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Spherical nanoindentation, modeling and transmission electron microscopy evidence for ripplocations in Ti_3SiC_2

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ABSTRACT

Herein we present experimental and modeling evidence for a new deformation micromechanism operating in layered solids termed a ripplocation. Select Ti_3SiC_2 grains were cyclically indented – either parallel or normal to the basal planes - with spherical tips with radii, R of 21 μm and 100 μm. When the load vs. displacement curves were converted to indentation stress vs. a/R curves, where *a* is the contact radius, fully and spontaneously reversible hysteresis loops were recorded. The energy dissipated per unit volume per cycle, W_d, was found to be a function of basal plane orientation; W_d was smaller when the basal planes were loaded edge on. Transmission electron microscope images of areas under the indentations revealed the existence of defects that previous work confirmed have a strain component along the c-axis and for which no g·b condition was found that resulted in their disappearance. These defects thus cannot be basal dislocations; their characteristics, however, are consistent with bulk ripplocations, BRs. It is the to-and-from movement of these BRs – and not basal dislocations as previously assumed - that is believed to be responsible for the fully and spontaneously reversible loops in Ti_3SiC_2 and possibly in most other layered solids. Consistent with the need of the basal planes to expand upon the introduction of BRs, the initial friction stress needed to move them was found to be almost three times lower when the basal planes were loaded edge-on. Molecular dynamics simulations on graphite at 10 K faithfully reproduce many features observed below the indenter in this, and previous, work on Ti_3SiC_2. The existence of BRs will require a revisiting and reassessment of our understanding of how layered solids - from geologic formations to 2D solids – deform.

1. Introduction

Layered solids, defined herein as solids whose deformation is, al least initially, constrained to two-dimensions, 2D, are ubiquitous in nature and our modern world. From the graphite used in nuclear reactors and Li-batteries, to geological formations of layered silicates, composite materials and those comprising the 2D materials, such as graphene and MXenes, that are showing great promise in a host of current and future applications. When the literature of the deformation of crystalline, layered solids is reviewed, however, it is clear that implicitly, or explicitly, the micromechanism responsible for their deformation is in all cases assumed to be the basal dislocation, BD [1–7]. Another commonality in the deformation of layered solids is their failure mode: when the basal planes are loaded edge-on, they almost always fail by the formation of kink bands, KBs [3–8]. In 1952 Frank and Stroh put forth a theory to explain how BDs can result in KBs [9]. We modified Frank and Stroh's theory of kinking to explain the deformation of a number of layered solids, including the MAX phases [10], graphite [11], and mica [12] among others [13].

This work deals with the constrained deformation of the $M_{n+1}AX_n$ (MAX) phase, Ti_3SiC_2. The MAX phases are so called because they are comprised of an early transition metal, M, an A-group element; X is C and/or N, and n ranges from 1 to 3. At room temperature, BDs have been postulated to exist in the MAX phases [14–16]. These BDs were presumed to be mobile, glide along their basal planes, self-assemble into dislocation arrays/pile-ups or low angle kink boundaries [16]. Non-basal dislocations would require inordinately high Burgers vectors due to their large c/a ratios (typically > 4), which renders their existence nearly impossible. Twins have never been observed in any MAX phase. In short, the MAX phases are layered as per our definition. It is thus not surprising that like other layered solids, kink bands form when the

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basal planes are loaded edge-on [15,17]. Indeed KBs in the MAX phases have been imaged at multiple lengths scales, from the submicrometer [15] to the centimeter [18]. What renders the MAX phases unique is the fact that the density of states at the Fermi level is substantial and therefore it is not unreasonable to think of them as nanolayered metals. As discussed herein, this is a key feature that allowed us to readily image BRs.

When the MAX phases are cyclically loaded in compression, they form fully, and spontaneously, reversible stress-strain hysteresis loops (Fig. 1a) [19]. Since part of the strain is fully reversible, viz. elastic, but non-linear, and the end result in most cases is the formation of kink boundaries/bands, we termed these solids kinking non-linear elastic or KNE. The mechanism invoked to explain these fully reversible stress-strain hysteresis loops was based on the aforementioned Frank and Stroh paper. In our model, the growth and annihilation of incipient kink bands, IKBs was postulated [9,10,20]. IKBs are BD loops, confined to the basal planes, that are extended when a load is applied, but shrink and annihilate when the load is removed as dislocations of opposite sign attract and combine. The to-and-fro motion of the IKB dislocations was postulated to explain the reversible, but non-linear elastic strain, ε_{NL}, and the energy dissipation per unit volume per cycle, W_d. The latter is given by the area of the fully, reversible stress-strain loop (hatched area in Fig. 1a). In light of the work presented here, this idea is no longer considered viable.

To study KNE solids in layered materials, such as the MAX phases [21], graphite [11] and mica [12] we developed a nanoindentation, NI, technique [22,23] wherein hemispherical indenters with radii, R, were repeatedly indented in the same location, of typically, single crystals. The load is then converted to a normal stress, σ_{NI}, and plotted vs. a/R, where a is the contact radius (see Fig. 1b). This technique is used here to study the mechanics of this phenomenon (see Appendix A).

This is not the first NI study of a MAX phase. In 2003, Molina-Aldareguia et al. used a Berkovich tip to study the deformation of Ti_3SiC_2 epitaxial thin films [24]. When they examined cross-sectional lift outs of the volume under the indentation in a transmission electron microscope, TEM, delaminations and kink bands, KBs, near the indentation edges were observed. In the same year, Kooi et al. [25] compared the response of Ti_3SiC_2 and SiC to Berkovich indenters as a function of basal plane orientation. Like Molina-Aldareguia et al. [24], they found that when the load was normal to the basal planes, a relatively large pileup of material accumulated near the indentation mark edges (Fig. 2a). Tellingly,

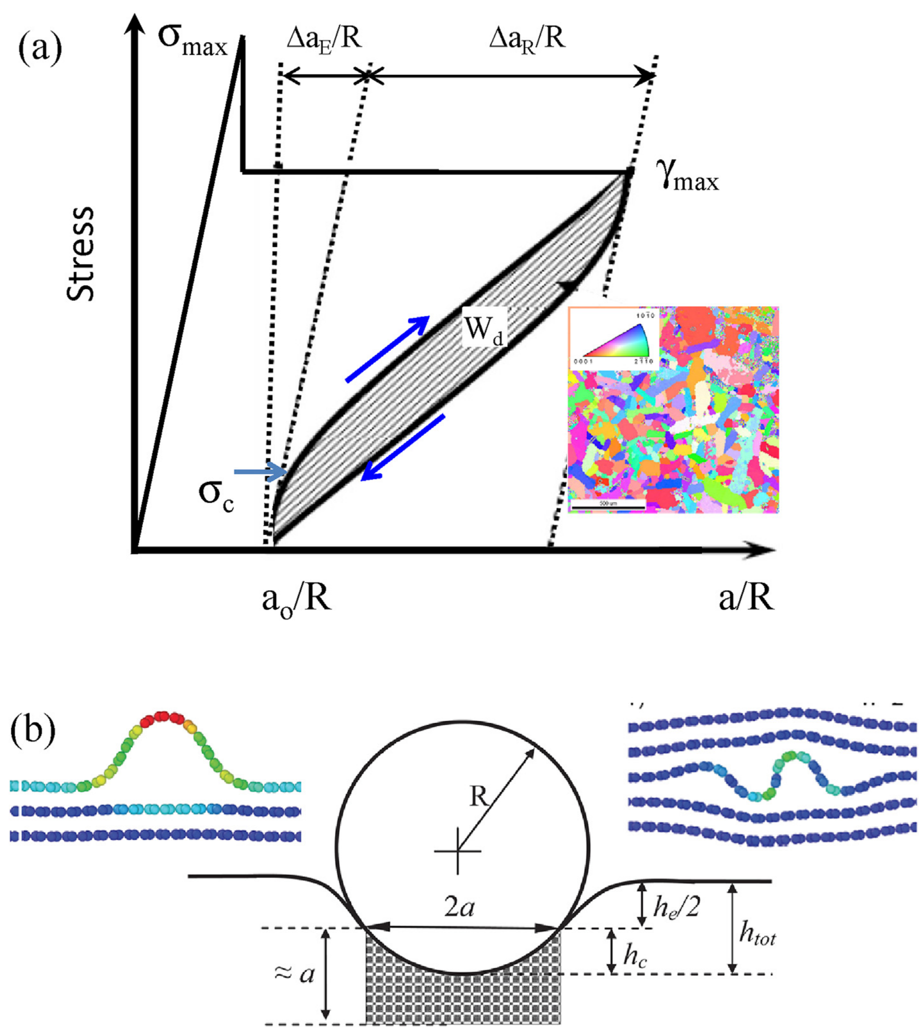

Fig. 1. Schematic of, **a)** Idealized NI stress vs. a/R plots typically observed. The total elastic strain at any stress is the sum of a linear, Δa_E/R, and a nonlinear, Δa_R/R, component. The energy dissipated per unit volume per cycle, W_d, is given by the area enclosed by the fully reversible stress-strain curves. Inset shows OIM map of sample used. **b)** Spherical NI geometry. The indenter radius, R, contact radius, a, elastic displacement, h_e, total displacement, h_{tot}, and contact depth, h_c, are labeled. Top left inset shows schematic of a surface ripplocation [32]; and top right inset shows schematic of a BR in graphite [33].