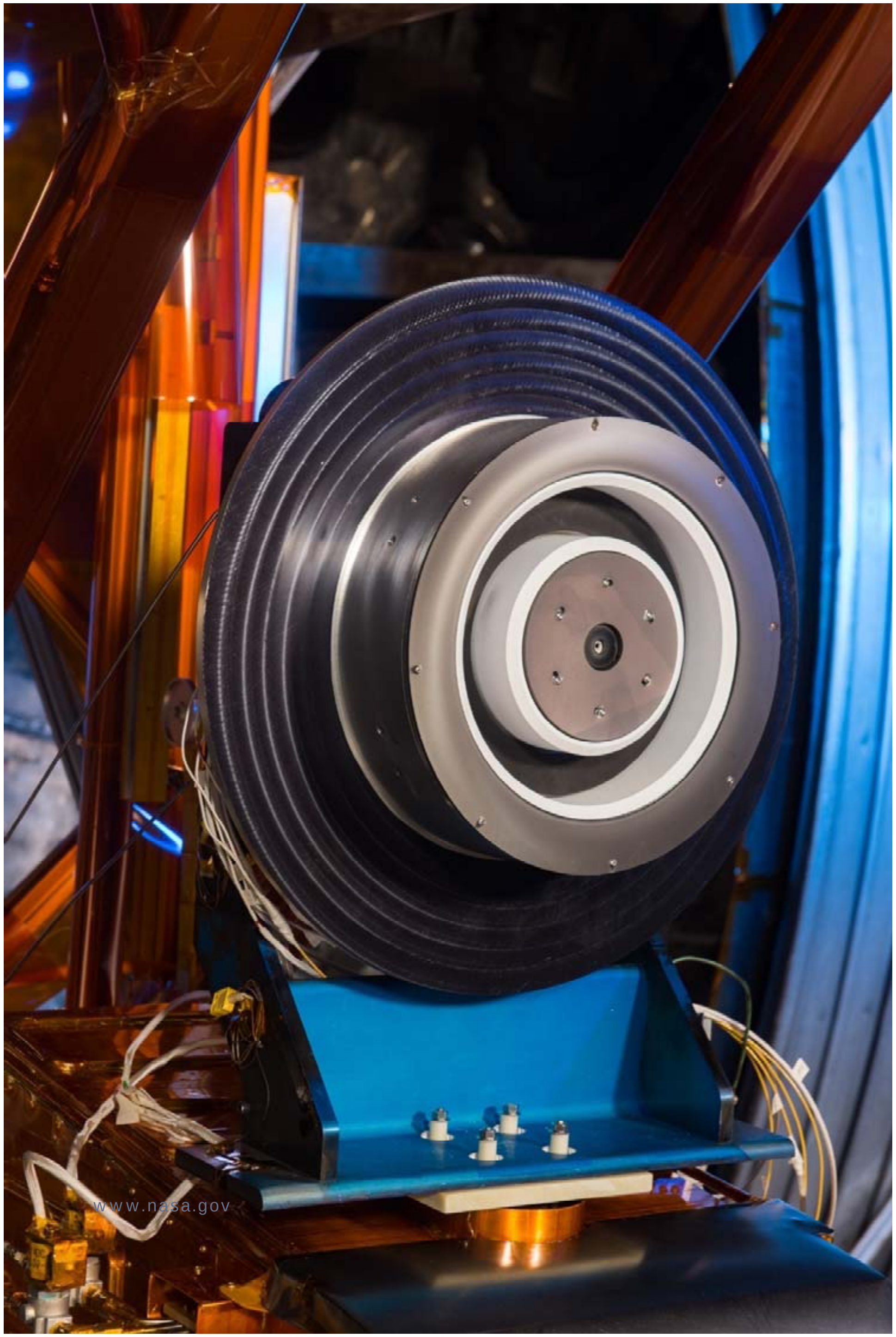

Slow crack growth of boron nitrides for electric propulsion components

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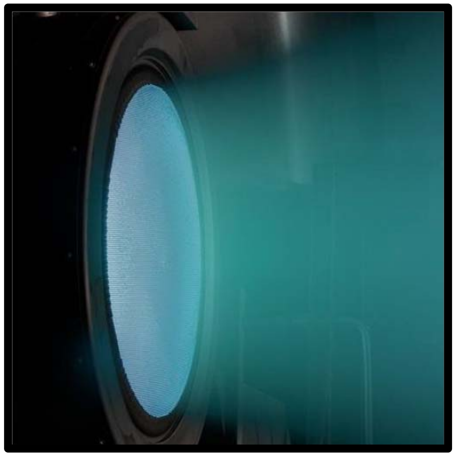
43nd International Conference and Expo on Advanced Ceramics and Composites

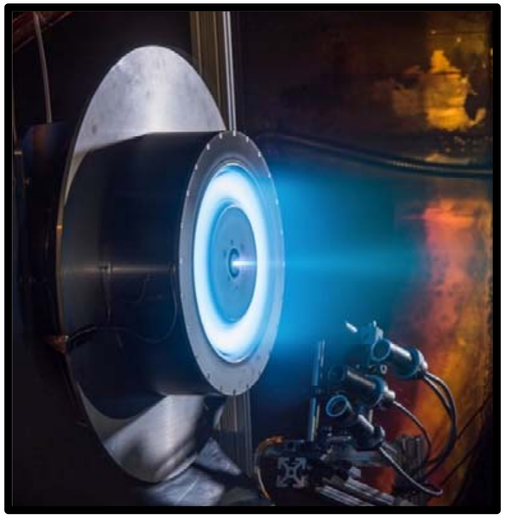
Outline

- Background
- Materials and properties of interest
- Past work
  - Chemistry, microstructure, texture, moisture absorption
  - Strength, modulus, CTE, conductivity
- Slow crack growth
  - procedure
  - failure sources
- Fracture toughness
- Summary

Background

- Electric propulsion systems subject components to harsh environments including:
  - High temperature plasma (600ºC)
  - low temperature (-200ºC), vacuum, and back-sputtered deposition.
- Both Hall and ion thrusters require ceramics:
  - electrical isolation
  - thermal management
  - structural performance.
- Ceramic components range in size from <¼" to >10".
- Historically, material selection has primarily been determined from cost, secondary electron emission yield, and sputtering yield.
  - ➢ Hot pressed hexagonal boron nitride





Materials of Interest

- The grades commercial hexagonal boron nitride being considered were selected from historical usage and/or geometric considerations.
- Similar costs w/exception of Tokuyama
- Several grades contain significant silica:

Grade Name*	Vendor*	Description	Relative Cost**
HP	Saint-Gobain	BN CaF_2 Binder, Hot Pressed	1.0
M26	Saint-Gobain	BN/SiO_2 Composite, Hot Pressed	1.1
M	Saint-Gobain	BN/SiO_2 Composite, Hot Pressed	1.0
BN-XX	Kennametal	BN/SiO_2/ZrO_2 Composite, Hot Pressed	1.0
Hi-M	Tokuyama	AlN/BN Composite, Hot Pressed	4.6

* Trade names and vendors are used for identification purposes only.

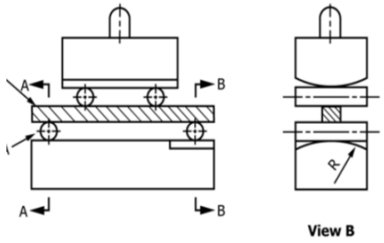
** Cost based on recent quotes for similar size lots of material, normalized to the cost of HP.

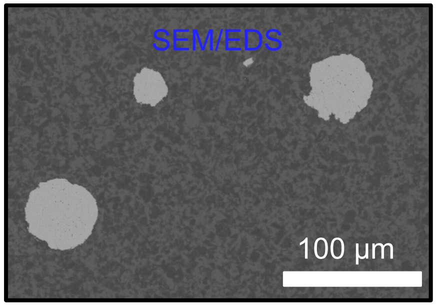
Factors of Interest

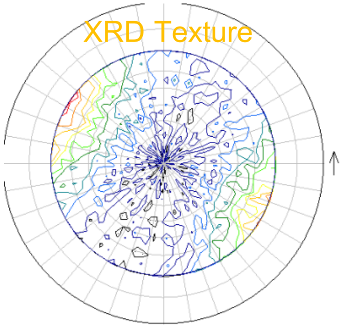
- Primary factors of interest:
  - dielectric properties
  - thermal properties and stability
  - mechanical properties
  - moisture sensitivity
  - secondary electron emission yield
  - erosion resistance in a plasma environment

- Secondary factors of interest:
  - Microstructure, crystal structure, details of processing, and mass spectroscopy.
- Additional factors to consider:
  - Hot press anisotropy, lot-to-lot and variability, billet uniformity/property variability, storage/handling concerns, and machining concerns.
- Beyond materials characterization work:
  - Component fabrication, component testing.

Property Testing

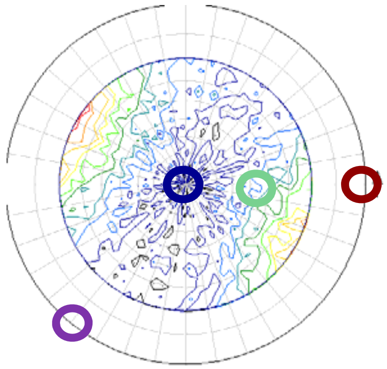


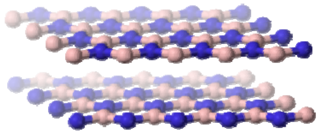




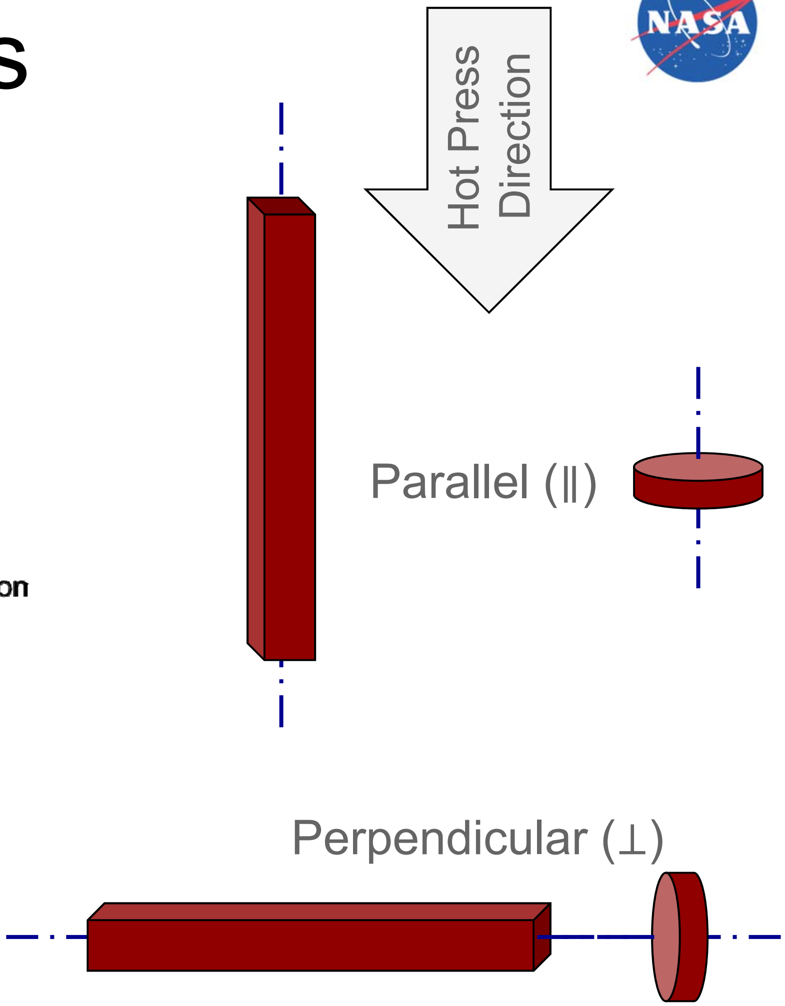
Property Measurements

- Building dataset to compare grades:
  - Collecting data from 25 to 900ºC .





hexagonal BN platelet orientation



- Collecting data on samples with orientation “Parallel ‖” or “Perpendicular ⊥” to the hot press direction.

NASA/TM—2018-219949
“Evaluation of Boron Nitride Materials for Hall Thruster Discharge Channels”
Jonathan A. Mackey, Jonathan A. Salem, and Hani Kamhawi…………

Property Trends & SiO$_2$ Content in BN

Property	**Method**	**HP** ∥ / ⊥	**M26** ∥ / ⊥	**BN-XX** ∥ / ⊥	**M** ∥ / ⊥
XRD BN Phase (wt%)	**Rietveld-refinement**	**98**	**70**	**56**	**45**
Porosity (%)	ASTM C830	<14	<4.7	<2.4	<3.0
CTE (μm/m-K)	Dilatometry	3.1 / 0.4	2.9 / 0.5	N/A	0.5 / 0.6
Dielectric Constant	Impedance Spectroscopy	4.7 / 4.6	4.6 / 4.7	4.1	4.0 / 4.2
Thermal Conductivity (W/m-K)	ASTM E1461	33 / 31	22 / 28	6	9 / 12
Elastic Modulus (GPa)	ASTM C1259	80 / 79	55 / 47	N/A	16 / 61

* All data collected at NASA GRC or California Institute of Technology

- Properties are quite different! Function of orientation.
- HP exhibits the largest values in all categories!

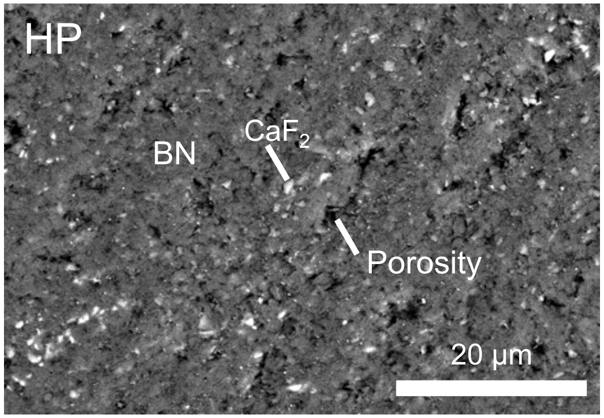
Microstructure Overview

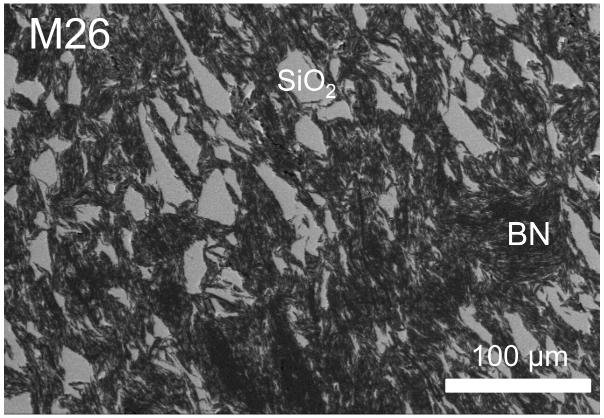
- Very different microstructure.
- Texture is not clearly apparent in SEM microstructure.
- Porosity is apparent in HP grade, less in other grades.
- Large silica content is a concern for crack growth.

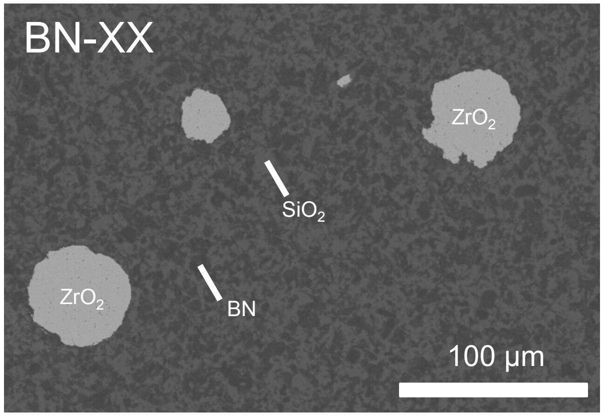
Powder XRD Rietveld Refinement (wt%)

Grade	BN	CaF_2	ZrO_2	AlN	Amorp.
HP	98	2	0	0	0
M26	68	0	0	0	32
BN-XX	56	0	1	0	43
M	41	0	0	0	59
Hi-M	27	0	0	72	0

*Amorphous content is likely SiO_2, confirmed with EDS.







Another Interesting Issue: Moisture Absorption

- Samples were subjected to one of three moisture levels for >20 days while mass change was tracked:
  - Drying Oven,100C, <5% rel. humidity.
  - Environmental Chamber, 50C, 90% rel. humidity.
  - Submerged Water Bath, 25C, 100% rel. humidity.
  - Each hot press orientation was investigated on high aspect ratio samples.

Drying Oven
100C, <5% rel. humidity, 50 days

Submerged in Water
25C, 100% rel. humidity, 90 days

Moisture Absorption (cont.)

- Mass change tracks with open pore porosity (high, medium, low).
- HP hot press orientation has influence on the transfer of moisture (high, low).
- HP samples produced a $CaB_6O_9(OH)_2(H_2O)_3$ salt on the surface of the submerged samples.

Sample	Porosity (%)	Dry Oven, 100C Mass Loss (%)	90% Chamber, 50C Mass Gain (%)	Submerged, 25C Mass Gain (%)
HP ∥	<14	1.1 ± 0.5	0.97 ± 0.07	4.6 ± 0.3
HP ⊥	<14	0.12 ± 0.01	0.33 ± 0.05	3.7 ± 0.5
M26 ∥	<4.7	0.025 ± 0.003	0.020 ± 0.005	2.7 ± 0.3
M26 ⊥	<4.7	0.035 ± 0.004	0.019 ± 0.008	3.2 ± 0.8
M ∥	<3.0	0.026 ± 0.005	0.018 ± 0.005	1.8 ± 0.1
M ⊥	<3.0	0.036 ± 0.003	0.005 ± 0.003	1.7 ± 0.1

% OP

BN wt%

Moisture Sensitivity on Strength

- Samples from moisture absorption study were tested for flexural strength and elastic modulus after soak.
- HP ‖, HP ⊥, and M ‖, all have significant changes in strength and elastic modulus properties with moisture exposure ($P<0.05$).

	<5% Rel. Humidity	~60% Rel. Humidity	90% Rel. Humidity	
Sample	**Dry Oven Strength (MPa)**	**As-machined Strength (MPa)**	**90% Chamber Strength (MPa)**	**P-Value [Oven>Chamber]**
HP ‖	52.1	42.5	27.5	0.000005
HP ⊥	80.1	76.1	69.7	0.005
M26 ‖	59.9	61.8	57.9	0.3
M26 ⊥	43.2	49.6	39.7	0.2
M ‖	23.9	24.7	22.3	0.01
M ⊥	60.1	62.4	59.2	0.3

Slow Crack Growth (SCG)

- Ceramics and glass exhibit loss of strength over time under static loads. The phenomenon is know as slow crack growth or "static fatigue" and is a form of stress corrosion.
- No data is the literature on BN.
- We need to know the SCG parameters for BN to see if stress corrosion should be a design consideration.
- Usual model: $v = \frac{da}{dt} = AK_I^n = A * [\frac{K_I}{K_{IC}}]^n$

<u>Sensitivity Parameter n</u>

< 20 high sensitivity (glasses)
< 40 intermediate (alumina's)
> 50 low (Si_3N_4)
> 100 ~ insensitive (Ge, Si, α SiC)

- v – crack velocity
- σ is Stress
- n & A are SCG parameters
- K_{Ic} is Fracture toughness

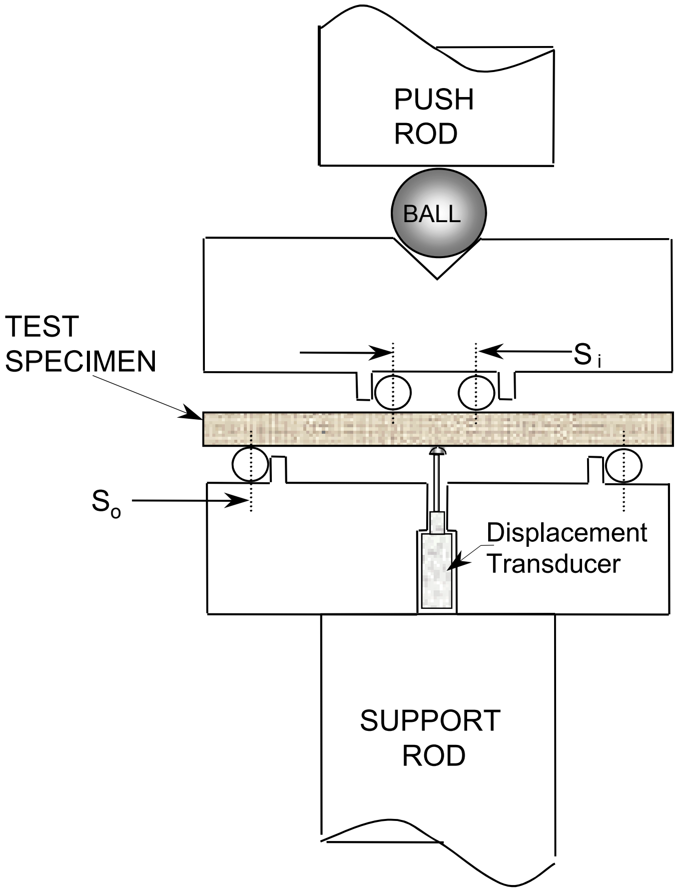
Rapid Technique for SCG Parameters

- Constant Stress Rate Testing (Dynamic fatigue):
  - well defined time-to-failure
  - can be rapid
  - simple

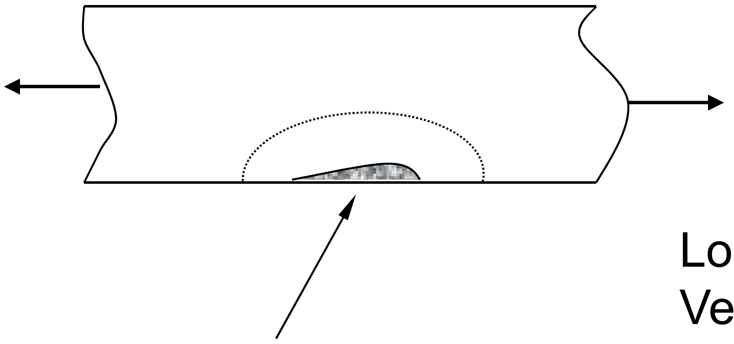
- Strength based approach with advantages & disadvantages:
  - samples the inherent, small flaws (length scale)
  - statistical scatter (many specimens needed)
  - averaging of fatigue regions
  - shorter time scale than application

Experimental Procedure

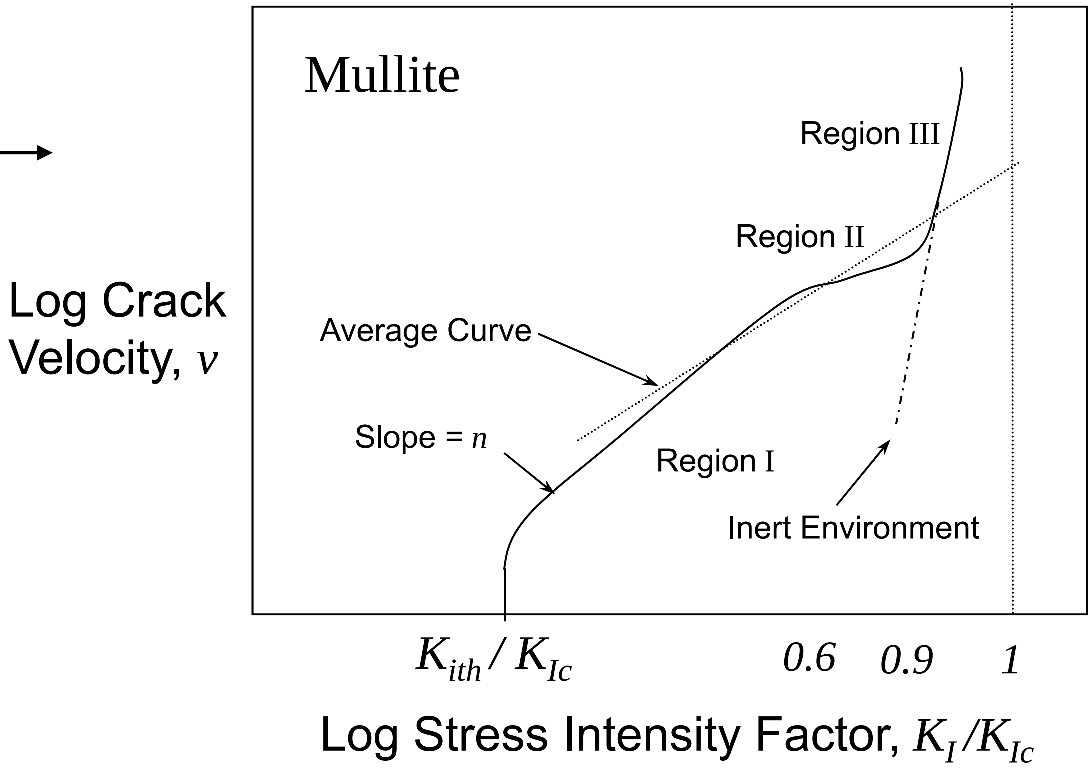
- Constant Stress Rate Tests (200 to 0.002 MPa/s)
- Uniaxial Flexure (4-point)
- Air : 60% RH
- As-machined surfaces
- 60 tests per condition



SCG FORMULATIONS



Defect/Damage



- ☐ Crack growth Function: $v = \dfrac{da}{dt} = AK_I^n = A^* \left[\dfrac{K_I}{K_{IC}} \right]^n$

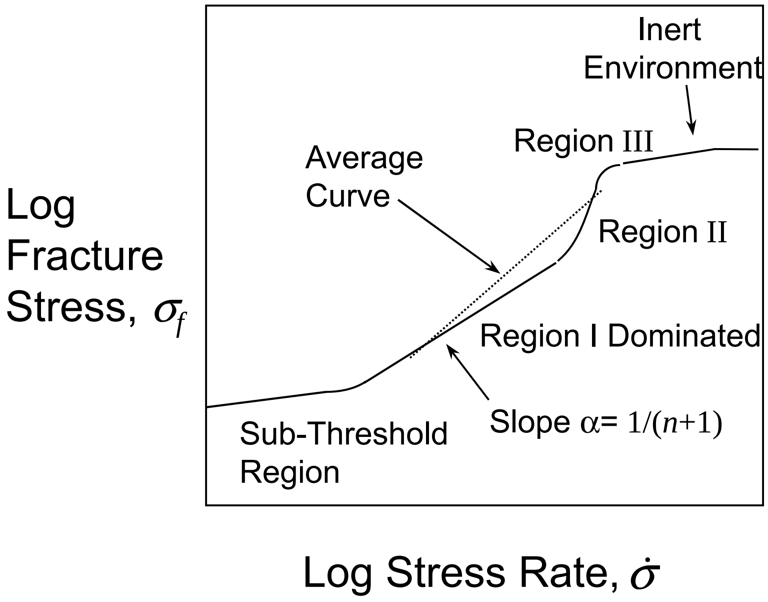
SCG Analysis

- Crack growth Function:

$$v = \frac{da}{dt} = AK_I^n = A * [\frac{K_I}{K_{IC}}]^n$$

- Constant Stress Rate Testing:

$$\sigma_f = \left[B(n+1)\sigma_i^{n-2}\dot{\sigma}\right]^{1/(n+1)}$$

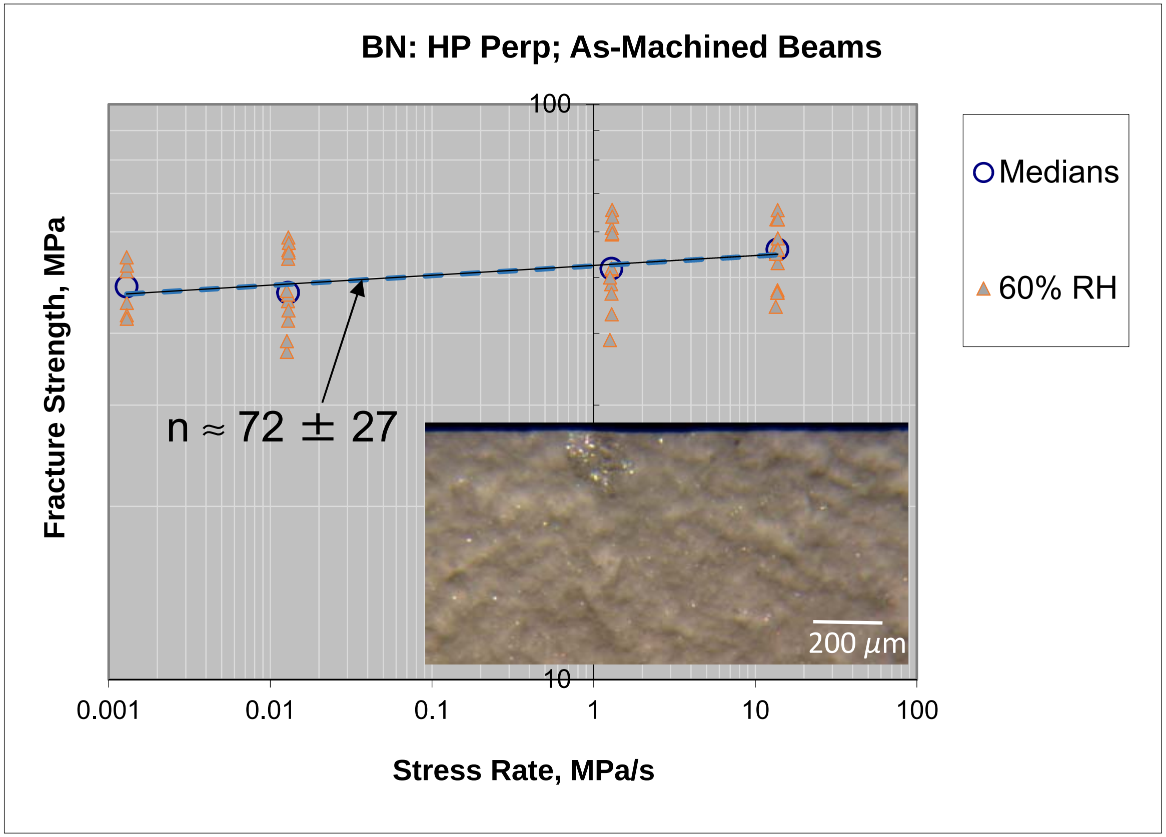


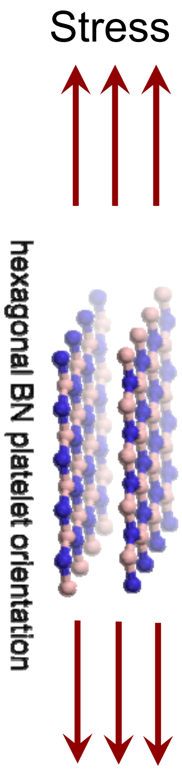
- Parameter extraction via regression:

$$\log_{10}\sigma_f = \frac{1}{n+1}\log_{10}\dot{\sigma} + \log_{10} D \qquad \log_{10} D = \frac{1}{n+1}\log_{10}\left[B(n+1)\sigma_i^{n-2}\right]$$

(Slope α) (Intercept β)

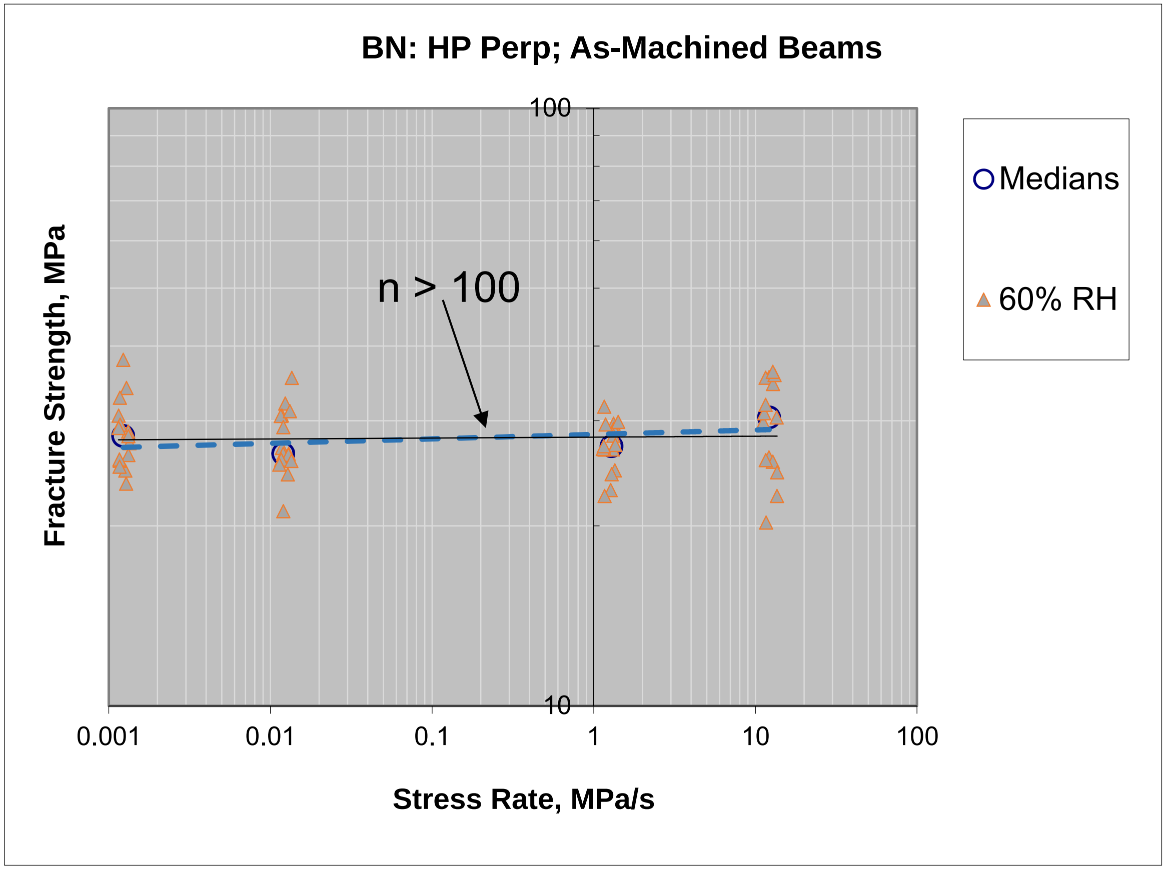
Results for HP BN Perpendicular

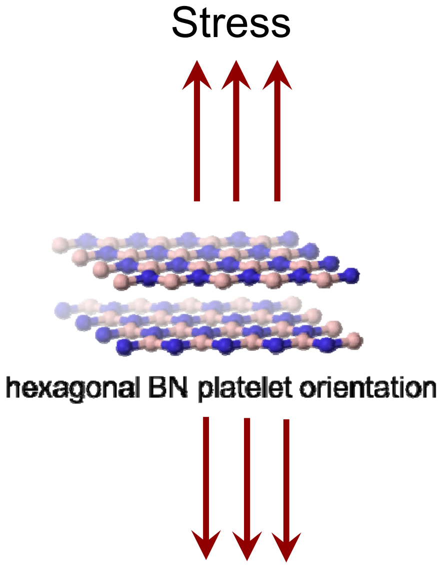




- SCG parameter *n* = ~72 ± 27
- Resistant to SCG.

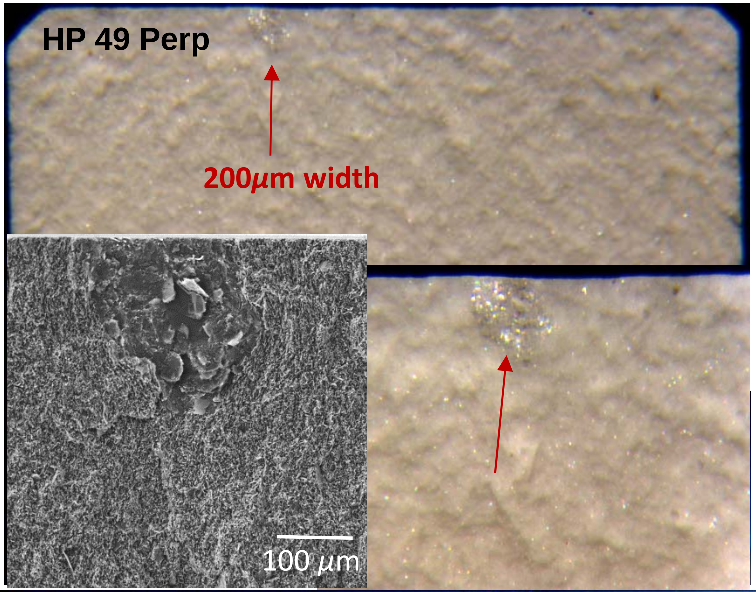
Results for HP BN Parallel

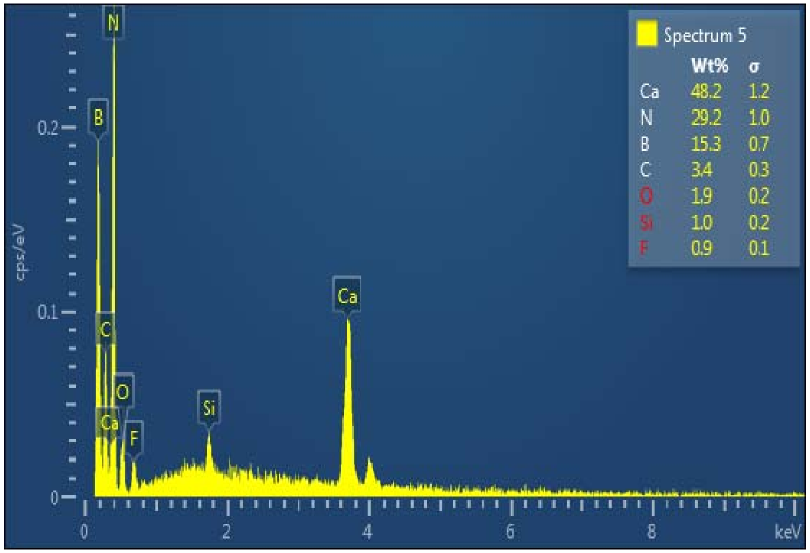




- SCG parameter *n* >100 is very high.
- Very resistant to SCG. …..platelets corossion.

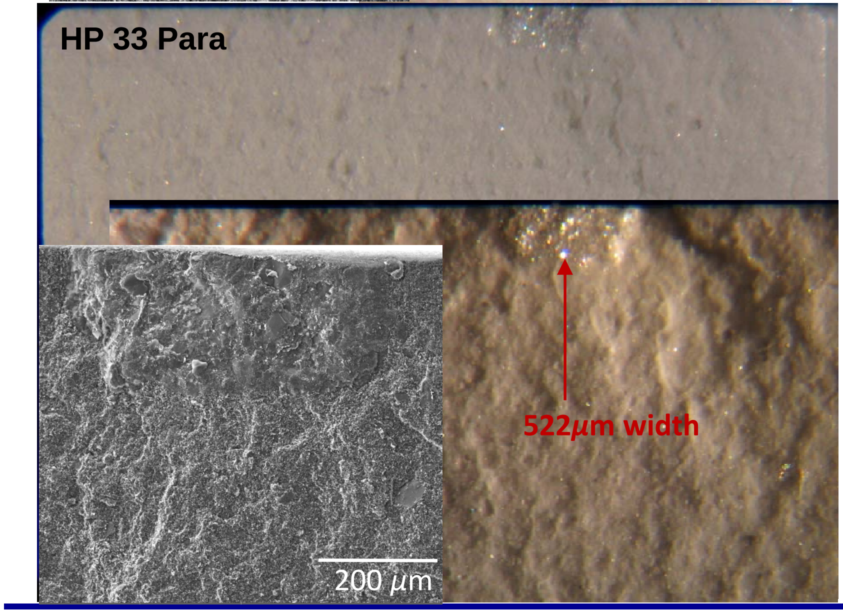
HP Failure Source: Ca rich agglomerates

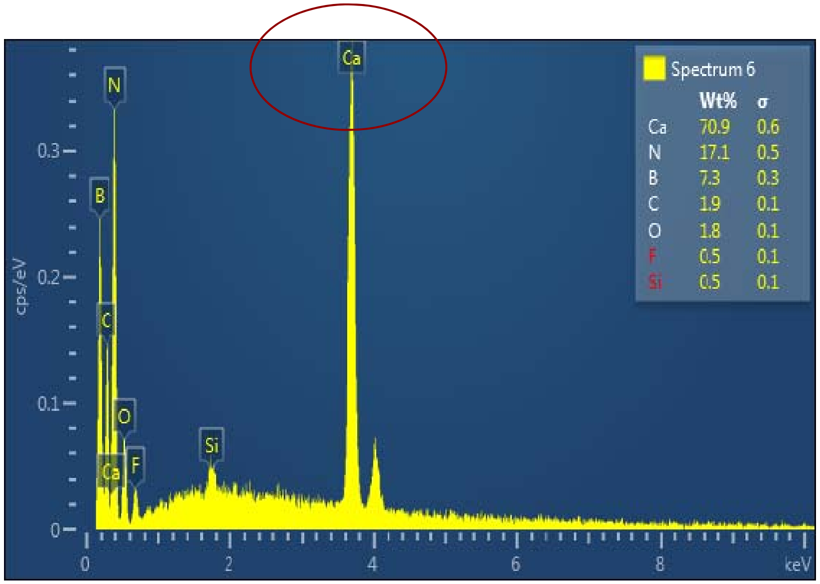




Spectrum 5

	Wt%	σ
Ca	48.2	1.2
N	29.2	1.0
B	15.3	0.7
C	3.4	0.3
O	1.9	0.2
Si	1.0	0.2
F	0.9	0.1

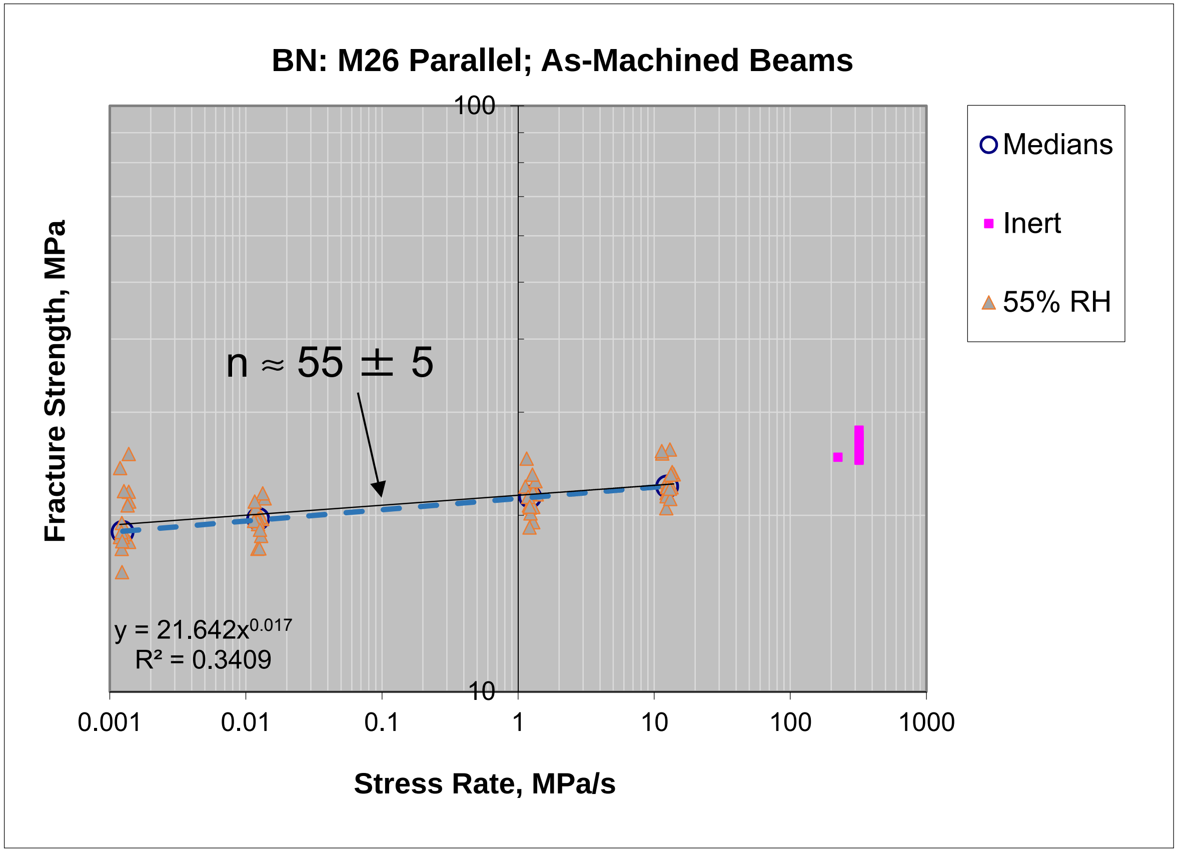


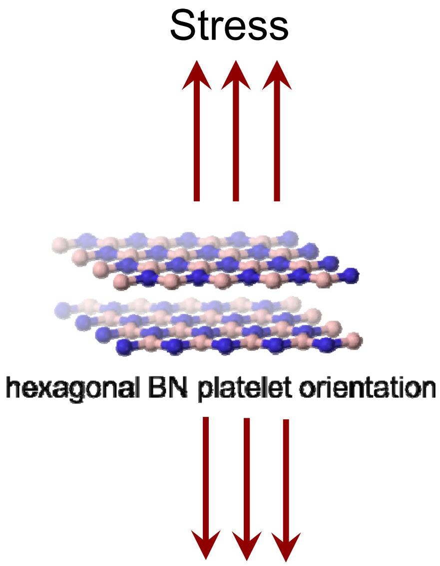


Spectrum 6

	Wt%	σ
Ca	70.9	0.6
N	17.1	0.5
B	7.3	0.3
C	1.9	0.1
O	1.8	0.1
F	0.5	0.1
Si	0.5	0.1

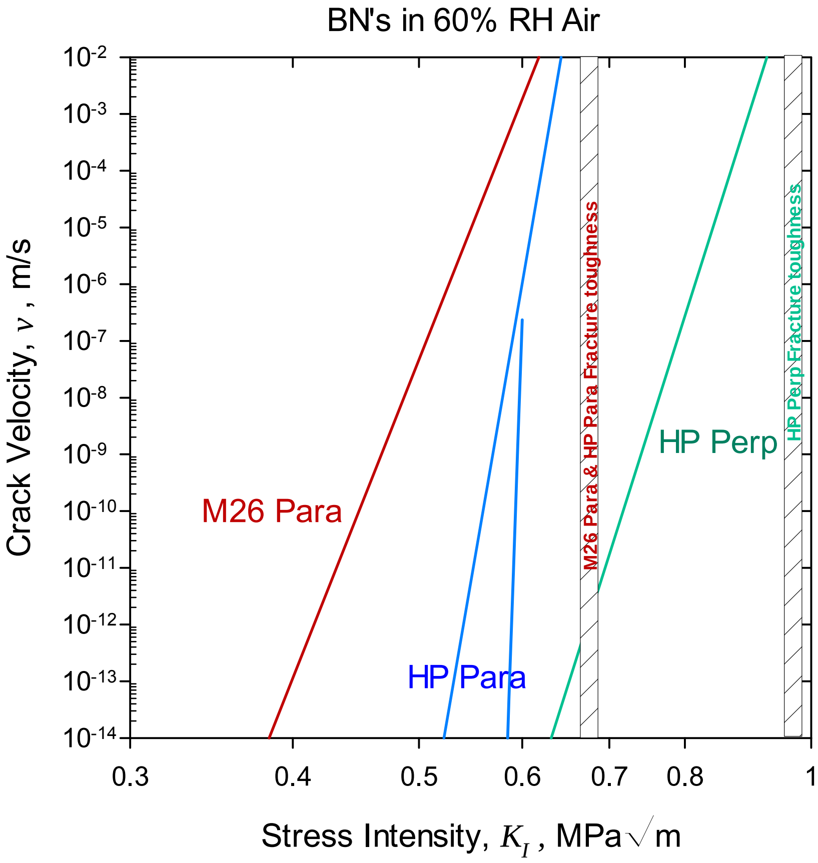
Results for M26 BN Parallel





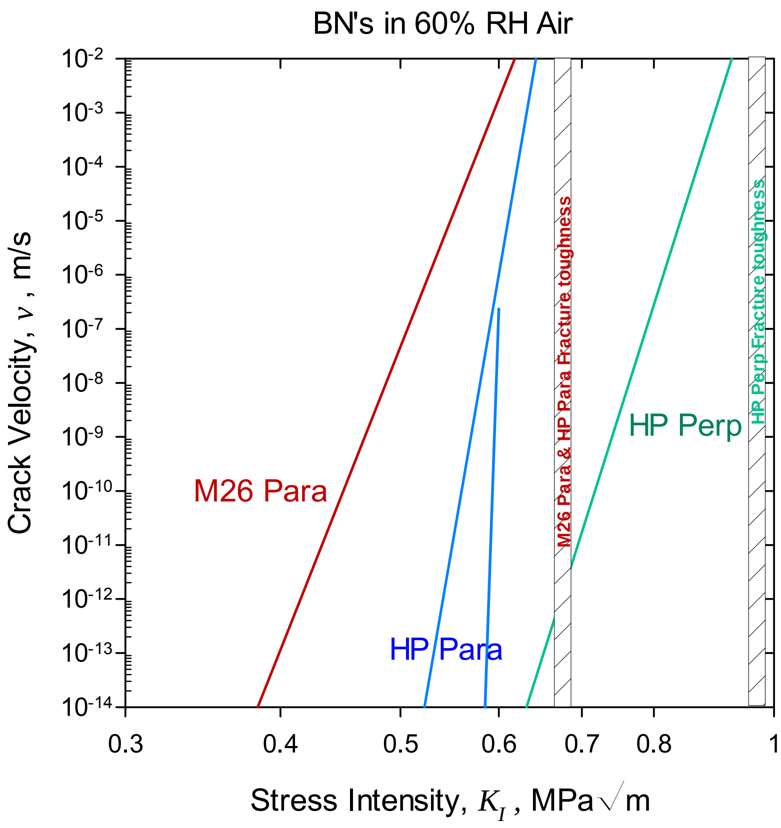
- SCG parameter *n* = 55 ± 5 is lower (more silica).
- Fairly resistant to SCG. …..

Crack Velocity Curves

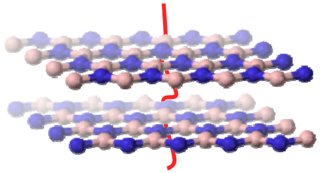


- M26 is the most sensitive to SCG: low *n* and low K_{Ic}.
- Crack growth in HP perp starts around the K_{Ic} of M26 and HP parallel.

Crack Velocity Curve



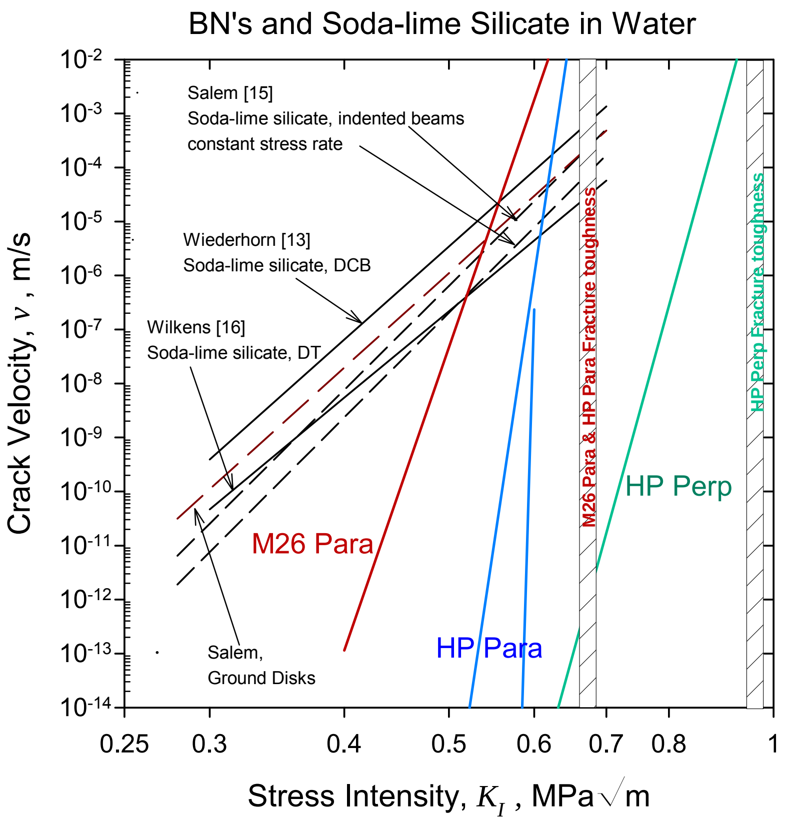
Material	n	Silica Content wt. %
HP Perp	72 ± 27	0
HP Para	>100	0
M26 Perp	58 ± 11	32
M26 Para	?	32



hexagonal BN platelet orientation

- SCG correlates with silica content……
- Bonds in HP between platelets are insensitive to water……….
- SCG mechanism across platelets may be ionic dissociation of bonds within platelets.

Crack Velocity Curve



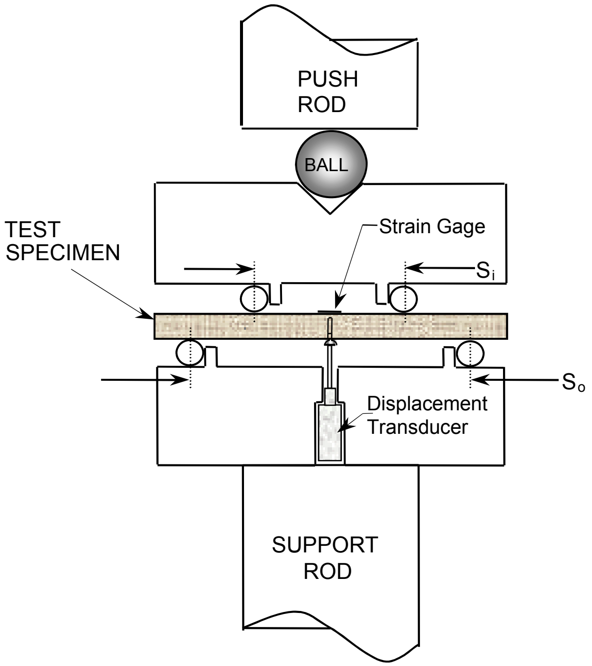
Glasses readily exhibit SCG and thus are a good comparison.

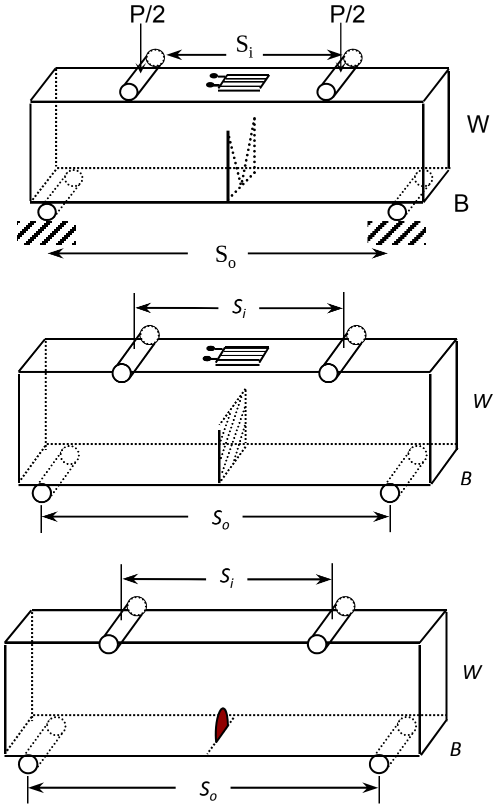
Material	**n**	**Silica Content wt. %**
HP Perp	72 ± 27	0
HP Para	>100	0
M26 Perp	58 ± 11	32
Glass	20	73
Fused SiO_2	40	100

- As compared to glass, M26 and HP parallel are less sensitive to changes in $K_{I,}$ but lower K_{Ic}.

Fracture Toughness

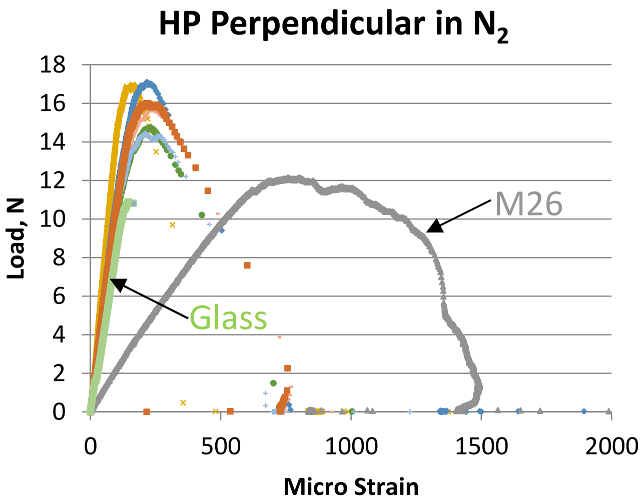
- Three standard methods are available.
- Indentation caused crushing w/o cracking.
- Used the chevron notch.

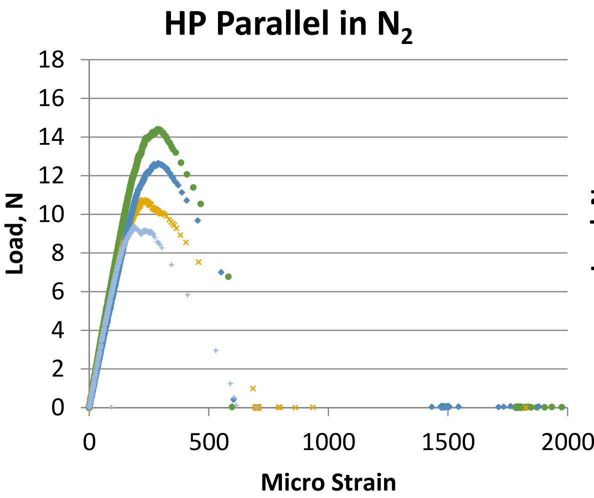


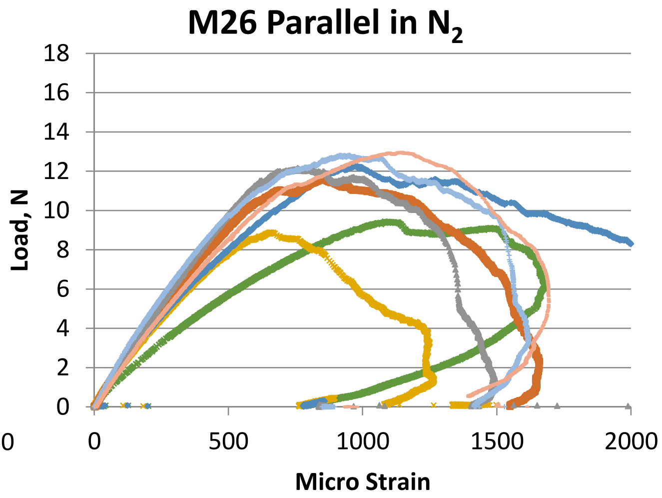


- Relatively simple fixtures: test frame, load cell, recording device.

Fracture Toughness

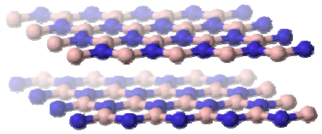

HP Perpendicular in N_2


HP Parallel in N_2


M26 Parallel in N_2

Material	K (60%)	K_{Ivb} (N_2) MPa√m
HP Perp		0.97 ± 0.07
HP Para		0.69 ± 0.08
M26 Perp		0.67 ± 0.05
M26 Para		?

Other Material	K_{Ivb}
Glass	0.78
Silca	0.75
SiC	2.8
Alumina	4


hexagonal BN platelet orientation

- Similar to glass. Easier to separate than split the platelets.

Summary

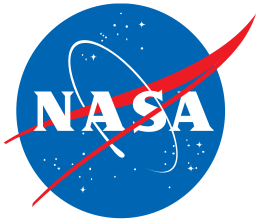
- BN's exhibits limited slow crack growth in humidity. Testing continues.
- SCG parameters correlate with silica content (?).
- Slow crack growth parameter are a function of test orientation due crystallographic texture & bond type.
- Bonds between platelet are not sensitive to water.
- Bonds within platelets are sensitive to water.
- Fracture toughness is low, around that of glass, and is a function of orientation.
- It is easier to drive a crack between hexagonal BN platelets than across platelets (weak bonds between platelets).

Summary

- Continuing work:
  - Lot-to-lot variability, fracture toughness, slow crack growth, compression strength, and secondary electron yield.

Acknowledgements

- Funding provided by NASA Space Technology Mission Directorate.
- Technical assistance provided by NASA Glenn Research Center.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