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Supporting Online Material for

Composite Materials with Viscoelastic Stiffness Greater than Diamond

T. Jaglinski, D. Kochmann, D. Stone, R. S. Lakes*

*To whom correspondence should be addressed. E-mail: lakes@engr.wisc.edu

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Composite materials with viscoelastic stiffness greater than diamond

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Methods

Tin (ingot, 99.8% metals basis) and barium titanate pieces (3-12 mm, 99.9% metals basis) were obtained from Alfa Aesar (Ward Hill, MA). Some particles were plated with nickel using an electroless method ([1]), rinsed with deionized water and baked dry. Dispersions were achieved through an ultrasonic casting technique ([2]). The tin was melted in a 75 ml alumina crucible, and the powders were preheated to the same temperature in a 23 ml alumina crucible. Molten matrix and particles were dispersed using an ultrasonic probe; care was taken to scrape the sides of the crucible, transducer and thermocouple to be sure that all particles which might have segregated to these areas were dispersed into the melt. Once dispersed, the melt was poured into an aluminum mold to create an ingot ~1.2 x 1.4 x 10 cm. Pure tin was cast into the same mold to obtain similar polycrystalline structure. Specimens for viscoelastic testing were sectioned from ingots using a low speed diamond saw into rectangular cross sections, typically 2 mm x 2 mm x 3.5 cm or were cut into cylinders, with diameters of 2.6 mm and 3 cm long, using a wire electron discharge milling machine (EDM).

Specimens for optical micrographs were potted in a two-part epoxy, and pucks were wet-ground using silica sandpaper, and polished using a 0.03-0.06 micron colloidal silica solution. Micrographs of composites were taken using an optical microscope (Nikon Eclipse ME600) with a digital camera (Diagnostic Instruments, SPOT model #2.2.1, St. Sterling Heights MI) and image capturing system (Metamorph 5.0r2, Universal Imaging Corp) on a PC.

Mechanical properties were determined in bending using broadband viscoelastic spectroscopy (BVS) ([3]). This instrument is capable of isothermal internal friction studies in torsion or bending over eleven orders of magnitude in frequency. It offers an exceptionally stiff platform for measurements of materials which exhibit changes of modulus of orders of magnitude. The support structure is massive (26 kg) and is orders of magnitude stiffer than the specimens, which in this series were 2 to 2.6 mm thick. The specimen was attached to a 25 mm diameter steel support rod. Since the structural rigidity in torsion or bending is proportional to the fourth power of the diameter, the support structure is at least several thousand times stiffer than the baseline structural stiffness of a typical specimen. The output signal of the silicon detector was input to a lock-in amplifier (Stanford Research Systems SR850 DSP) and a digital oscilloscope. During dynamic measurements, slow deformation including spontaneous strain was concurrently measured using a wide angle, 2 axis silicon sensor (Pacific Silicon Sensor Inc. DL100-7PCBA, Westlake, CA) with a detector area of 1 cm^2. Temperature was governed by a flow of heated air over the specimen.

The protocol is typical of that used in characterizing viscoelastic solids including those which undergo a phase transformation. The time scale of the imposed sinusoidal sub-resonant torque was much shorter than the time scale of the temperature changes. Therefore the complex dynamic modulus formulation is appropriate.

The large peaks in stiffness were verified as follows. In addition to the lock-in amplifier measurements, the torque-angle trace was observed on an oscilloscope and was verified to be consistent with a large increase in stiffness. The position of the laser beam on the detector was monitored. The beam was verified to be on the detector, and in the linear region of behavior throughout measurement of the peaks.

Analysis and interpretation: Anomalies at temperatures offset from phase transformation temperatures are interpreted as follows. Using composite theory based on the Hashin-Shtrikman coated sphere model for inclusions, multiple peaks and doublets are obtained if one allows softening of bulk modulus to zero and negative values, and of shear modulus to zero. Shear modulus less than zero gives rise to instability associated with domain formation; since the present inclusions were much larger than the domain size, their shear modulus is assumed to be positive. Indeed, no anomalies were observed in shear (torsion) in the present results. Anomalies in predicted bending properties appear well below T_c if we assume a base modulus of 50 GPa for tin matrix and 100 GPa for inclusions. This is in contrast to the VO_2 examined in prior studies, in which the inclusions were much stiffer than matrix.

Shift of peaks with thermal cycling is interpreted as follows. Negative specific heat was observed as a brief reversal of the heating or cooling trend of temperature vs. time. The temperature sensor in these studies was placed in the air flow about 1 mm from the specimen rather than in contact with it, to avoid interference with mechanical property measurements. Calibration studies upon normal specimens mounted but not tested mechanically disclosed less than 1 °C difference between the temperature of a sensor in contact with the specimen and one near it in the air flow. However a larger difference is likely to occur in specimens which exhibit anomalous thermal properties such as negative specific heat since in that case, the rate of change of temperature is greater than in the case of natural heating or cooling. Changes in the interface between inclusion and matrix therefore are reflected in the thermal properties, giving rise to a shift of the peaks with temperature as thermal cycling alters the interface. The theoretical specific heat depends on constituent bulk moduli (4) as follows.

$$c_p^{cmp} = c_p^{avg} + 9T \left[\frac{(\alpha_2 - \alpha_1)}{\frac{1}{K_1} - \frac{1}{K_2}} \right]^2 \left[\frac{1}{K}\Big|_{avg} - \frac{1}{K^{cmp}} \right]$$

in which c_p^{cmp} is the composite specific heat, c_p^{avg} is the volume average specific heat of the phases, T is temperature, α_1 is thermal expansion of phase 1, K_1 is the bulk modulus of phase 1, K^{cmp} is the composite bulk modulus and K^{avg} is the volume average bulk modulus of the phases. When one phase has negative bulk modulus, the composite compressibility $1/K^{cmp}$ can substantially exceed the volume average compressibility in magnitude, therefore negative specific heat can result in the composite.

The Landau free energy function $F = \alpha\varepsilon^6 - \beta\varepsilon^4 + \gamma(T - T_1)\varepsilon^2$ of temperature T with α, β, γ and T_1 as positive constants depending on the material is associated with the modulus as follows (5). Formally, the relation between stress σ and strain ε is $\sigma = \partial F/\partial \varepsilon$. Therefore at low temperature, the effective modulus is negative.

Negative compressibility or heat capacity is unstable in equilibrium thermodynamics of homogeneous systems, but if there is heterogeneity (6), as in the case of gravitating systems (7), negative susceptibilities can occur.

References

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1. Endplate NI-426 A and 426 B (Enthone, West haven, CT)
2. Y. Yang, J. Lan, X. Li: Study on bulk aluminum nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy, *Mater. Sci. Eng.* A **380** 378-383 (2004).
3. T. Lee, R. S. Lakes, A. Lal, Resonant ultrasound spectroscopy for measurement of mechanical damping: comparison with broadband viscoelastic spectroscopy. *Rev. Sci. Instrum.* **71**, 2855-2861 (2000).
4. B. W. Rosen and Z. Hashin, "Effective thermal expansion coefficients and specific heats of composite materials", *Int. J. Engng. Sci.* **8**, 157-178, (1970).
5. F. Falk, . Model free energy, mechanics, and thermodynamics of shape memory alloys. *Acta Metall.* **28**, 1773-1780 (1980).
6. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 2nd edition, Addison Wesley, Reading, MA, (1969)
7. W. Thirring, "Systems with negative specific heat", *Z. Physik*, **235**, 339-352 (1970).