Lot-to-lot variability of BN grades for space electric propulsion applications

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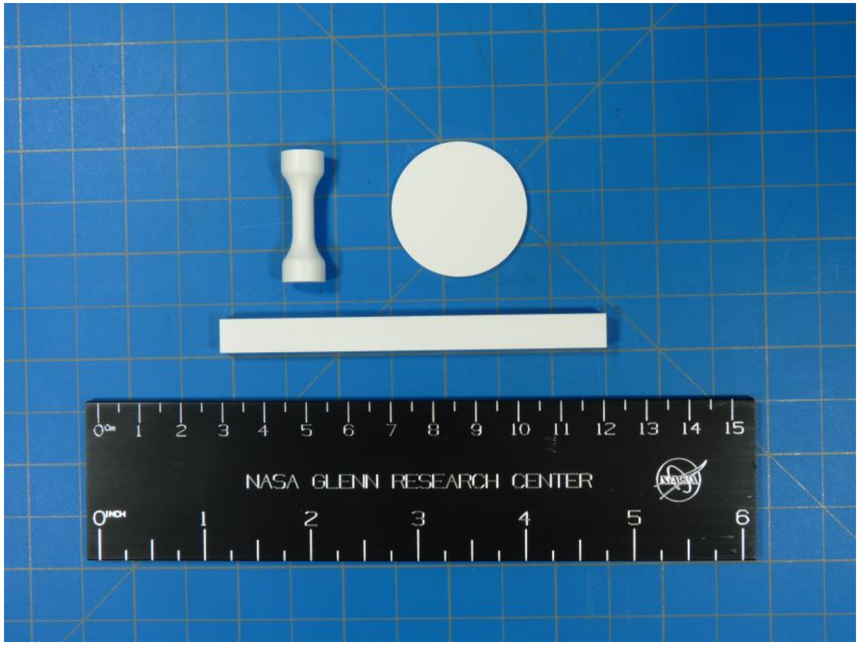
Background

- Focus of this work are commercially available machinable ceramics for electric propulsion components.
  - Specifically interested in hot pressed boron nitride.
- Electric propulsion applications may subject ceramics to harsh environments including:
  - Plasma erosion, high temperature, low temperature, vacuum, and back-sputtered deposition.
  - Components may need to provide electrical isolation, thermal isolation, or some limited structural support.
- This work investigates material properties of various commercially available ceramic materials with a focus on lot-to-lot variation.



Materials of Interest

- Several commercial hexagonal boron nitride grades are being considered in this study.
- Grades considered were selected from geometric considerations for typical components.
- Previous study focused on “Lot 1”, this work investigates differences for “Lot 2” compared against “Lot 1”.

Grade*	Vendor*	Description	Relative Cost**	Lot 1	Lot 2
HP	Saint-Gobain	BN $Ca(BO_2)_2$ Binder	1.0	HP6073, HP6035	T3044
M26	Saint-Gobain	BN/SiO_2 Composite	1.1	M266072	M266037, M268032
M	Saint-Gobain	BN/SiO_2 Composite	1.0	M5118	M6011
BN-XX	Kennametal	$BN/SiO_2/ZrO_2$ Composite	1.0	N/A	N/A
Hi-M	Tokuyama/ Precision Ceramics	AlN/BN Composite	4.6	N/A	N/A

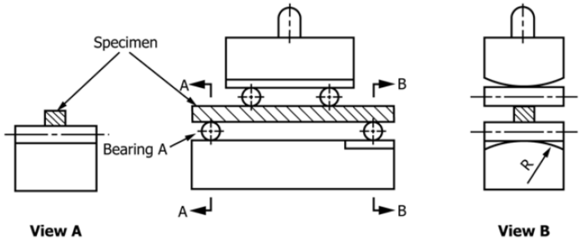
* Trade names and vendors are used for identification purposes only.

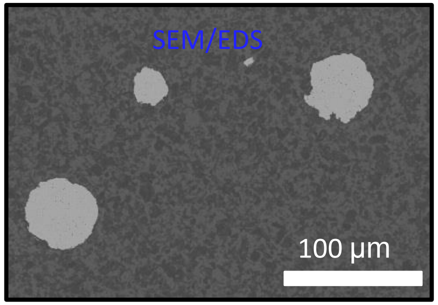
** Cost normalized to HP grade for comparable lot sizes.

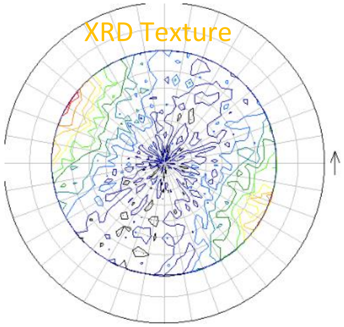
Factors of Interest

- Primary factors of interest:
  - Dielectric properties, thermal properties, mechanical properties, moisture sensitivity, secondary electron emission yield, thermal stability, and 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 property variability, billet uniformity/property variability, storage/handling concerns, and machining concerns.
- Beyond materials characterization work:
  - component fabrication and testing.

Property Testing

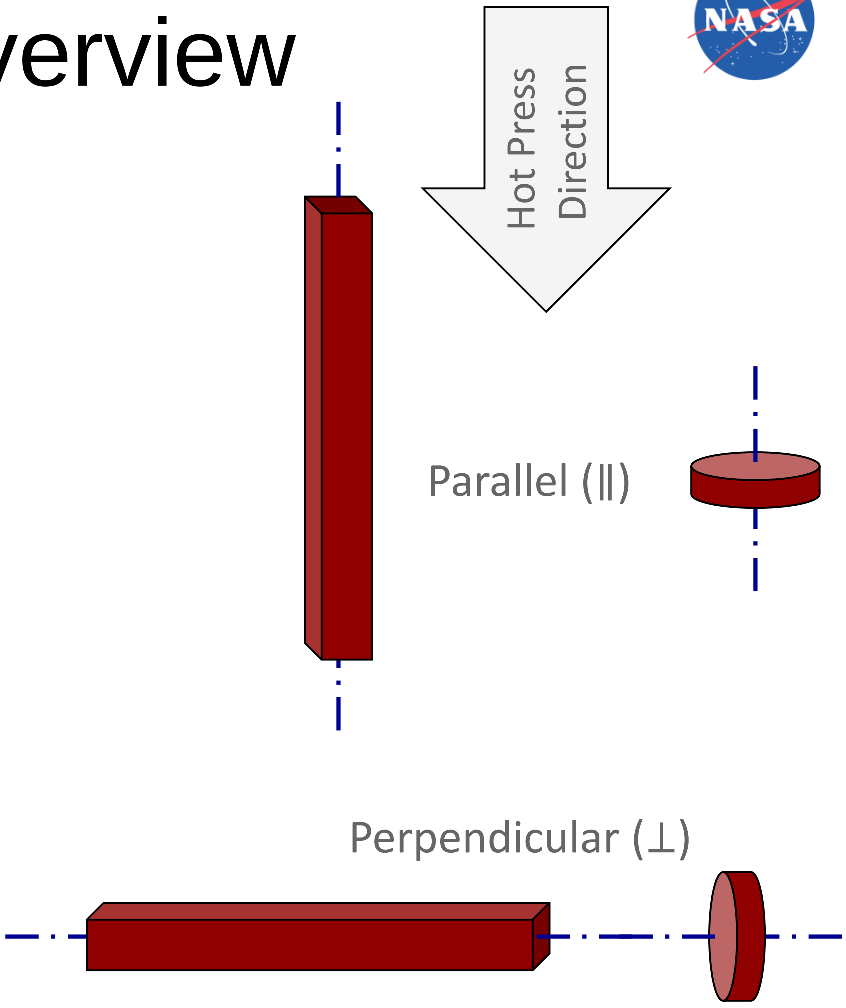


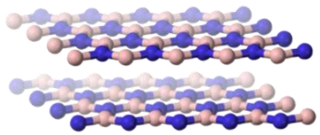




General Properties Overview

- Building dataset to contrast between different grades and against corporate literature.
  - Estimating measurement uncertainty from instrument uncertainty and sample size statistics.
  - Collecting data over a range of temperatures from 25 to 900ºC whenever possible.
  - Following ASTM standards whenever possible.
- Collecting data on samples with primary measurement direction “Parallel ∥” or “Perpendicular ⊥” to the hot press direction.





hexagonal BN platelet orientation

General Properties Overview (cont.)

Property trends in BN/SiO_2 content

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

General Properties Overview (cont.)

Property trends in BN/SiO_2 content

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

General Properties Overview (cont.)

Pro

Property	X	M ∥ / ⊥
XRD BN Phase (wt%)		**45**
Porosity (%)		<3.0
CTE (μm/m-K)		0.5 / 0.6
Dielectric Consta		4.0 / 4.2
Thermal Conduc (W/m-K)		9 / 12
Elastic Modulus (GPa)		16 / 61

* All data ... gy

Density

Lot 1

Grade	Geometric Density (g/cm^3)	Archimedes Density (g/cm^3)	Archimedes Porosity (%)
HP	1.95-1.99 [0.01]	1.95-1.98 [0.01]	12.7-14.4 [1]
M26	2.10-2.13 [0.01]	2.10-2.12 [0.01]	0.7-4.6 [1]
M	2.12-2.13 [0.01]	2.12-2.13 [0.01]	0.3-3.0 [1]

Lot 2

Grade	Geometric Density (g/cm^3)	Archimedes Density (g/cm^3)	Archimedes Porosity (%)
HP	1.96-2.07 [0.01]	1.95-2.07 [0.01]	9.6-13.8 [1]
M26	2.03-2.10 [0.01]	2.03-2.07 [0.01]	6.7-9.2 [1]
M	2.08-2.14 [0.01]	2.09-2.13 [0.01]	0.9-4.5 [1]

More variability observed in Lot 2

General Properties Overview (cont.)

Property ... nt

Property	Me...	BN-XX ‖ / ⊥	M ‖ / ⊥
XRD BN Phase (wt%)	Riet...	...6	45
Porosity (%)	AST...	<2.4	<3.0
CTE (µm/m-K)	Dila...	N/A	0.5 / 0.6
Dielectric Constant	Imp...	4.1	4.0 / 4.2
Thermal Conductivity (W/m-K)	AST...	5	9 / 12
Elastic Modulus (GPa)	AST...	N/A	16 / 61

* All data collected a... ...nology

Thermal

Lot 1

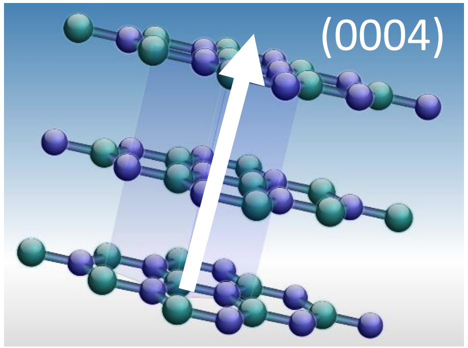
Grade	Emissivity 630ºC	CTE 400-800ºC (10^{-6}/K)
HP ‖	0.82 [0.01]	3.1 [0.5]
HP ⊥	0.81 [0.01]	0.4 [0.4]
M26 ‖	0.80 [0.01]	2.9 [0.1]
M26 ⊥	0.75 [0.01]	0.5 [0.2]
M ‖	0.76 [0.01]	0.5 [0.1]
M ⊥	0.71 [0.01]	0.6 [0.1]

Lot 2

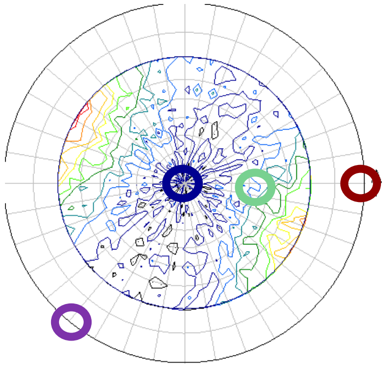
Grade	Emissivity 630ºC	CTE 400-800ºC (10^{-6}/K)
HP ‖	0.85 [0.01]	3.4 [0.5]
HP ⊥	0.81 [0.01]	0.5 [0.4]
M26 ‖	0.79 [0.01]	2.8 [0.1]
M26 ⊥	0.80 [0.01]	0.6 [0.2]
M ‖	0.82 [0.01]	1.8 [0.2]
M ⊥	0.83 [0.01]	0.8 [0.1]

Hot Press Anisotropy

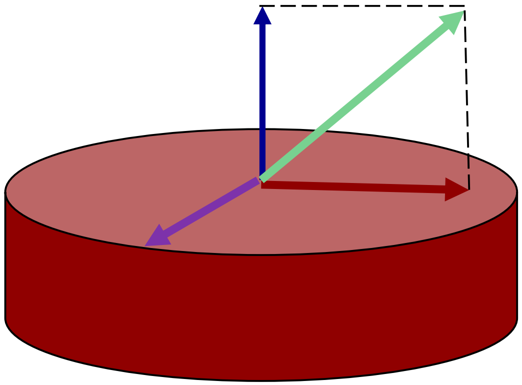
- Hot pressed BN platelets tend to align during processing.
- Property anisotropy strongest in CTE, Thermal conductivity, and Flexural strength data.
- Characterize crystallographic texture with XRD pole figures.
  - Can also be used to identify unknown hot press direction.



Crystallographic Direction

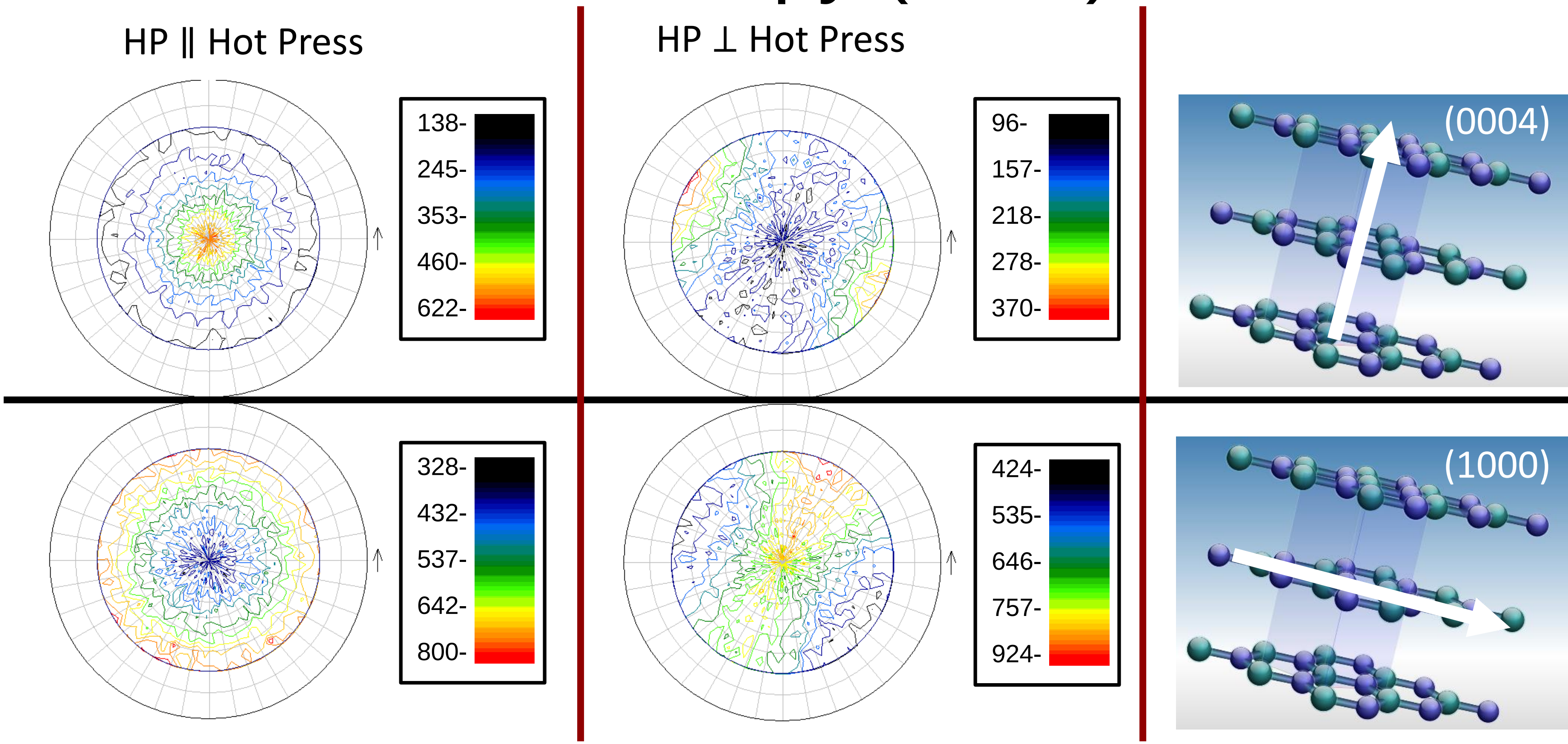


Stereographic Projection



Sample

Hot Press Anisotropy (cont.)

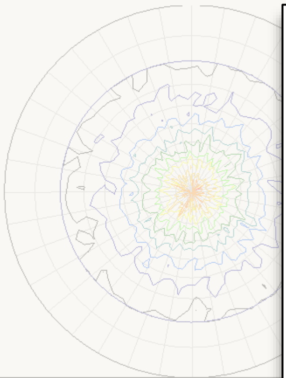


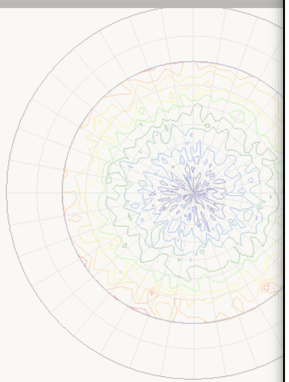
- HP, M26, and M grades evaluated with XRD pole figures.
- HP & M26 (98 & 70 wt% BN) show similar level of texturing, M (45 wt% BN) is less textured based on maximum intensity.
- Texture is consistent with hot press orientation in all samples tested.
  - Some samples have up to 10º mis-alignment between axial direction and maximum (0004) direction.

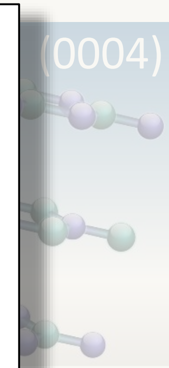
Hot Press Anisotropy (cont.)

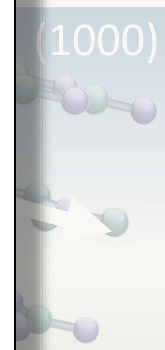
HP || Hot Press

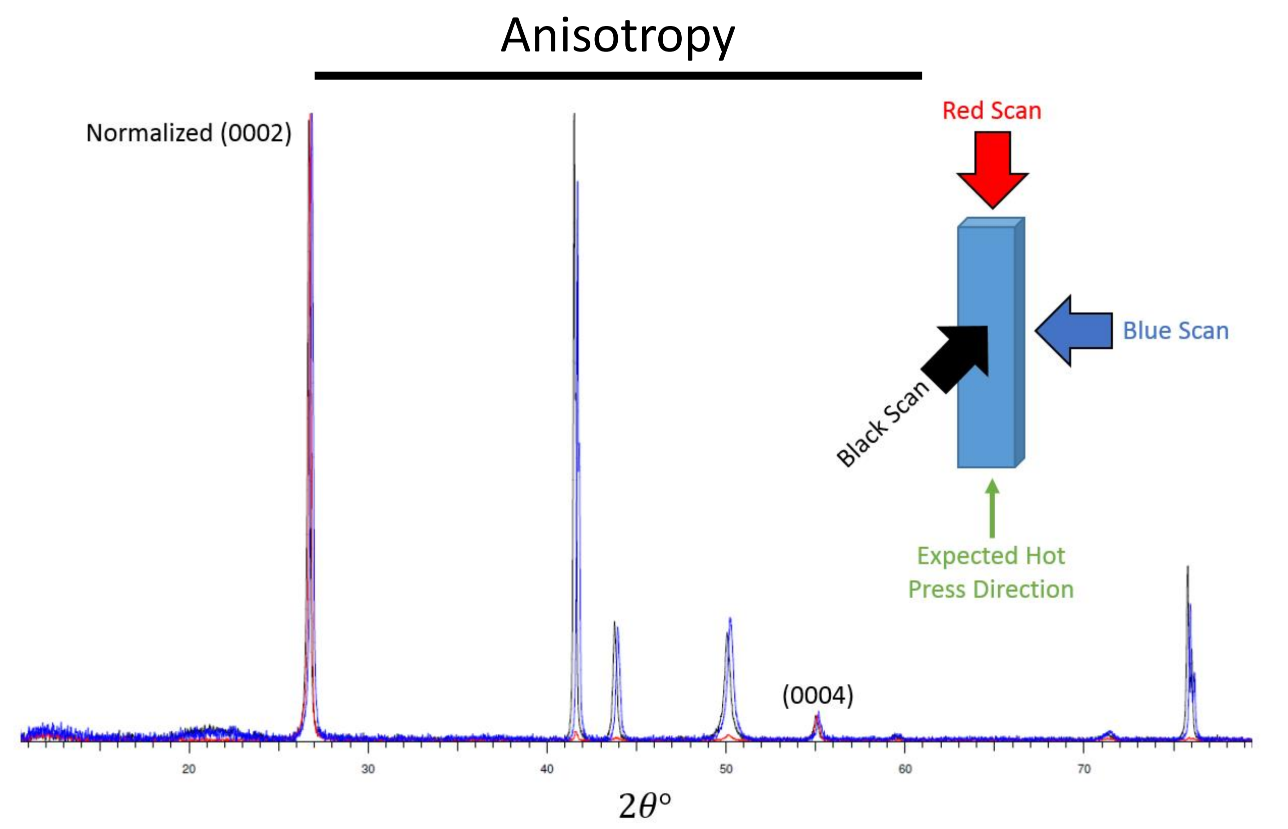
HP ⊥ Hot Press











Lot 2 was confirmed to have similar hot press anisotropy

- HP, M26, a
- HP & M26 textured ba
- Texture is consistent with hot press orientation in all samples tested.
  - Some samples have up to 10º mis-alignment between axial direction and maximum (0004) direction.

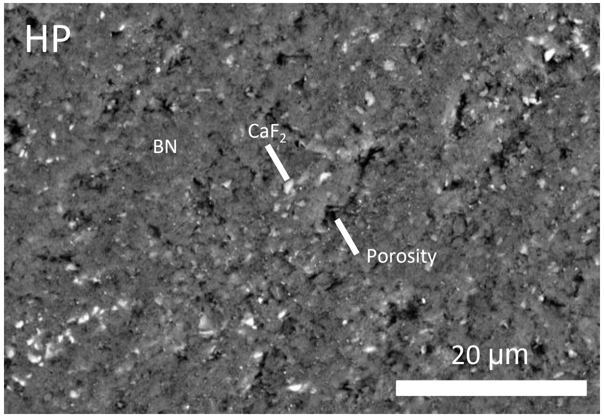
Microstructure Overview

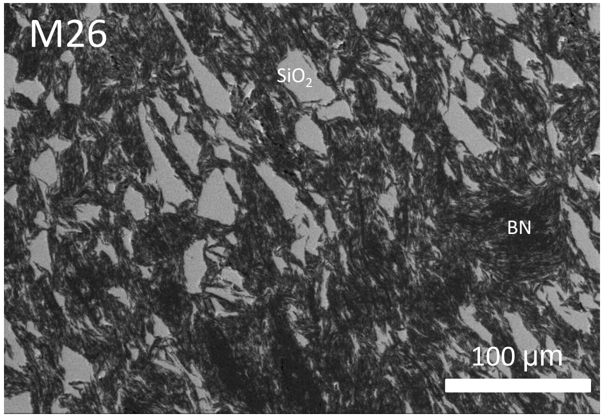
- SEM microstructure is not clearly textured by hot press direction.
- Porosity is apparent in HP grade, less in other grades.
- M26, BN-XX, and M have similar BN/SiO2 structure.
- XRD phase analysis matches with micrograph area analysis.

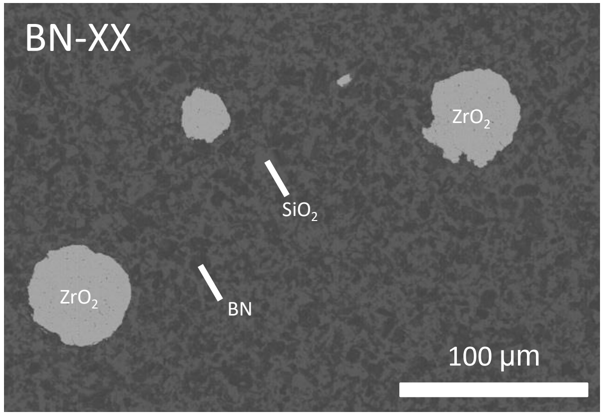
Powder XRD Rietveld Refinement

Grade	BN (wt%)	CaF_2 (wt%)	ZrO_2 (wt%)	AlN (wt%)	Amorp. (wt%)*
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.





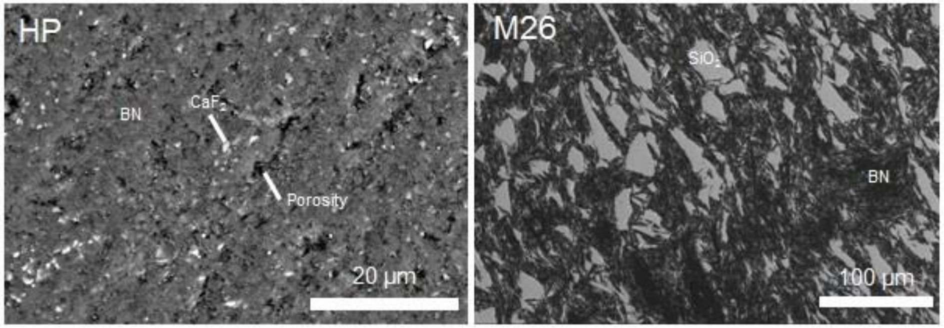


Microstructure Overview

Microstructure

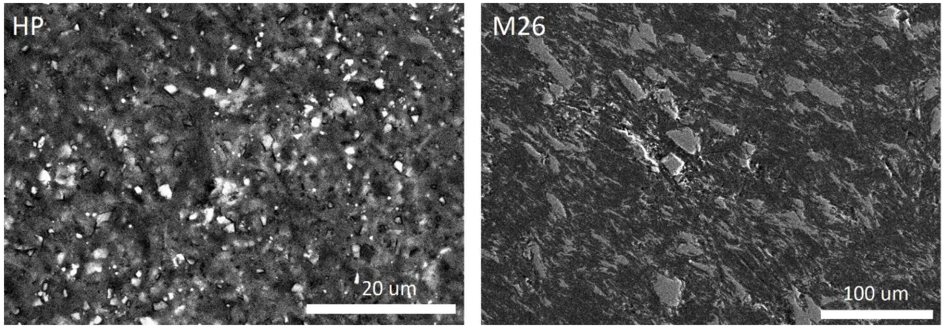
Lot 1

Grade	BN (wt%)	CaF_2 (wt%)	ZrO_2 (wt%)	AlN (wt%)	Amorp. Bal. (wt%)*
HP	98	2	0	0	0
M26	68	0	0	0	32
M	41	0	0	0	59



Lot 2

Grade	BN (wt%)	CaF_2 (wt%)	ZrO_2 (wt%)	AlN (wt%)	Amorp. Bal. (wt%)*
HP	98	2	0	0	0
M26	74	0	0	0	25
M	38	0	0	0	62



Lot 2 similar within expected capability to determine amorphous content

Lot 2 microstructure qualitatively and semi-quantitatively similar

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

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

Moisture Absorption (cont.)

Moisture Absorption

Lot 1

Grade	Dry Oven Mass Change (%)	Environment Chamber Mass Change (%)
HP ∥	-1.1 [0.5]	0.97 [0.07]
HP ⊥	-0.12 [0.01]	0.33 [0.05]
M26 ∥	-0.025 [0.003]	0.020 [0.005]
M26 ⊥	-0.035 [0.004]	0.019 [0.008]
M ∥	-0.026 [0.005]	0.018 [0.005]
M ⊥	-0.036 [0.003]	0.005 [0.003]

Lot 2

Grade	Dry Oven Mass Change (%)	Environment Chamber Mass Change (%)
HP ∥	-0.697 [0.596]	-0.241 [0.245]
HP ⊥	-0.208 [0.064]	0.056 [0.012]
M26 ∥	-0.043 [0.005]	0.017 [0.005]
M26 ⊥	-0.043 [0.011]	0.099 [0.081]
M ∥	-0.012 [0.006]	0.046 [0.024]
M ⊥	-0.013 [0.004]	0.047 [0.011]

Lot 2 dry oven results are similar to Lot 1.

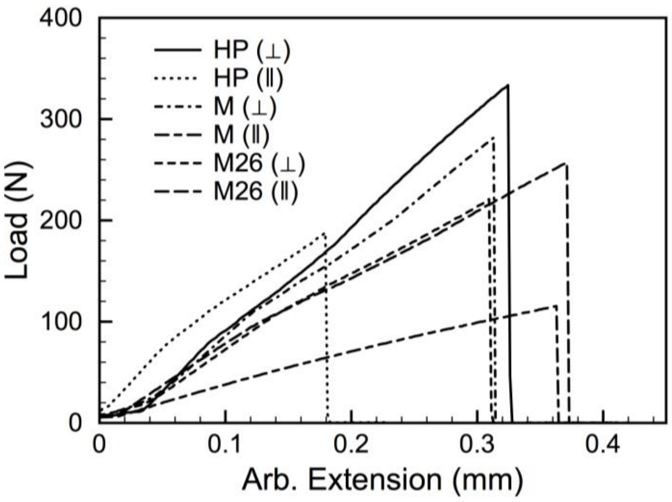
Lot 2 environmental chamber results are inconsistent and have standard deviations as large as 100% of average.

Lot 2 environmental chamber settings were different from lot 1.

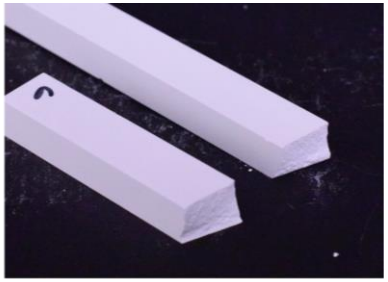
Flexural Testing

- 4-point bend testing performed on HP, M, and M26.
  - 26+ room temperature samples and 10 high temperature samples per configuration.
  - ∥ and ⊥ hot press orientations, as-machined, dry oven, and humidity chamber samples.
- All grades exhibited brittle failure at room temperature (25ºC).
- HP exhibited significant deflection at 600ºC.
  - Possibly CaF_2 or $CaB_6O_9(OH)_2(H_2O)_3$ related mechanism.
- HP ∥ suffered significant decrease in strength at 600ºC.

Representative load extension curves



HP ∥
25ºC



HP ∥
600ºC

Flexural Testing (cont.)

- Weibull modulus of all grades ranged from 7 to 22.
  - M and M26 have similar Weibull modulus at 600ºC as room temp.
- M ‖ strength is significantly below literature values (103 MPa Literature), consistent at room temperature and 600ºC.

	Room Temperature			600ºC		
Sample	**Average (MPa)**	**Std. Dev. (MPa)**	**Weibull Modulus**	**Average (MPa)**	**Std. Dev. (MPa)**	**Weibull Modulus**
HP ‖	39.7	2.3	19.3	9.8	4.7	-
HP ⊥	70.5	3.6	22.3	70.1	9.7	-
M26 ‖	55.6	7.3	8.6	66.3	6.7	10.7
M26 ⊥	45.0	6.6	7.0	56.2	8.1	7.6
M ‖	23.6	2.0	13.4	27.7	1.8	15.2
M ⊥	59.1	5.9	11.2	71.4	8.7	8.6

Flexural Testing (cont.)

- Weibull m...
  - M and ... temp.
- M || stre... 103 MPa Lite... d 600ºC.

Mechanical

Lot 1		
Grade	**Flexural Strength 25ºC (MPa)**	**Dynamic Modulus (GPa)***
HP ‖	39.7 [2.3]	80 [3]
HP ⊥	70.5 [3.6]	79 [3]
M26 ‖	55.6 [7.3]	55 [11]
M26 ⊥	45.0 [6.6]	47 [7]
M ‖	23.6 [2.0]	16 [1]
M ⊥	59.1 [5.9]	61 [3]

Lot 2		
Grade	**Flexural Strength 25ºC (MPa)**	**Dynamic Modulus (GPa)**
HP ‖	22.8 [4.0]	36.9 [1.0]
HP ⊥	57.6 [3.7]	75.1 [1.0]
M26 ‖	19.9 [0.9]	83.9 [4.1]
M26 ⊥	47.9 [1.7]	49.8 [6.2]
M ‖	39.1 [7.1]	58.3 [3.3]
M ⊥	65.0 [6.1]	26.5 [3.4]

Lot 2 differences are significant for strength and modulus of all grades.

Sample						**...ull ...ulus**
HP ‖						
HP ⊥						
M26 ‖	55.6	7.3	8.6	66.3	6.7	10.7
M26 ⊥	45.0	6.6	7.0	56.2	8.1	7.6
M ‖	23.6	2.0	13.4	27.7	1.8	15.2
M ⊥	59.1	5.9	11.2	71.4	8.7	8.6

Moisture Sensitivity

- 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

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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

Moisture Sensitivity

Lot 1

Grade	Dry Oven Strength (MPa)	As-Machined Strength (MPa)	Environment Chamber Strength (MPa)	P-Value [Oven>Chamber]
HP ∥	52.1 [5]	42.5 [3]	27.5 [2]	<0.005
HP ⊥	80.1 [3]	76.1 [4]	69.7 [6]	0.005
M26 ∥	59.9 [9]	61.8 [10]	57.9 [7]	0.3
M26 ⊥	43.2 [8]	49.6 [8]	39.7 [8]	0.2
M ∥	23.9 [1]	24.7 [1]	22.3 [1]	0.01
M ⊥	60.1 [2]	62.4 [4]	59.2 [6]	0.3

Lot 2

Grade	Dry Oven Strength (MPa)	As-Machined Strength (MPa)	Environment Chamber Strength (MPa)	P-Value [Oven>Chamber]
HP ∥	32.2 [5]	22.8 [4]	18.8 [3]	<0.005
HP ⊥	67.3 [8]	57.6 [4]	62.9 [5]	0.07
M26 ∥	22.0 [1]	19.9 [1]	20.6 [1]	0.02
M26 ⊥	53.6 [4]	47.9 [2]	47.0 [1]	<0.005
M ∥	35.9 [6]	39.1 [7]	36.8 [7]	0.3
M ⊥	37.2 [5]	65.0 [6]	60.8 [10]	<0.005

Lot 2 is more moisture sensitive.

Summary

- So far only two lots have been characterized, so the following statements should be interpreted appropriately.
- Properties with significant lot-to-lot variation:
  - Flexural strength, elastic modulus, moisture sensitivity
- Properties with minimal lot-to-lot variation:
  - Density, moisture absorption
- Properties with no lot-to-lot variation:
  - CTE, emissivity, microstructure, surface roughness, trace contaminates, anisotropy, composition
- Properties not yet characterized on multiple lots:
  - Slow crack growth, fracture toughness, compression strength, coefficient of sliding friction, thermal conductivity, electrical properties, specific heat
- Lot testing is strongly recommended for critical applications.

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