constant frequency $f = 1$ Hz.

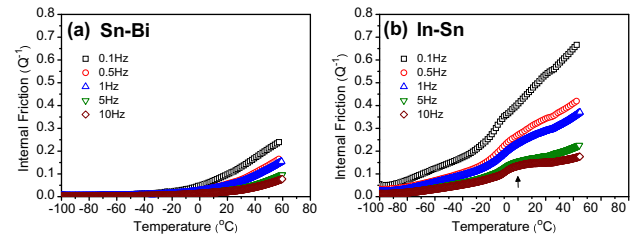


Figure 2. Heating $Q^{-1}(T)$ curves for eutectic (a) Sn–Bi and (b) In–Sn solders measured with different frequencies from 0.1 to 10 Hz.

($\varepsilon = 2.06 \times 10^{-4}$) and heating rate (3 °C min^{-1}), with different frequencies from 0.1 to 10 Hz. Here, the applied strain is set as $\varepsilon = 2.06 \times 10^{-4}$, which is higher than the critical strains of Sn–Bi and In–Sn solders, to obtain a conspicuous $Q^{-1}(T)$ curve. Figure 2a reveals that the Q^{-1} value of each $Q^{-1}(T)$ curve for Sn–Bi solder remains almost constant at temperatures below -40 °C, then increases gradually up to 60 °C. Consequently, these $Q^{-1}(T)$ curves can be divided into an athermal damping background (ADB) at temperatures between -100 and -40 °C and an exponential damping background at temperatures higher than -40 °C. The exponential damping background is also called the high-temperature damping background (HTDB), and has also been observed in other metals and alloys [4,9]. Compared to Sn–Bi solder, as shown in Figure 2b, In–Sn solder possesses only a very narrow ADB temperature range, from -100 to -80 °C, but subsequently its $Q^{-1}(T)$ curves increase dramatically in the HTDB temperature range. Figure 2b also demonstrates that the damping capacity of In–Sn solder is much higher than that of Sn–Bi solder, i.e. the maximum Q^{-1} value of In–Sn solder approaches 0.67 under $f = 0.1$ Hz while that of Sn–Bi is only 0.24. In addition, the $Q^{-1}(T)$ curves of In–Sn solder shown in Figure 2b exhibit an inconspicuous internal friction peak at around 0 °C, as indicated by the arrow in the figure. This internal friction peak could originate from grain boundary sliding, and has also been observed in some Mg alloys and soft solders [4,8].

Figure 2a and b also reveals that Q^{-1} values of the HTDB for eutectic Sn–Bi and In–Sn solders increase with decreasing frequency f at the same temperature. This feature indicates that the HTDBs for Sn–Bi and In–Sn solders exhibit a viscoelastic relaxation characteristic, which can be described by Schoeck's equation as [10,11]:

$$Q^{-1}(T) = Q_{at}^{-1} + \frac{K}{[\omega \exp(H/kT)]^n} \quad (2)$$

where Q_{at}^{-1} is the damping capacity of the ADB, H is the activation energy, ω is an angular frequency ($\omega = 2\pi f$, f is the applied frequency), k is the Boltzmann constant, T is the absolute temperature, and n and K are constants. It is convenient to use the logarithmic representation of Eq. (1) for the analysis of the HTDB as:

$$\ln[Q^{-1}(T) - Q_{at}^{-1}] = \ln K - n \ln \omega - n \frac{H}{kT} \quad (3)$$

Figure 3a plots the logarithmic plot ($\ln[Q^{-1}(T) - Q_{at}^{-1}]$ vs. $\ln \omega$) for various temperatures of the HTDBs for Sn–Bi and In–Sn solders, which are determined at different

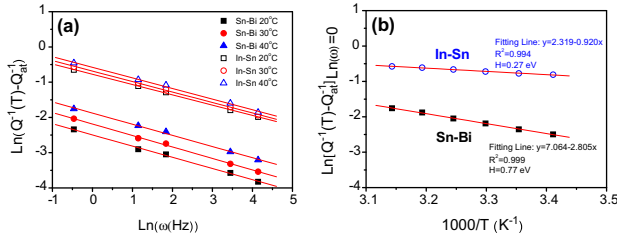


Figure 3. (a) The plot of $\ln[Q^{-1}(T) - Q_{at}^{-1}]$ vs. $\ln \omega$ for eutectic Sn-Bi and In-Sn solders measured at different temperatures. (b) The plot of $\ln[Q^{-1}(T) - Q_{at}^{-1}]|_{\ln \omega=0}$ vs. $1/T$ for eutectic Sn-Bi and In-Sn solders.

temperatures above 20 °C. Here, Q_{at}^{-1} is the stable damping capacity of the ADB measured at 10 Hz and –100 °C. Figure 3a reveals that the dependence of $\ln[Q^{-1}(T) - Q_{at}^{-1}]$ vs. $\ln \omega$ for Sn-Bi and In-Sn solders is linear, which is in accordance with the expectation of the viscoelastic relaxation behavior. From the slopes of the fitting lines, the n values can be measured at each temperature and their mean values are 0.32 and 0.29 for Sn-Bi and In-Sn solders, respectively. Figure 3b plots the $\ln[Q^{-1}(T) - Q_{at}^{-1}]|_{\ln \omega=0}$ vs. $1/T$ for Sn-Bi and In-Sn solders, in which $\ln[Q^{-1}(T) - Q_{at}^{-1}]|_{\ln \omega=0}$ is the value determined at $\ln \omega \rightarrow 0$ for each fitting line in Figure 3a. From the slope of the fitting line shown in Figure 3b, the H values of the HTDBs for Sn-Bi and In-Sn solders can be calculated as 0.77 and 0.27 eV, respectively. Table 1 lists the n and H values of the HTDB for eutectic Sn-Bi and In-Sn solders determined from Figure 4 as well as those for other soft solders [4], magnesium alloys [8,12,13] and TiAl/NiAl intermetallics [14]. Weller et al. [14–16] stated that the HTDB in TiAl alloys is associated with the diffusion-assisted climb of dislocations since the activation energies of TiAl alloys calculated from the high-temperature damping experiments and from the creep experiments are comparable. Therefore, as demonstrated in Table 1, the diffusion-assisted increase in dislocations should occur more readily in the group of soft solders and magnesium alloys ($H < 2.0$ eV) than in the TiAl and NiAl intermetallics ($H > 3.0$ eV). Table 1 also shows that In-Sn solder possesses the lowest H value of only 0.27 eV. This feature may correspond to the fact that the In element has the lowest melting temperature (melting temperature for In: 156.8 °C, Bi: 271.4 °C and Pb: 327.5 °C) and the easiest diffusion for smaller atomic radius (atomic radius for In: 0.144 nm, Bi = 0.182 nm and Pb = 0.175 nm) [17]. The extremely low H value of In-Sn solder implies that the accelerated diffusion process

Table 1. The n and H values of the HTDB for soft solders, magnesium alloys and TiAl/NiAl intermetallics.

	n	H (eV)
<i>Soft solders</i>		
Pure Sn (99.99%) [4]	0.12	0.98
Pb–Sn solder alloy [4]	0.23	0.43
Sn–Bi solder alloy	0.32	0.77
In–Sn solder alloy	0.29	0.27
<i>Mg alloys</i>		
As hot-extruded AZ80 alloy [12]	0.27	1.69
After 20% Cold-rolled AZ80 Alloy [12]	0.31	1.37
Mg–1Ca (wt.%) alloy [13]	–	1.35
Mg–9.5Li–0.5Zn (wt.%) alloy [9]	–	0.59
<i>TiAl and NiAl intermetallics</i>		
Ti–46Al–9Nb (at.%) [14]	–	4.2–4.3
Ti–46.5Al–4 (Cr, Nb, Ta, B) (at.%) [14]	–	3.8–3.9
Ni _{49.5} Al _{50.5} single crystal [14]	–	3.3

at HTDB temperature region simultaneously promotes creep development. Therefore, the effect of creep resistance deterioration in In-Sn solder should be carefully considered when In-Sn solder is used in the HTDB temperature region.

Figure 4a plots the heating $Q^{-1}(T)$ curves of different soft solders measured under $f = 1$ Hz. Figure 4a shows that Sn–3Ag–0.5Cu solder exhibits an extremely low damping capacity below 0.025 without any conspicuous internal friction peak or HTDB. Also, in view of practical high damping applications, the Q^{-1} value measured at room temperature (25 °C) for In-Sn (0.297) is much higher than those of pure Sn (0.074), Sn–Pb (0.067), Sn–Bi (0.056) and Sn–3Ag–0.5Cu (0.017) solders. That In-Sn solder possesses a much higher damping capacity at room temperature is a direct consequence of its melting temperature being lower than the others.

Figure 4b plots the heating $Q^{-1}(T)$ curves as a function of the homologous temperature for the soft solders shown in Figure 4a. Figure 4b indicates that both pure Sn metal and In-Sn solder possess good damping capacity at 0.5 T_m ($Q^{-1} = 0.041$ and 0.036 for pure Sn metal and In-Sn solder, respectively). However, Sn–Pb and Sn–Bi solders can exhibit comparable damping capacity only when they are heated to temperatures around 0.6 and 0.7 T_m , respectively. Figure 4b also reveals that pure Sn metal, Pb–Sn and In-Sn solders all exhibit HTDBs at temperatures above 0.5 T_m , while damping in Sn–Bi does not take place unless the temperature is above 0.65 T_m . It is also interesting to note that the addition of heterogeneous metals (except In) to Sn decreases the damping capacity of the solder alloy at the same homologous temperature. This could be because In metal itself is also a high damping material [18].

In conclusion, eutectic Sn–Bi and In-Sn solders both exhibit better damping capacities and conspicuous HTDBs than Sn–Ag–Cu lead-free solders at temperatures above room temperature. The Q_0^{-1} and critical strain values of Sn–Bi solder determined at room temperature are comparable to those of Mg alloys measured at the same temperature. The damping capacity of In-Sn solder is primarily dominated by $Q_H^{-1}(\varepsilon)$ rather than Q_0^{-1} at room temperature. The activation energies H values of the HTDBs for Sn–Bi and In-Sn solders are 0.77

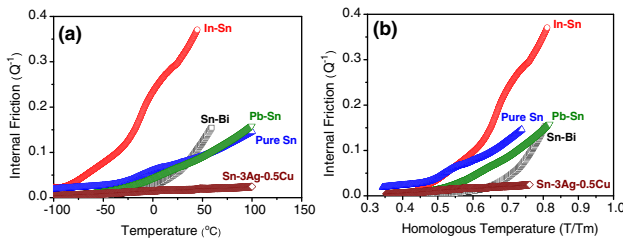


Figure 4. (a) Heating $Q^{-1}(T)$ curves of different soft solders [4] measured under $f = 1$ Hz. (b) Heating $Q^{-1}(T)$ curves as a function of the homologous temperature for the soft solders in (a).

and 0.27 eV, respectively. The extremely low H value of In–Sn solder indicates that the diffusion-assisted increase in dislocations in In–Sn solder is accelerated in the HTDB temperature region. The deterioration of creep resistance should be carefully considered when In–Sn solder needs to be used in the HTDB temperature region.

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