Non-Destructive Characterization of Dense Ceramics

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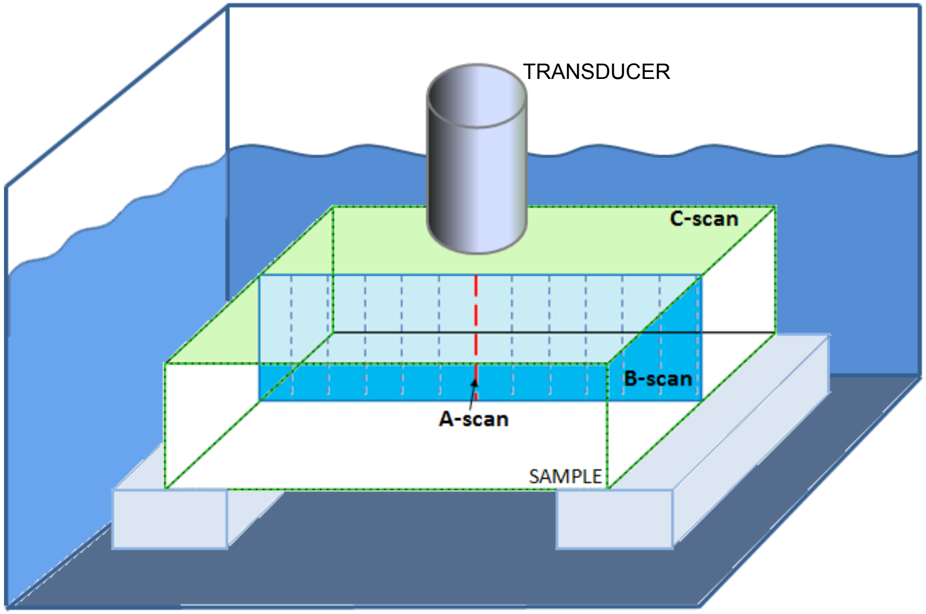
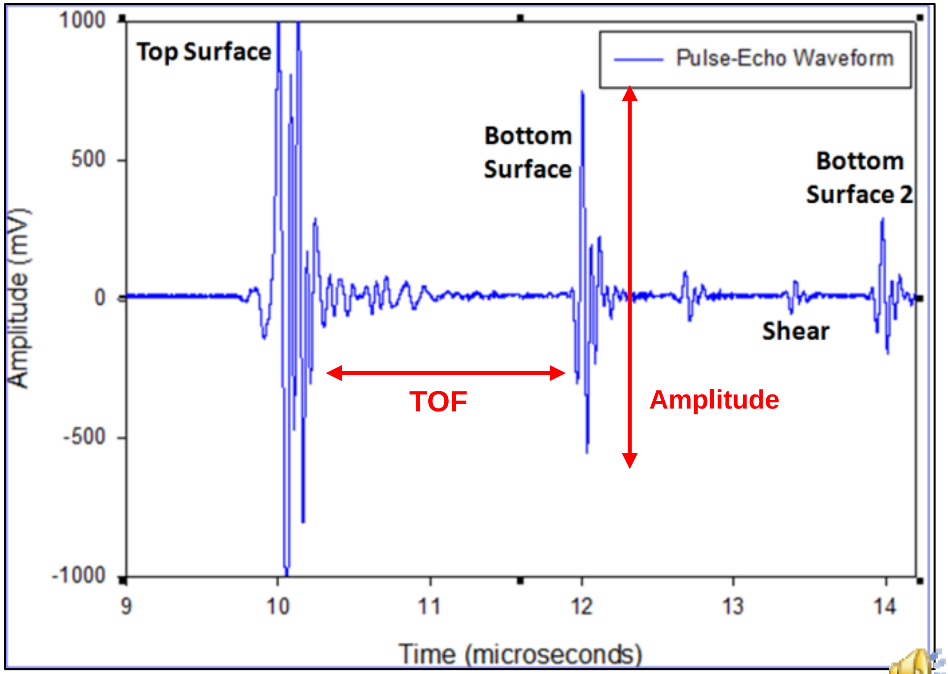
Ultrasound NDE Basics



- Immersion-based, pulse-echo system
- A-scans point measurements useful for quickly evaluating properties
- C-scan imaging mode useful for mapping material property variations

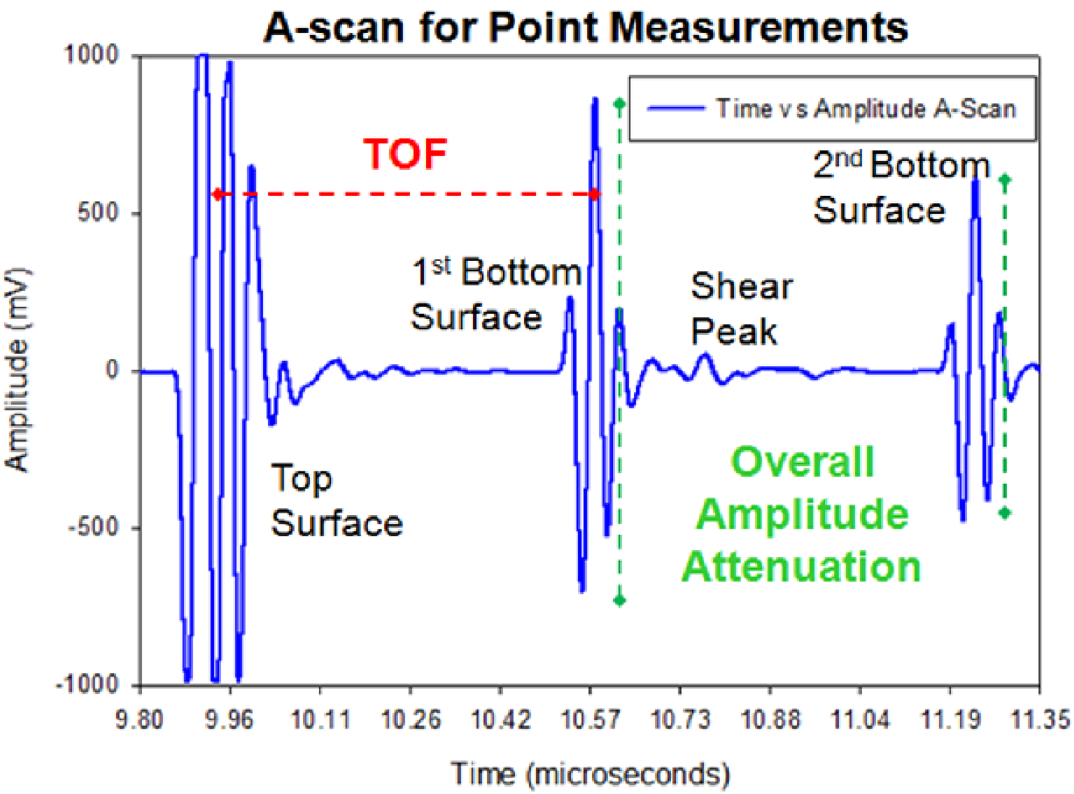
- Analysis of time of flight (TOF) can determine speed of sound in material → elastic properties
- Analysis of amplitude variations can determine acoustic attenuation in material



A-scan Point Measurements

Time-of-Flight Based Measurements

- Measures Longitudinal TOF and Shear TOF
- Dependent on density of material
- Can tolerate non-ideal sample surfaces
- Can quickly determine:
    - Longitudinal and shear speeds of sound
    - Poisson ratio
    - Young's modulus
    - Shear modulus
    - Bulk modulus



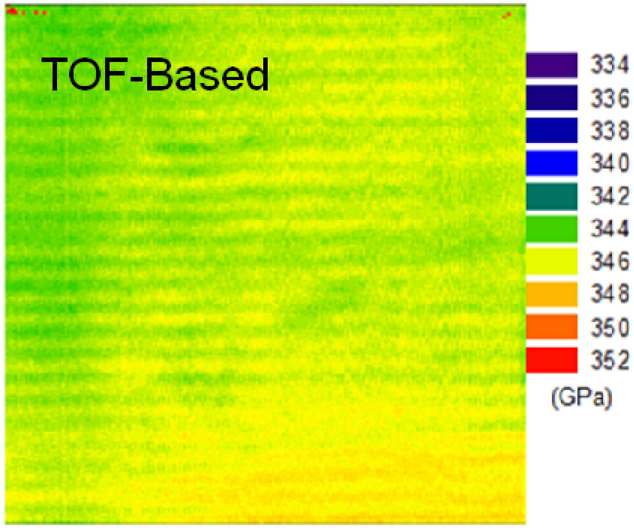
Amplitude Based Measurements

- Measures average drop in intensity over all frequencies
- Useful in determining sample heterogeneities

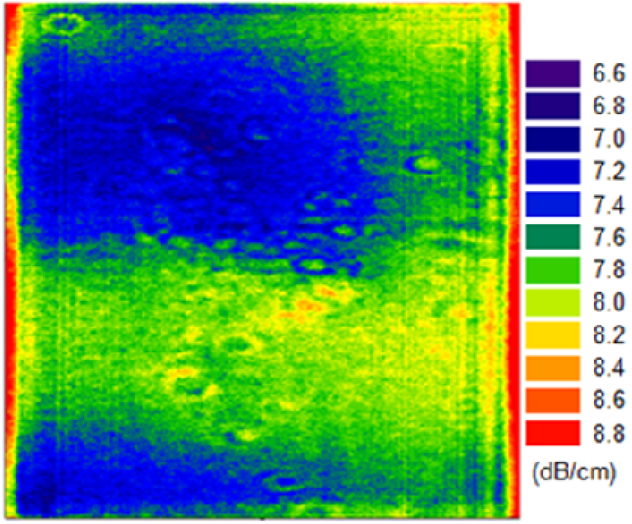
Information comes from a single point → What if the sample is not uniform?

C-scan Property Mapping

C-scans for Area Property Maps



Young's Modulus Map

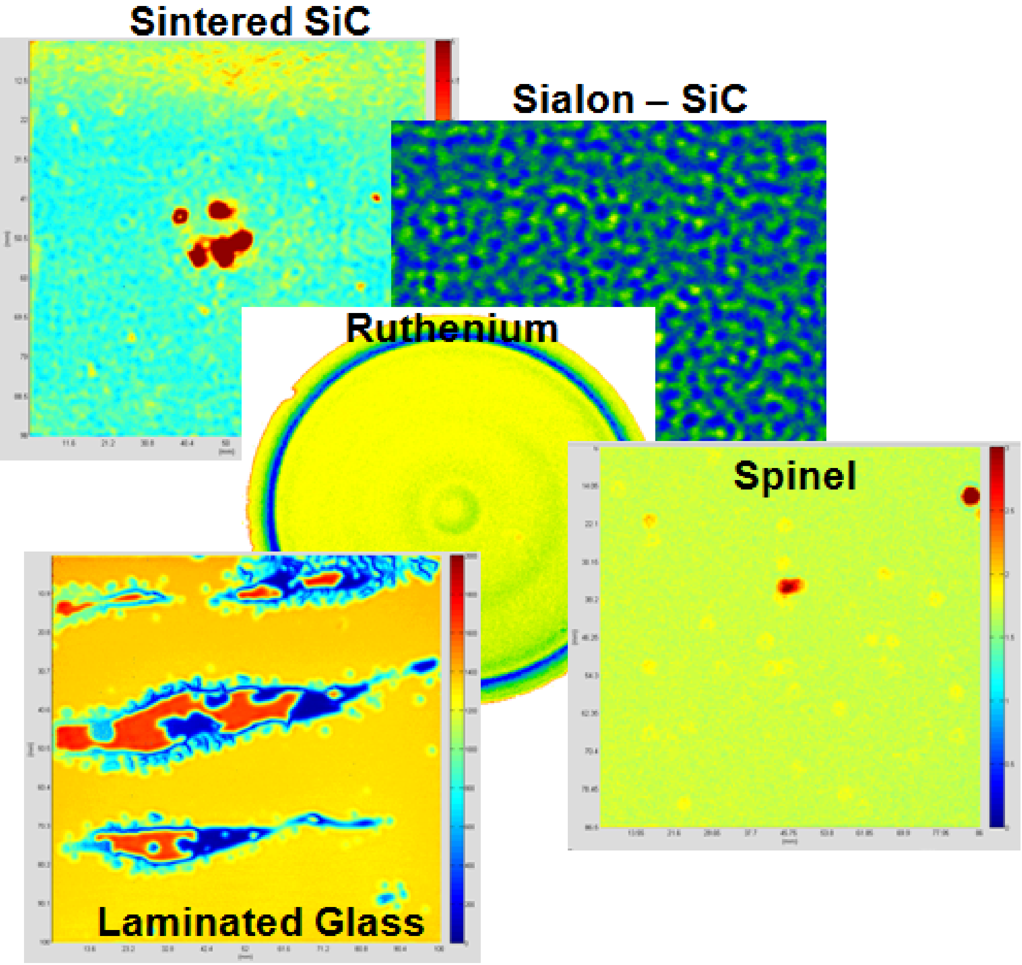


Attenuation Coefficient Map

C-scan Mapping

- Determining elastic property variations → Semblance of porosity variations
- Spatially locating large, anomalous features
- C-scans → Sensitive to sample nonuniformities
  - Surface scratches 100μm and greater apparent
  - Thickness gradient of 100μm and greater apparent
  - Sample thickness greater than 2”
  - Porosity greater than 10%
- 4” x 4” tile scan in 30 minutes

Evaluation vs. Characterization



- mapping of velocity and amplitude variations
- Rapid identification of anomalous defects

- NDE identifies anomalous defects
  - Composition?
  - Effect on local microstructure?
- NDE measures elastic properties
  - Relate to density
  - New batch compositions introduce elements that reduce density but improve microstructure
- Which values are ‘good’?
- What is the cause of variations?
- ***What about microstructure?***
  - ***Grain size***
  - ***Solid inclusions***
  - ***Secondary phases***

Develop Characterization Method To Answer These Questions

Characterization-Based Measurements

Acoustic Attenuation

- Exponential decrease in acoustic energy defined by Beer-Lambert Law
- Very sensitive to wavelength (frequency)
- Attenuation caused by a multitude of loss mechanisms *controlled by microstructure*

Beer-Lambert Law

Acoustic intensity after propagation

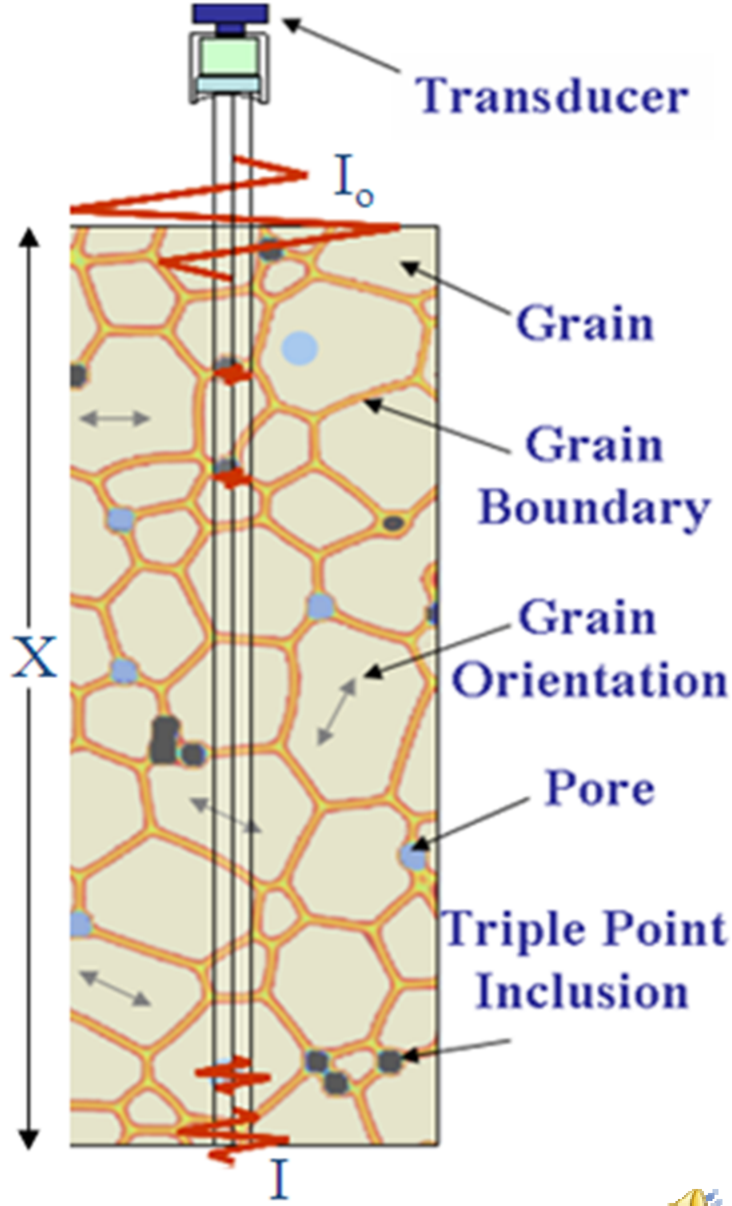
Attenuation coefficient

$$I = I_o \, e^{-\alpha x}$$

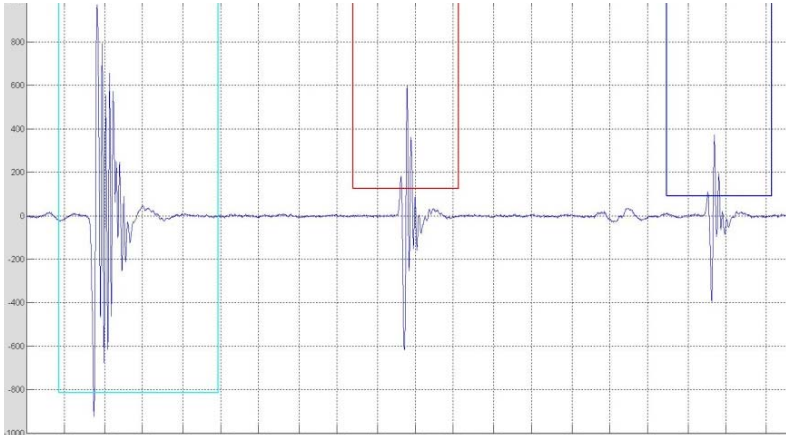
Acoustic intensity before propagation

Path length (sample thickness)

α measured in dB/cm

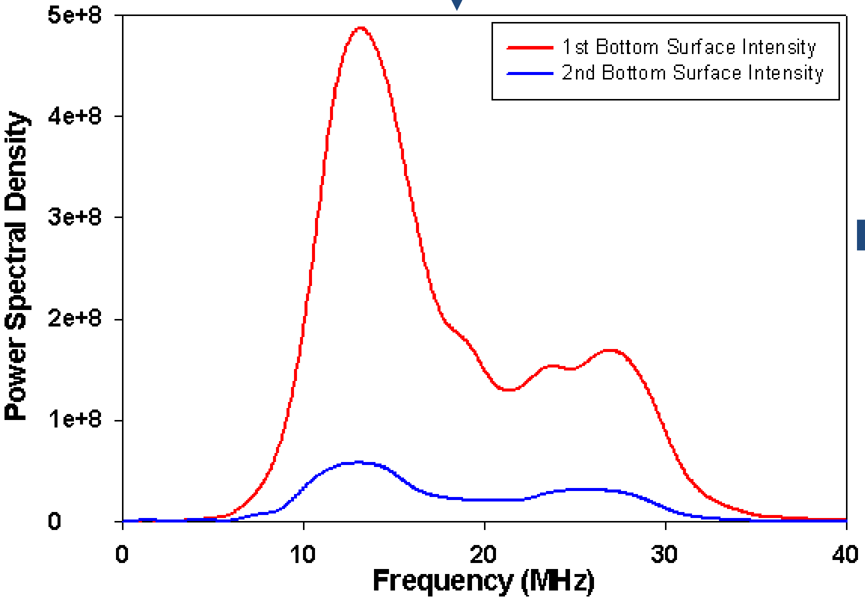


From NDE to NDC: Acoustic Spectroscopy

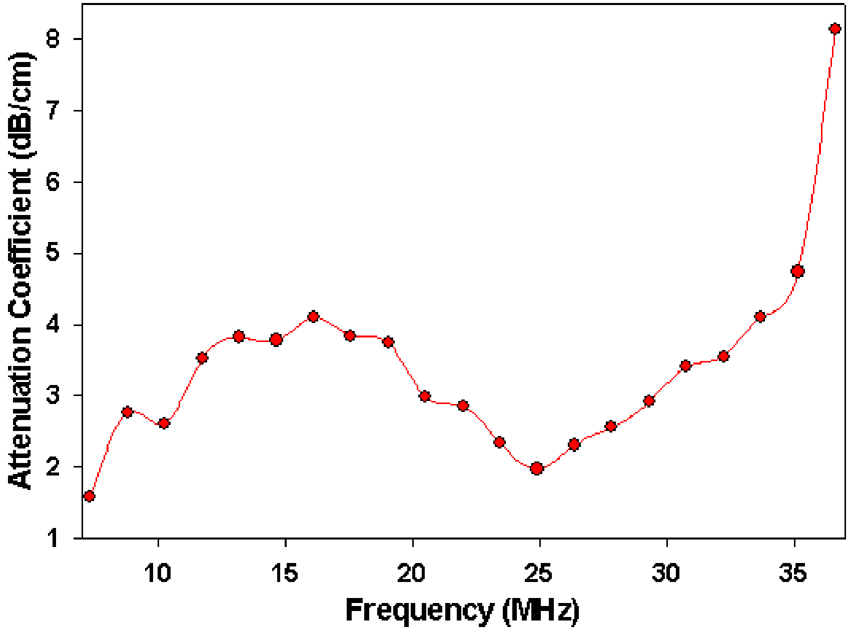


A-scan of sample

- Measures energy loss at each measured frequency
- Possible to characterize microstructure through knowledge of loss mechanisms within material
- Total attenuation is a summation of absorption and scattering effects



FFT of bottom surface peaks

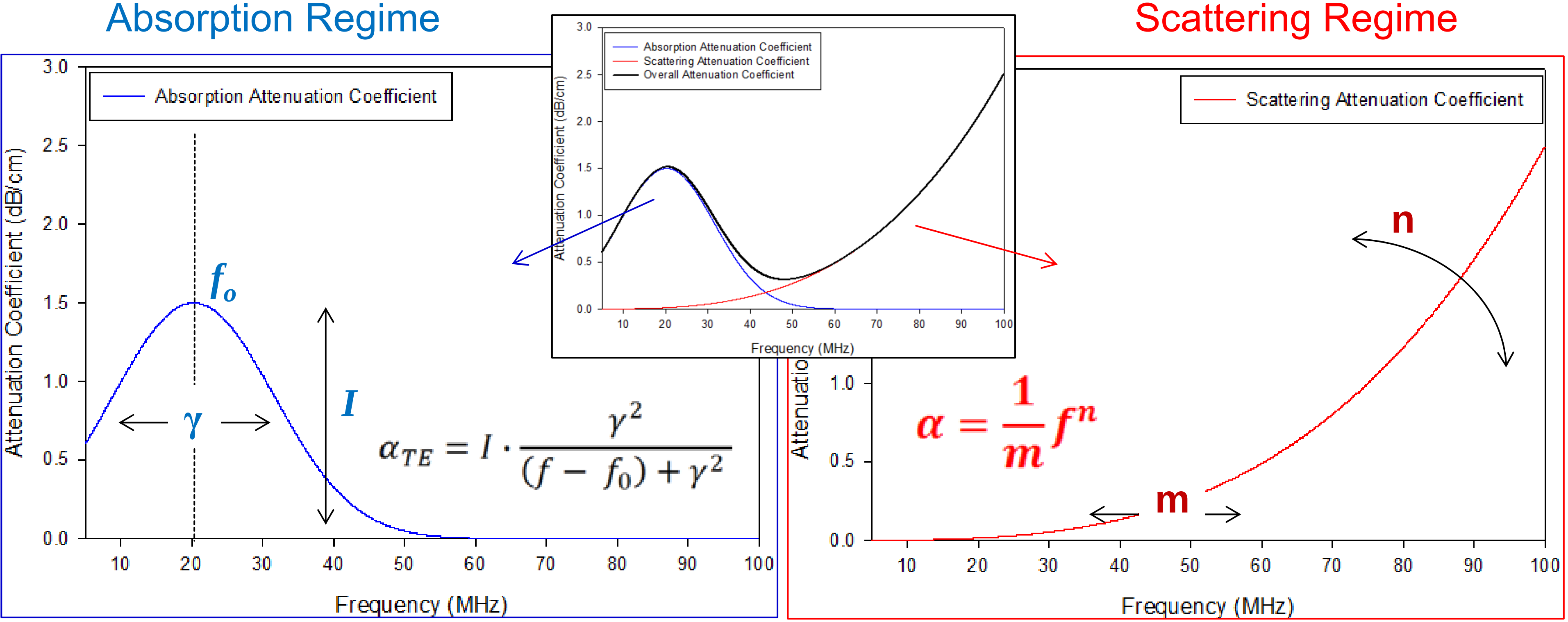


Attenuation Coefficient Spectrum

Acoustic Spectroscopy

Absorption Regime

Scattering Regime



$$\alpha_{TE} = I \cdot \frac{\gamma^2}{(f - f_0) + \gamma^2}$$

$$\alpha = \frac{1}{m} f^n$$

$$f_o = \frac{\pi\, X}{2\, \rho\, C_V\, a^2}$$ †

a - diameter
C_v – specific heat

X – thermal conductivity
ρ – density

Material	ρ (kg/m^3)	X (W/mK)	C_V (J/kgK)	a (μm) (F_o=10MHz)	a (μm) (F_o =30MHz)
SiC	3210	145.64	667	3.27	1.89
Carbon	2266	131.81	704	3.60	2.08
B_4C	2510	28	968	1.35	0.78

$$\alpha = C_R a^3 f^4$$

Rayleigh scattering
(a<<λ)

$$\alpha = C_S a f^2$$

Stochastic scattering
(a~λ)

$$\alpha = \frac{C_D f^0}{a}$$

Diffuse scattering
(a>λ)

Can we use ultrasound to predict microstructural characteristics?

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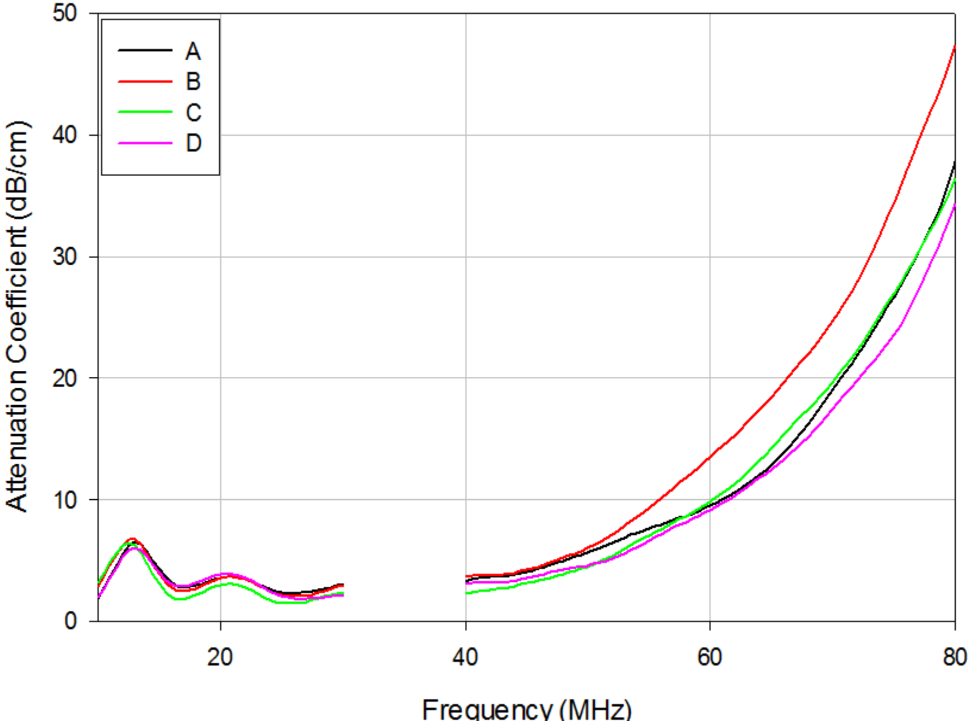
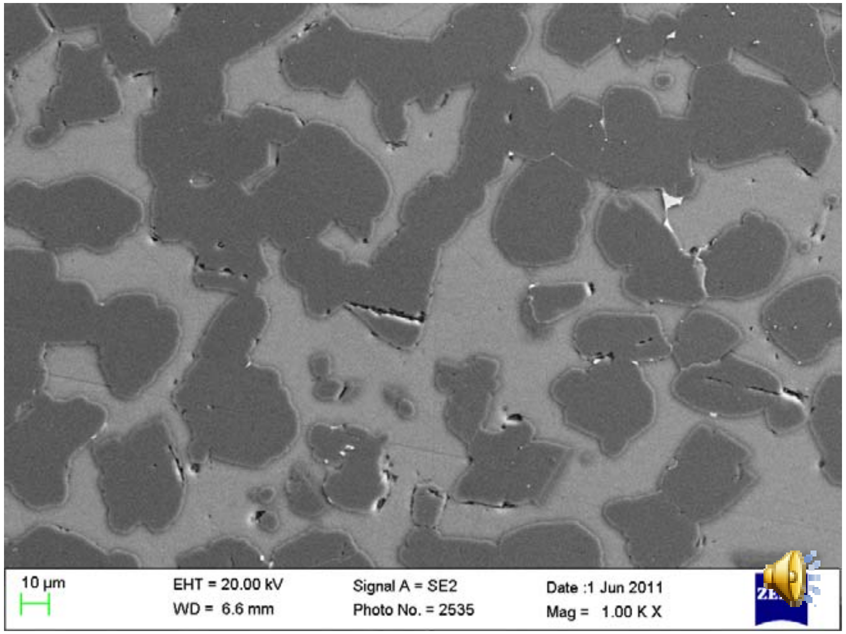
†Zener, C., “Internal Friction in Solids.” Proceedings of the Physical Society, vol. 52, pp. 152-167, 1940.

Acoustic Spectroscopy Example



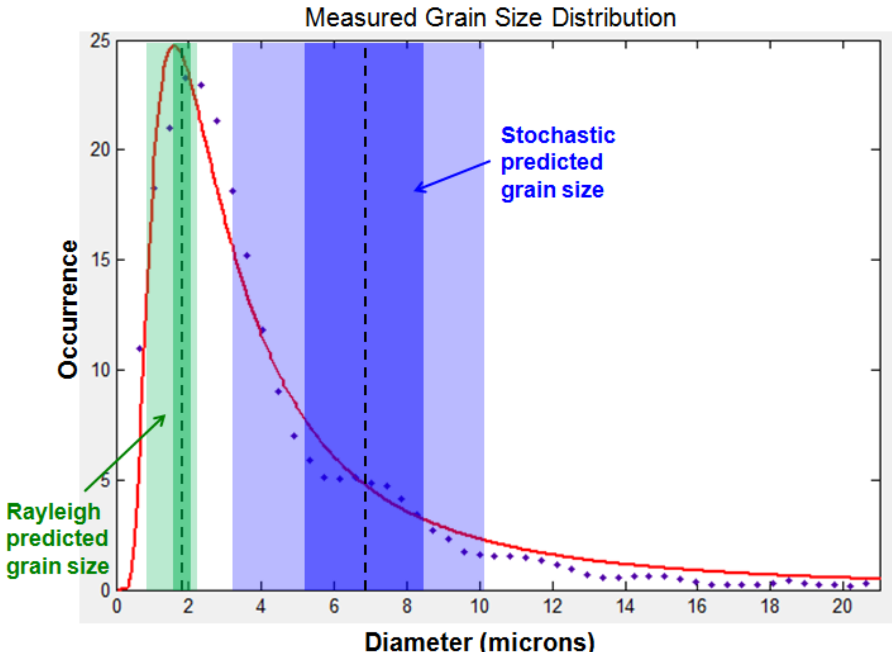
- Reaction bonded SiC samples
- Well defined absorption peaks at lower frequencies
- Smooth transition to power law behavior at higher frequencies
  - Exponent of ~4 indicative of predominantly Rayleigh scattering

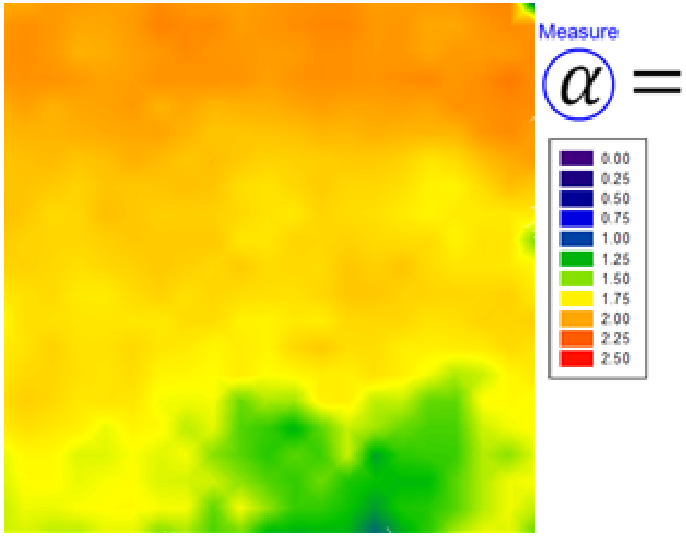
- Absorption peaks predict secondary phase particles of ~8-10μm
- Rayleigh scattering behavior predicts SiC grain size of ~10-50μm
- FESEM imaging shows that predictions are reasonable



Acoustic Spectroscopy Example

- Extracting microstructural information is not trivial
- Requires knowledge of material
  - Secondary phases
  - Inclusions
  - Concentration
  - Composition
  - Scattering prefactors
- **Need standard reference materials**

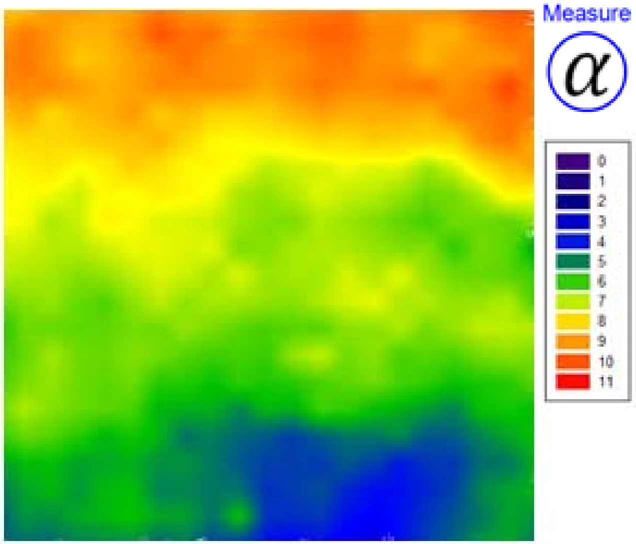




Measure — Created Standard — Frequencies: 40 – 70MHz

$$\boxed{\alpha} = \boxed{C_R} a^3 \boxed{f^4}$$

Mean Grain Size Map (µm)
Assuming Rayleigh



Measure — Created Standard — Frequencies: 40 – 70MHz

$$\boxed{\alpha} = \boxed{C_S} a \boxed{f^2}$$

Mean Grain Size Map (µm)
Assuming Stochastic

Goals

- SPS SiC samples using several different types of B_4C additives with varying size and morphology
  - Commercial B_4C powders from ESK, H.C. Starck
  - B_4C powder made at Rutgers via rapid carbothermal reduction

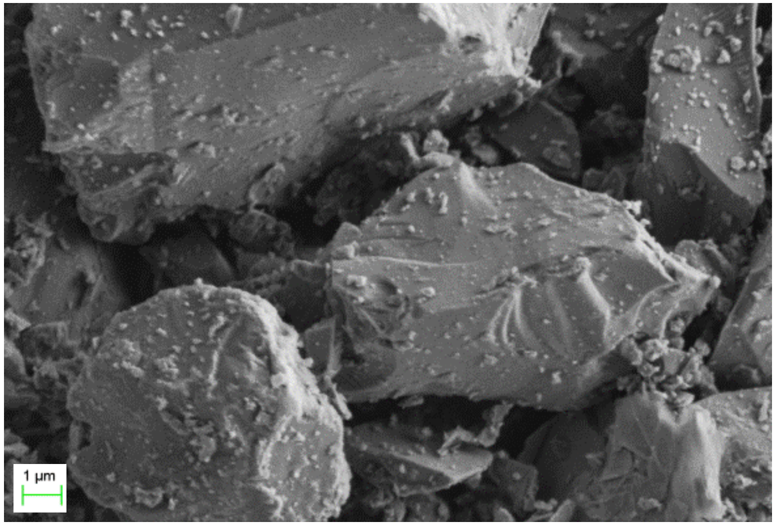
- SPS SiC samples using different processing methods
  - Dry mixing in SpectroMill
  - Filter press from ball milled slurry

- Use ultrasound methods to determine elastic properties and predict microstructural features
  - Use both conventional ultrasound NDE techniques and Acoustic Spectroscopy

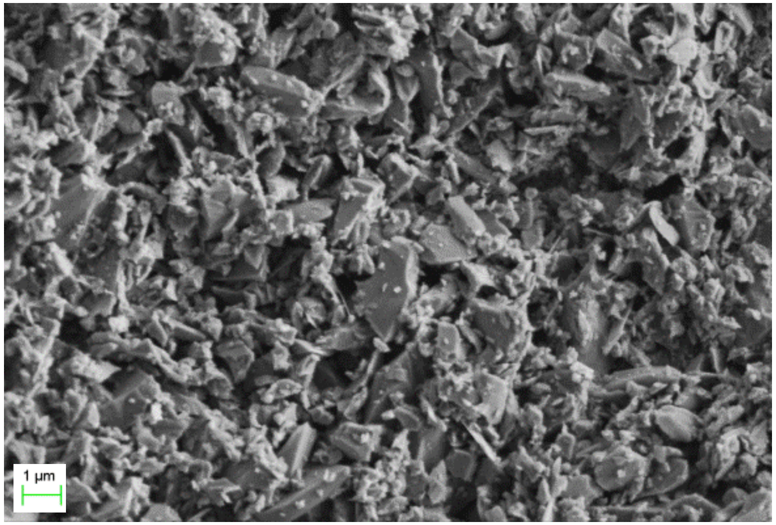
- Perform FESEM imaging to characterize microstructure
  - Compare NDE predictions with FESEM images

- Examine relationship between additive size/morphology and processing methods and SiC microstructure and acoustic properties

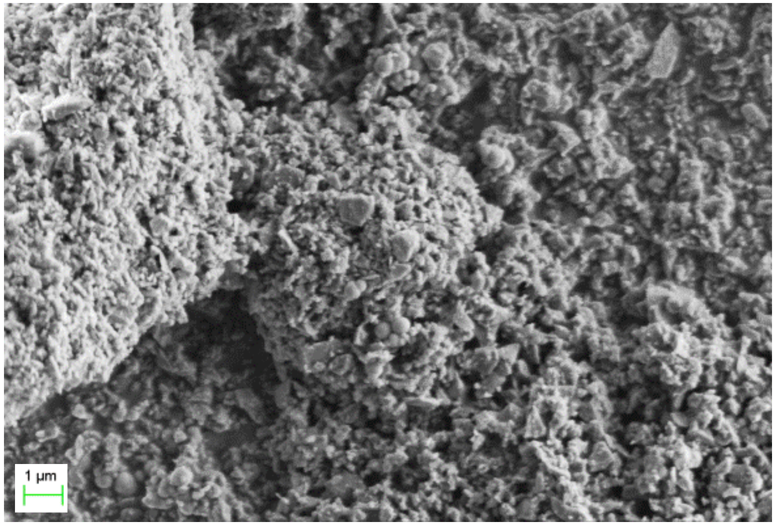
Boron Carbide Additives



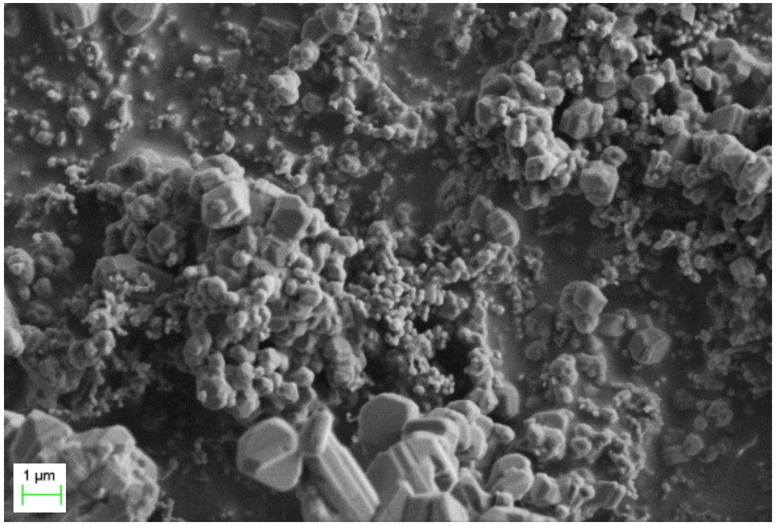
ESK Tetrabor 1250 mesh
(d50: approx 6µm)



ESK Tetrabor 3000F
(d50: approx 1µm)



H.C. Starck HD20
(d50: 0.3 - 0.6µm)

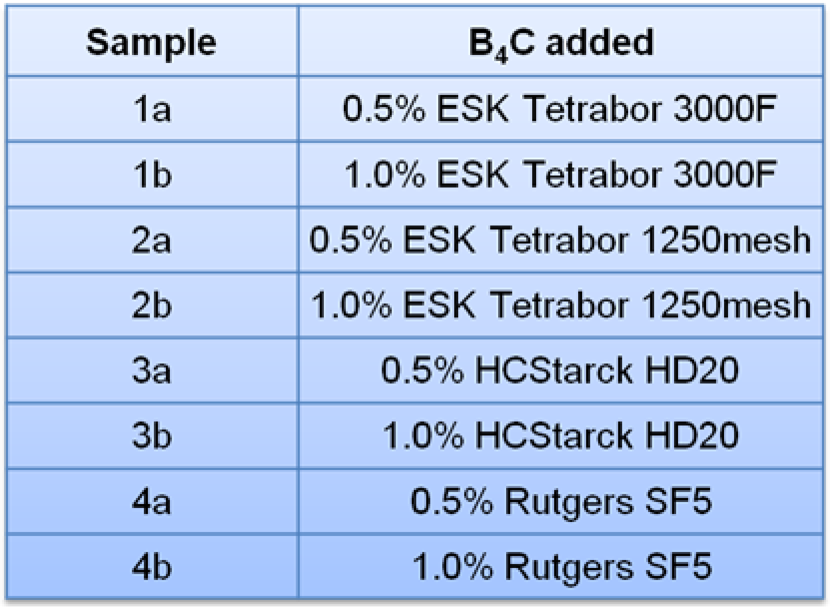


Rutgers RCR SF5
(d50: 0.59µm)

SiC with Different Additive Size and Morphology

- Ball milled in ethanol 3 hours
- H.C. Starck UF-25 SiC
- 0.5% or 1.0% B_4C
- 1.5% Fisher Lamp Black

- Different types of B_4C additives
  - ESK Tetrabor 3000F
  - ESK Tetrabor 1250 mesh
  - H.C. Starck HD20
  - Rutgers RCR SF5



Sample	B_4C added
1a	0.5% ESK Tetrabor 3000F
1b	1.0% ESK Tetrabor 3000F
2a	0.5% ESK Tetrabor 1250mesh
2b	1.0% ESK Tetrabor 1250mesh
3a	0.5% HCStarck HD20
3b	1.0% HCStarck HD20
4a	0.5% Rutgers SF5
4b	1.0% Rutgers SF5

- Sintered in Thermal Technologies SPS 10-4 unit
  - Argon atmosphere
  - 50MPa pressure

Ramp to 1400°C at 200°C/min

Hold at 1400°C for 1min

Ramp to 1850°C at 200°C/min

Hold at 1850°C for 5min

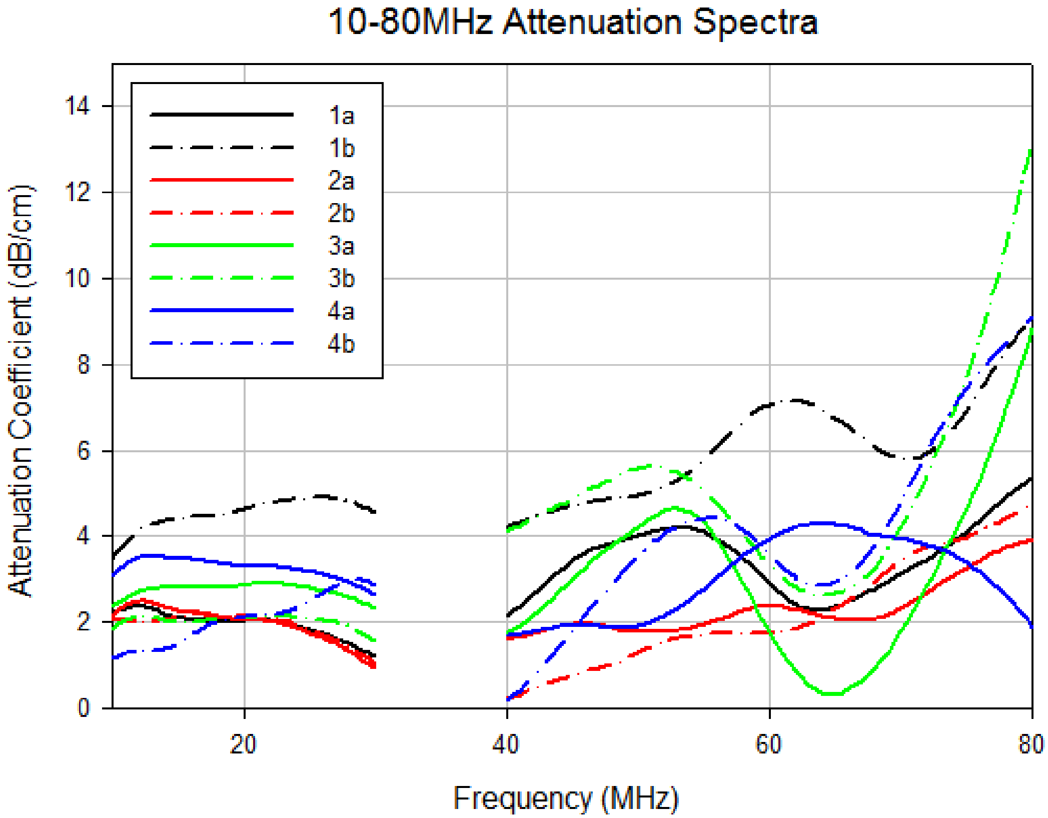
Ramp to 1950°C at 200°C/min

Hold at 1950°C for 13min

Off

Ultrasound NDE, mechanical sectioning and FESEM imaging for characterization

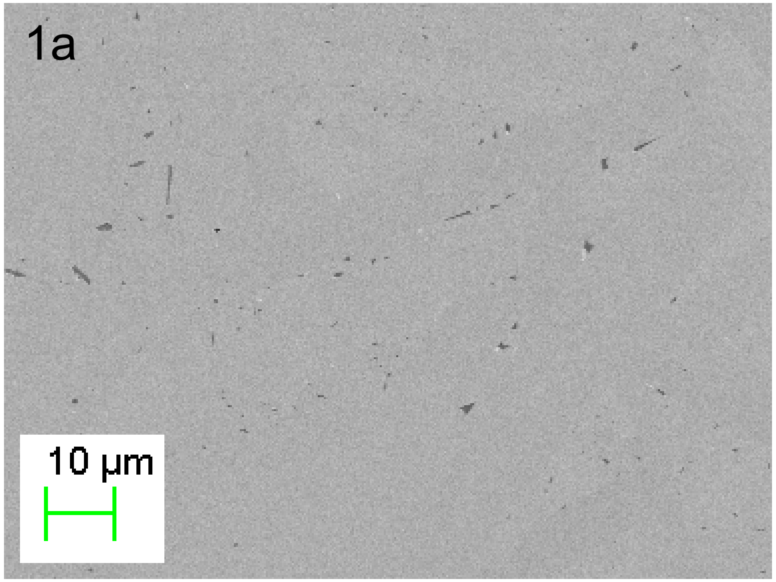
Ultrasound Results



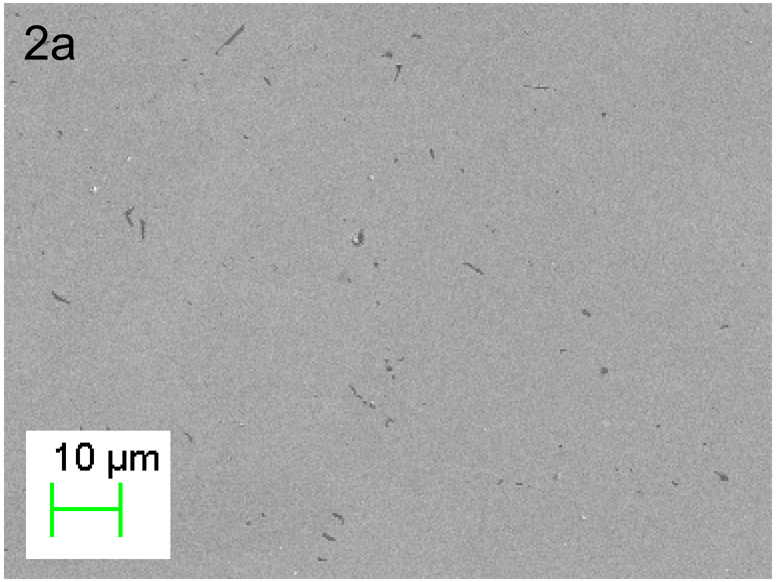
- No sharp peaks at lower frequencies
  - Broad inclusion size distribution
  - Inclusions too large/small
- Anomalous behavior at higher frequencies
  - Non-uniform grain size distribution
  - Surface effects
- Both absorption and scattering assume spherical particles – what if we don't have these?

Sample	cL (m/s)	cS (m/s)	Poisson	Density	E (GPa)	G (GPa)	K (GPa)
1a (0.5% ESK Tetrabor 3000F)	12293	7496	0.204	3.20	433	180	244
1b (1.0% ESK Tetrabor 3000F)	12211	7484	0.199	3.19	429	179	237
2a (0.5% ESK Tetrabor 1250 mesh)	12324	7475	0.209	3.20	432	179	248
2b (1.0% ESK Tetrabor 1250 mesh)	11974	7376	0.194	3.19	415	174	226
3a (0.5% HCStarck HD20)	12184	7590	0.183	3.20	436	184	229
3b (1.0% HCStarck HD20)	12384	7471	0.214	3.20	434	179	253
4a (0.5% Rutgers SF5)	12295	7478	0.207	3.20	432	179	24[illegible]
4b (1.0% Rutgers SF5)	12270	7443	0.209	3.20	429	177	245

0.5% B_4C Additive

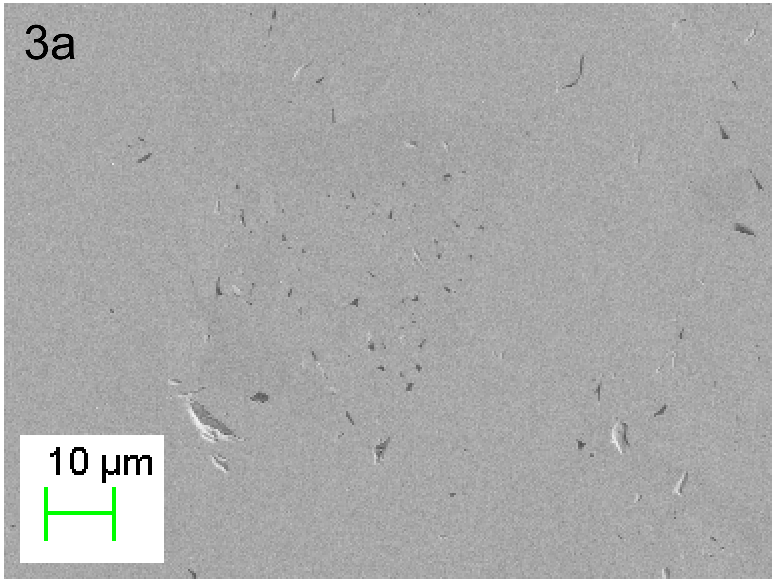


0.5% ESK Tetrabor 3000F

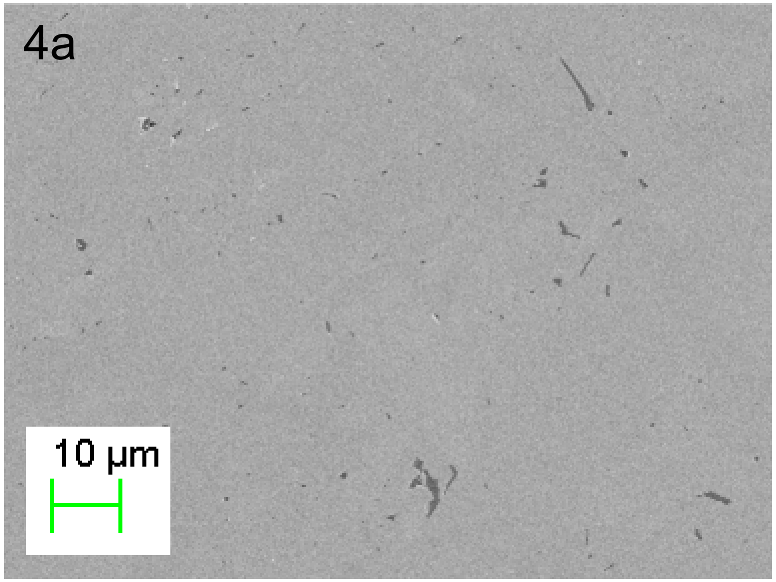


0.5% ESK Tetrabor 1250 mesh

Size of inclusions are fairly consistent, even with different additive sizes



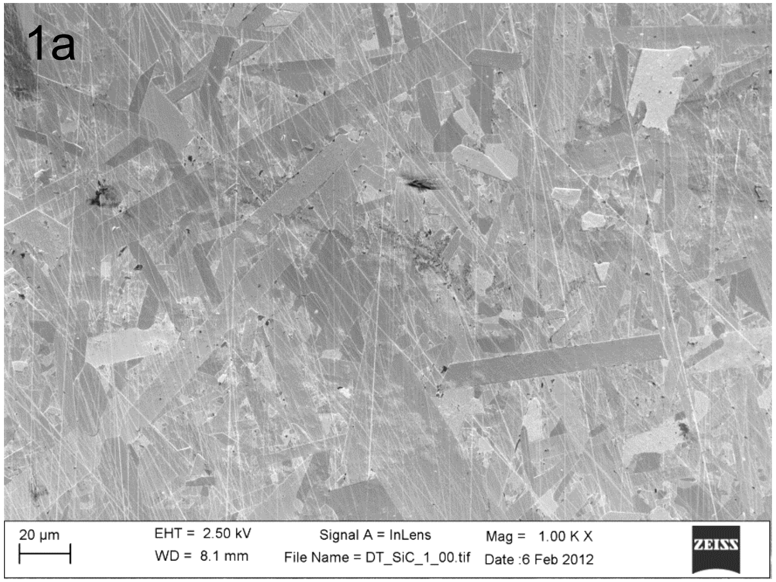
0.5% HC Starck HD20

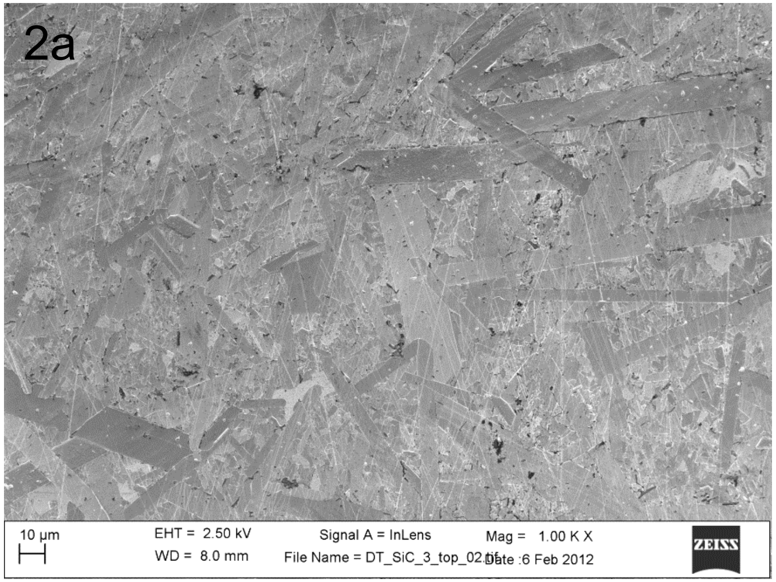


0.5% Rutgers SF5

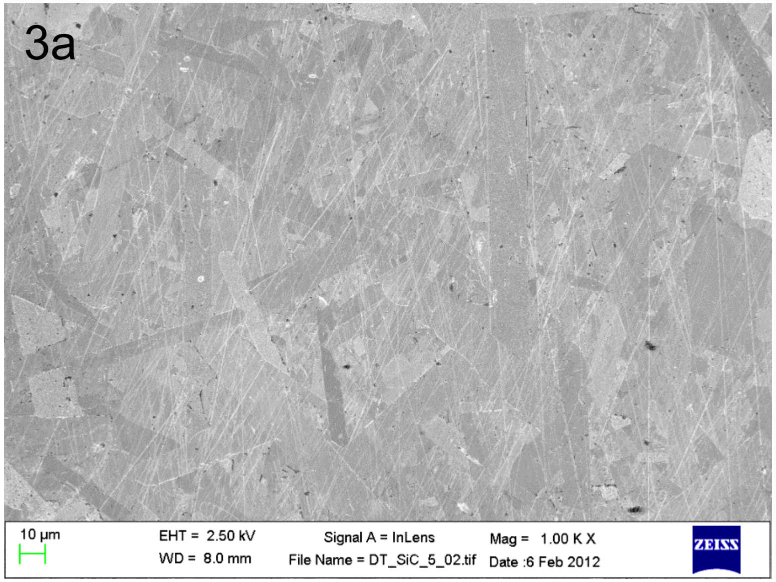
All samples fully dense with little if any visible porosity

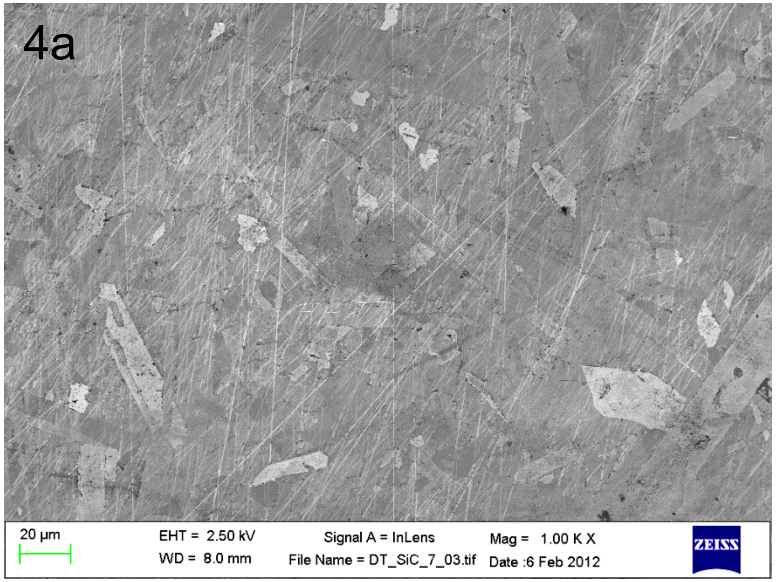
0.5% B_4C Additive





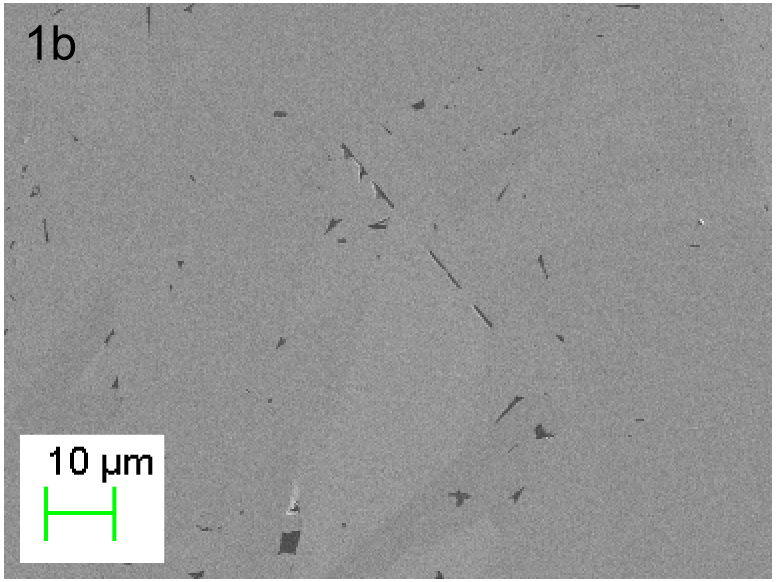
All samples show large, elongated grains



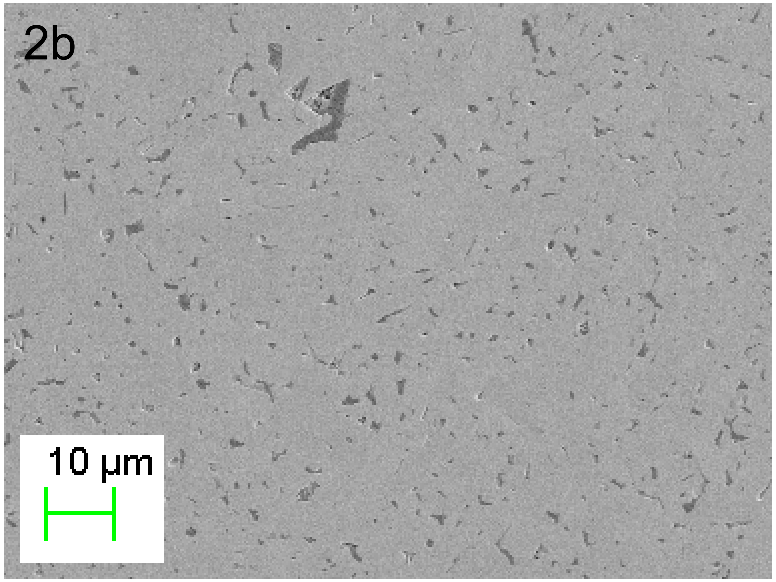


Sample 2a shows smaller average grain size, fewer very large grains

1.0% B_4C Additive

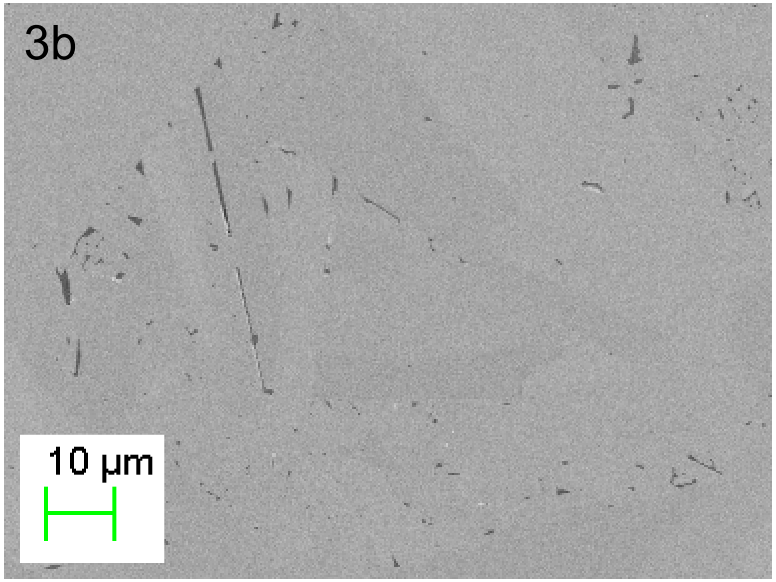


1.0% ESK Tetrabor 3000F

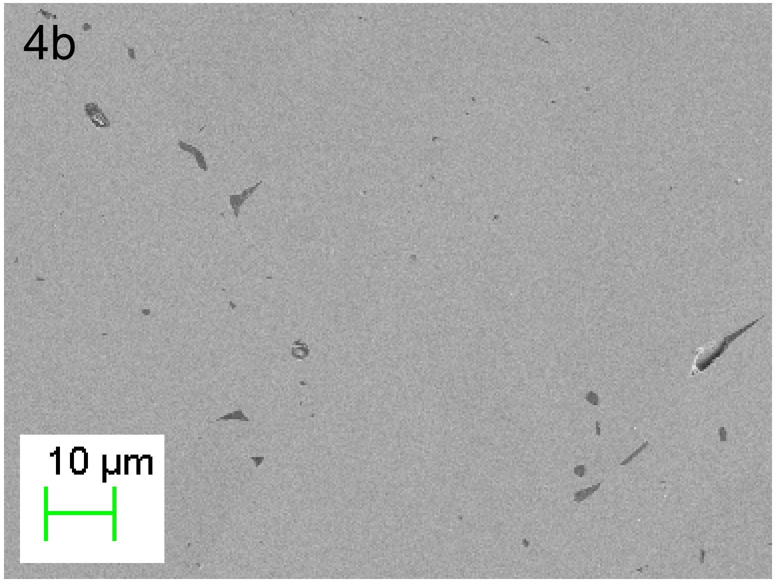


1.0% ESK Tetrabor 1250 mesh

More additives → more inclusions, larger inclusions



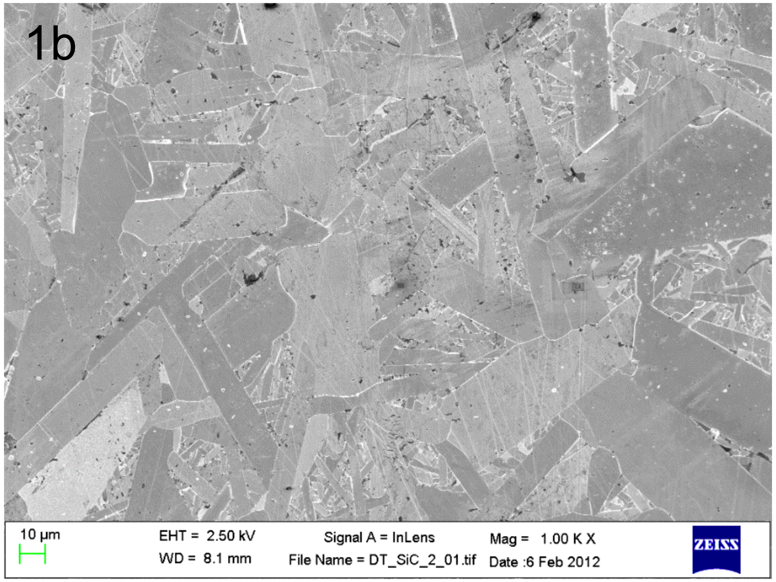
1.0% H.C. Starck HD20

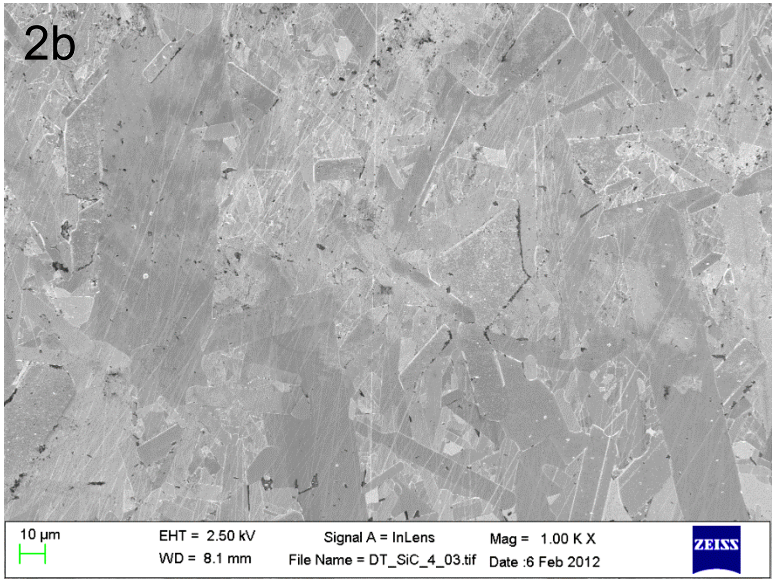


1.0% Rutgers SF5

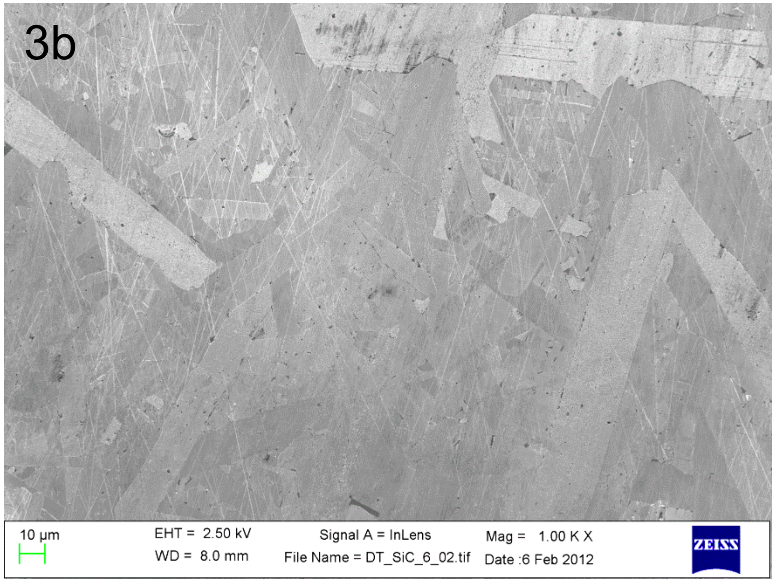
All samples fully dense with little if any visible porosity

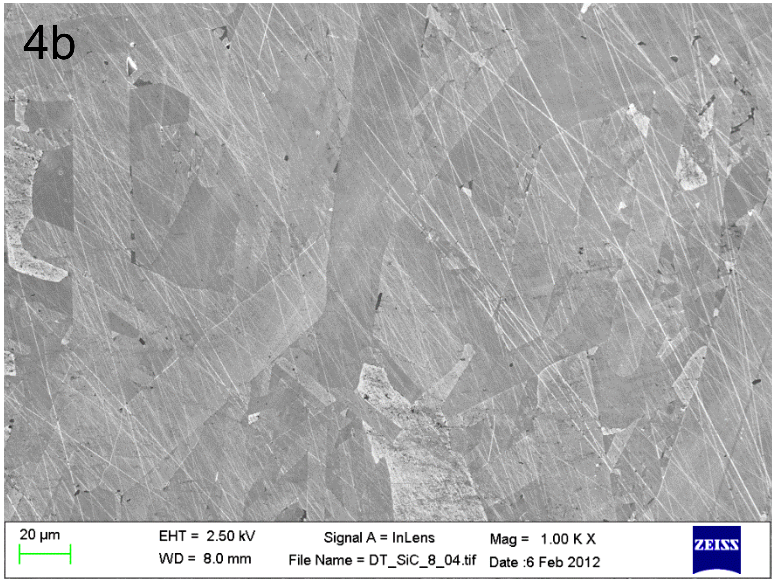
1.0% B_4C Additive





Samples still show elongated grains





Again, larger B_4C additive seems to reduce average grain size

SiC Made with Different Processing Methods

- Mark I - Baseline sample
  - Dry mixed in SpectroMill
  - H.C. Starck UF-25 SiC
  - 0.5% ESK Tetrabor 3000F B_4C
  - 1.0% Fisher Lamp Black C
- Mark II - Filter-pressed samples
  - Ball milled in ethanol 24 hours
  - Filter pressed at 15psi
  - H.C. Starck UF-25 SiC
  - 0.5% Rutgers SF5 B_4C
  - 1.5% Fisher Lamp Black C

- Sintered in Thermal Technologies SPS 10-4 unit
  - Argon atmosphere
  - 50MPa pressure

Ramp to 1400°C at 200°C/min

Hold at 1400°C for 30min

Cool down for 30min

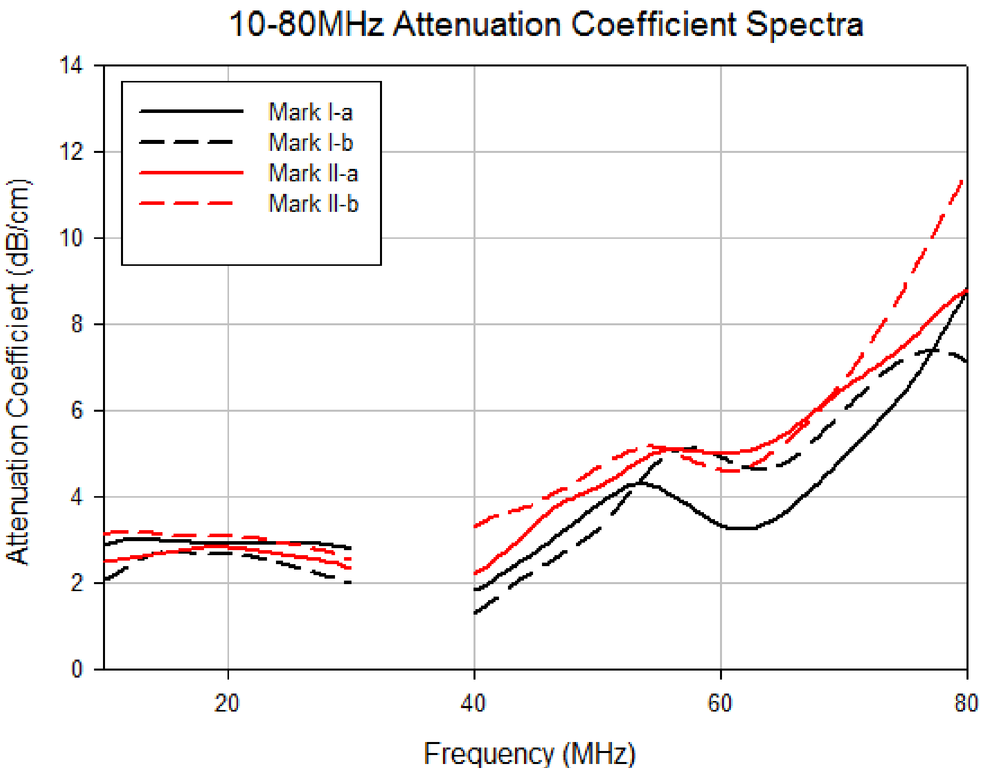
Ramp to 2000°C at 500°C/min

Hold at 2000°C for 15min

Off

Ultrasound Evaluation

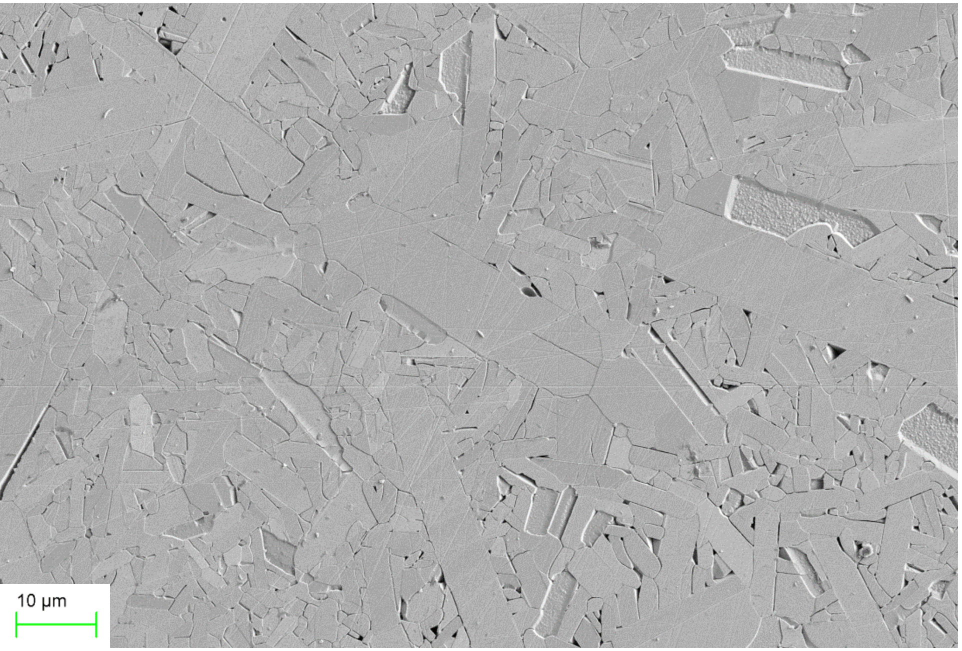
Sample	cL (m/s)	cS (m/s)	Poisson	Density (g/cc)	E (GPa)	G (GPa)	K (GPa)
Mark I-a	12196	7589	0.184	3.20	437	185	231
Mark I-b	12072	7486	0.188	3.20	426	179	227
Mark I-c	12054	7459	0.190	3.21	424	178	228
Average	**12107**	**7511**	**0.187**	**3.20**	**429**	**181**	**229**
Mark II-a	12258	7451	0.207	3.21	430	178	245
Mark II-b	12213	7455	0.203	3.21	429	178	241
Mark II-c	12209	7394	0.210	3.21	425	176	244
Average	**12227**	**7433**	**0.207**	**3.21**	**428**	**177**	**243**



- Sample elastic properties comparable to commercial materials
- Attenuation behavior similar at low frequencies
- Behavior differs at higher frequencies, due to grain size and shape effects

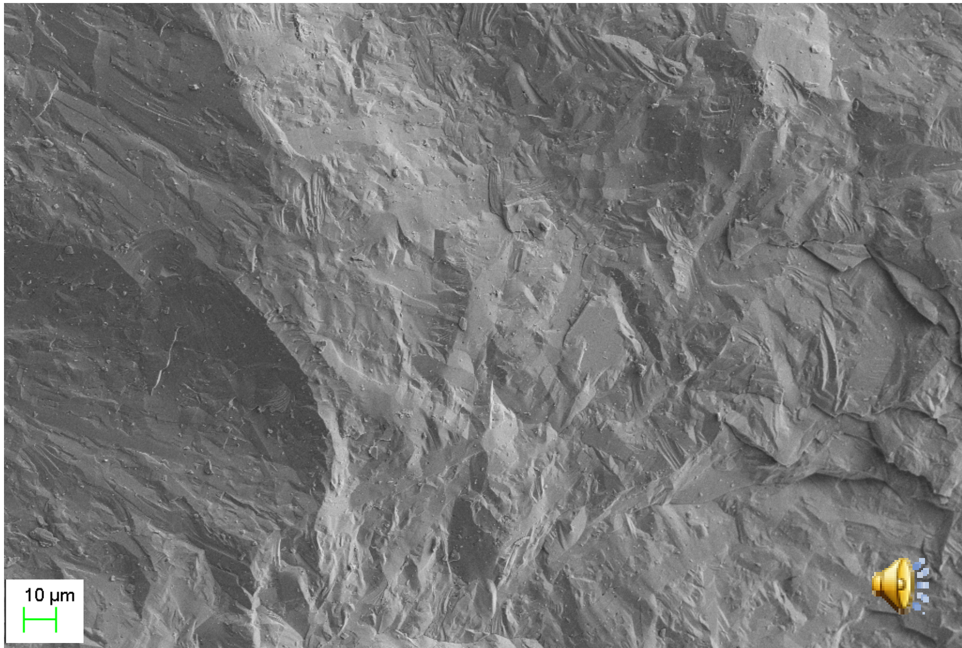
Mark I SEM

Mark I etched



- Some elongated, high aspect ratio grains present
- Appears to have a bimodal grain size distribution
- Mainly smaller grains with some larger ones

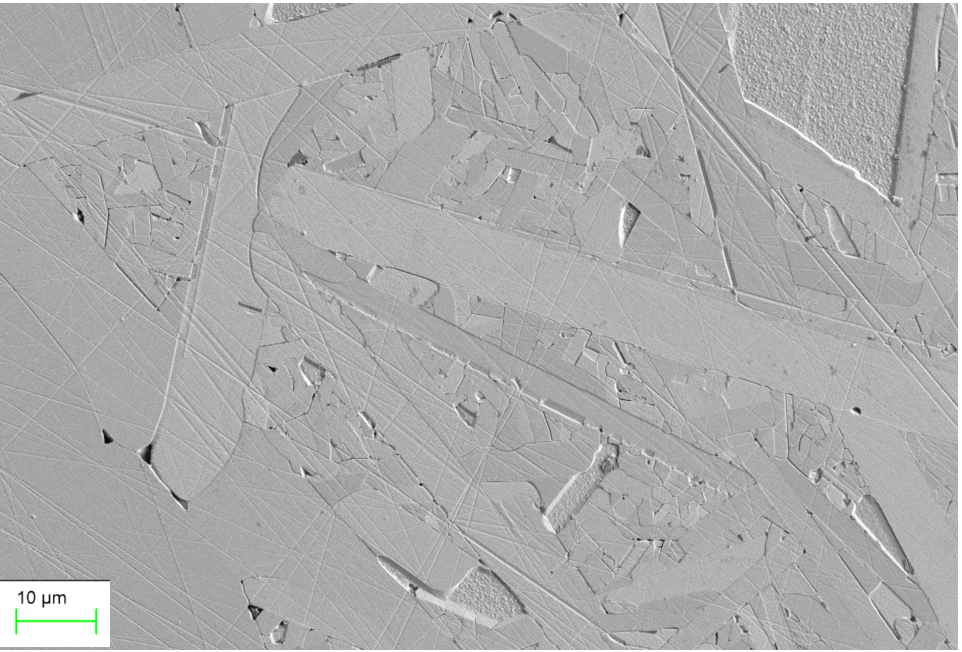
Mark I fracture surface



- Fragment from dynamic testing
- Predominantly transgranular fracture

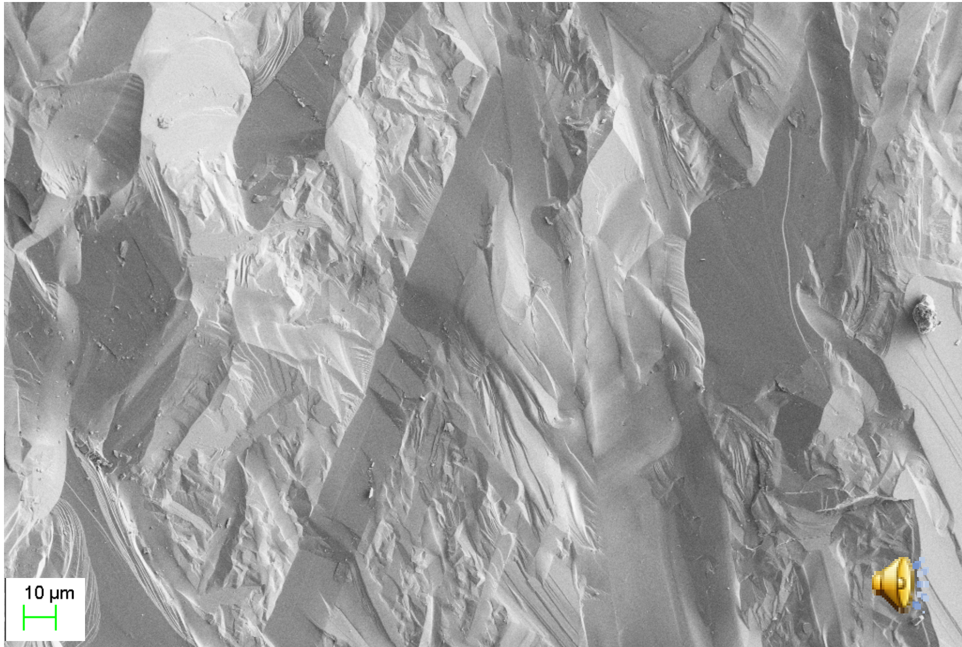
Mark II SEM

Mark II etched



- Many elongated, high aspect ratio grains present
- Appears to have a bimodal grain size distribution
- Many large grains with smaller grains between them

Mark II fracture surface



- Predominantly transgranular fracture
- Clean fracture surfaces – no C or B_4C evident

Summary

- Ultrasonic testing was performed to measure elastic properties, predict microstructural characteristics of SPS SiC samples
  - Anomalous behavior precluded quantitative estimates of secondary phase inclusion and SiC grain size

- FESEM imaging showed predominantly large, high aspect ratio grains

- Different additive samples
  - Smaller B_4C additives show much cleaner microstructures, even with higher additive content
  - Larger additive size appears to decrease SiC grain size
  - Additive morphology doesn’t appear to have much of an effect

- Different processing method samples
  - Samples show similar elastic properties and acoustic behavior, but show very different microstructures

- Irregular grain shapes and wide grain size distribution must be corrected before definitive conclusions can be made

Future Work

- Fabricate SiC samples with B_4C and C additions via SPS
  - Use different sintering cycles to produce more equiaxed grains
    - Prepare samples using different processing methods
    - Use different size/purity B_4C, C starting materials
    - Generate standard samples with varying grain sizes, additives
- Ultrasound characterization of standard samples to determine:
  - Scattering prefactors
    - Grain size measurements
  - Absorption mechanisms
    - Secondary phase size distributions, concentrations
- Expand transducer library to fill frequency gap between 30 – 40 MHz, expand capabilities to lower, higher frequencies