



VISCOELASTIC BEHAVIOR OVER A WIDE RANGE OF TIME AND FREQUENCY IN TIN ALLOYS: SnCd AND SnSb

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Introduction

All materials exhibit some viscoelastic response, which can manifest itself as creep, relaxation, or, if the load is sinusoidal in time, a phase angle δ between stress and strain. In polymers (1), large viscoelastic effects (the loss tangent, $\tan \delta$ from 0.1 to 1 or more) are common at ambient temperature, but in structural metals (2,3) such as steel, brass, and aluminum, viscoelastic effects are usually small ($\tan \delta$ of 10^{-3} or less); some aluminum alloys may exhibit very small loss, e.g. type 6061-T6, with $\tan \delta = 3.6 \times 10^{-6}$ (4).

Metals which exhibit substantial viscoelastic behavior are of interest in a variety of contexts. For example, materials with a high loss tangent are of use in damping vibration in structures and vehicles. Since structural metals have low damping, polymer layers are of use as attached layers in providing damping. Polymer layers are of little use in dealing with compressional vibration and have drawbacks in aggressive environments. Stiff materials with high damping would be of use in such situations. Homogeneous materials with high stiffness and high damping are not known. Composite materials may provide a way of combining these desired material properties. As another example, alloys of low melting point are used in soldering (5). Such alloys can exhibit substantial viscoelasticity. The effective performance of these solders in electronic devices is related to their viscoelastic behavior (creep); flow or cracking of a solder joint can lead to failure of the device that utilizes that solder joint.

It is well known that mechanical damping increases rapidly with temperature in metals at homologous temperature $T_H > 0.5$, where

$$T_H = \frac{T_{\text{abs}}}{T_{\text{melt}}} \quad (1)$$

T_{abs} is the absolute temperature and T_{melt} is the melting temperature (6). For structural metals, $T_H > 0.5$ corresponds to elevated temperature, but for some elements and alloys of low melting point, a high

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homologous temperature occurs at room temperature. Recently, a study of pure elements with low melting points, Cd, In, Pb, and Sn (7) disclosed that cadmium exhibited a substantial loss tangent of 0.03 to 0.04 over much of the audio range of frequencies, combined with a moderate stiffness $G = 20.7$ GPa. Lead, by contrast, exhibited $\tan \delta$ of 0.005 to 0.016 in the audio range. Indium exhibited a high loss tangent exceeding 0.1 at very low frequency. A eutectic alloy of indium and tin was found to exhibit substantial damping exceeding 0.1 below 0.1 Hz (8), and this alloy was used to make a composite exhibiting high stiffness and high damping (9). It is the purpose of this communication to present viscoelastic properties of two additional low melting point alloys, SnCd and SnSb. Both InSn and SnSb are used as solders. Although the melting point of Sb is 630.74°C , $T_H > 0.55$ at ambient temperature for the alloy of SnSb (95 wt% Sn/5 wt% Sb) which melts near 240°C . Eutectic SnCd melts at 177°C so $T_H \approx 0.65$ at room temperature.

Materials and Methods

Cd (99.99+% pure) was obtained in a 12.7 mm diameter rod-shaped form, and Sn (99.985% pure) was obtained in the form of a 63 mm diameter rod (Alfa, Johnson Matthey, Ward Hill, MA) and cut into small pieces under water irrigation. Cd was cleaned using a 10% solution of Nitol and mechanically agitated ultrasonically to remove surface oxide. Cd and Sn were rinsed in acetone and then in methanol. After cleaning, the elements were weighed and combined in a eutectic combination [67.75 wt% Sn/32.25 wt% Cd (10)]. The metal elements were then placed in a Pyrex tube with an inner diameter of 3.175 mm. During the alloying, the elements were heated in an environment that had been evacuated with a mechanical vacuum pump and backfilled with standard purity argon to provide an inert gas environment and prevent possible oxidation. The furnace was heated to 350°C which is above the melting point of both Sn and Cd. Temperature was held constant for 1 h, during which the alloying elements were occasionally agitated to ensure complete alloying. The resulting SnCd specimen was then removed from the tube, and its ends were cut to form a cylinder with a diameter of 3.2 mm (0.126 in) and a length of 37.4 mm (1.473 in).

The SnSb alloy specimen was obtained from a roll of 2.31 mm (0.091 in) diameter wire (Litton, Kester solder, Des Plaines, IL) intended for soldering use. The alloy is rather malleable, so a length was straightened manually and cut from the roll. The resulting SnSb alloy specimen was 2.31 mm (0.091 in) in diameter and 46.9 mm (1.847 in) in length.

Testing on the SnCd specimen was performed using the modified (8) apparatus (Figure 1) of Chen and Lakes (11). A ten decade frequency range up to 10 kHz under isothermal conditions was used with the original instrument for the dynamic characterization of foams, polymers, and viscoelastic elastomers. Recent modifications make possible experiments on stiffer and lower-damping materials such as metals. Testing of the SnSb specimen was performed using a smaller apparatus that utilizes the principles developed by Chen and Lakes but differs in the method of supporting the testing components. The wide frequency range capability of this apparatus is particularly useful in testing composites and other materials which are thermorheologically complex. The top of each cylindrical specimen was attached to its support rod. A high magnetic intensity neodymium iron boron magnet was glued to the bottom end of each specimen. They were allowed to set at room temperature for up to 24 h before testing. Mounting was achieved through the use of a cyanoacrylate cement.

Dynamic experiments were conducted by applying an amplified sinusoidal voltage from a digital function generator to the Helmholtz coil. This coil imposed a magnetic field on the permanent magnet and transmitted an axial torque on the specimen. The angular displacement of the specimen was measured using laser light reflected from a mirror mounted on the magnet to a split-diode light detector. The detector signal was amplified with a wideband differential amplifier. Torque was inferred from the Helmholtz coil current. Torque calculations were supported by calibrations using the well-characterized 6061-T6 Al alloy ($E=68.9$ GPa, $G=25.9$ GPa, $\tan \delta \approx 3.6 \times 10^{-6}$) (4). Input and output voltages were

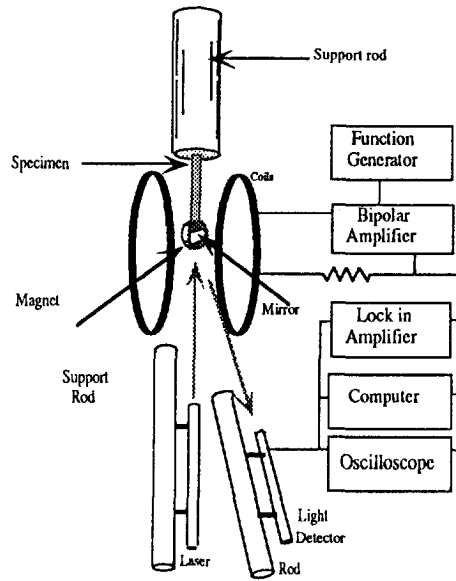


Figure 1. Schematic diagram of apparatus.

recorded using a digital data acquisition system containing a Macintosh IIfx computer and LabVIEW® interface hardware and software. Quasistatic (creep) experiments were conducted by applying a step function of current and monitoring both the current and the angular displacement signal as a function of time. Near resonances, signals were measured using a digitizing oscilloscope. Surface strain amplitude at acoustic frequencies was typically 10^{-6} or less. The phase angle between torque and angular displacement was determined from the width of elliptical Lissajous figures.

Data reduction was conducted using the relationship for the torsional rigidity (ratio of torque M^* to angular displacement θ) of a viscoelastic cylinder of radius R , length L , and density ρ with an attached mass of mass moment of inertia I_{at} at one end and fixed at the other end. The exact relationship is (12):

$$\frac{M^*}{\theta} = \left[\frac{1}{2} \pi R^4 \right] \left[\rho \omega^2 L \right] \frac{\text{ctn } \Omega^*}{\Omega^*} - I_{at} \omega^2, \tag{2}$$

in which

$$\Omega^* = \sqrt{\frac{\rho \omega^2 L^2}{G^*}} \tag{3}$$

with G^* as the complex shear modulus $G^* = |G^*| (1 + i \tan \delta)$ and $\omega = 2\pi\nu$, with ν as frequency. For the present data of relatively low loss below the first resonance, it was sufficient to use a simpler lumped approximation; for high loss materials near resonance, the exact relation is required (11). We remark that for very low frequency, stiffness is given by $|G^*| \approx \frac{|M^*|L}{\theta J_t}$, and loss by $\tan \delta \approx \tan \Phi$ where J_t is the second moment of area about the neutral axis in torsion, and Φ is the observed phase difference. At the torsional resonance angular frequencies ω_o , damping was calculated using the width $\Delta \omega$ at half maximum of the frequency response curve as follows.

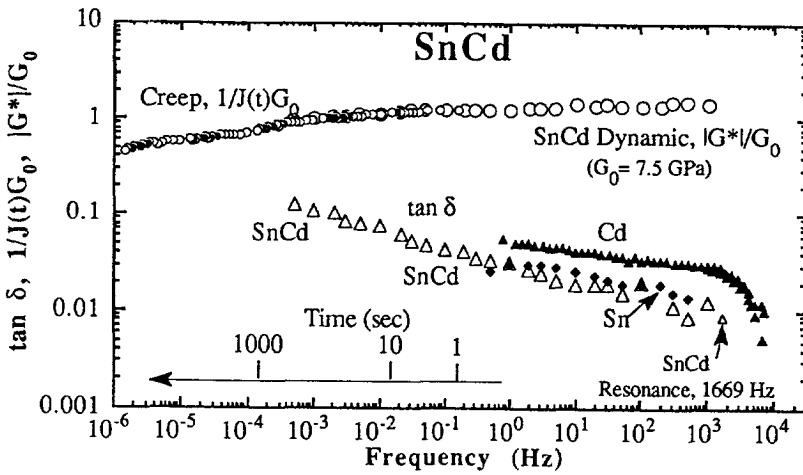


Figure 2. Viscoelastic properties of SnCd compared with those of Cd and Sn (7). G_0 (0.001 Hz) = 7.5 GPa.

$$\tan \delta \approx \frac{1}{\sqrt{3}} \frac{\Delta \omega}{\omega_0} \tag{4}$$

Each specimen was tested at a temperature of 23°C. In most experiments, input voltage (and thus shear stress) was held constant.

Results and Discussion

Phenomena

The absolute value of the complex dynamic shear modulus G^* and the loss tangent $\tan \delta$ are plotted on a common scale along with the normalized inverse of the creep compliance $J(t)$ (Figures 2,3). Errors are mostly comparable to or less than the size of the data points. Time t in creep is related to frequency ν in

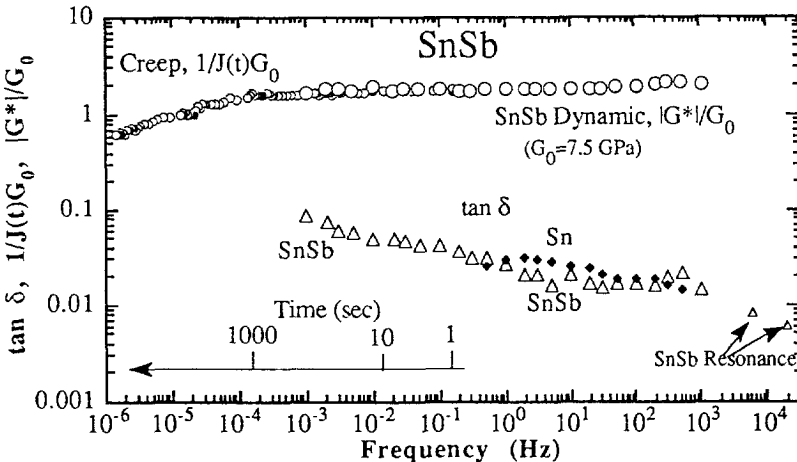


Figure 3. Viscoelastic properties of SnSb compared with those of Sn (7).

dynamic tests by $2\pi\nu = 1/t$. $\tan \delta$ approximately followed a ν^{-n} dependence at higher frequency for both alloys with n values given below. Deviations from this pattern may be in the form of peaks; if so they are poorly defined. The value of n was 0.17 for SnCd and 0.12 for SnSb, compared with 0.28 for InSn examined earlier (8). The creep compliance showed a t^m behavior at long times with no evidence of an asymptotic stiffness. The value of m for time greater than 100 sec was 0.10 for SnCd and 0.21 for SnSb, compared with 0.28 for InSn. Since $m \neq 1$, the strain rate is not constant so the creep is not secondary creep; it is still primary creep even at long times. The SnCd and SnSb alloys overall exhibited substantially less viscoelastic response at the lower frequencies than did InSn.

Alloy Properties in Relation to Constituent Properties

In an ideal eutectic, the constituents form a composite microstructure in which each phase is a pure element. Viscoelastic composites are reasonably well understood in that the elastic-viscoelastic correspondence principle may be applied to the known analytical elastic modulus results for composite structures to obtain the complex modulus of the material (13,14), and maps of stiffness vs loss developed for various composite structures (15). Rigorous bounds are available for the complex bulk modulus of viscoelastic composites (16) but not for the shear modulus. The Voigt (arithmetic mean) and Reuss (harmonic mean) composite formulae are not bounds, but they are realizable, and they approximate the bounds. The SnCd alloy considered here does not form an ideal eutectic; there is some solid solubility as was the case for InSn. Nevertheless, the properties of composites containing the pure constituents are of interest for comparison in considering possible mechanisms.

Damping of the SnCd alloy is slightly less than that of Sn (7) over most of the audio frequency range and is substantially less than that of Cd, however there is a 33% decrease in stiffness when compared to Sn at 100 Hz. Damping and stiffness of the SnCd are below both the Voigt and Reuss values for composites of Sn and Cd. Consequently the solid solubility has the effect of reducing the damping in this alloy. This is in contrast to the eutectic InSn alloy in which damping (8) was considerably higher than the range expected for a composite or ideal eutectic. SnSb exhibits a higher shear modulus at 100 Hz (15.0 GPa) than Sn, but its damping is lower ($\tan \delta = 0.017$); a comparison based on composite theory is precluded by a lack of data for Sb.

Mechanisms

Several mechanisms give rise to viscoelastic damping in metals at high homologous temperature (2,3). Viscous slip at the grain boundaries as well as rearrangement of pairs of atoms in an alloy (Zener mechanism) give rise to peaks in $\tan \delta$ which approximate the Debye form.

$$\tan \delta = \Delta \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (5)$$

with τ as a relaxation time and $\omega = 2\pi\nu$, with ν as frequency and Δ as a constant. Such peaks cover about one decade of time or frequency.

There is also a high temperature background which follows a power law in frequency.

$$\tan \delta = A \nu^{-n} \quad (6)$$

where A and n are constants. A superposition of Zener and high temperature background processes was observed in a CdMg alloy (17); the Zener peak dominated.

Nowick and Berry (3) discussed the high temperature background in their classic reference on anelastic behavior, in which they observe:

- that its magnitude is highly structure sensitive in that it is smaller in single crystals than in polycrystals,
- that its magnitude is smaller in coarse-grained polycrystals than in fine-grained polycrystals,
- it is enhanced in deformed and partially recovered or polygonized samples, and
- it is reduced by annealing treatments at successively higher temperatures.

High temperature background is thought to be caused by a combination of thermally activated dislocation mechanisms (18). Schoeck, Bisogni, and Shyne assumed a generic thermally activated dislocation-point-defect mechanism; for a distribution of activation energies and negligible restoring force on the dislocations, the following was obtained.

$$\tan \delta = \frac{Q}{[v \exp(U_o/kT_{abs})]^n} \quad (7)$$

where U_o is the activation energy of the rate-controlling process, v is frequency, T_{abs} is the absolute temperature, and Q and n are constants. This relaxation process is, however, not well enough understood to permit prediction of the magnitude of the viscoelastic response of a given pure metal or alloy.

The SnCd and SnSb alloys considered here exhibit behavior dominated by damping as a power law in frequency, which is consistent with a high temperature background (dislocation) mechanism. In that sense they are similar to eutectic InSn, but they exhibit less damping. No Debye peaks which could be attributed to solid solubility according to the Zener mechanism, were evident. Reduced damping in these alloys may be attributed to pinning of dislocations.

Conclusions

Damping of SnCd was lower than that of Cd and at most frequencies lower than that of Sn. Damping of SnSb was lower than that of Sn over most audio frequencies. Both alloys had lower damping than eutectic InSn. $\tan \delta$ approximately followed a v^{-n} dependence over a wide range of frequency for these alloys.

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