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Deformation of layered solids: Ripplocations not basal dislocations

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ABSTRACT

It has long been assumed that basal dislocations were responsible for the deformation of layered, crystalline solids. Herein we make the case that, with the notable exception of some metals that kink, ripplocations - not basal dislocations - are the operative micromechanism. The reasons are: i) clear evidence for c-axis strain at multiple length scales including in transmission electron microscopy images; ii) strong influence of confining pressure on the compressive strengths of poly-, and especially single crystals; iii) ripplocations are a topological imperative if the layers are to move relative to each other, without breaking the in-plane bonds.

1. Introduction

Layered solids, defined herein as solids in whose deformation, at least initially, is constrained to two-dimensions (2D) are ubiquitous in nature and our modern world. From graphite used in nuclear reactors and Li-batteries, to geological formations of layered silicates in foliated rocks, composite materials and those comprising the *2D materials revolution*, such as graphene, that are showing great promise in a host of current/future applications due to their remarkable properties. This point of view deals strictly with crystalline materials. For reasons discussed below, it excludes layered materials in which <c + a> dislocations or twins are nucleated. And while not discussed herein, the conclusions reached are nonetheless important and applicable to layered composite materials.

It is well established that when the basal planes of layered solids are loaded edge-on, they generally fail by the formation of kink bands (KBs) (top left inset in Fig. 1a). KBs have been extensively studied in the geological [1–7], ice [8], composites [9–11], graphite [12], metallurgical literature [13–16], as well as confined sheets of paper, [17,18], among many other systems. In short, most materials wherein buckling and KB formation have been observed, KBs have been modeled and experimentally studied.

However, when the literature on the deformation of layered crystalline solids is reviewed, it is clear that - implicitly or explicitly - the micromechanism responsible for their deformation is, in all cases, assumed to be the *basal dislocation* (BD) [1–5,19,20]. The purpose of this article is to make the case that ripplocations [21,22] and not BDs are the operative micromechanism.

Our interest in kinking was triggered by the early realization that one of the preferred deformation modes of the MAX phases was KB formation [23–26]. The $M_{n+1}AX_n$ (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 [27]. These phases are important here for several reasons:

- Nanolaminated topology at the atomic level (bottom left inset in Fig. 1a).
- Density of states at Fermi level is substantial and thus it is not unreasonable to think of them as "nanolayered metals" [27].
- Fully, and spontaneously reversible stress-strain hysteresis loops are observed when cyclically loaded in compression [28], both at the macro- (Fig. 1a) and the micro-scales (Fig. 1b).
- Since part of the strain is fully reversible, viz. elastic, but non-linear, and the end result in most cases is the formation of KBs, these solids were described as being *kinking non-linear elastic* (*KNE*) materials.
- Due to their high c/a ratios (4 to 6), the energetic cost of non-BDs is prohibitive and has never been implicated in their deformation. Twins have also never been observed.

It follows that the MAX phases represent the ideal layered solid in that the deformation is unambiguously 2D. It is thus not surprising that like other layered solids, KBs form when the basal planes are loaded edge-on [23,29], and have been imaged at multiple length scales, from the sub-micrometer (lower right inset in Fig. 1a) [23] to the millimeter (top inset in Fig. 1a) [30].

Before proceeding, it is important to summarize what is known about the confined deformation of layered solids. A simple but powerful way to study confined deformation– especially of weakly bonded solids such as graphite and mica - is to carry out repeated spherical

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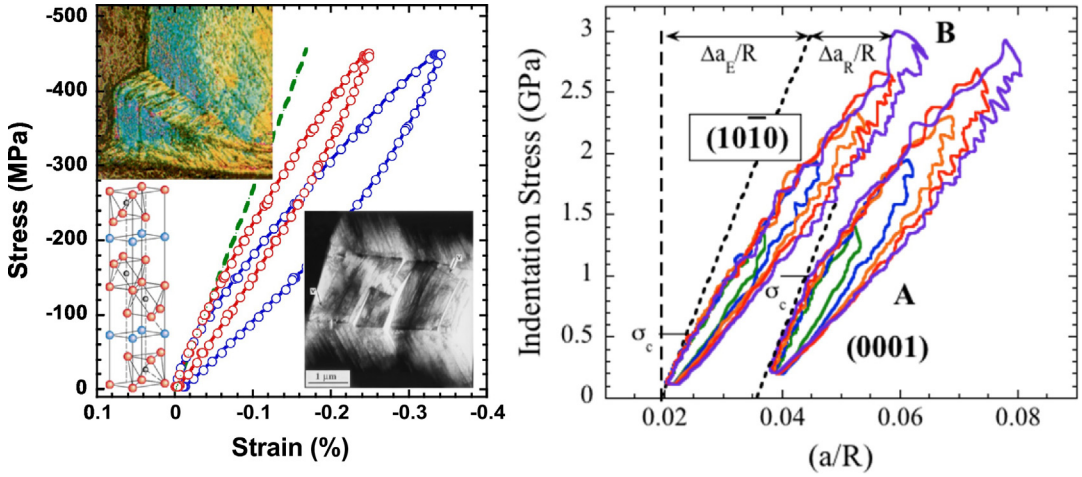

Fig. 1. a) Macroscopic stress-strain curves for highly oriented Ti_2AlC samples wherein the basal planes are loaded edge-on (red) or normal to basal planes (blue) [43]. Top left inset shows an optical microscope micrograph of a KB of extra large Ti_3SiC_2 grains deformed at RT when the basal planes were loaded edge-on. Picture width ≈0.2 mm [30]. Lower left inset shows unit cell of Ti_3SiC_2. Bottom right inset shows TEM of a KB in Ti_3SiC_2 deformed at RT [23]. b) Typical nanoindentation stress vs. a/R curves obtained when a 100 μm radius sphere is indented normal, or parallel, to the basal planes of Ti_3SiC_2 [41]. Dotted inclined lines in both figures represent the linear elastic response if BRs were not nucleated. Note that at both scales, less energy is dissipated when the basal planes are loaded edge-on. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nanoindentation (NI) experiments in the same location and measure the resulting load displacement curves. The load is then converted to a stress which is plotted vs. a/R, where R is the radius of the indenter and a is the contact radius [31,32]. Whenever possible, the basal planes are loaded either edge-on or along [0001]. From over a decade of work, mostly on single crystals, the following conclusions have been gleaned: When indented with spherical indenters, layered solids and/or plastically anisotropic solids respond in one of two ways:

1.1. Metallurgical indentation marks

If <c + a> slip and/or twins are nucleated, the indentation mark is 'metallurgical' in that little to no buildup of material around the indentation edges or cracks are observed. This is best seen in Fig. 2a–f, where typical indentation marks in Zn (0001), Zn (10$\bar{1}$0) [34] Mg (0001) [34], ZnO (0001), ZnO (10$\bar{1}$0) [33] and $LiTaO_3$ (0001) [35] surfaces are shown, respectively.

To differentiate between nucleation of twins and activation of <c + a> slip is straightforward: In the former, the indentation shape takes on the geometry of the twins. This is best seen in Fig. 2f, where (000l) $LiTaO_3$ surfaces are loaded [35]. The same is true of $LiNbO_3$ [36]. Here, despite the fact that the indenter was a hemisphere, the indentation mark is triangular in shape (Fig. 2f).

When the (000l) ZnO surface is loaded, clear evidence for pyramidal slip is seen [33]. That such slip occurs was unambiguously shown by Bradby et al. [37] In other words, a mechanism for c-strain was available. In contradistinction, when the basal planes of ZnO are loaded edge-on (Fig. 2e), <c + a> activation is *not* required, since c-strain is not

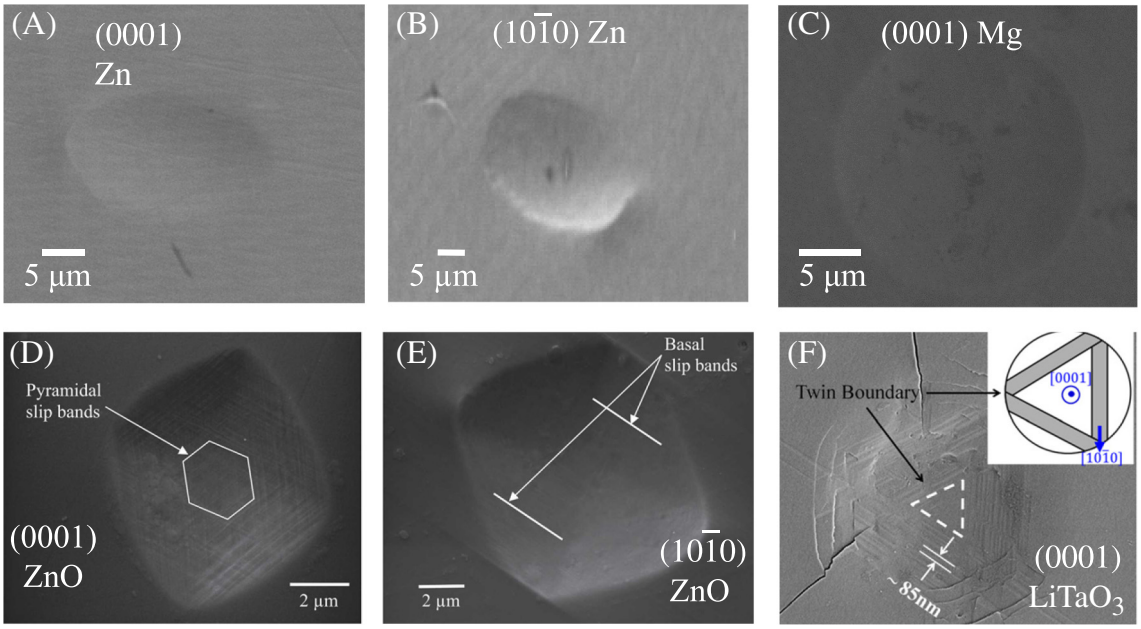

Fig. 2. Residual indentation marks on, a) (0001) Zn [34], b) (10$\bar{1}$ 0) Zn [34], c) (0001) Mg, [34], d) (0001) ZnO [33], e) (10$\bar{1}$ 0) ZnO [33] and, f) (0001) $LiTaO_3$ [35] surfaces. Inset in f shows orientation of twins nucleated that result in the formation of a triangular indentation, despite the fact that the indenter used was spherical. Note absence of pileups or delamination cracks. Lines in d trace pyramidal slip lines; lines in e trace basal slip lines.

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