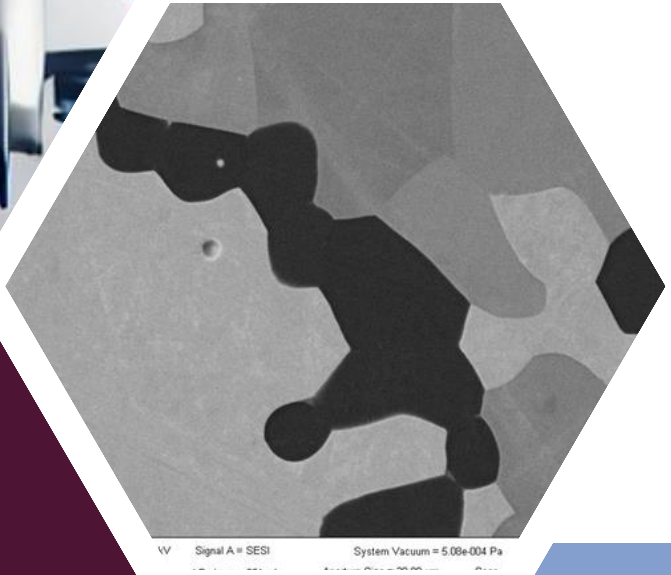


Toughening of high-entropy ceramics by low-dimensional nanomaterials

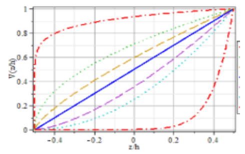
Presented by: Ines Sara Moussaoui

Supervised Ján Dusza and By Péter Pinke

23/01/2025

PLAN

Introduction — I



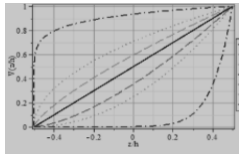
Experimental procedure — II

Results and discussions — III

Conference participation and on going research — IV

PLAN

Introduction I



Experimental procedure II

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High-Entropy Ceramics dual definition

Based on elemental composition

•**Definition:** HECs typically consist of **equiatomic or near-equiatomic ratios** of **five or more principal elements**.

•**Composition**: Each element contributes **5% to 35%** of the atomic composition.

.

Based on configurational entropy

•**Threshold for High Entropy:**

- •Configurational entropy typically **exceeds 1.61 R** (where R is the gas constant).
- •In some formulations, it may be **1.5 R**.

Stabilizing Mechanisms

- High entropy
- Lattice distortion
- Sluggish diffusion
- Cocktail effect

Properties and applications

DPHECs Composition: Combines two high-entropy phases for enhanced performance.

Carbides (TaC, HfC, ZrC): Contribute to high hardness, melting points, and thermal stability.

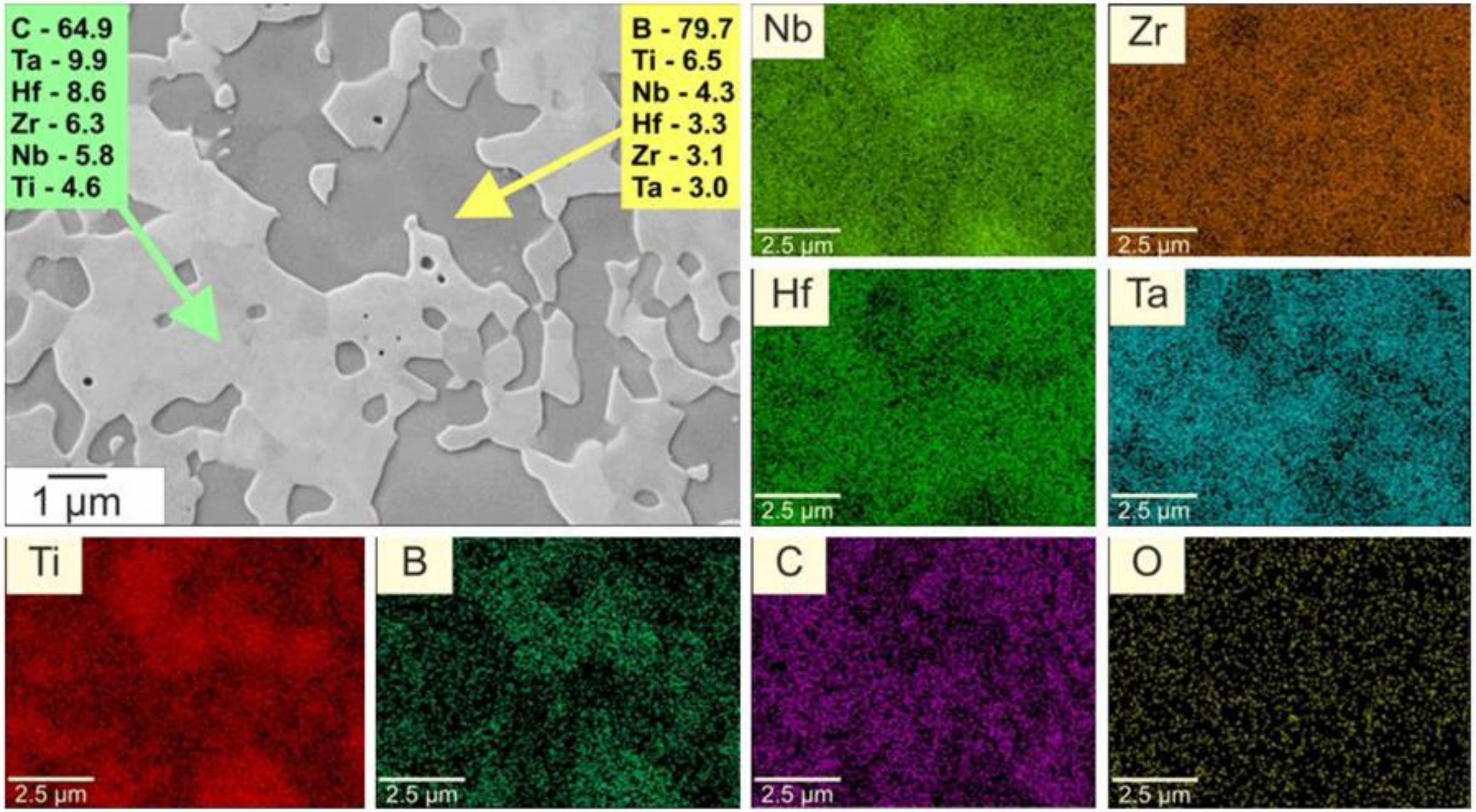
Borides (ZrB_2, NbB_2, TiB_2): Offer excellent oxidation resistance and thermal shock tolerance.

Enhanced Mechanical Properties: Improved toughness and thermal resistance compared to single-phase ceramics.

Ideal for Extreme Environments: Suitable for ultra-high-temperature and high-stress applications. such as: **abrasive, erosive, corrosive and high-temperature environments**

Typical microstructure

$(Ti_{0.14}Zr_{0.2}Nb_{0.2}Hf_{0.2}Ta_{0.26})C$ and $(Ti_{0.38}Zr_{0.18}Nb_{0.22}Hf_{0.115}Ta_{0.105})$

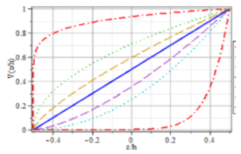


Characteristic microstructure of the dual-phase high-entropy carbide/boride system with SEM-EDS analyses of the individual grains and elemental mapping of constituent elements.

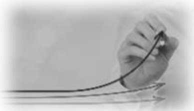
Annamaria Naughton-Duszovaa et al. "Dual-phase high-entropy carbide/boride ceramics with excellent tribological properties." Journal of the European Ceramic Society 44.9 (2024): 5391-5400.

PLAN

Introduction — I



Experimental procedure — II



Results and discussions — III

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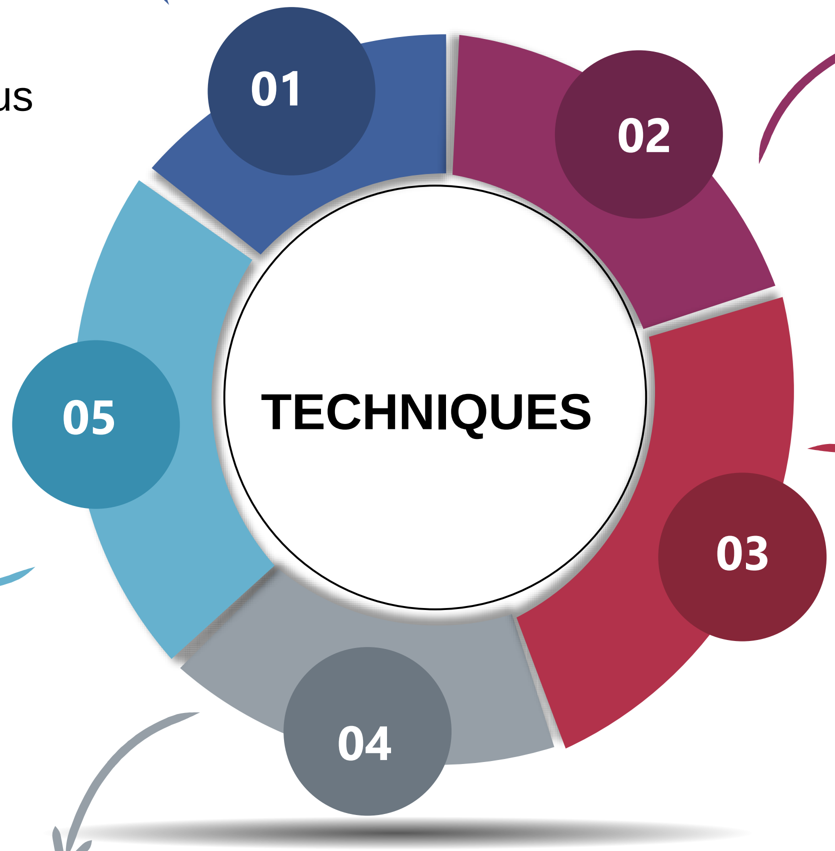
Processing methods of DPHEC

Reactive Spark Plasma Sintering (ReaFSPS): Directly synthesizes ceramics from powders with simultaneous reaction and sintering.

Boro/Carbothermal Reduction: Uses boron carbide and graphite under vacuum, followed by SPS to densify boride/carbide powders.



Reactive Sintering: Combines borides and carbides, then mills and hot-presses to form ceramics with tailored phases.

Sequential Carbothermal Reduction: Creates carbide powders, then partially converts to borides, using milling and sintering for dense ceramics.

Ultra-Fast High-Temperature Sintering (UHS): Rapid Joule heating enables quick synthesis at high temperatures up to 3000°C, while preserving volatile elements.

Preprocessing of DPHEC

Starting powders

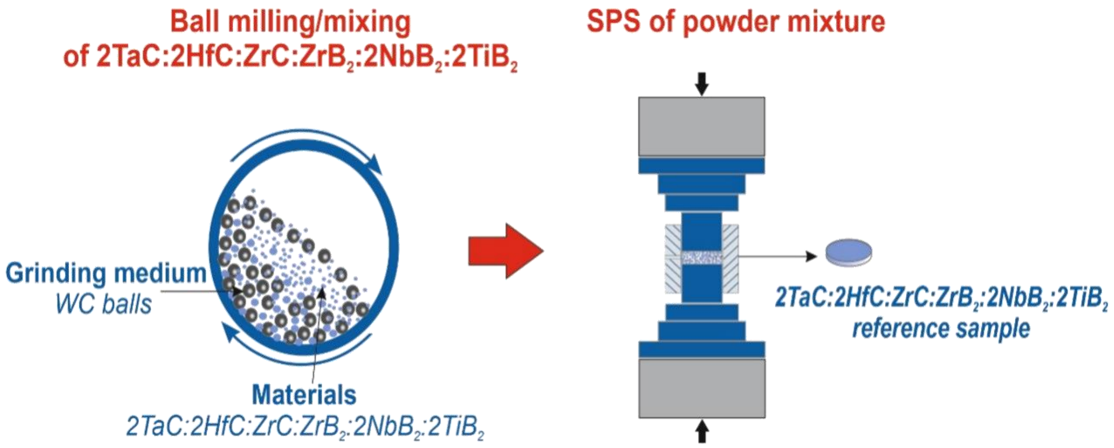
Alfa Aesar (Producer)	TaC	HfC	ZrC	ZrB2	NbB2	TiB2
Purity Average Particle Size/Laser Diffraction d_{50} µm	99.5% <325 mesh	99.5 % ~325 mesh	99.5% ~325 mesh	99.5 % 15 µm APS	purity 99%	99.5 % ~325 mesh

Mixtures preparation of material for sintering

Mixing/milling: Planetary mill (PM 100, Retsch) at 250 rpm for 4 h in a tungsten carbide jar, using isopropanol as a solventWC-Co grinding balls φ 10 mm, the powder to ball ratio was 1:10

Drying: After milling, the powder is thoroughly dried to remove any residual solvents. The required mass of the powder is weighed based on the sample volume and material density to ensure the precise composition targeted.

compaction for SPS: The powder is thoroughly mixed again to ensure homogeneity for preserving the high-value nanostructures and enhancing the functionality of the resulting dual-phase high entropy ceramics. The mixed powder is then molded via a manual hydraulic press, 70 MPa, discs φ 20mm

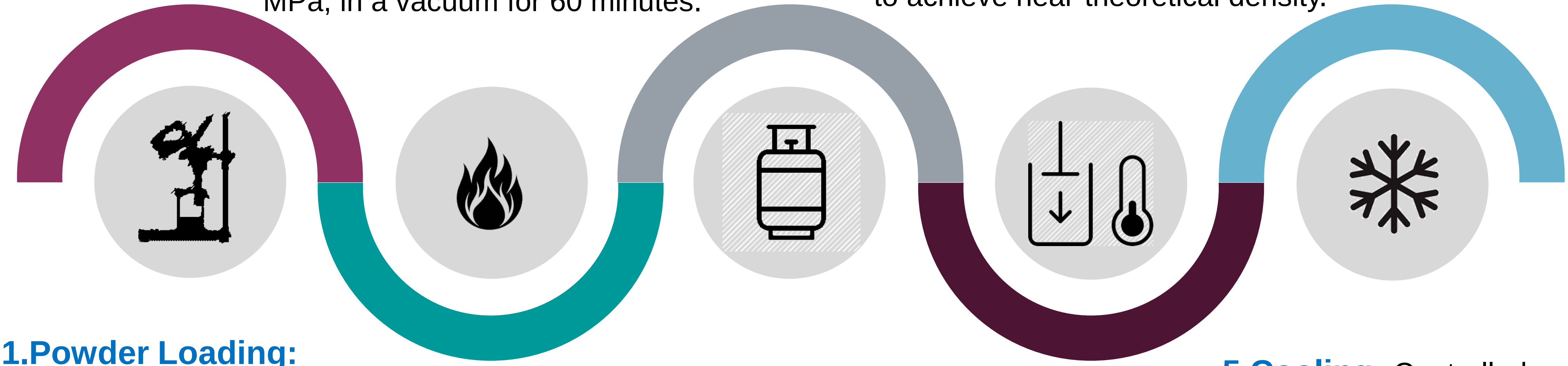


Processing of DPHEC

Force up to **70 MPa**, temperature up to **2100 °C**
Sintering time of **5 min, 10 min and 20 min**

2.Initial SPS Consolidation:
Powder consolidated at 1650°C, 3 MPa, in a vacuum for 60 minutes.

4.Final SPS Consolidation:
Temperature increased to 2100°C and 70 MPa for 5, 10, or 20 minutes to achieve near-theoretical density.

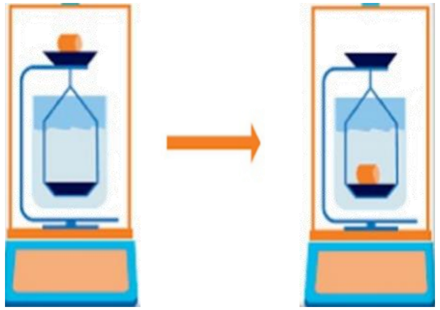


1.Powder Loading:
Milled powder loaded into a graphite-lined die to prevent reactions and ease sample removal.

3.Outgassing and Oxide Reduction:
Temperature raised to 1800°C for 10 minutes to remove trapped gases and reduce oxides.

5.Cooling: Controlled cooling at 50°C/min under argon to prevent oxidation.

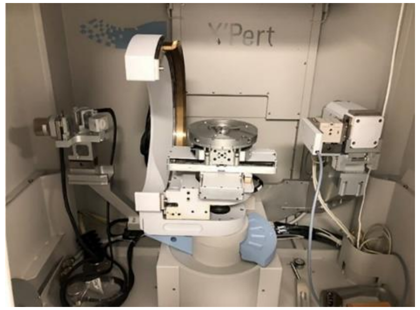
CARACTERIZATION



01

Density Measurement (Archimedes' Principle)

- Weigh the sample in air.
- Immerse in distilled water and measure the apparent weight.
- Calculate density using the weight difference.



02

Crystalline Phase Composition (X-Ray Diffraction)

Instrument: Philips X'PertPro

- Utilizes Cu Kα radiation.

Procedure:

- Prepare the sample and mount it on the XRD stage.
- Collect diffraction patterns.
- Analyze peaks to identify crystalline phases.

03

Microstructure Analysis (Scanning Electron Microscopy)

Instruments:

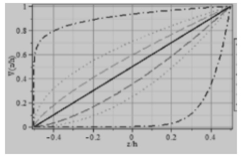
- EVO SEM for general surface morphology observation.
- FIB-SEM ZEISS AURIGA Compact, a focused Ion Beam (FIB) for cross-sectional analysis.

Procedure:

- Prepare the sample surface (e.g., polishing).
- Place in SEM chamber.
- Capture images at various magnifications.

PLAN

Introduction — I



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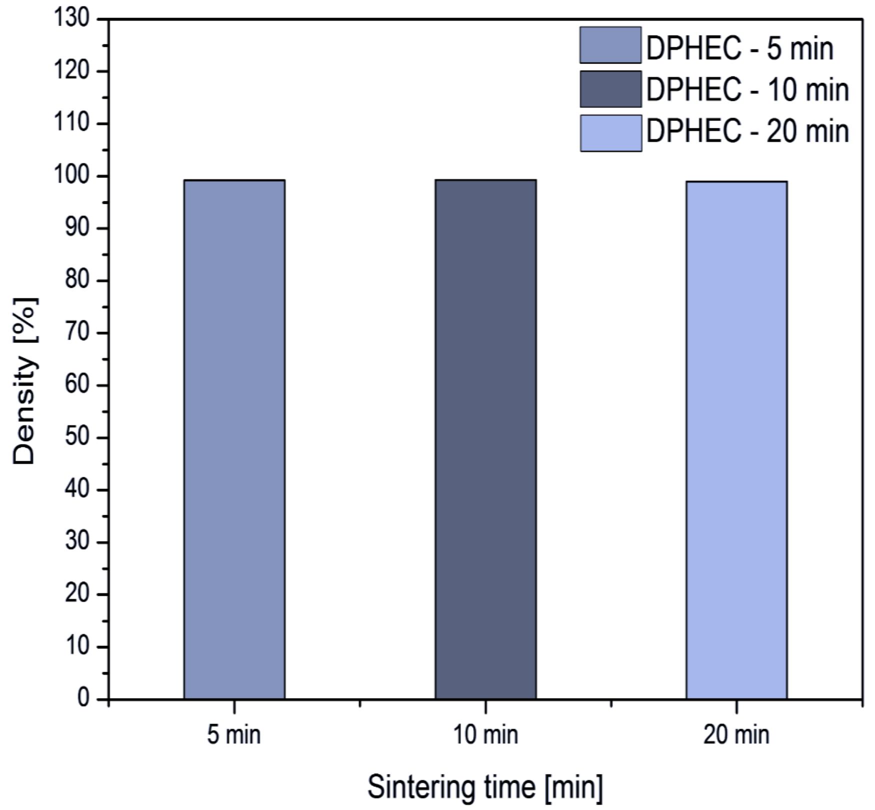
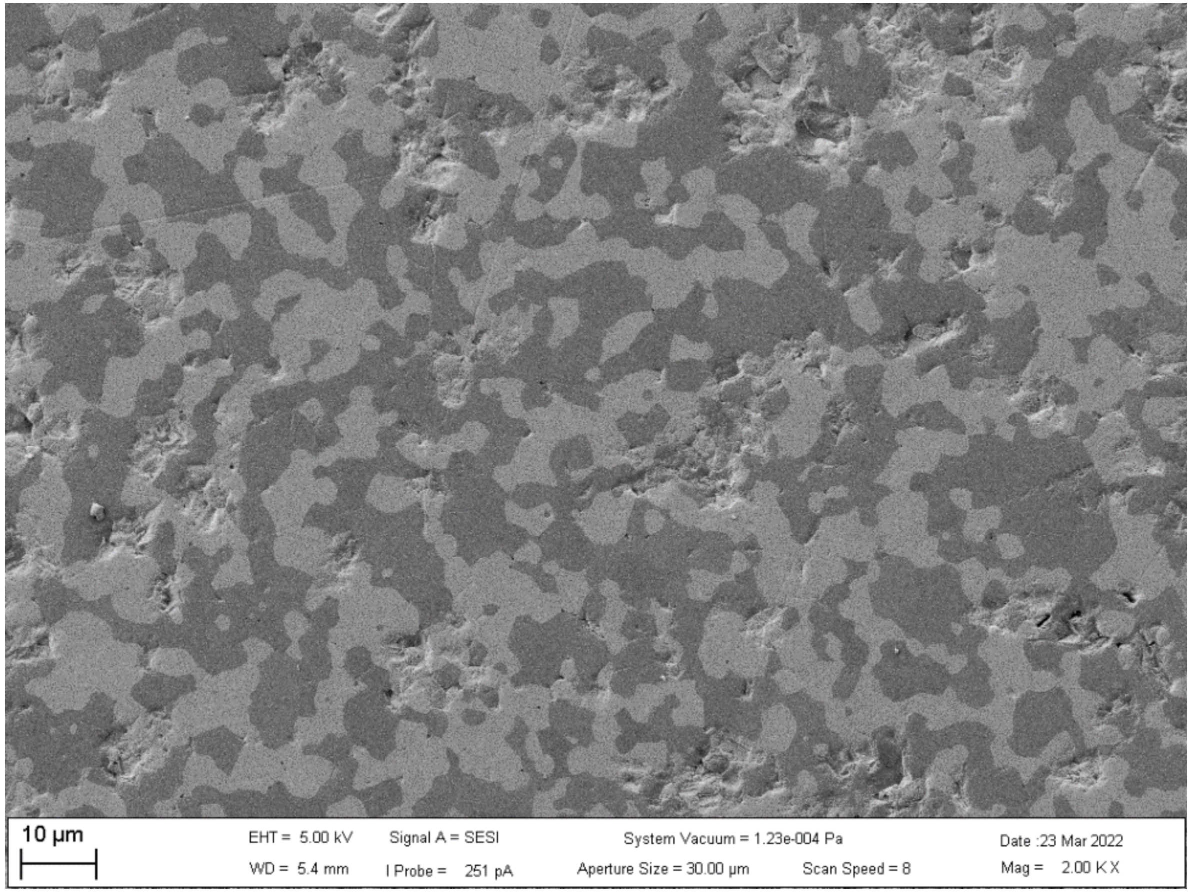
Influence of processing parameters on density

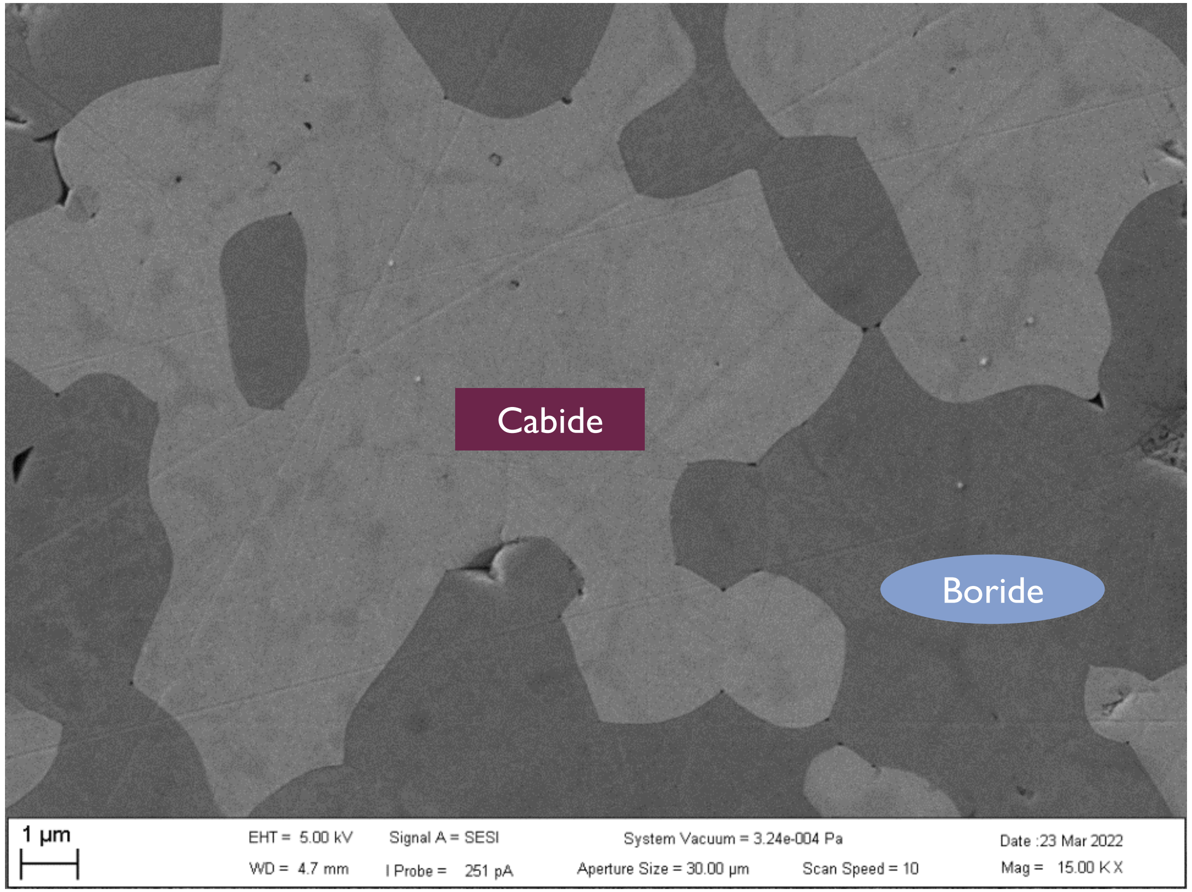
Sintering parameters	Density [g/cm^3] (%)	Hardness HV1[GPa]	Young modulus [GPa]	Fracture toughness [MPa m$^{1/2}$]
Temp.: 2100 °C Pressure: 75 MPa Time: 5 min	5,9313 (99.25)	21.73±1.3	580±39	6.04±0.93
Temp.: 2100 °C Pressure: 75 MPa Time: 10 min	5,8939 (99.32)	21.52±1.8	611±23	4.68±0.56
Temp.: 2100 °C Pressure: 75 MPa Time: 20 min	6,0377 (98.98)	19.82±0.4	608±13	5.83±0.81



It is evident that the highest hardness and fracture toughness are achieved after a sintering time of 5 minutes. A detailed study was conducted on this system, with the results presented in the following section.

Microstructure of optimized system





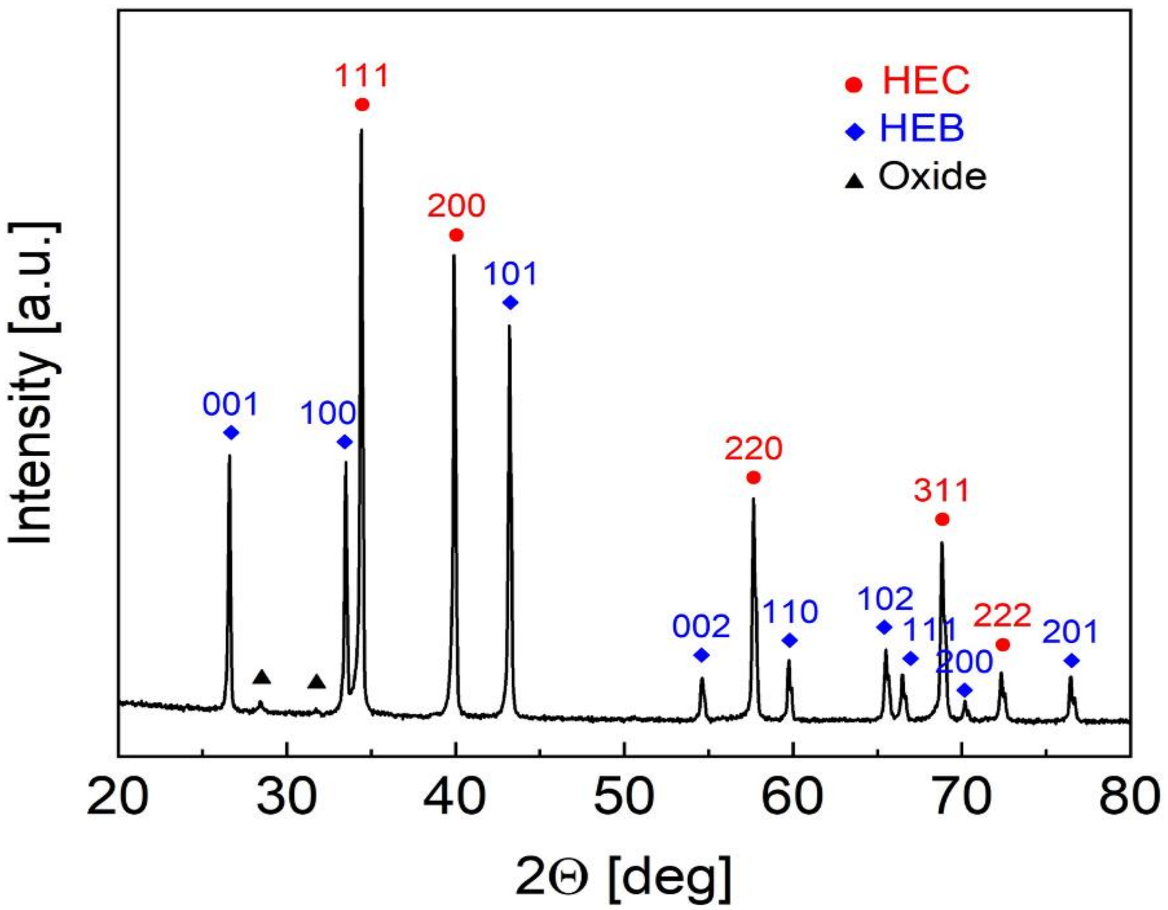
Here we can see two separate phases with a dense structure. According to the results the HEC (lighter) and the HEB (darker) phases are evenly distributed, with relatively large clustering of the phases and without predominantly large grain size. No visible porosity except very few impurities (Pullout of grains during the preparation) either because grinding damage do to the material characteristics or some inclusions during sintering.

X – ray measurement

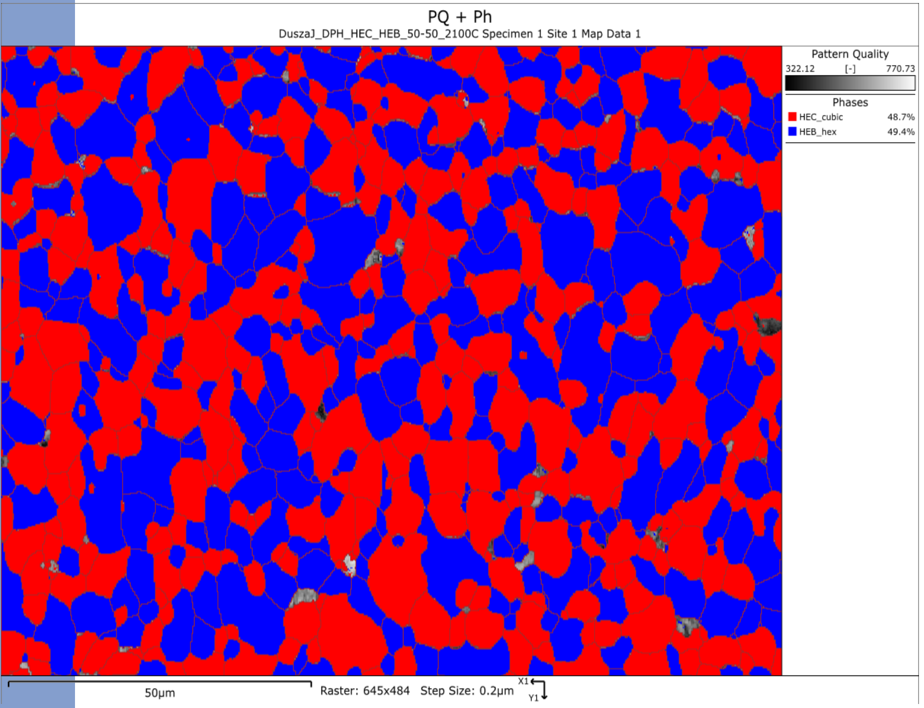
- ❑ Fig shows the recorded XRD pattern of the (Ta-Hf-Zr-Nb-Ti)C-(Ta- Hf-Zr-Nb-Ti)B2 composite ceramics with indexed peaks.

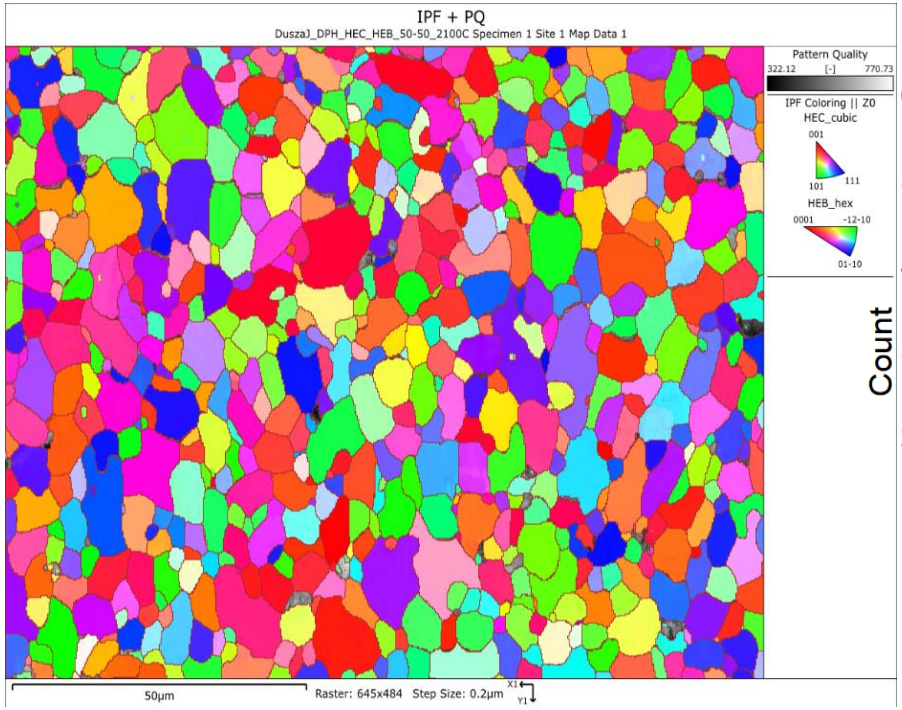
- ❑ The XRD pattern confirms that a dual-phase high-entropy system was synthesized with a negligible amount of oxides (HfO2/ZrO2 < 1 wt%) where the carbide and boride phases are denoted by HEC and HEB in the present work.

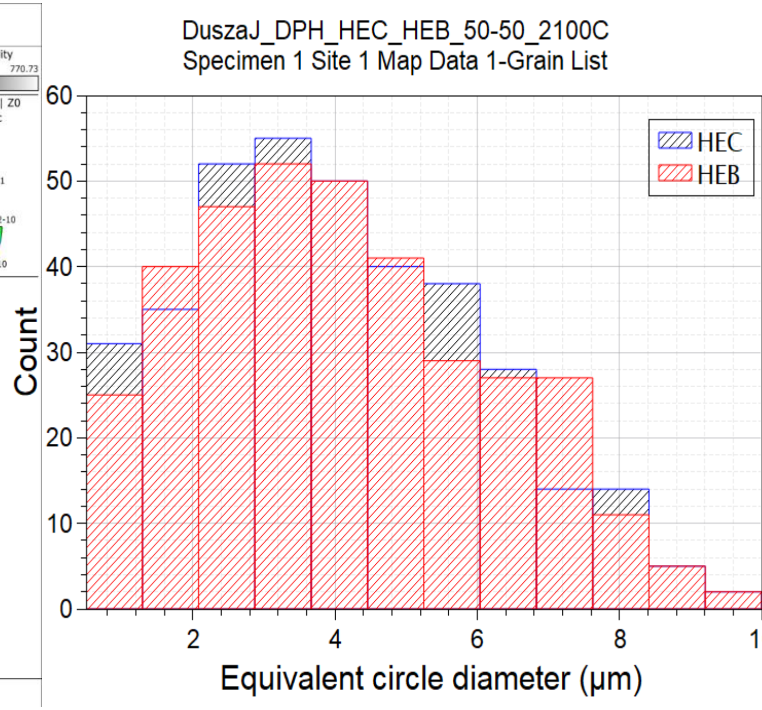
- ❑ The lattice constants are a= 4.5246(7) Å for the cubic carbide (Fm-3 m) and a= 3.0974(6) Å, c= 3.3643(8) Å for the hexagonal boride (P6/mmm) phases.



EBSD ANALYSIS

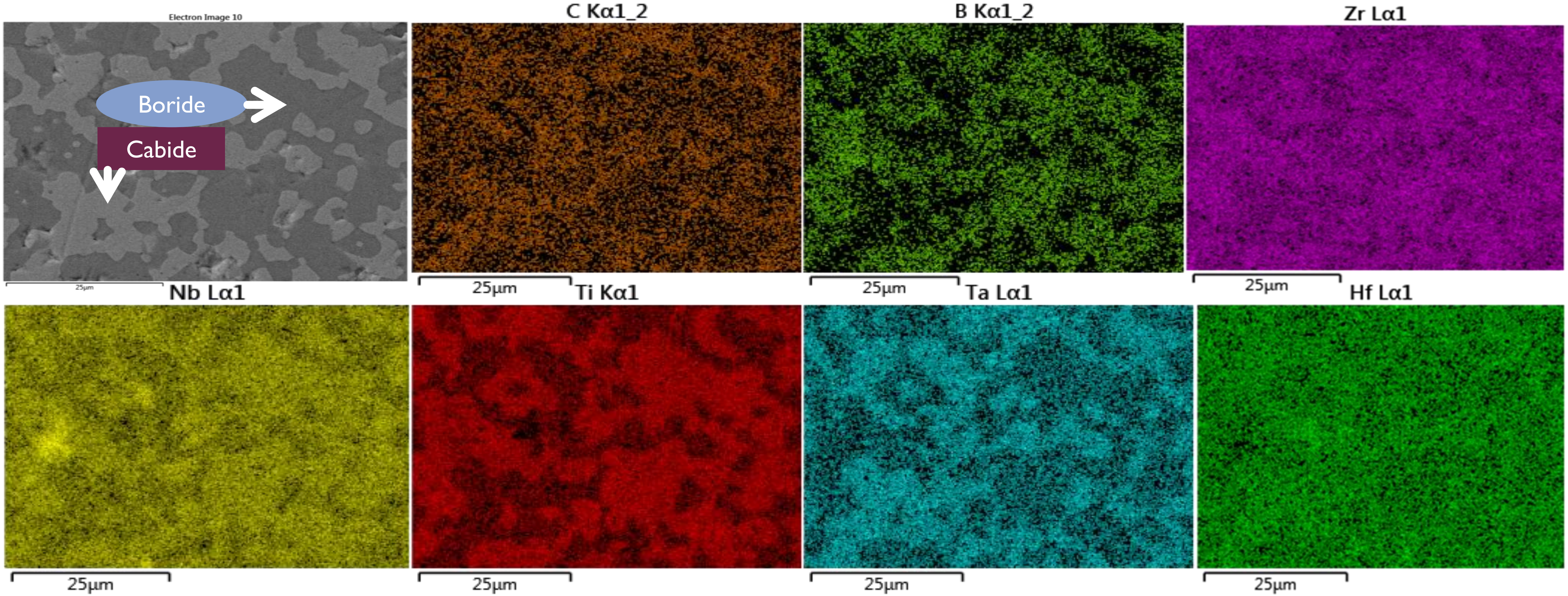






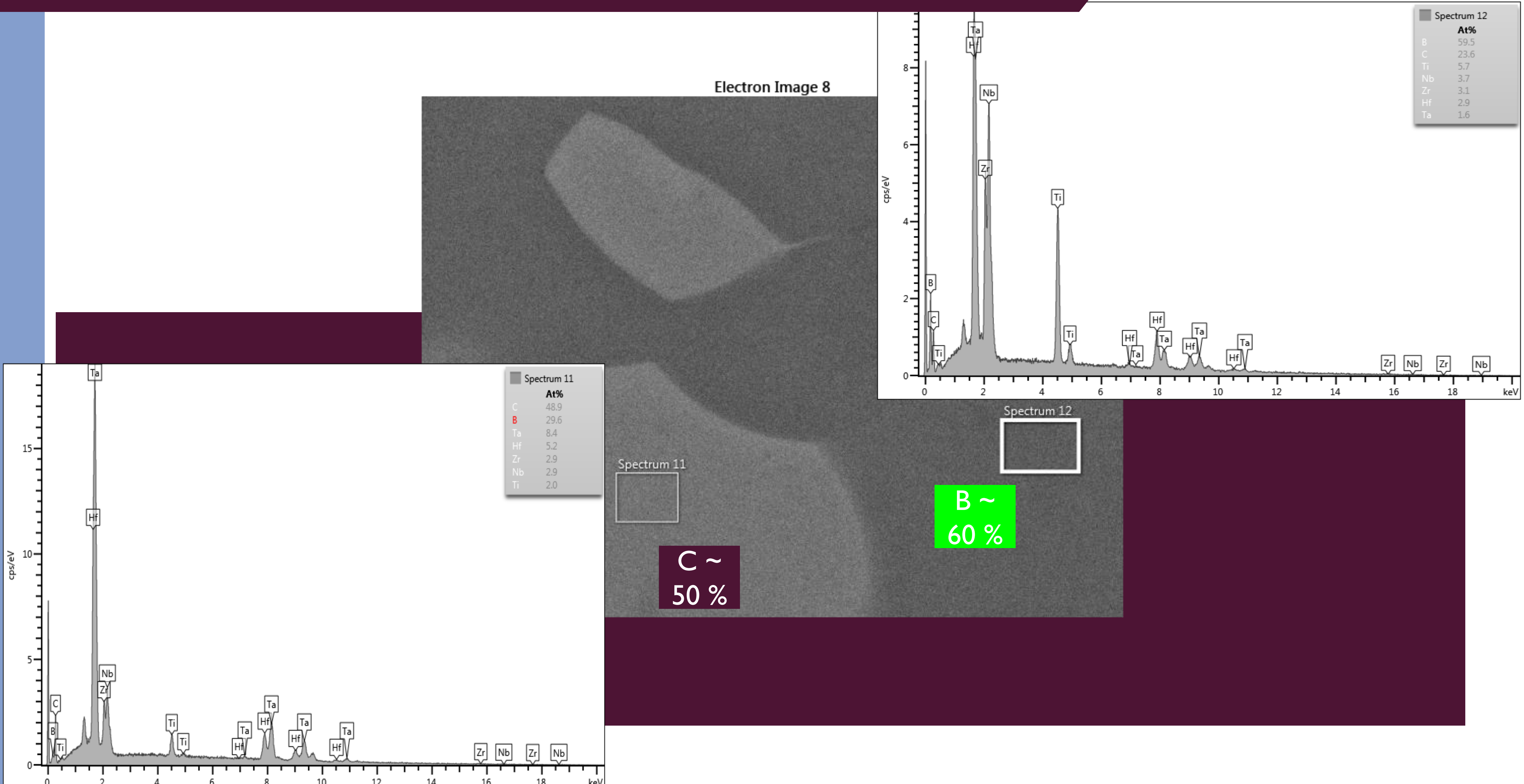
- The material consists of a hexagonal high-entropy boride (HEB) phase and a cubic high-entropy carbide (HEC) phase.
- The middle image is an IPF map showing diverse, equiaxed grains with random crystallographic orientations, indicating a randomized texture in the material.
- The average grain size of the HEC and HEB phases were measured to be 2 µm and 3 µm, respectively.

EDX ANALYSIS



Ti, Zr, and Nb are enriched in the HEBoride phase, while Ta and Hf are concentrated in the HECarbide phase. A minor amount of W contamination was also detected, likely originating from the milling media.

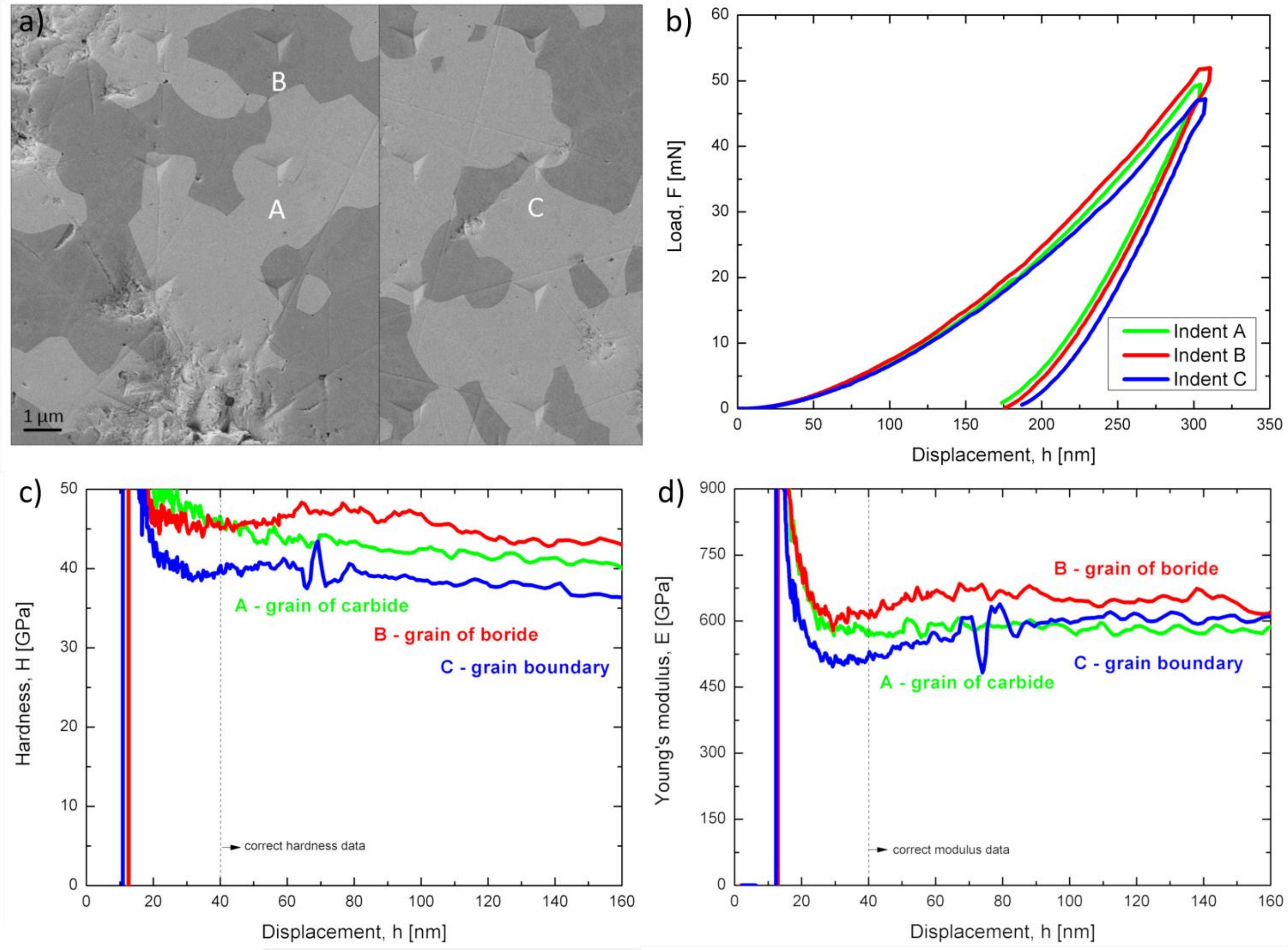
EDX ANALYSIS



Nanoindentation

- The sample exhibits phase-dependent mechanical properties. The **boride grains (B)** are the hardest and most rigid, which corresponds to higher load resistance and minimal displacement. The carbide **grains (A)** show intermediate properties, while the **grain boundaries (C)** are the least hard and exhibit the lowest Young's modulus, indicating greater compliance under load.

- These variations are typical in multi-phase ceramics and can impact the overall behavior of the material under mechanical stresses. The grain boundaries are the weakest points, which could influence crack initiation and propagation in the material.



Constituent	Carbide grains	Boride grains	Grain boundaries
Nanohardness, *H* (GPa)	*39.3 ± 1.6*	*41.1 ± 1.8*	*35.7 ± 1.9*
***Young's modulus, E* (GPa)**	*577 ± 37*	*628 ± 19*	*592 ± 15*

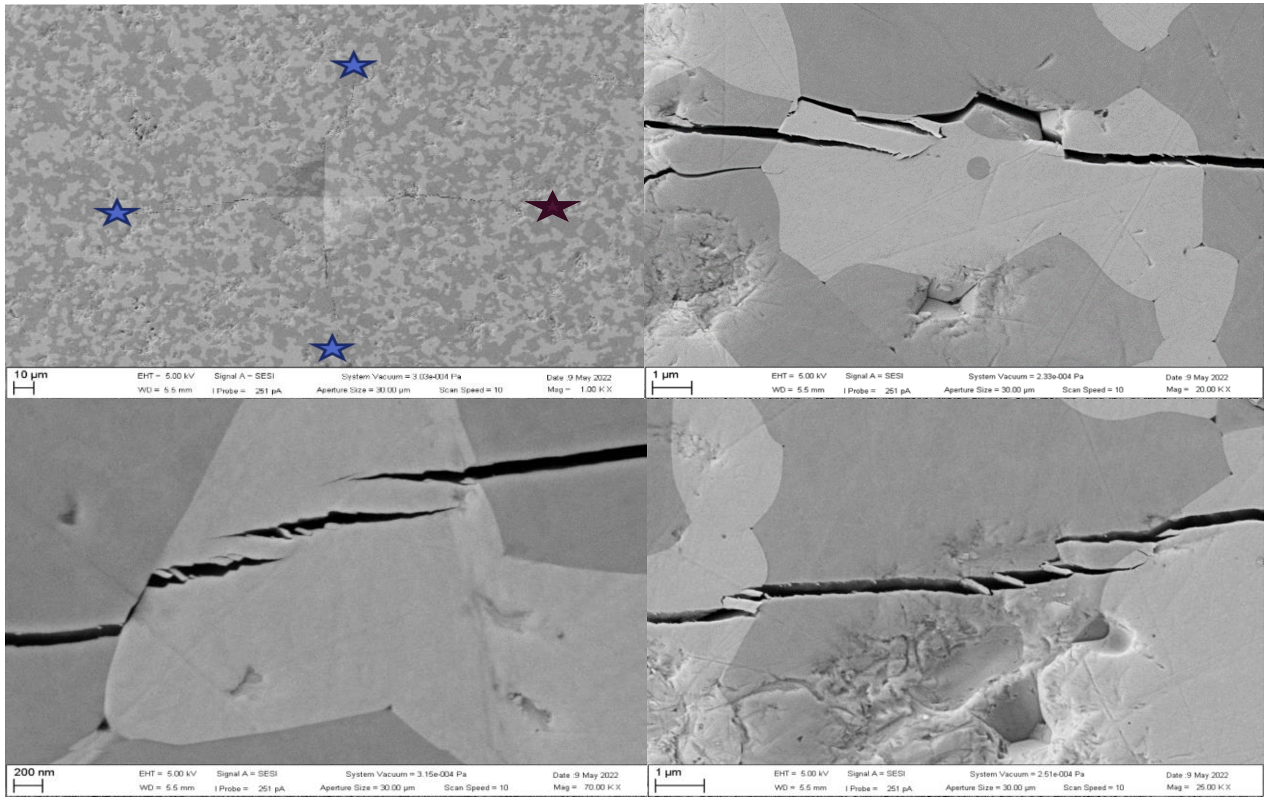
Microindentation

- **The microhardness and the indentation** fracture resistance of the systems is the highest at 5 min. of the sintering time with a value of 21.73 GPa and 6.04 MPa.m$^{0.5}$

- Crack branching, a phenomenon where a main crack splits into two or more smaller cracks, was frequently observed, especially at the grain boundaries and within the carbide and boride grains. This behavior is not typically seen in non-HEC ceramics.

- **Crack Deflection**: By initiating at grain boundaries, cracks are often deflected as they encounter different phases or orientations. This deflection contributes to increased energy absorption, enhancing the material's resistance to fracture.

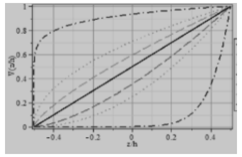
fracture toughness and crack propagation



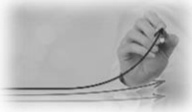
- The images indicate that cracks often deviate from their original path (crack branching) or span across grains with material bridging the crack (crack bridging). These phenomena suggest a crack-resistance mechanism inherent to the grain structure.

PLAN

Introduction I



Experimental procedure II



Results and discussions III

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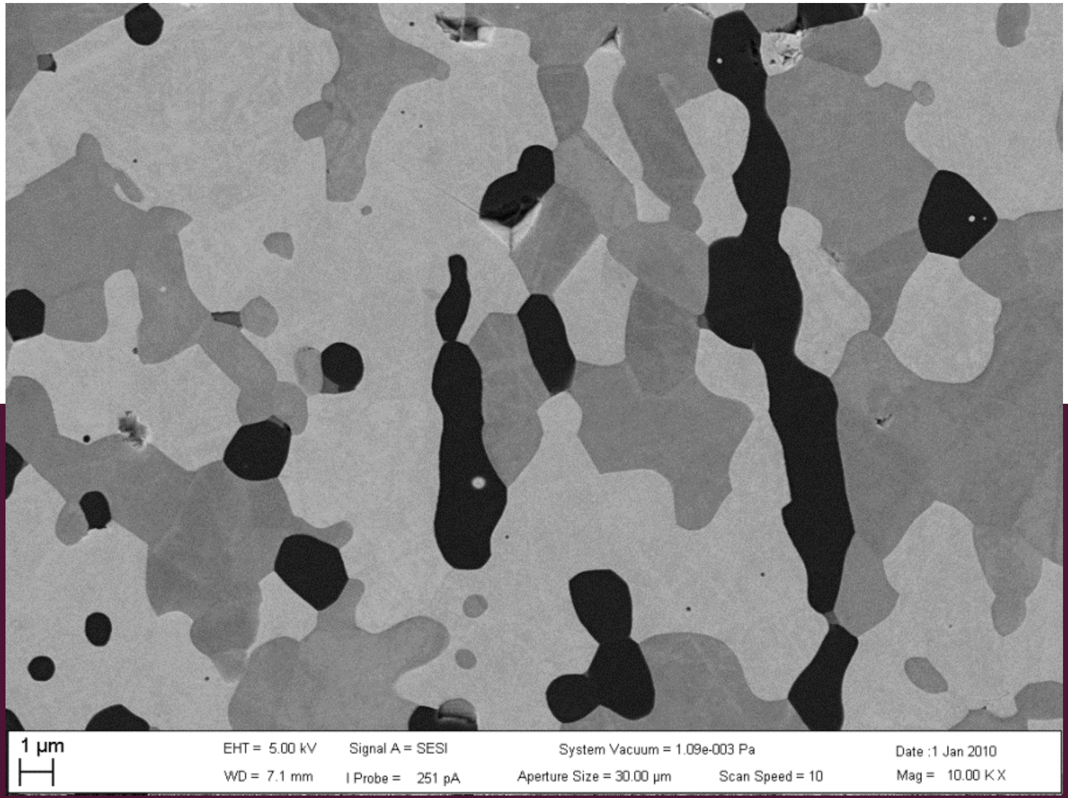
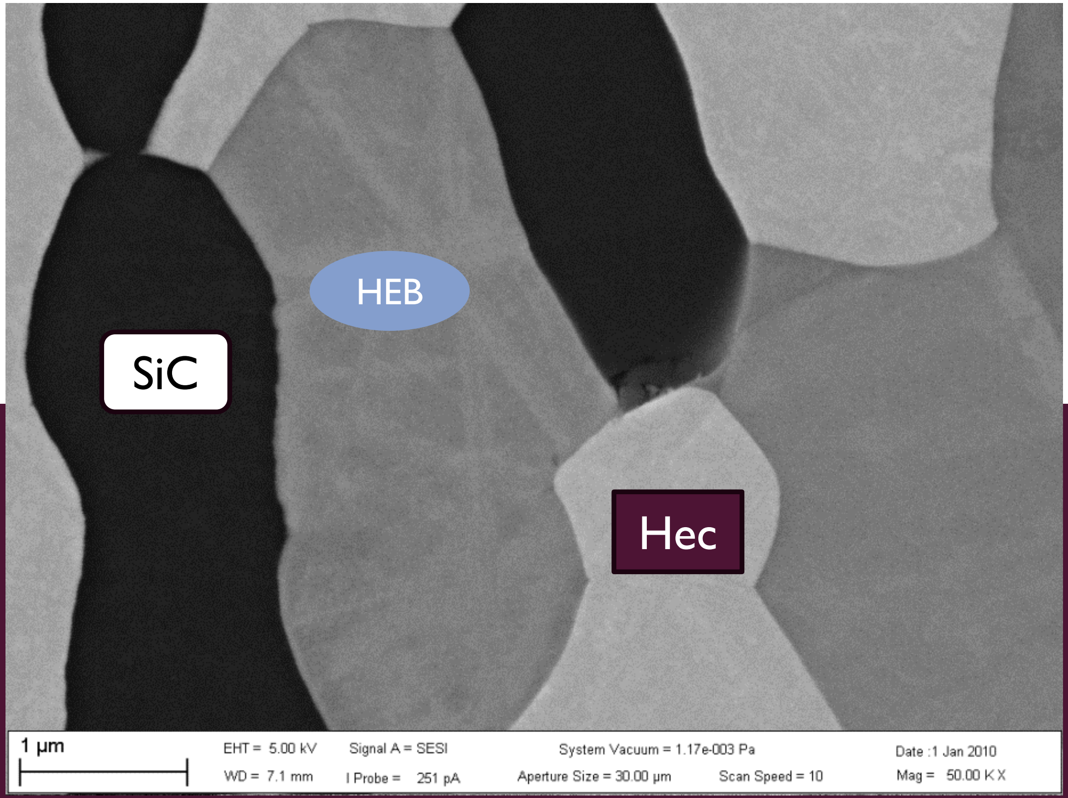
5% SiC

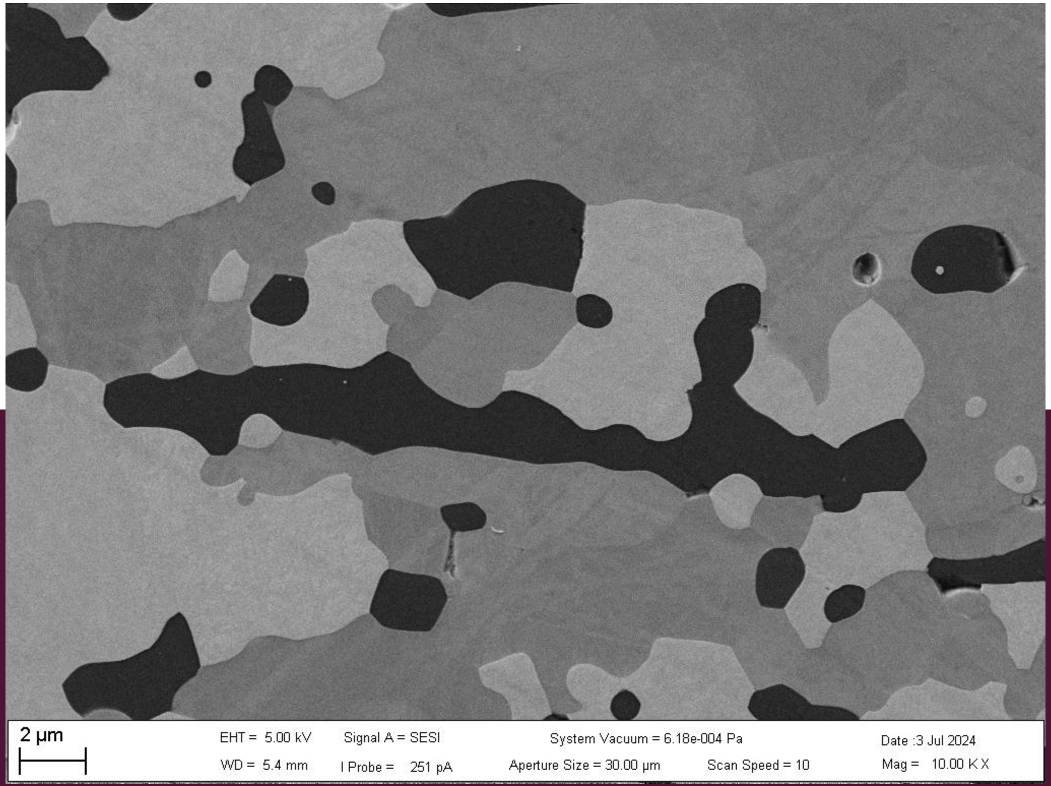
Microstructure of DPHE-UHTC + SiC whiskers composites

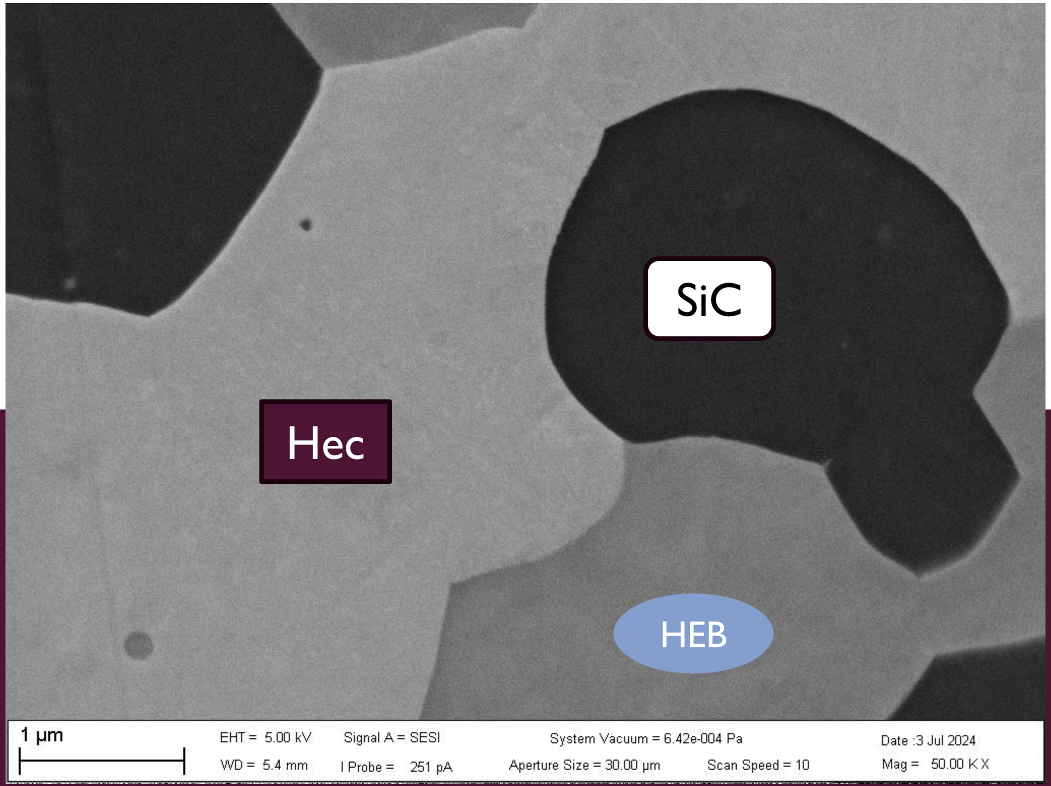




Microstructure of DPHE-UHTC + SiC whiskers composites

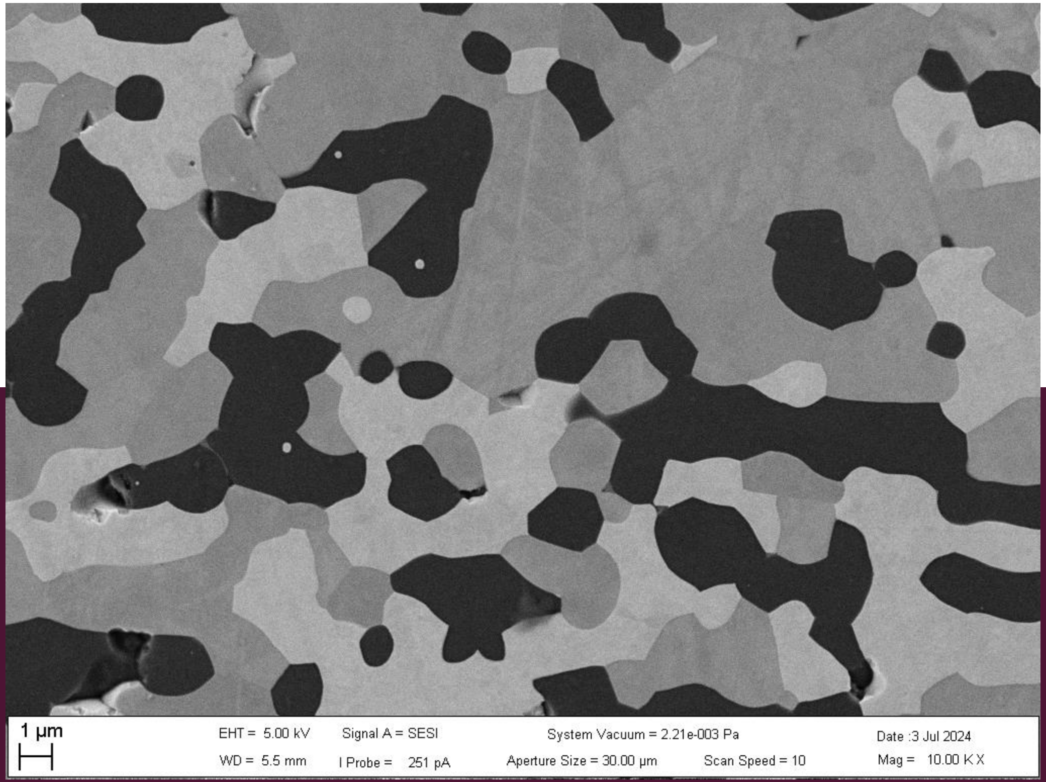
10% SiC

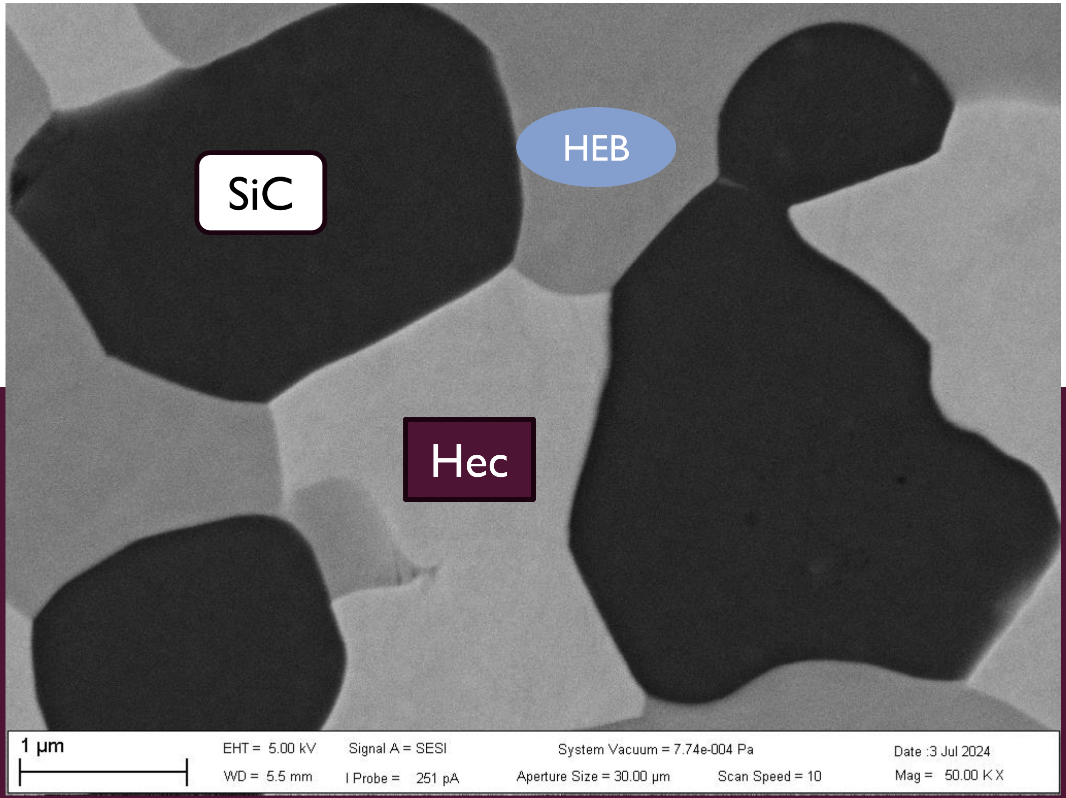




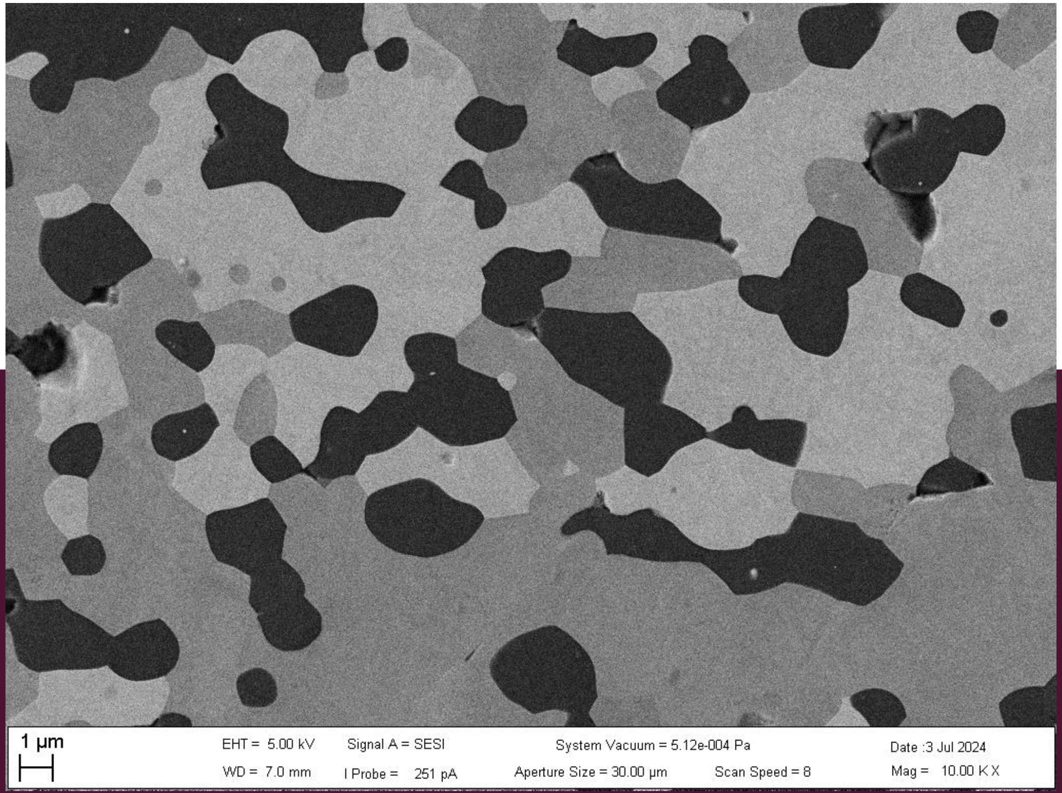
15% SiC

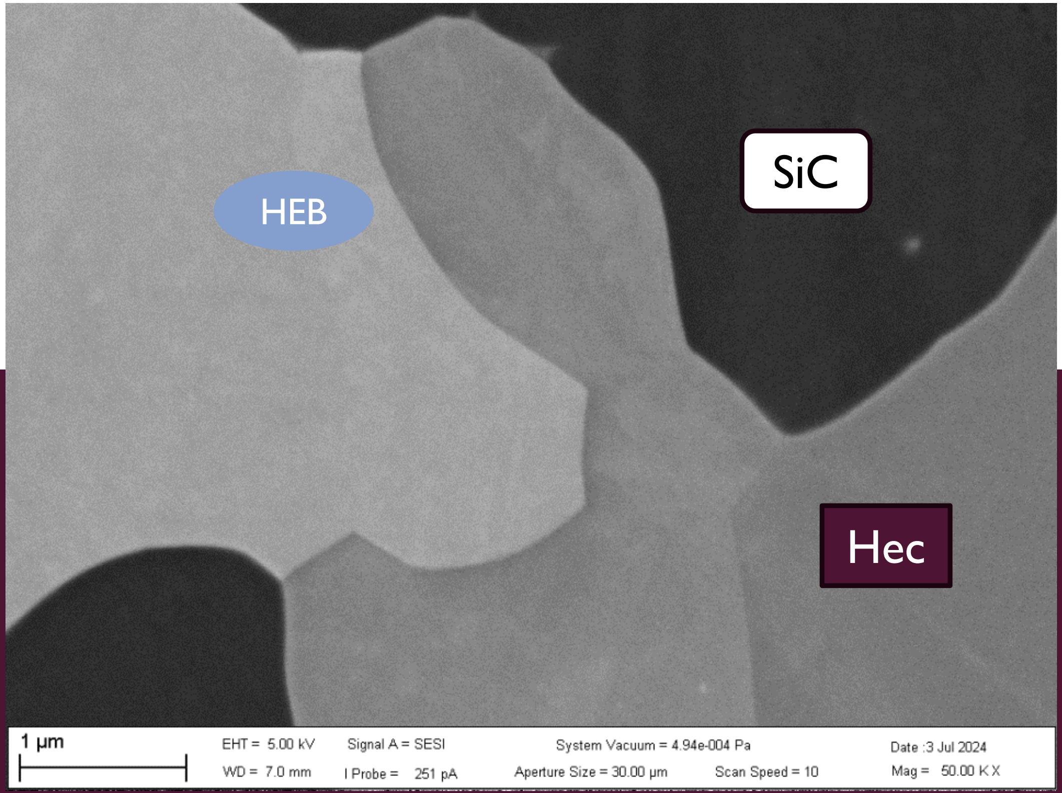
Microstructure of DPHE-UHTC + SiC whiskers composites





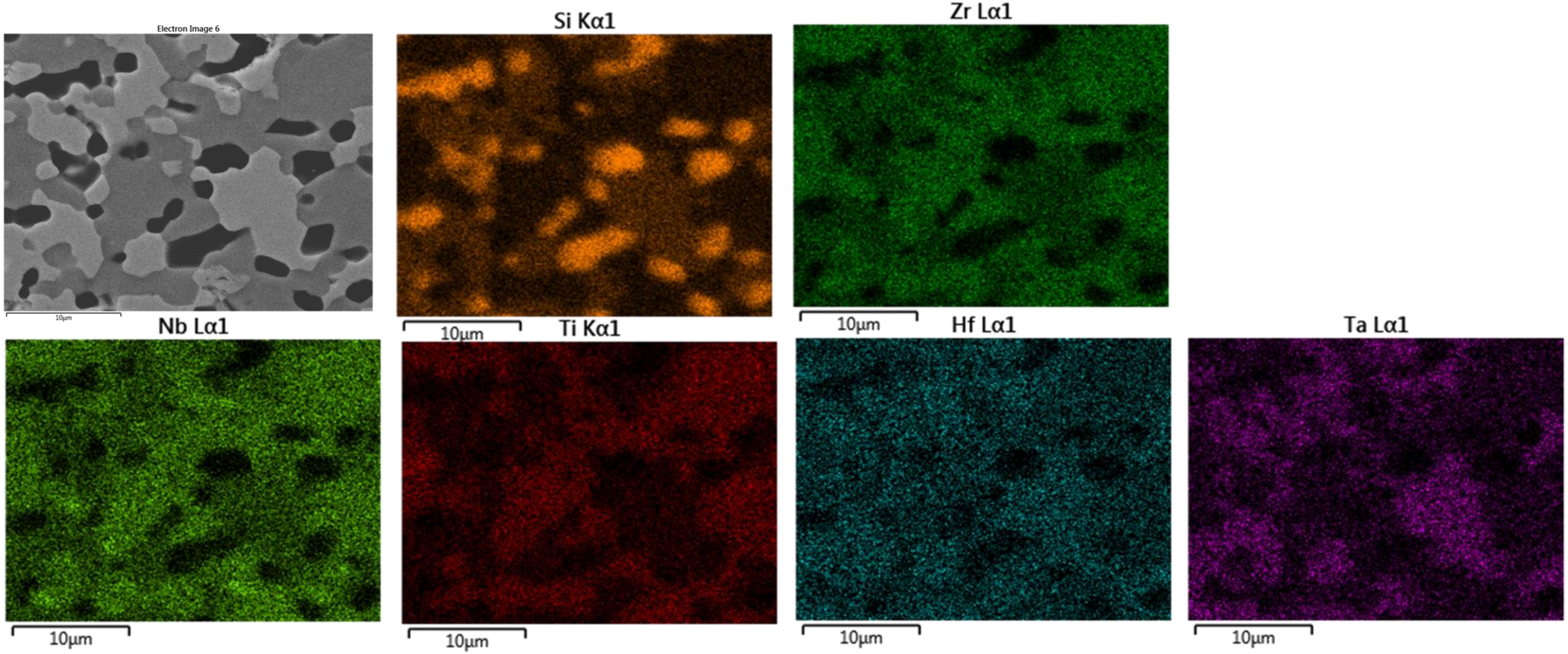
Microstructure of DPHE-UHTC + SiC whiskers composites



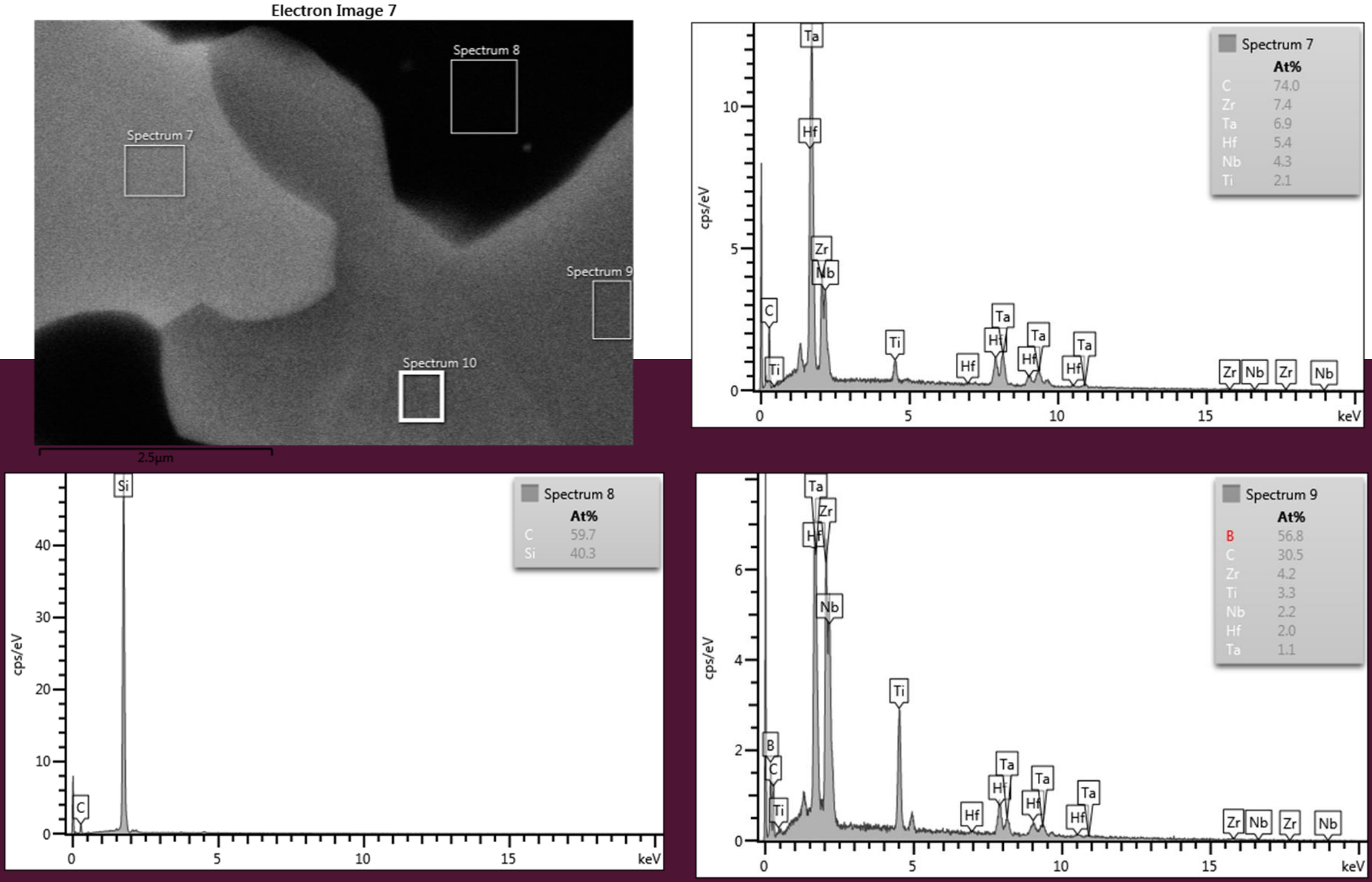


Processing of DPH+SiCw composites

10% SiC



20% SiC

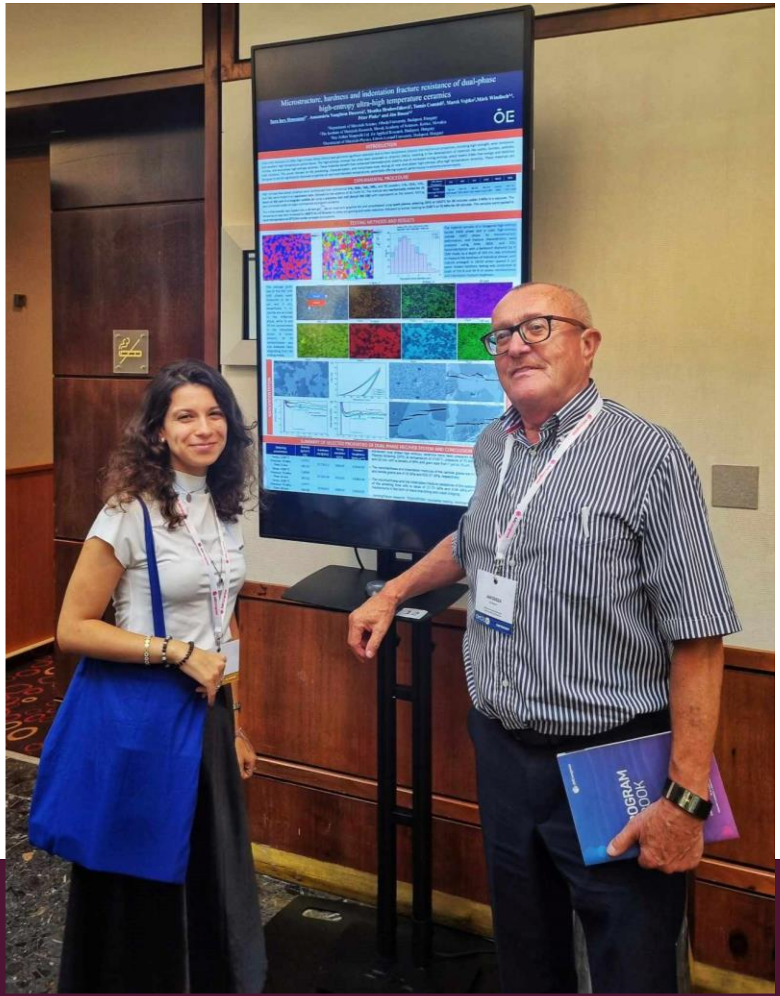


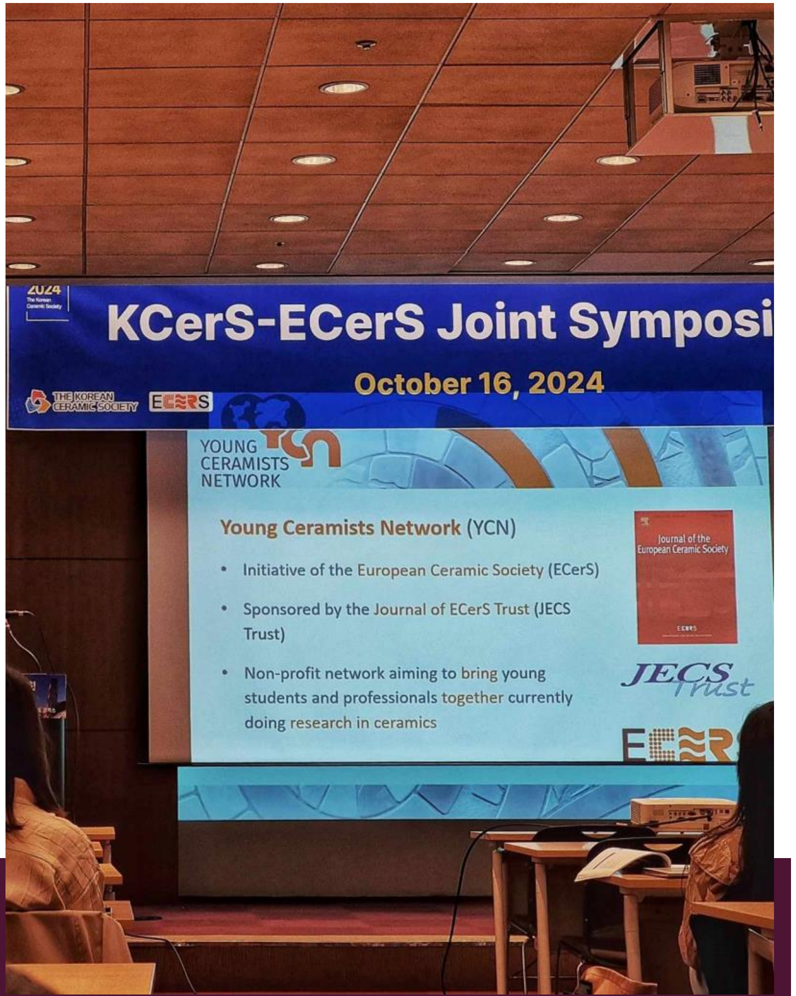
Electron Image 7
Spectrum 7
Spectrum 8
Spectrum 9
Spectrum 10
2.5µm
Spectrum 7
At%
C 74.0
Zr 7.4
Ta 6.9
Hf 5.4
Nb 4.3
Ti 2.1
Spectrum 8
At%
C 59.7
Si 40.3
Spectrum 9
At%
B 56.8
C 30.5
Zr 4.2
Ti 3.3
Nb 2.2
Hf 2.0
Ta 1.1
cps/eV
keV

Conference participation

- **15th Engineering Symposium in Bánkiban (ESB)** (November 2024, Hungary): Presented ongoing research findings in an oral presentation titles " Microstructural investigation of dual phase boride/carbide based high-entropy ceramics."
- **2024 Fall Meeting of the Korean Ceramic Society** (October 2024, Seoul,Korea): Delivered an oral presentation on the "Development of boride/carbide dual-phase high-entropy ceramics."
- **14th International Conference on Ceramic Materials and Components for Energy and Environmental Systems (CMCEE)** (August 2024, Budapest): Presented a poster on the "Microstructure, hardness, and indentation fracture resistance of dual-phase high-entropy ultra-high temperature ceramics."
- **14th Engineering Symposium in Bánkiban (ESB)** (November 2023, Budapest): Gave an oral presentation and published work titled " High Entropy Ceramics: A Brief Introduction."


CMCEE 14
14TH INTERNATIONAL CONFERENCE ON CERAMIC MATERIALS AND COMPONENTS FOR ENERGY AND ENVIRONMENTAL SYSTEMS


Microstructure, hardness and indentation fracture resistance of dual-phase high-entropy ultra-high temperature ceramics


2024
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October 16, 2024
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YOUNG CERAMISTS NETWORK
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Sponsored by the Journal of ECerS Trust (JECS Trust)
Non-profit network aiming to bring young students and professionals together currently doing research in ceramics
Journal of the European Ceramic Society
JECS Trust

Upcoming events

- The 2025 edition of the young Ceramists Additive Manufacturing Forum (yCAM) will take place at INP-ENSIACET, Toulouse, France, from 23rd to 25th April 2025.
- The second International Conference of the Croatian Ceramic Society "Advanced Configurations in Derivative Ceramics" will be organised in ŠIBENIK, Croatia, from 30th April to 3rd May 2025.
- The 8th International Conference on the Characterization and Control of Interfaces for High Quality Advanced Materials (ICCCI2025) will be held from July 8th to 11th, 2025, Fujiyoshida, Japan.
- The XIX ECerS Conference and Exhibition will be held from 31th August to 4th September 2025 in Dresden, Germany.
- The 19th Unified International Technical Conference on Refractories will be hosted by ALAFAR (Latin American Association of Refractories Manufacturers) on 27-30 October 2025 in Cancun, Mexico.

THANK YOU