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Anelastic instability in composites with negative stiffness inclusions

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ABSTRACT

Composites with VO_2 particulate inclusions as a negative stiffness phase were fabricated through powder metallurgy. The composites are predicted to exhibit enhanced anelastic damping by virtue of the partially constrained negative stiffness of the inclusions in the vicinity of a ferroelastic phase transformation, and are predicted to become unstable for sufficiently high concentration (5 vol%) of inclusions. Composite specimens with 5 vol% inclusions studied in subresonant dynamic torsion displayed various manifestations of mechanical instability during cooling in a temperature range including the inclusion transformation temperature. Instability was manifested as macroscopic specimen undulations (slow thrashing) and fluctuation of the damping $\tan\delta$. Material instability occurs at high inclusion volume fraction in harmony with predictions from composite theory.

§ 1. INTRODUCTION

Composite material properties depend on the properties of the constituents and the geometry of the microstructure. Usually, a formulation of particles, fibers, or platelets as the stiffer or harder structural component is used to stiffen or strengthen a matrix material. The performance of these composites can be analysed using composite theory. Bounds for behaviour of composites of any microstructure are calculated (Hashin and Shtrikman 1963) assuming both phases are in their lowest energy state. If one phase has negative stiffness, it is not in an energy minimum. Such a composite can have anelastic properties greater than those of either constituent. Negative stiffness is manifested by a reversal in the usual directional relationship between causal forces and ensuing deformations, and is normally unstable without physical constraint.

As for other aspects of reversal physics, negative stiffness differs from negative Poisson's ratio (Lakes 1987), which refers to the transverse deformation of a material due to a longitudinal load. Negative stiffness as considered here is a result of elastic

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stored energy at equilibrium; it is not a result of resonance or other inertial effects. By contrast, negative dielectric permittivity (Shelby *et al.* 2001) in lattices of resonant elements occurs only over a narrow frequency range. Extreme behaviour in designed dielectric composites at high frequency (Nicorovici *et al.* 1994) also depends on structural resonance. The present concept does not depend on inertial terms: it is not resonant.

Composite theory analysis of materials with inclusions of negative stiffness predicts anomalies in the modulus and large peaks in the mechanical damping (Lakes 2001a), properties greater than those of either constituent. However, negative stiffness entails instability. An object with negative stiffness can be stabilized by a constraint. For example, the axial force-displacement relation of a buckled tube under displacement constraint exhibits negative stiffness. Material damping orders of magnitude larger than constituent damping and approaching a singularity, was observed in a constrained unit cell containing a post-buckled tube by Lakes (2001b). A composite inclusion constrained by a stiff matrix can under some circumstances be stable (Lakes and Drugan 2002).

Ferroelastic phase transformations (Salje 1990), or temperature induced, structural phase transformations, possess negative stiffness characteristics. This has been understood in the context of the free energy (Falk 1980) in the Landau (1965) theory having a relative maximum, corresponding to unstable equilibrium, below the material's transformation temperature T_c. The force is proportional to the gradient of the energy, so the region near an energy maximum corresponds to negative stiffness. Interplay between the positive and negative stiffness constituents leads to interesting and extreme behaviour as observed experimentally in a composite with ferroelastic inclusions (Lakes *et al.* 2001) and analysed by Lakes and Drugan (2002).

This letter will concentrate on the experimental observation of mechanical instability, or stability, in a composite with inclusions having negative stiffness, specifically particulate vanadium dioxide (Maurer *et al.* 1999) (VO_2), which undergoes a ferroelastic phase transformation (Heckingbottom and Linnett 1962) at 67°C, embedded in tin (Sn) as the stabilizing, positive stiffness matrix. It is believed that this is the first report of observed mechanical instability in the material properties themselves, and not simply structural instability.

§ 2. Experiment

Composites were made by powder metallurgy. Powdered tin (Alfa, 99.95%, 325 mesh, 44 μm or less) and VO_2 (Alfa, 100 mesh, 150 μm or less) were measured according to the intended volume fraction, mixed by hand and then consolidated. Cold consolidation of the powder was carried out by pressing in a steel compression die with one movable punch and a hydraulic press. After cold pressing at a nominal stress of 180 MPa, the green compact was sintered in argon at 220°C for 12 hrs. Composites were made with different volume fractions of inclusions, including zero, 0.5 and 5 vol% VO_2. This method, using 15–20 g of powder, produced thin slabs approximately 50 by 12 by 3–5 mm thick. Out of these slabs 4–5 strips of approximately square cross section were cut out using a low-speed abrasive diamond saw. The pressing procedure creates composites without the need for a rapid cooling step as used in the casting (Lakes *et al.* 2001) method to prevent segregation of the inclusions.

Specimens were tested in torsion using broadband viscoelastic spectroscopy (BVS) as outlined by Lee *et al.* (2000) with refinements allowing elevated temperature control and ability to measure the relatively large deformations associated with instability. Sm-Co magnets were glued to the free end of the specimen using Micro Measurements MBond 610 strain gage cement according to the curing and pressure schedule provided by the manufacturer. The fixed end of the specimen was clamped by tungsten adapters and set screws. The driving torque via a Helmholtz coil was oriented for torsion at 100 Hz, well below the fundamental resonance of the specimens (typically 6 kHz). Strain amplitude was about 5×10^{-7}. Specimens were heated via a resistive micro-tube furnace within the apparatus and were cooled from about 120 to 40°C, with cooling rates on the order of 1 to 2°C/min. Specimen temperature was measured using a type-K thermocouple attached to the base of the specimen, and the voltage recorded by a digital oscilloscope.

Internal friction (tan δ) and shear modulus measurements were taken using a Stanford Research Systems lock-in amplifier (SR850 DSP) by measuring the subresonant phase angle ϕ (equivalent to δ far below resonance) between the torque and displacement signals as well as signal amplitude. To measure the slow large amplitude component of the deformation signal due to material instability, a wide-angle two-axis photodiode position sensor with a detector area of 1 cm^2 was used (Pacific Silicon Sensor Inc. DL100-7PCBA, Westlake, CA). This was accomplished by splitting off a portion of the laser beam and recording the detector output voltage for both the horizontal and vertical directions with a digital oscilloscope. Specimen instability was detected (using the wide angle detector) as a change in the vertical and horizontal location of the laser light beam reflected off the free end of the specimen. The horizontal motion of the light beam corresponds to specimen torsion, and vertical motion corresponds to bending.

§ 3. Results

The structure of the composite material, a particulate composite with vanadium dioxide (VO_2) as the negative stiffness inclusion, and tin (Sn) as the stabilizing, positive stiffness matrix is shown in figure 1a. The composite exhibited a thrashing instability, i. e. slow aperiodic cyclic deformation independent of any excitation, for sufficiently high concentration of VO_2. The instability of 5 vol% VO_2–Sn composite in comparison with pure Sn is shown in figure 1b. Thrashing occurred in both torsion and bending in the composite but not in the pure tin. Slow, monotonic deformation is attributed to thermal drift. Thrashing undulations occurred over a range of time scales, principally 3 to 300 s. The instability was dependent on thermal cycling.

Thrashing of the specimen is also accompanied by fluctuations in the mechanical damping tan δ, a measure of internal friction (Lakes 1998), of the composite. Although the 5% particulate specimens exhibited instability not seen in the 0.5% specimens or in the pure Sn, the detailed form of the instability differed among specimens. Figure 2 illustrates an oscillatory instability in the tan δ of 5 vol% composite for several cooling cycles. Observe that tan δ undulates and briefly becomes negative. Since composite properties are intermediate between those of the constituents, the baseline damping of the composite is lower than that of the pure Sn.

It was observed that the unstable response emerges and dissipates with thermal cycling. This cycle dependence is illustrated in figure 2 by the change in amplitude of the peaks and dips in tan δ, and in figure 3 by the change in the time dependence of the thrashing (slow undulations in strain). Furthermore, as seen in figure 1b, specimen thrash precedes anomalous behaviour in tan δ during cooling.

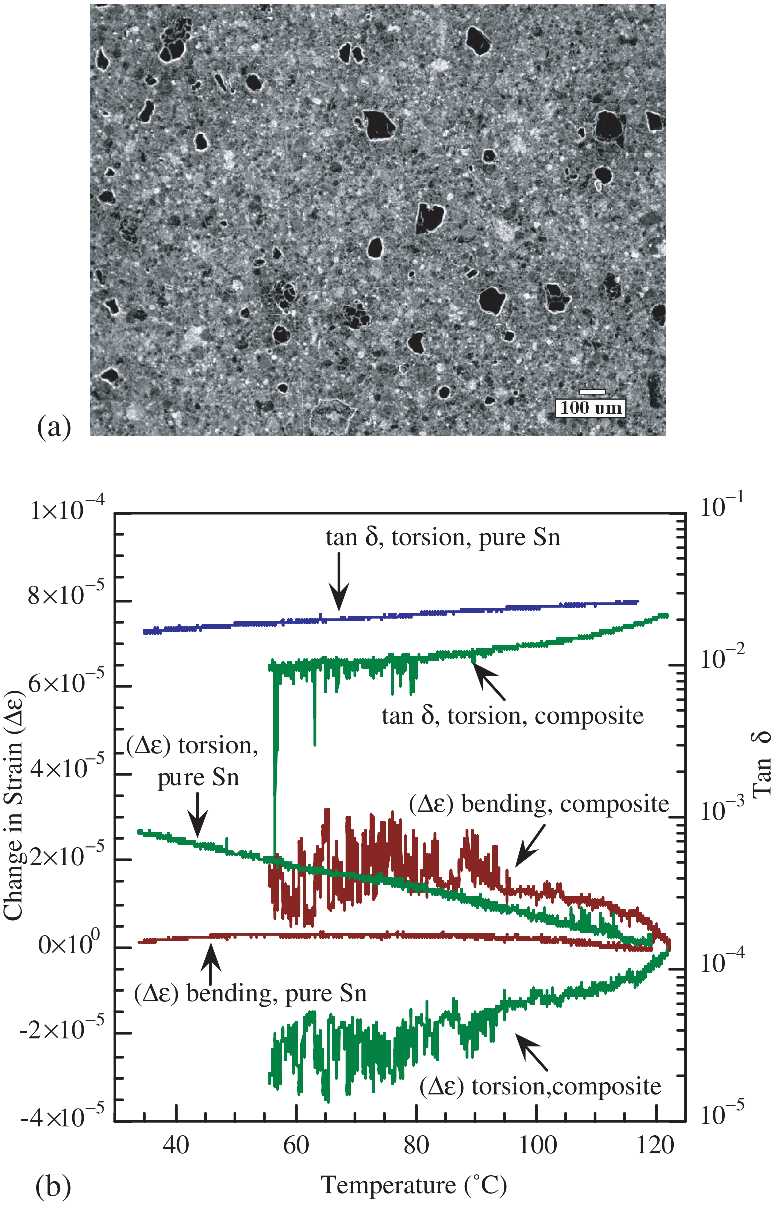

Figure 1. (a) A dark-field optical micrograph of the composite showing VO_2 as the black inclusions. (b) Plots of the change in torsion and bending maximum surface strains and torsional tan δ for 5 vol% VO_2–Sn particulate composite as a function of temperature in cooling (cycle 4) compared to a pure Sn specimen.

§ 4. ANALYSIS

For the composite, viewed as a continuum, to be stable, it must obey the stability criteria for an unconstrained object. In isotropic elastic solids, the range of Poisson's ratio ν for stability is (Timoshenko and Goodier 1970)

$$-1 < \nu < 0.5, \qquad (1)$$

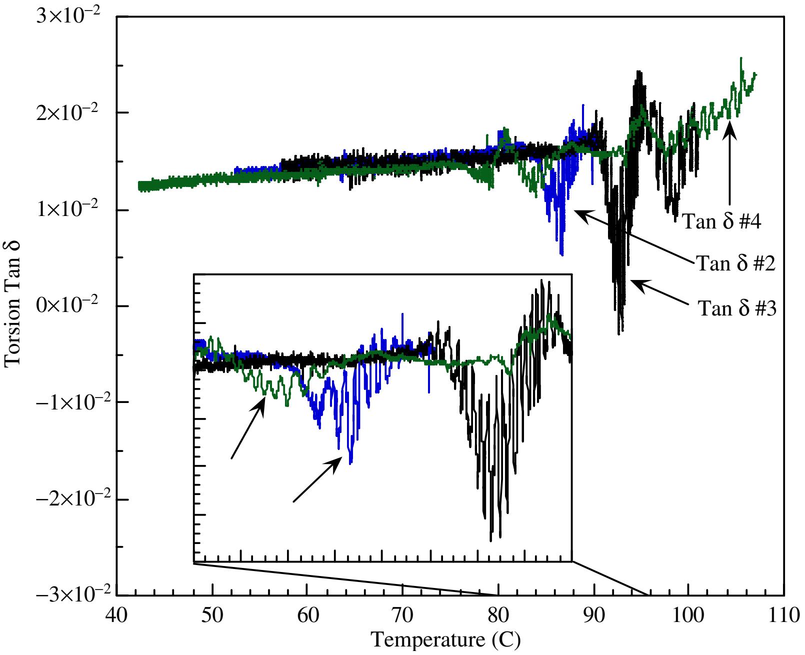

Figure 2. Oscillatory instability of tan δ of 5 vol% VO_2–Sn particulate composite during second, third, and fourth cooling cycles.

corresponding to the requirement that the shear G and bulk K moduli be positive. Using this criterion, the volume fraction range of inclusions for stability can be predicted using the Hashin-Shtrikman (1963) formula for the lower bound on the composite shear modulus $\boldsymbol{G}_{\mathrm{L}}$.

$$G_{\mathrm{L}} = G_2 + \frac{V_1}{(1/G_1 - G_2) + (6(K_2 + 2G_2)V_2)/(5(3K_2 + 4G_2)G_2)}, \tag{2}$$

in which K_1, K_2, G_1 and V_1, and G_2 and V_2 are the bulk modulus, shear modulus and volume fraction of phases 1 (inclusions), and 2 (matrix), respectively. This is an exact solution for a hierarchical coated sphere morphology and is a good approximation for a composite with dilute near-spherical inclusions. For viscoelastic solids, the moduli are complex; tan δ is the ratio of the imaginary part to the real part G'. The imaginary part G'' must be positive (Christensen 1972) if the material exhibits a non-negative rate of dissipation of energy, hence stability. Based on the experimental results, the powder composites have a tan δ of about 0.01 at room temperature and about 0.015 at elevated temperature, therefore a value of 0.015 was assumed in the analysis for the matrix damping. Negative values of the modulus G_1 are not measured directly; they are inferred from the composite behaviour. A dilute suspension of spherical inclusions of positive stiffness has minimal effect on the composite properties but if inclusion stiffness becomes negative, large effects are predicted (Lakes 2001a) and observed (Lakes *et al.* 2001). The theory predicts (figure 4) that 5 vol% VO_2 specimens will be unstable during the inclusion phase transformation, since G' or tan δ of the composite becomes negative. By contrast, 0.5 vol% VO_2 specimens will be stable.

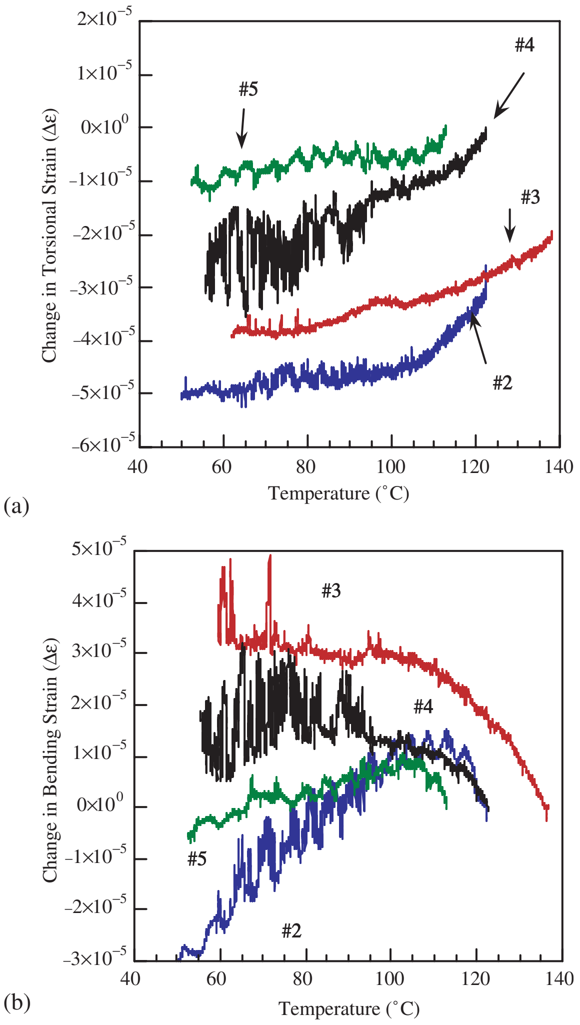

Figure 3. Effect of thermal cycling: strain for four cooling runs on a 5 vol% VO_2–Sn particulate composite. (a) Change in torsion strain. (b) Change in bending strain. Curves have been shifted vertically for clarity.

The behaviour of a composite with a distribution of inclusion stiffness values was also calculated, according to the following, with $N = 20$ and $\{G_1\}_k = G_1(1 + 0.05\,k)$.

$$G_L = G_2 + \sum_{k=1}^{N} \frac{V_1}{(1/\{G_1\}_k - G_2) + (6(K_2 + 2G_2)V_2/5(3K_2 + 4G_2)G_2)} \frac{1}{N}. \tag{3}$$

The peak damping is reduced, though the 5% composite is still unstable. Ripples occur in the modulus and damping calculated via equation (2) owing to the discrete values of inclusion modulus G_1 assumed.

Such ripples are observed in the experiments (e.g. figure 2). The experimental results are consistent with these predictions since instability was observed in 5 vol% specimens. The 1/2 vol% composites showed no signs of instability, but they do exhibit peaks in damping. As with the 5% specimens, the effects of the inclusions

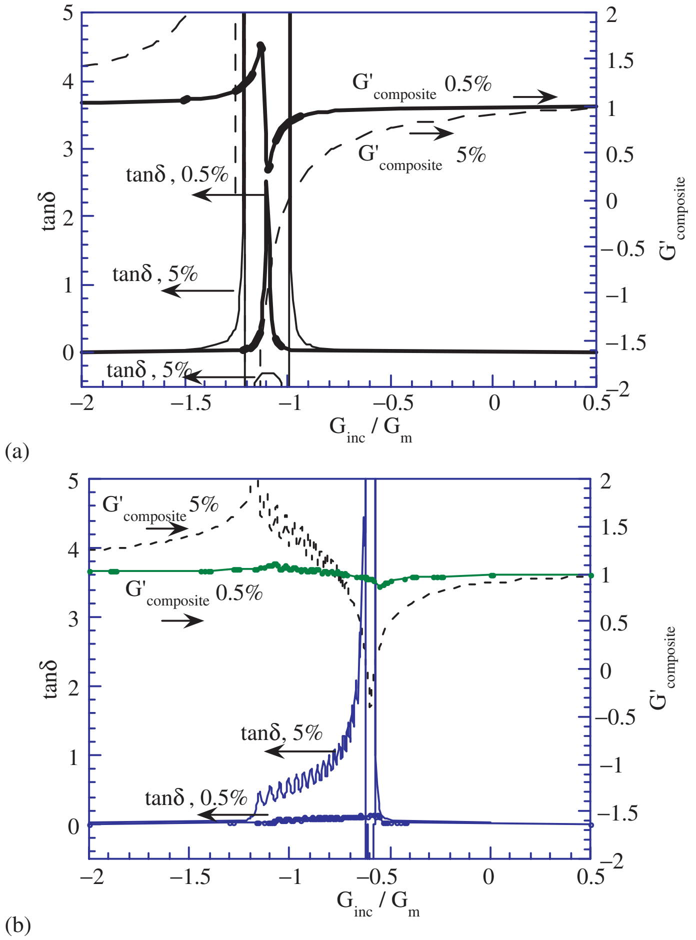

Figure 4. Theoretical predictions of composite stability assuming matrix tan $\delta = 0.015$. Negative composite shear modulus G' or negative tan δ implies instability. (a), single value of inclusion stiffness based on Hashin-Shtrikman equation (2) for 0.5 vol% (solid thick curves) and 5 vol% (dash curve, modulus, thin solid curve, tan δ) inclusions; (b), distribution of 20 discrete inclusion stiffness values. G' and tan δ for 5% composite exhibits undulations due to discrete values of inclusion stiffness in equation (3).

occur over a substantial range of temperature. This is in contrast to the sharp (less than 1°C) peak in tan δ observed in a cast 1% composite by Lakes *et al.* (2001), and is also in contrast to damping peaks about 5°C wide observed in polycrystalline VO_2 by Zhang *et al.* (1995) The broadening of the behaviour is attributed to heterogeneous residual stress introduced in the pressing procedure used in the present work. Phase transformations are known to depend on both temperature and on stress (Salje 1990). The pressed specimens contain substantial nonuniform residual stress and pores containing entrapped gas under pressure (Hirschhorn 1969) due to the processing, and this stress is heterogeneous. Thermal cycling has the effect of annealing and redistributing the residual stress, therefore, via the effect of such stress on the inclusion transformation temperature, a change in the behaviour due to partially constrained phase transformation of the inclusions.

§ 5. Summary and Conclusions

Sn–VO_2 particulate composites with 5 vol% inclusions displayed various manifestations of mechanical instability as the specimens were cooled through the transformation temperature of the inclusions; 1/2 vol% specimens showing no signs of unstable behaviour. This concentration dependence is in harmony with predictions from composite theory.

Instability was manifested as (i) macroscopic specimen undulations, and (ii) instability in the mechanical damping tan δ. Instability occurred over a broader range of temperature than either polycrystalline VO_2 or a cast Sn–VO_2 composite. Instability also emerged and dissipated with thermal cycles. This behaviour indicates a role for heterogeneous residual stress in the present composite prepared by powder metallurgy.

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