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

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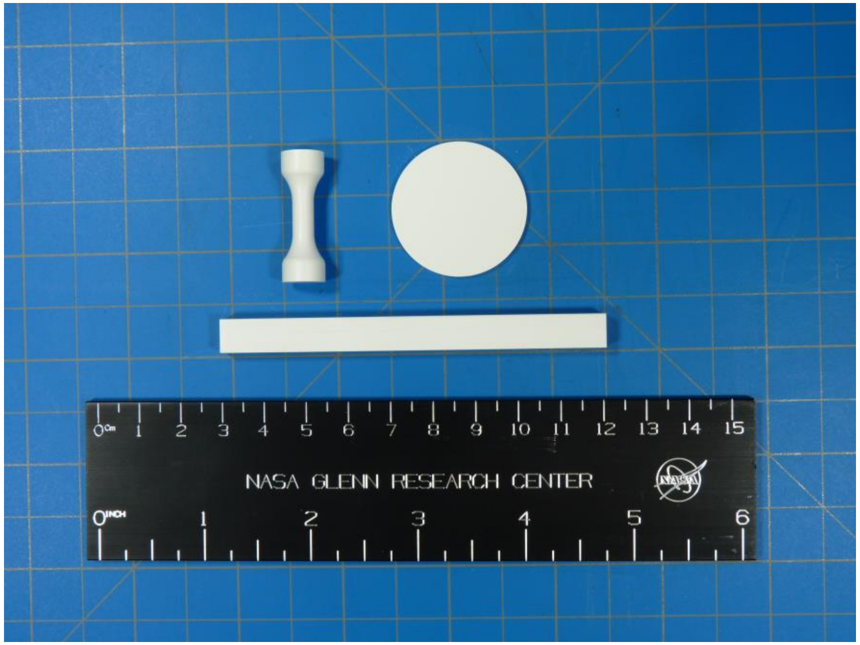
44th International Conference and Expo on Advanced Ceramics and Composites (ICACC)

Daytona Beach, Florida, 2020

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

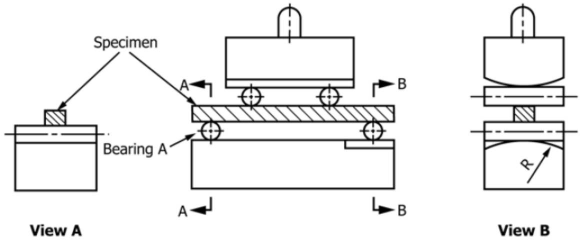
* Trade names and vendors are used for identification purposes only.

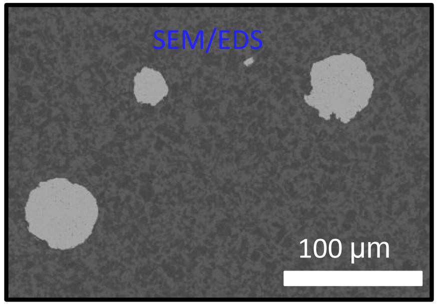
** Cost normalized to HP grade for comparable lot sizes.

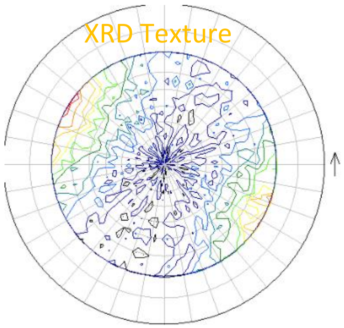
Factors of Interest

- 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

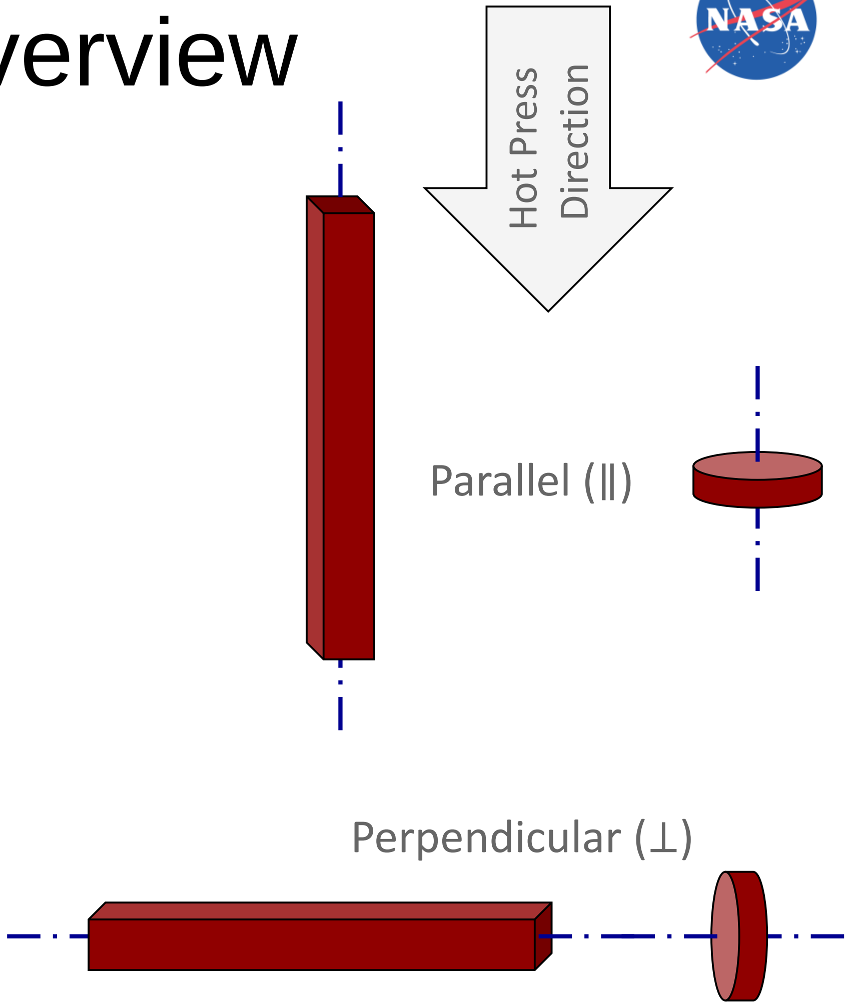


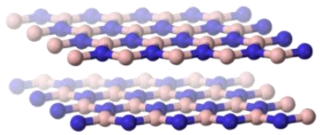




General Properties Overview

- 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 ǁ” 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	/A	0.5 / 0.6
Dielectric Constant	Imp	.1	4.0 / 4.2
Thermal Conductivity (W/m-K)	AST	5	9 / 12
Elastic Modulus (GPa)	AST	/A	16 / 61

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

Thermal

Lot 1

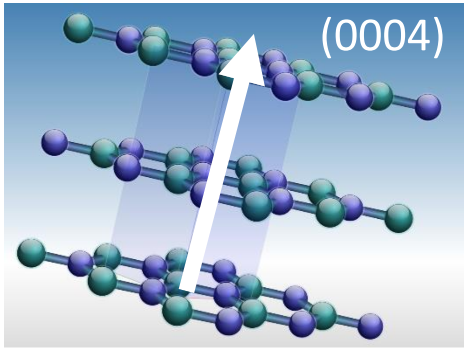
Grade	Emissivity 630ºC	CTE 400-800ºC (10^{-6}/K)
HP ‖	0.82 [0.01]	3.1 [0.5]
HP ⊥	0.81 [0.01]	0.4 [0.4]
M26 ‖	0.80 [0.01]	2.9 [0.1]
M26 ⊥	0.75 [0.01]	0.5 [0.2]
M ‖	0.76 [0.01]	0.5 [0.1]
M ⊥	0.71 [0.01]	0.6 [0.1]

Lot 2

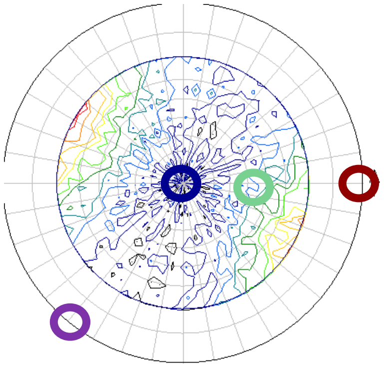
Grade	Emissivity 630ºC	CTE 400-800ºC (10^{-6}/K)
HP ‖	0.85 [0.01]	3.4 [0.5]
HP ⊥	0.81 [0.01]	0.5 [0.4]
M26 ‖	0.79 [0.01]	2.8 [0.1]
M26 ⊥	0.80 [0.01]	0.6 [0.2]
M ‖	0.82 [0.01]	1.8 [0.2]
M ⊥	0.83 [0.01]	0.8 [0.1]

Hot Press Anisotropy

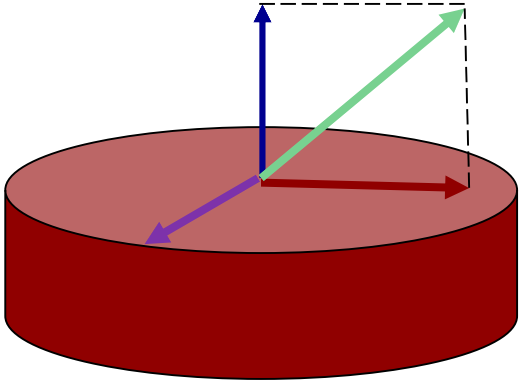
- Hot pressed BN platelets tend to align during processing.
- Property anisotropy strongest in CTE, Thermal conductivity, and Flexural strength data.
- Characterize crystallographic texture with XRD pole figures.
  - Can also be used to identify unknown hot press direction.



Crystallographic Direction

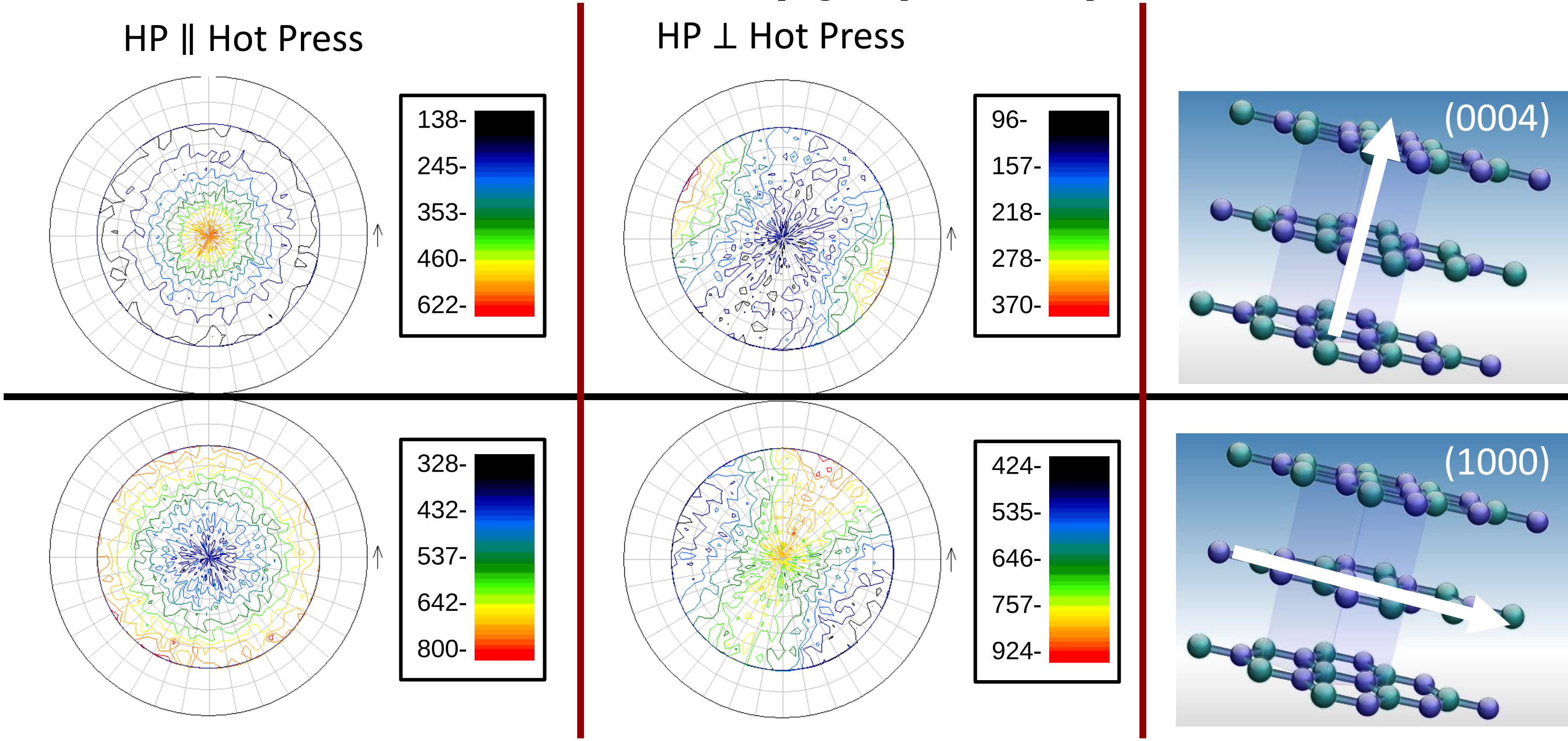


Stereographic Projection



Sample

Hot Press Anisotropy (cont.)

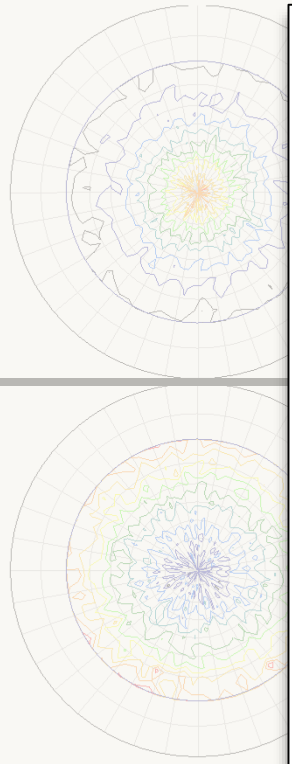


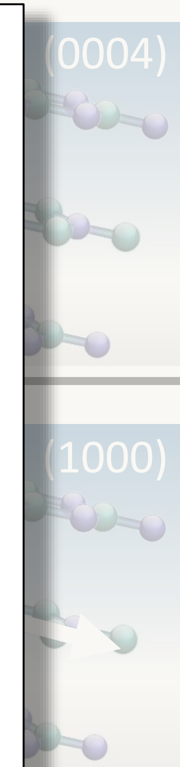
- HP, M26, and M grades evaluated with XRD pole figures.
- HP & M26 (98 & 70 wt% BN) show similar level of texturing, M (45 wt% BN) is less textured based on maximum intensity.
- Texture is consistent with hot press orientation in all samples tested.
  - Some samples have up to 10º mis-alignment between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

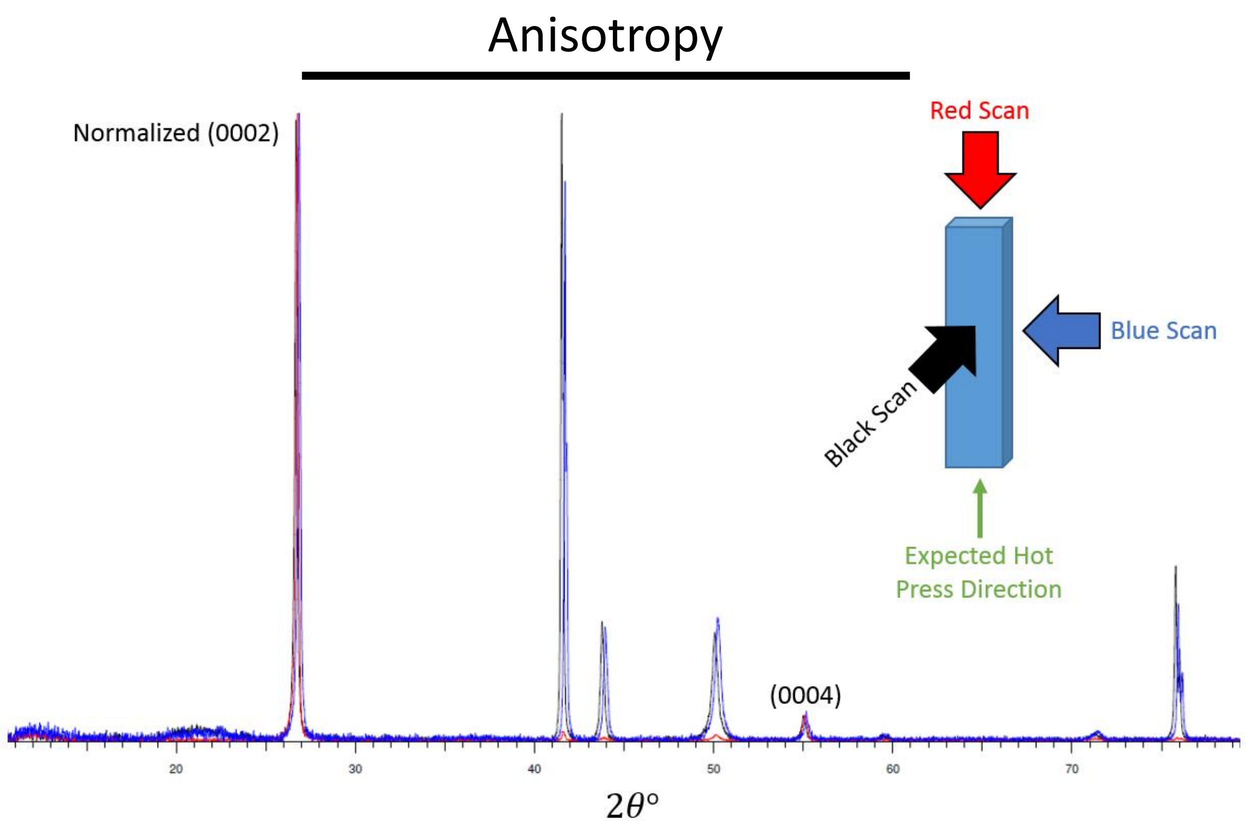
Hot Press Anisotropy (cont.)

HP || Hot Press

HP ⊥ Hot Press







Lot 2 was confirmed to have similar hot press anisotropy

- HP, M26, a
- HP & M26 … s 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.

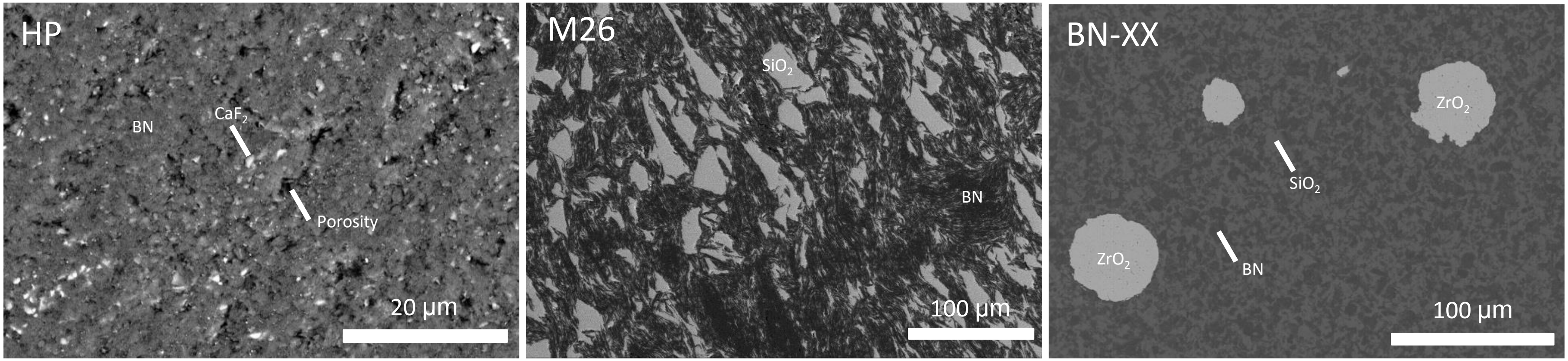
Microstructure Overview

- 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.

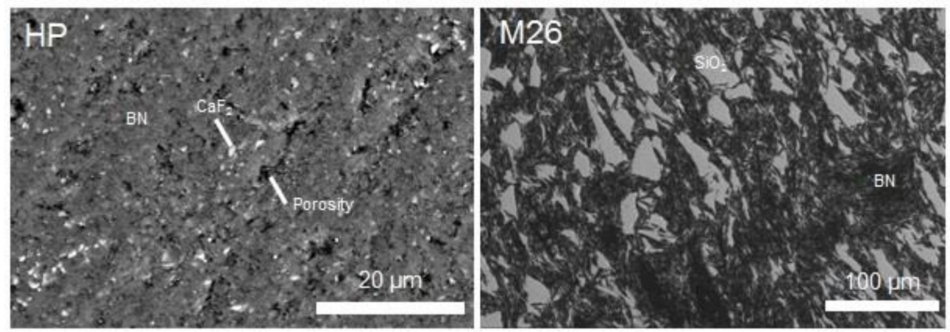


Microstructure Overview

Microstructure

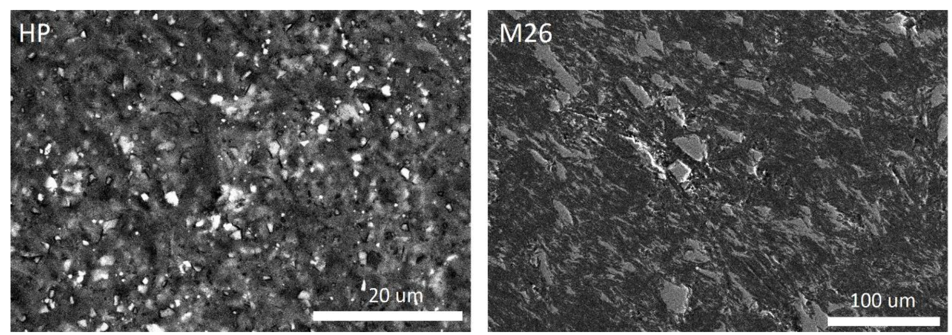
Lot 1

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 (%)
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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.

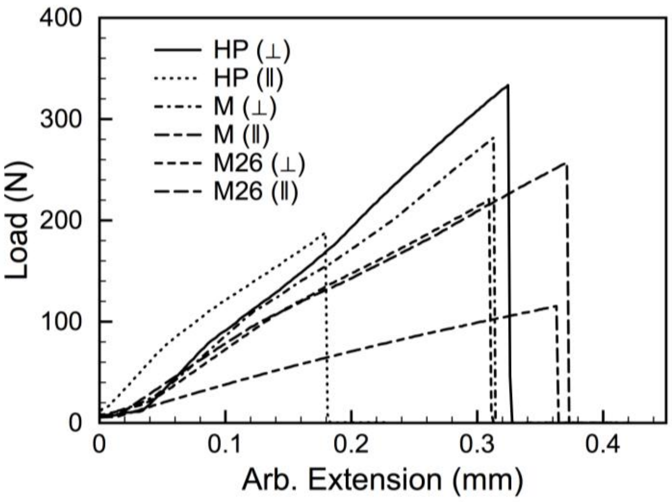
Lot 2 environmental chamber results are inconsistent and have standard deviations as large as 100% of average.

Lot 2 environmental chamber settings were different from lot 1.

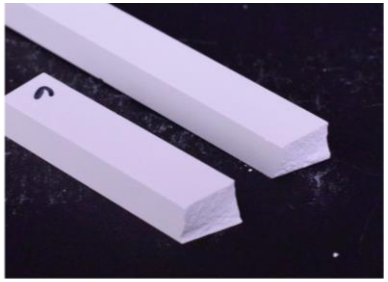
Flexural Testing

- 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 ǁ 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 ǁ	39.7	2.3	19.3	9.8	4.7	-
HP ⊥	70.5	3.6	22.3	70.1	9.7	-
M26 ǁ	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 ǁ	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.

Sample						Weibull Modulus
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

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.

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.

Acknowledgements

- Funding provided by NASA Space Technology Mission Directorate.
- Technical assistance provided by NASA Glenn Research Center, NASA Jet Propulsion Laboratory, and California Institute of Technology (Contract #NNN17D002T).

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