Dynamic Elastic Hysteretic Solids and Dislocations

M. W. Barsoum,[1] M. Radovic,[2] T. Zhen,[1] P. Finkel,[3] and S. R. Kalidindi[1]
[1]*Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104, USA*
[2]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[3]*Thomson TTW R&D Center, Lancaster, Pennsylvania 17601, USA*
(Received 12 September 2004; published 1 March 2005)

Recently we showed that the quasistatic response of nonlinear mesoscopic elastic solids to stress can be explained by invoking the formation of dislocation-based incipient kink bands. In this Letter, using resonant ultrasound spectroscopy, we confirm that the dynamical behavior of these nonlinear elastic systems is due to the interaction of dislocations with the ultrasound waves, thus resolving a long-standing mystery.

DOI: 10.1103/PhysRevLett.94.085501 PACS numbers: 62.20.Dc, 61.72.Hh, 62.80.+f

Nonlinear mesoscopic elastic (NME) solids are of fundamental importance in geology since many rocks have been thus classified [1,2]. The quasistatic response of NME to relatively large strains ($\approx 10^{-3}$) and low frequencies ($\approx 10^{-2}$ Hz) is characterized by hysteresis and end-point memory [1]. Currently, this response is modeled phenomenologically by invoking the presence of hysteretic mesoscopic units (HMUs), whose physical underpinnings were until recently unknown [3]. Very recently, we have shown that these HMUs are nothing but dislocation-based incipient kink bands (IKB) [4]. Furthermore, we have shown that the active phases (see below) in NME solids belong to a much larger class of layered solids that we termed kinking nonlinear elastic (KNE) solids. KNEs include the *MAX* phases (see below), graphite, hexagonal BN, sapphire, layered semiconductors, ice, mica, and other layered silicates, hence their importance to geology among many other fields [4]. We further claimed that a sufficient but not necessary condition for a solid to be a KNE solid is a *high* c/a *ratio*, which per force renders them plastically anisotropic and hence prone to kinking.

The ternary carbides with the general formula $M_{n+1}AX_n$ (where $n = 1$ to 3, M is an early transition metal, A is an A-group element, and X is C and/or N) are best described as thermodynamically stable nanolaminates [5]. The vast majority of the more than 50 *MAX* phases known to exist were discovered in the 1960s by Nowotny and co-workers [6]. Since then two more were added to the list [7,8]. As a class, these solids are excellent electric and thermal conductors, exceptionally thermal shock resistant, and damage tolerant [5,9–15]. Despite being elastically quite stiff, they are all readily machinable. Recently developed Ti_2AlC-based compounds are also exceptionally oxidation resistant and can be used in air to temperatures up to 1400 °C [16].

There are two other characteristics of KNE solids that are germane to this work. First, the slopes of stress-strain curves in compression are strong functions of grain size [17]. This apparent dependence of the Young moduli on microstructure is a direct consequence of the ease by which IKBs nucleate, especially in coarse-grained samples. As the grain size shrinks, the slopes of the stress-strain curves approach those measured by ultrasound [17]. Second, because the dislocations are restricted to the basal planes, they do not entangle and thus can move back and forth over significant distances. This results in the dissipation of large amounts of energy per cycle. The energy dissipated also *increases* as the square of the applied stress [17].

Resonant ultrasound spectroscopy (RUS) is a relatively novel, highly accurate technique developed by Migliori *et al.* [18,19] for determining the complete set of elastic constants (moduli) from the resonant spectra of freely suspended solids [20,21]. The technique is based on measuring the frequency of resonance peaks, which are dependent on density, elastic moduli, and shape, of a freely suspended solid. The location of the peaks can, in principle, yield the elastic moduli of a solid. The mechanical damping is manifested as an increase in the widths of the peaks and is defined as [18,19,21]

$$Q_k^{-1} = \Delta\omega_k/\omega_{ko} \tag{1}$$

where ω_{ko} is the frequency associated with the kth eigenmode, and $\Delta\omega_k$ is the full width at half maximum (FWHM) of that mode.

The underlying physics of the dynamic response of NME solids—at small strains (10^{-8} to 10^{-6}) and frequencies in the kHz range—is currently not understood [1,2,22–24]. The dynamic response is characterized by a frequency shift downward, and widening and changes in shape of the resonance peaks as the amplitude of the strain field is increased [2,22]. Another unusual feature is slow dynamics, i.e., the slow recovery of the linear material properties after a sample is subjected to a force [25,26]. These nonlinear effects are believed to be due to the presence of soft regions, such as microcracks, etc., bonding together hard aggregate, viz., linear elastic, particles [1,2,23]. As noted above, we identified these soft regions to be the KNE phase. To date these solids have been modeled phenomenologically [1–3,22–24].

The purpose of this Letter is to show that this nonlinear dynamic response is due to dislocations. This was demonstrated by carrying out RUS experiments on the ternary carbide, Ti_3SiC_2. The processing details have been presented elsewhere [14,15]. Two microstructures were tested: coarse- (CG) and fine-grained (FG). The CG microstructure was composed of large (100–300 μm) platelike grains with some fine grains ($\approx$ 2–8 μm) between them. The FG samples had a more uniform distribution of grain sizes ($\approx 8 \pm 4$ μm). All samples were almost single phase (<2 vol % of inclusions) and fully dense. RUS was carried out using commercially available equipment (Quasar International [27], Albuquerque, NM). The experimental details are described elsewhere [20].

Young's, E, and shear, μ, moduli were found to decrease linearly with increasing temperature up to the highest temperature recorded [see inset in Fig. 2(b)]. The values were in excellent agreement with previous results [10] and were independent of grain size. In contradistinction, Q^{-1} remained more or less constant up to $\approx$ 1173 K, before it increased dramatically [Fig. 1(a)]. Moreover, and as important, Q^{-1} was *not* a function of grain size [Fig. 1(b)]. Also plotted in Fig. 1(b) are the room temperature Q^{-1} values measured after a CG Ti_3SiC_2 sample was compressively deformed by 4% at 1573 K and 25 MPa. This relatively modest deformation resulted in roughly an order of magnitude increase in Q^{-1} [Fig. 1(b), solid circles].

The fact that the changes in E and μ with temperature are small, as the imaginary component, viz., Q^{-1}, increases dramatically above $\approx$ 1273 K is unusual. The strong function of deformation history on damping [Fig. 1(b)] is compelling evidence that it is dislocation based. When combined with the fact that the 4% predeformation also results in a stiffening and hardening of the solid [17]—a fact that can only be accounted for by the presence of dislocations—the evidence becomes almost irrefutable. The increase in Q^{-1} after deformation must thus be due to an increase in dislocation density. It is important to note that the independence of Q^{-1} on grain size shown in Fig. 1(b) rules out grain boundaries or microcracking as sources of damping. Additionally, RUS is one of the most sensitive techniques to detect microcracking that manifests itself through a decrease in moduli [18–20].

Before proceeding further it is crucial to underscore the differences, apart from the obvious increases in frequency, alluded to earlier, between the results obtained in this work and those obtained in our quasistatic tests [12,17]. The strains generated during RUS are orders of magnitude lower than those in quasistatic tests [17]. It follows that the ultrasound energy applied during RUS is insufficient to nucleate mobile IKBs in Ti_3SiC_2 at least up to $\approx$ 1173 K. The fact that the elastic moduli do not drop dramatically at $\approx$ 1173 K, as they do in tension [12], compression [17], or bending [15] (a drop attributed to

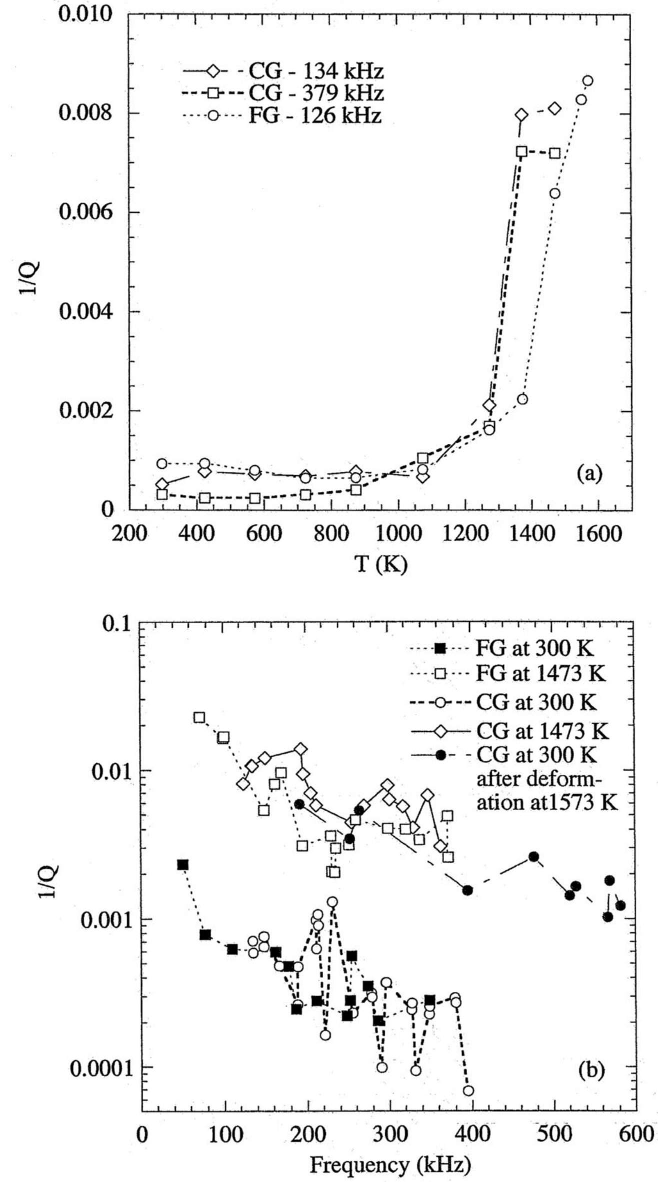

FIG. 1. Effect of microstructure on (a) $1/Q$ vs temperature, and (b) $\ln(1/Q)$ vs frequency at room temperature and 1473 K. Also included are the room temperature results of a sample that was deformed at 1573 K by 4% in compression.

the formation of KBs, mobile dislocation walls, and dislocation arrays [17]) is further evidence that IKBs are not nucleated here.

The ultrasound energy must thus couple with dislocation line segments causing them to either vibrate (string model) and/or move (hysteretic model) [28]. It is important to note that the variations in Q^{-1} with frequency shown in Fig. 1(b) are not noise. The uncertainty in the determination of Q^{-1} from the resonance spectra [i.e., Eq. (1)] is smaller than the width of the data points. These variations reflect the various eigenmodes of the sample and are quite typical of RUS results.

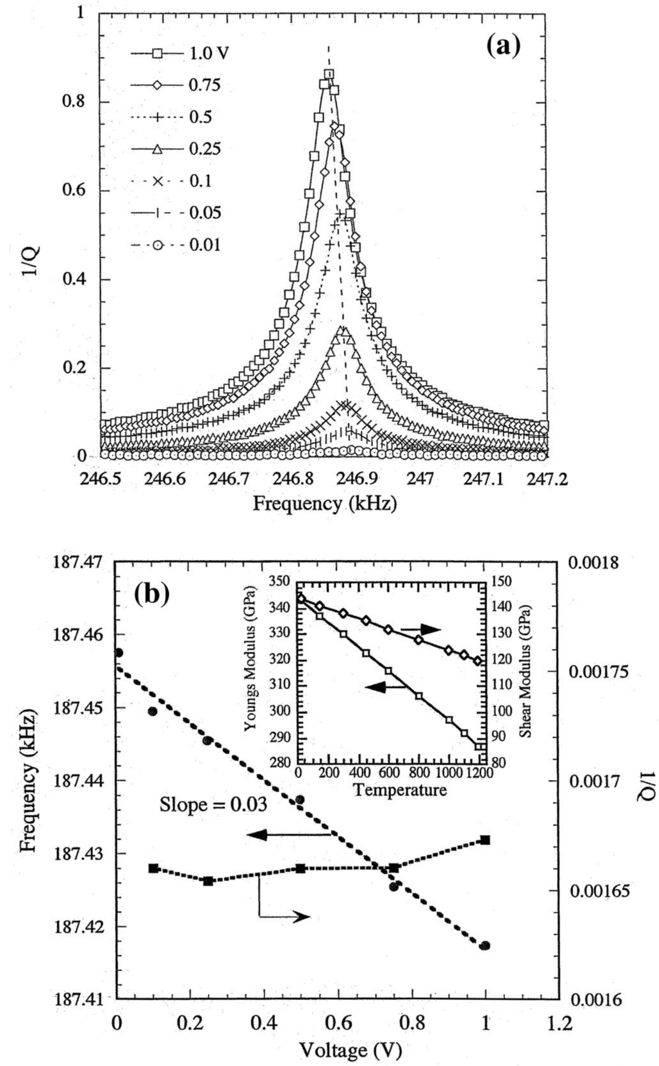

FIG. 2. Effect of drive amplitudes in volts on the room temperature: (a) resonant peaks for deformed Ti_3SiC_2, and (b) peak positions and $1/Q$. Inset in (b) shows changes in Young's and the shear moduli with increasing temperatures for Ti_3SiC_2.

The reason for the sharp and dramatic increase in Q^{-1} at temperatures greater than ≈ 1173 K [Fig. 1(a)] is unclear at this time. However, since this increase is fully reversible (when the samples are cooled the original spectra are recovered) it is fair to conclude that the microstructure does not change either. In other words, the increase cannot be due to the formation of KBs, dislocation pileups, or an increase in dislocation density. Hence, the increase in damping must be due to an increase in dislocation mobility. Note mobility here does not imply long-range glide of dislocations, but a localized hopping in response to the ultrasound waves.

The dynamic response of the deformed Ti_3SiC_2 sample at 298 K [Fig. 2(a)] and 1473 K (not shown) to increasing transducer driving voltages, i.e., increasing strains, results in a linear downward shift in the frequencies of the resonant peaks [Fig. 2(b)]. In other words, the response is qualitatively identical to that of NME solids [1,2,22–24]. This observation is in accord with our conclusion that the dynamic losses are indeed due to dislocations. This decrease is most probably due to the softening of the solid as a result of the motion of the dislocations. Note these changes in stiffnesses are quite small relative to the changes due to variations in temperature, i.e., those shown in the inset of Fig. 2(b).

Typically in the geologic literature the shifts in resonance peaks are quite small (1–20 Hz) [1,2,23]. As far as we are aware, the shifts observed here [e.g., 50 Hz in Fig. 2(b)] have never been reported before and are consistent with our conjecture. This dislocation-based softening will depend on the volume fraction of the material that is a KNE solid; in our case the entire sample is. As noted above, because in the geologic literature the KNE phases are usually found in small quantities, as binding phases their effect on softening is much more limited. Furthermore, the fact that the frequency shift at 1473 K (not shown) is roughly 5 times that at 298 K [Fig. 2(b)] is consistent with the greater mobility of dislocation segments discussed above [Fig. 1(a)].

In contrast to the peak positions, the increase in applied voltage had no effect on $1/Q$ [Fig. 2(b)]. Typically such behavior is observed only in ultrapure metals in which dislocations are not pinned by impurity atoms [29]. Since we do not believe our samples were particularly pure, the results shown in Fig. 2(b) suggest that, for reasons that are unclear at this time but are probably related to the long loop lengths present in KNE solids (see below), the role of impurities in KNE solids is not as pronounced as in metals. Another possibility is that the strain amplitudes used here (estimated to be in 10^{-6} to 10^{-8} for RUS) are too small to cause breakaway. Note that in our previous work [17] we have shown that, at larger amplitudes, $1/Q$ does indeed increase significantly with increasing applied stress. Interestingly and in total accord with our conclusions the values of $1/Q$ obtained from measuring the area enclosed by stress-strain curves in Zn [30], which is known to kink, are much larger than the ones measured in the kilocycle range [29].

The large damping properties of KNE materials do *not* necessarily result from exceptionally large dislocation densities, but rather from the relatively large areas swept by the dislocation segments. Said otherwise, because of their layered nature and the confinement of the dislocations to the basal planes, the lengths of the unpinned dislocation segments can be unusually long. Working on mica, Meike [31] directly observed basal dislocation motion in the TEM and reported dislocation separations, attributed to stacking faults, of the order of 100–500 nm. In the same paper, Meike showed dislocation segments of the order of 20 μm. Similarly, Kronenberg *et al.* [32], working with biotite single crystals, concluded that the activation areas, i.e., areas swept by the dislocation lines, were "enormous" and irreconcilable with the dearth of stacking faults found in TEM foils of deformed samples.

It is also important to note here that we are not claiming that the response of all rocks or concrete can be attributed to dislocations. Clearly, they must contain a KNE phase and the role of microcracking, if any, has to be well understood and accounted for.

The ramifications of this work cannot be overemphasized. The geologic literature is replete with some very elegant and powerful phenomenological models that accurately capture the response of nonlinear elastic materials [1–3,22–26,33,34]. The identification of the underlying physics, however, should lead to major and rapid advances in this important field, especially since so much is already known about dislocations and their interactions. In conclusion, we have shown that the dynamic response of nonlinear elastically hysteretic solids is due to the interaction of dislocation segments with ultrasound waves, thus solving a long lasting mystery.

We thank Dr. Edgar Lara-Curzio of Oak Ridge National Laboratory (ORNL) for his support. This research was sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Freedom Car and Vehicle Technologies as part of the High Temperature Materials Laboratory User Program, ORNL. ORNL is managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. This work was also partially funded by the Division of Materials Research of the NSF (Grant No. DMR 0072067) and ARO (Grant No. DAAD19-03-1-0213). This work was also supported in part by the Higher Education Research Experiences Program at ORNL.

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