JOURNAL OF MATERIALS SCIENCE 31 (1996) 6577–6581

Viscoelastic behaviour in indium alloys: InSn, InBi, InCd and InSnCd

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Experimental studies of dynamic and transient viscoelastic response were conducted at 24 °C on the indium alloys InSn, InBi, InCd and InSnCd. The experiments were conducted in torsion using an instrument capable of determining viscoelastic properties over ten decades of time and frequency. The damping, tan δ, followed a ν^{-n} dependence at higher frequency ν and was essentially constant at low frequency. Creep at long times followed a power law dependence upon time: t^m. The damping is attributed to a dislocation-point defect mechanism.

1. Introduction

Viscoelastic materials are used in many applications which involve vibration damping and sound absorption. The tangent of the phase angle δ between stress and strain in sinusoidal loading, is referred to as the loss tangent, and is a useful measure of dynamic viscoelastic response. Many polymers exhibit large loss tangents, on the order of one, over frequency ranges suitable for damping applications [1]. Structural metals, by contrast, typically exhibit loss tangents of 10^{-3} or less [2, 3].

In some structural applications it would be helpful to have materials which exhibit both high stiffness and high damping. Composite materials represent one possibility in achieving such behaviour. It is possible to predict the viscoelastic behaviour of composites from that of the constituents [4, 5]. Composite microstructures which exhibit high stiffness and high damping have been considered theoretically [6, 7] and experimentally [8, 9]. Many materials are available for the stiff phase of such a composite. A polymer could be used for the high-loss phase, but the volume fraction would have to be unrealistically small to achieve a composite with high stiffness and high damping. A better choice for the high-loss phase would be a material with moderate stiffness. The alloys of low melting point considered here are candidate materials for such a composite.

Alloys of low melting point are also of interest in connection with the "high temperature background" damping which is observed in metals at high homologous temperature $T_H > 0.5$ in which $T_H = T/T_{melting}$, and T is the absolute temperature. Kê [10] systematically examined this effect since it was superposed on the damping peak under study, attributed to grain boundary sliding in metals. In structural metals such as steel, aluminium and brass, the melting point is high, so viscoelasticity associated with the 'high-temperature background' occurs only at elevated temperatures. Metals of low melting point can be expected to exhibit high-temperature background damping at room temperature, therefore this damping mode is accessible for applications and is also readily studied in these metals.

Low melting point alloys are used in solders [11]. Viscoelastic behaviour, particularly creep, of solders is relevant to their performance in electronic devices, since flow or cracking of a solder joint can lead to failure of the device.

2. Experimental Procedure

Metal ingots were cut, under water irrigation, into sections using a low speed diamond saw. The InSn alloy was obtained from Johnson Matthey Alfa in a eutectic composition, while the other alloys were prepared by melting the constituents, also obtained from Johnson Matthey Alfa. The sections were then placed into a glass tube which was evacuated and backfilled with standard purity argon. The furnace was ramped to a temperature above the melting point of each alloy and allowed to soak for one hour. The specimen tube was shaken vigorously at times during the melting. By this method specimens were cast into glass tubular molds 3.1 mm in diameter. The resulting ingot was then removed from the glass tube and its ends finished to form a circular cylindrical specimen about 35 mm long. The compositions by weight were InSn, eutectic, 52:48%; InBi, eutectic 66:34%; InCd, 25:75% (eutectic is 75% indium); InSnCd, 26:24:50%.

Viscoelastic measurements were performed using a modified [12] version of the apparatus of Chen and Lakes [13] as shown in Fig. 1. This device permits measurements over an unusually wide range of time and frequency. This is particularly useful in composites and other materials which are not thermorheologically simple. The modifications allow improved phase resolution so that measurements are

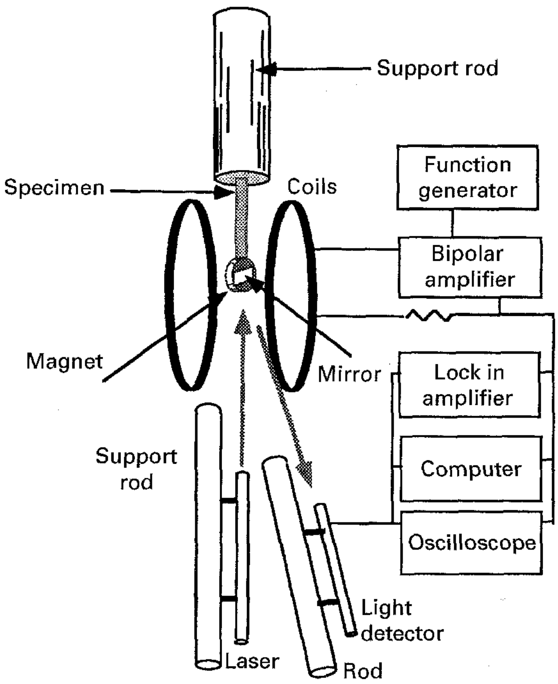

Figure 1 Schematic diagram of the instrumentation for viscoelastic experiments.

not limited to high-loss elastomers. One end of the specimen was glued (with a cyanoacrylate cement) to a tungsten rod, 12.7 mm in diameter, fixed to a stiff framework of rods. The other end of the specimen was cemented to a permanent magnet made of high intensity neodymium-iron-boron. Dynamic experiments were conducted by applying an amplified sinusoidal voltage from a digital function generator to a Helmholtz coil which generated a magnetic field. This field acted upon the specimen magnet to provide an axial torque. Light from a helium neon laser was reflected from a small mirror upon the magnet to a split-diode light detector. The output from the detector was amplified by a differential amplifier. Torque was inferred from the Helmholtz coil current. Torque calculations were supported by calibrations using the well-characterized 6061-T6 aluminium alloy ($E = 68.9$ GPa, $G = 25.9$ GPa, $\tan\delta \approx 3.6 \times 10^{-6}$) [14]. The phase angle between torque and angular displacement was determined using a lock-in amplifier at higher frequencies and from the width of elliptic Lissajous figures at low frequencies. At resonant frequencies, material damping was inferred from the width of the dynamic compliance curve or from free decay of vibration. Quasistatic (creep) experiments were conducted by applying a step function current and monitoring both the current and the angular displacement signal as a function of time. Several short term creep tests were conducted and recovery following creep was examined. The surface shear strain at 1 Hz was 6.7×10^{-6} for InSn, 1.2×10^{-5} for InBi, 9.0×10^{-6} for InCd and 5.7×10^{-6} for InSnCd. Specimen ages (following casting) at the beginning of the tests reported in the graphs were: InSn 192 days; InBi 77 days; InCd 104 days; InSnCd, 190 days. An ageing study was also conducted in which InSn of age 15 days following casting was compared with InSn of age 192 days and greater. The test temperature was 24 °C ± 1 °C.

3. Results

Viscoelastic spectra over wide ranges of time and frequency are plotted in Figs 2–5. In these figures, the absolute value of the complex dynamic shear modulus and the loss tangent tan δ are shown as functions of frequency. The dynamic properties are plotted on a common scale with the inverse of the creep compliance; time t in creep is related to frequency ν in dynamic tests by $2\pi\nu = t$. Tan δ followed a ν^{-n} dependence at higher frequency for all the alloys. The value of n was 0.28 for InSn, 0.21 for InBi, 0.16 for InCd and 0.24 for InSnCd. Dynamic behaviour was linear over a range of strain exceeding values reported above: neither stiffness nor tan δ depended significantly on the strain level, from 2.2×10^{-6} up to 1.8×10^{-5} for InSn. Moreover, the tan δ values were considerably higher than those observed by others for structural metals. The creep behaviour showed a t^m behaviour at long times with no evidence of an

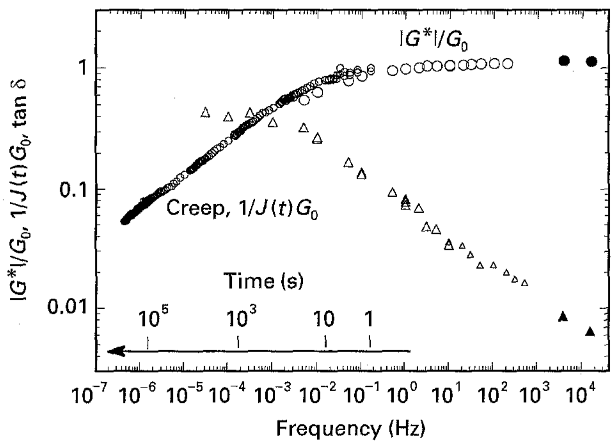

Figure 2 Viscoelastic behaviour of indium–tin eutectic alloy at room temperature [$G_0 = 7.56$Pa). Creep as a function of time t and dynamic results as a function of frequency ν shown on the same plot using the relation $2\pi\nu = t$. (△) damping, tan δ; (▲) resonance.

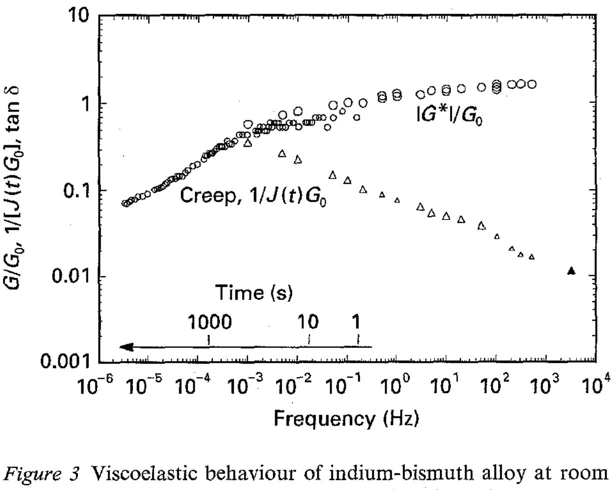

Figure 3 Viscoelastic behaviour of indium-bismuth alloy at room temperature [$G_0 = 3.86$Pa). Creep as a function of time t and dynamic results as a function of frequency ν shown on the same plot using the relation $2\pi\nu = t$. (△) damping, tan δ; (▲) resonance.

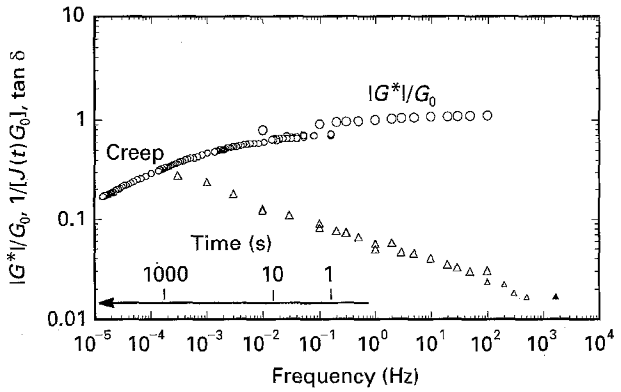

Figure 4 Viscoelastic behaviour of indium-cadmium alloy at room temperature [$G_0 = 3.96$Pa). Creep as a function of time t and dynamic results as a function of frequency ν shown on the same plot using the relation $2\pi\nu = t$. (△) damping, tan δ; (▲) resonance.

Figure 6 Reflected light micrograph of indium–tin alloy.

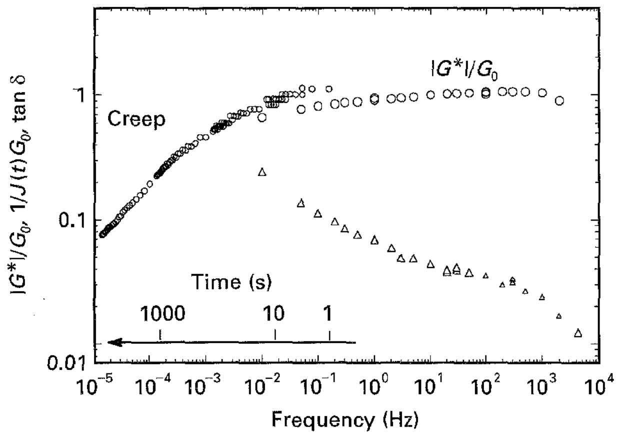

Figure 5 Viscoelastic behaviour of indium-tin–cadmium alloy at room temperature [$G_0 = 11.76$Pa). Creep as a function of time t and dynamic results as a function of frequency ν shown on the same plot using the relation $2\pi\nu = t$. (△) damping, tan δ; (▲) resonance.

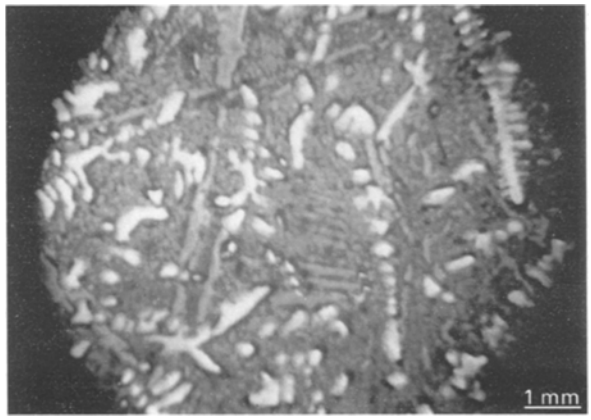

Figure 7 Reflected light micrograph of indium–tin–cadmium alloy.

asymptotic stiffness. The value of m for times greater than 100 s was 0.28 for InSn, 0.32 for InBi, 0.27 for InCd and 0.44 for InSnCd. 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. Moreover, recovery following short term creep was essentially complete. Creep of a power law form in a linearly viscoelastic material implies a loss tangent which is essentially constant at low frequency: $\tan\delta \approx m\frac{\pi}{2}$. Dynamic results for InSn at very low frequency are in reasonable agreement with the $\tan\delta \approx 0.44$ expected from the slope of the creep curve as shown in Fig. 2.

InSn exhibited little temperature dependence over the range 23.5–25.5 °C: at 1 Hz, the shear modulus decreased by about 1% per °C; changes in tan δ were too small to resolve.

Some ageing was observed in InSn. From 15 to 192 days, the shear modulus at 100 Hz increased by 8% and 1 Hz by 17%; tan δ decreased by 17% at 100 Hz and by 26% at 1 Hz. From 192 to 225 days no further evidence of ageing was evident. These results suggest a slow conversion to a more ordered microstructure. The micrographs shown in Figs 6 and 7 show representative heterogeneous structures.

4. Discussion

4.1 Indium properties

The properties of indium are relevant to understanding the characteristics of its alloys. Polycrystalline cast indium is viscoelastic and has a shear modulus of 4.1 GPa and a loss tangent of 0.035 at 100 Hz and at 23 °C [15]. The loss tangent increases substantially at lower frequency, exceeding 0.2 at 10^{-4} Hz. Single-crystal indium is highly anisotropic. Its moduli, measured ultrasonically at 300K, are, in the reduced notation, $C_{11} = 45.2$ GPa, $C_{12} = 41.9$ GPa, $C_{33} = 45.1$ GPa, $C_{44} = 6.5$ GPa, and $C_{66} = 12.1$ GPa [16]. The shear modulus $\frac{1}{2}(C_{11} - C_{12}) = 2.6$ GPa differs from C_{44}, a further manifestation of crystal anisotropy. For pure indium, the value of $\frac{1}{2}(C_{11} - C_{12})$ is small and it decreases with increasing temperature. This modulus, as well as the others must be positive if a crystal is to be stable. It is thought that indium would undergo a martensitic transformation at high temperature if it did not melt first [17].

4.2 Relation of alloy properties to constituent properties

In the simplest possible 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 [4, 5]. No known composite structure gives rise to a composite tan δ exceeding that of each constituent [6]. Rigorous bounds are available for the complex bulk modulus of viscoelastic composites [7] but not the shear modulus. The alloys considered here do not form simple eutectics: there is some solid solubility as described below. Nevertheless, the properties of composites containing the pure constituents are of interest for comparison in considering possible mechanisms.

InSn has a shear modulus of 8.1 GPa at 100 Hz, a value which lies between the Voigt and Reuss moduli of 9.67 and 6.35 GPa for composites of indium ($G = 4.1$ GPa at 100 Hz) and tin ($G = 15.7$ GPa at 100 Hz). The tan δ for InSn exceeds the values observed for pure cast indium [15], a situation which does not occur in any known composite. As for InCd, its shear modulus ($G = 3.98$ GPa at 100 Hz) is lower than the Voigt modulus 16.6 GPa, the Reuss modulus 10.3 GPa, as well as the modulus of either constituent, a situation which does not occur in any known composite.

The phase diagram of InSn discloses substantial solid solubility, quoted to be 6.5 wt% indium in tin at room temperature [18]. Therefore the "extra" damping beyond the upper bound of what might be expected of a composite of pure indium and pure tin, may be attributed to atomic-scale processes in the solid solution. Possible viscoelastic mechanisms are discussed below. The eutectic temperature of InSn is 117 °C. InBi exhibits a eutectic point at 72 °C, but solid solubility of 20.5 wt% bismuth was reported [18]; moreover it was suggested that indium hardens bismuth. The solid solubility of indium in cadmium is quoted as less than 1% at the eutectic temperature, 123 °C. The solid solubility of cadmium in indium is quoted as 4.5 at% at 20 °C. The solid solubility is considered to be linked to the reasons why these materials do not obey the composite theory which would apply to an ideal eutectic.

As for specific viscoelastic mechanisms, the atom-pair reorientation process of Zener [19] can give rise to substantial damping in alloys. It is considered unlikely that this mechanism is involved in the present alloys since a Debye type peak in the tan δ (covering about one decade in frequency) is predicted while the present results disclose a broad distribution of damping.

4.3 Stability in indium alloys

For a crystal to be stable, it is necessary, amongst other conditions, that, $C_{44} > 0$, $\frac{1}{2}(C_{11} - C_{12}) > 0$ and also that $C_{33} > 0$. Alloying indium with thallium gives rise to a martensitic phase transition from a tetragonal structure to a cubic structure. The quantity $\frac{1}{2}(C_{11} - C_{12})$ tends to zero as a function of composition in InTl alloys and as a function of temperature at a fixed composition [16]. Peaks in ultrasonic attenuation, and hence the viscoelastic damping, are observed in the vicinity of the phase transformation. A phase transition is also observed in indium-rich InCd alloys with 6.5 at% cadmium [17]. The transition temperature depends on composition, from 40 °C at 5.83 at% to 6 °C at 6.23 at%, to −6 °C at 6.97 at% indium [20]. Since the InCd alloy examined here is cadmium rich, and since small temperature fluctuations did not give rise to large changes in stiffness, it is unlikely that the observed damping is associated with proximity to a phase transition.

4.4 High temperature background

High temperature background damping in metals is known to depend on structure in that it is smaller in single crystals than in polycrystals. It is also smaller in coarse-grained polycrystals than in fine-grained polycrystals whilst it is enhanced in deformed and partially-recovered or polygonized samples. It is also reduced by annealing treatments at successively higher temperatures. It is thought that the background is caused by a combination of thermally-activated dislocation mechanisms. The dependence of the background loss upon temperature and frequency has been discussed by Schoeck *et al* [21]. They considered a generic thermally-activated dislocation-point defect mechanism. If the dislocation experiences a restoring force represented by q, then the damping follows a Debye peak in angular frequency $\omega = 2\pi\nu$, with ν as frequency:

$$\tan\delta = \frac{\gamma\Lambda G\mathbf{b}}{q}\frac{\omega\tau}{1 + \omega^2\tau^2} \tag{1}$$

in which G is the shear modulus. The dislocation has length Λ and a Burgers vector magnitude $\mathbf{b}$; γ is a geometrical orientation factor of order of magnitude 0.1. $\tau = 1/pq \exp U_0/kT$ in which U_0 is an activation energy, T is the absolute temperature (in K), k is Boltzmann's constant and p solely depends on temperature. If there is no restoring force q, tan $\delta \propto \nu^{-1}$. For a *distribution* of activation energies, the following can be obtained.

$$\tan\delta \propto \nu^{-n} \tag{2}$$

In the present results the tan δ indeed follows a ν^{-n} dependence over the upper part of the frequency range. However at lower effective frequencies, the power-law form of the creep curve implies a constant tan δ, so the tan δ must level off at sufficiently low frequency, and low frequency dynamic studies on InSn confirm that implication. Moreover, full recovery observed after short term creep suggests the dynamic dependence on frequency cannot be pure ν^{-n}. Therefore the assumptions used in obtaining ν^{-n} or Debye type damping are to be critically examined. It is possible, as recognized by Schoeck *et al* [21], that there is a distribution in some or all of p, q and U_0.

Other experiments disclosing high temperature background have been focused primarily on other damping mechanisms such as grain boundary slip or the Zener mechanism for atom movement in alloys. Moreover it is more common, and experimentally easier, to scan temperature rather than frequency. For example, in brass, damping versus temperature was studied at constant frequency for various concentrations of zinc, between 5–30% [22]. The Zener peak due to atom-pair reorientation increased with zinc concentration as might be expected, but the high temperature background also increased with concentration. A direct comparison with the present work is difficult since different variables are involved, however the alloys studied here tend to have higher damping than the highest damping constituent, indium.

The alloys considered in this study exhibit damping at the higher frequencies which is consistent with the concept of a dislocation based high homologous temperature "background". These alloys are at high homologous temperature at room temperature. The phenomenology of this damping has been explored over wide frequency range but the understanding in terms of mechanisms is still incomplete.

5. Conclusions

(1) Tan δ followed a ν^{-n} dependence at higher frequency and was essentially constant at low frequency for these alloys.

(2) Creep behaviour followed a t^{m} dependence on time and exhibited no asymptotic limiting stiffness.

Acknowledgement

We thank the ONR and EARDA for their support of this work. We also thank the University of Iowa for a University Faculty Scholar Award to one of the authors (RSL).

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Received 9 May 1995
and accepted 13 June 1996