RIPPLOCATIONS: A NEW MICROMECHANISM IN THE DEFORMATION OF LAYERED SOLIDS

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Drexel University

- **Founded** in 1891 by financier Anthony J. Drexel
- **Student Enrollment:** 13,500 UG; 9,000 G
- **Materials Dept.** ranked 11 in US in NRC ranking a few years ago.
Mechanical Properties of Solids

Increase load and measure deformation
Deformation of Materials

Brittle solids (ceramics)

Ductile solids (metals)

Polymers
How does plastic deformation occur at the atomic level?

The first idea is that atomic planes simply glide over each other.

IMPOSSIBLE

1930 Taylor, postulated the presence of a crystal defect he called a DISLOCATION.
Edge Dislocation

https://www.youtube.com/watch?v=quGSfmt4V6Y
Layered Solids

Deformation is confined to 2D

Easy to visualize
but CANNOT lead to ductility
Crystalline Solids Made up of Small Grains

Five slip systems needed for ductility.

Layered solids have only 2 systems.

So they are brittle.

**NO** deformation mechanism to basal planes.
Nature's Solution is to Kink

Kinks displace material perpendicular to the basal planes.
ALL Layered Materials Kink

Layered silicates: geology
Wood
Laminated Composites
Graphite
Card Decks
Rubber Laminates
Phone Books*
MAX Phases

Kinking is a buckling phenomenon
Mostly occurs under compression
Occurs at **ALL** Scales
Kink Band & Kink Boundaries

$\text{Ti}_3\text{SiC}_2$

Barsoum et al. Met. Trans. 1999
Some make music!
$M_{N+1}AX_N$ Phases

M: Early transition metal

A: Group A (IIIA and IVA)

X: C and/or N

211
$\text{Ti}_2\text{AlC}$
$\text{Cr}_2\text{GeC}$

312
$\text{Ti}_3\text{SiC}_2$
$\text{Ti}_3\text{AlC}_2$

413
$\text{Ti}_4\text{AlN}_3$
$\text{Nb}_4\text{AlC}_3$
Thermodynamically Stable Nanolaminates

211

312

413

MAX/MXene Research Group
Layered Solids with Metallic Bonding

Ti$_3$SiC$_2$
Inorganic Wood

2 µm

Gilbert, et al. Scripta 2000
Ti$_3$SiC$_2$
Kinks Due to Buckling

2 µm
Mechanical Properties

- Lack of 5 independent slip systems = not ductile
- BUT as you load, you generate large stresses that cause fully reversible kinks to form.

Results in kinking nonlinear elasticity.
Kinking Nonlinear Elasticity
Fully Reversible Loops up to 1 GPa

Room Temperature

FG Ti$_3$SiC$_2$

Kinking Nonlinear Elastic

Elastic
Nonlinear
Kinking
Compressive Stress-Strain Curves

- Fine Grain Ti$_6$SiC$_2$
- Al$_2$O$_3$
  - $E = 360\, \text{GPa}$
- Coarse Grain Ti$_6$SiC$_2$
- T2024 (Al alloy)
  - $E = 66\, \text{GPa}$

Room Temperature
No Effect of Strain Rate

Barsoum, MAX Phases (2013)
Room Temperature Cyclic Tests

Fine grain Ti$_3$SiC$_2$

Coarse grain Ti$_3$SiC$_2$

Dense and 10% Porous Ti$_2$AlC

Porous sample dissipates MORE energy!
Since 2003, I tried to explain observations in formalism everybody was using: **Basal Dislocations**

It was not working!
Ripplocations in van der Waals Layers

Same-sign Ripplocations: attract

Same-sign Dislocations: repel
Ripplocations in MoS$_2$
Ripplocations in Graphite

a)

b)

c)

d)

Fully constrained

\[ \Delta E (eV/A) \]

- a) Constrained Surface
- b) Unconstrained Surface
- c) Constrained Bulk
- d) Unconstrained Bulk
Graphite

Color is a measure of strain
Ripplocation/Ripplocation Interactions

a) 

b) 

c) 

d)
Ripplocation Vacancy Interaction
Kink Band Formation Magic
Response to Remote Stress
Ripplocations are Alive in Graphite!

@ 10 K
Buckling of Graphite on Peeling

(f) [Image showing multiple layers of graphite]

(g) [Image showing multiple layers of graphite]

(a) [Diagram showing peeling graphite flake and kink]
Repeated Spherical Nanoindentation

Measure load and displacement
Convert to stress vs. a/R (strain)
**Ti$_3$SiC$_2$ - Relatively Low Loads**

100 μm tip  
50 cycles
Relatively Low Stresses

Indentation Stress (GPa)

(a/R)

(0001) (1010) \( \sigma_y \) \( \sigma_y \)

100 \( \mu m \) tip

5 \( \mu m \)

NO indentation mark especially in samples loaded edge on!

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Griggs, PhD Thesis Drexel 2105
Relatively High Loads
Relatively High Stresses

\[ E = 325 \text{ GPa} \]

\[ \frac{\sigma_c}{\Delta(a_c/R)} \]

\[ \frac{21 \mu m}{21 \mu m} \]

BOOK

PRAYER
Permanent Kink Bands
TEM of Prayer Direction after High Stresses

Kinks
Cracks

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Book Orientation

[Diagram showing a Berkovich indenter, free surface, delaminations, and bulk structure]
Vickers Indentation of Ti$_3$SiC$_2$
TEM of Book Direction after High Stresses

Near Edge Pileup

Kink Boundaries
Taking a Closer Look

Indent crater
No cracking
No delamination

Evidence for c-axis Strain!
TEM Evidence
How to Distinguish Between D and R?

Ripplocations have to nucleate at a free surface.


With \( \langle c+a \rangle \) Dislocations

**Mg**

- No pileups

**ZnO**

- No delamination cracks

Griggs et al. Sub. for publication.
Kinks Everywhere

Tallman et al. Scripta 2012
Summary and Conclusions

Ripplocations are the micromechanism operative during the mechanical deformation of layered solids.

Ripplocations are a topological imperative!

Ripplocations can self assemble into kink boundaries

Acknowledgments

MAX/MXene Group
Thank you for your attention
**Buckled Layers Analysis**

**Elastic Energy**

\[ \delta U = -4Db s^{-1}(\pi - 2\alpha) \delta \alpha. \]

- **D** = bending stiffness
- **b** = width of ribbon
- **s** = length of bend

**Dissipated Energy**

\[ \delta W = \tau_s b L |\delta d| = \frac{\tau_s h b L}{\sin^2 \alpha} \delta \alpha \]

- **\( \tau \)** = shear resistance
- **L** = length of kink
- **d** = sliding distance
- **h** = thickness between layers

\[ L \geq \frac{4D}{\tau_s h s} \]
Molecular Dynamics Details


All configurations were periodic in the y-axis only. All configurations spanned 20 unit cells in the x-axis and 2 unit cells in the periodic y-axis.
TEM Analysis Details

• JEOL 2100 LaB$_6$ with a HR objective-lens pole piece.
• Geometric Phase Analysis, GPA, was performed using algorithms described by Hýtch et al. (Hýtch, Snoeck & Kilaas, *Ultramicroscopy* (1998))
• A plug-in designed for the Gatan Microscopy Suite and licensed through HREM Research Inc.
• Strain and rotation maps were produced by performing GPA using 6 or more spots in the FFT obtained from the corresponding HRTEM image. Reference frames were chosen to represent undeformed lattice and are noted within images.
R-Curve and Crack Bridging

\[ \text{Crack growth Resistance, } K (\text{MPa} \sqrt{\text{m}}) \]

\[ \text{Crack Extension, } \Delta a (\text{mm}) \]

- \( a_0 = \text{initial flaw size} \)
- \( a_0 \sim 13 \text{ mm} \)
- \( a_0 \sim 10 \text{ mm} \)
- \( a_0 \sim 8.3 \text{ mm} \)
- \( a_0 \sim 7.8 \text{ mm} \)
- \( a_0 \sim 3.8 \text{ mm} \)

Compact tension
Kinky Creep in Ti$_2$AlC

Tensile Creep
1100 °C, 30 MPa
Strain to failure = 16%
Time to failure = 3 h
Effect of Strain Rate on Tensile Response

1200 °C

Strain exponent = 0.5.
This is not superplasticity

No necking

Microcracked Swiss cheese
Psuedo-Single Crystals

Macro, oriented grains fabricated by a sinter forging technique

Stress-Strain vs. Orientation

Engineering Stress (MPa)

Compression along z-axis

Compression along x-axis

Basal planes are parallel to the x-axis

25°

Hot pressing direction

Engineering Strain
Kink Bands and Dislocations

It is basically a buckling phenomenon.

KNE solids are hugely plastically anisotropic

Basal slip, and **only**, basal slip

Type A: High c/a ratio solids

Type B: 2D solids with low $c_{44}$

No mechanism for strain normal to the layers

NONE
Energy Gain

Definition of Burger vector has to change.
Uniaxial Compression

Ti$_3$SiC$_2$ at High T

Temperature dependent decohesion strength
Explain Mechanical Properties of Layered Solids

Two simple ideas:

Reversible Buckling = KNE, not a f(T) or time!
Decohesion strength = f(T) = BPTT
Cyclic Hardening After HT Deformation

Important result: HT softening is fully reversible!

Easier to buckle large grains than small grains
Specific Stiffness

Be
Al
SiC
Al₂O₃
Ti
Fe
TiC
Si₃N₄
Ti₃SiC₂

Specific Stiffness (GPa/gm/cc) vs. Density (gm/cm³)

Toxic
Non-machinable
Superb Machinability

Machinability decoupled from high temperature mechanical properties.