Ultra-High Temperature Ceramics: Materials For Extreme Environment Applications V

Proceedings

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Ultra-high temperature ceramics with exceptional strength at elevated temperature

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ULTRA-HIGH TEMPERATURE CERAMICS WITH EXCEPTIONAL STRENGTH AT ELEVATED TEMPERATURE

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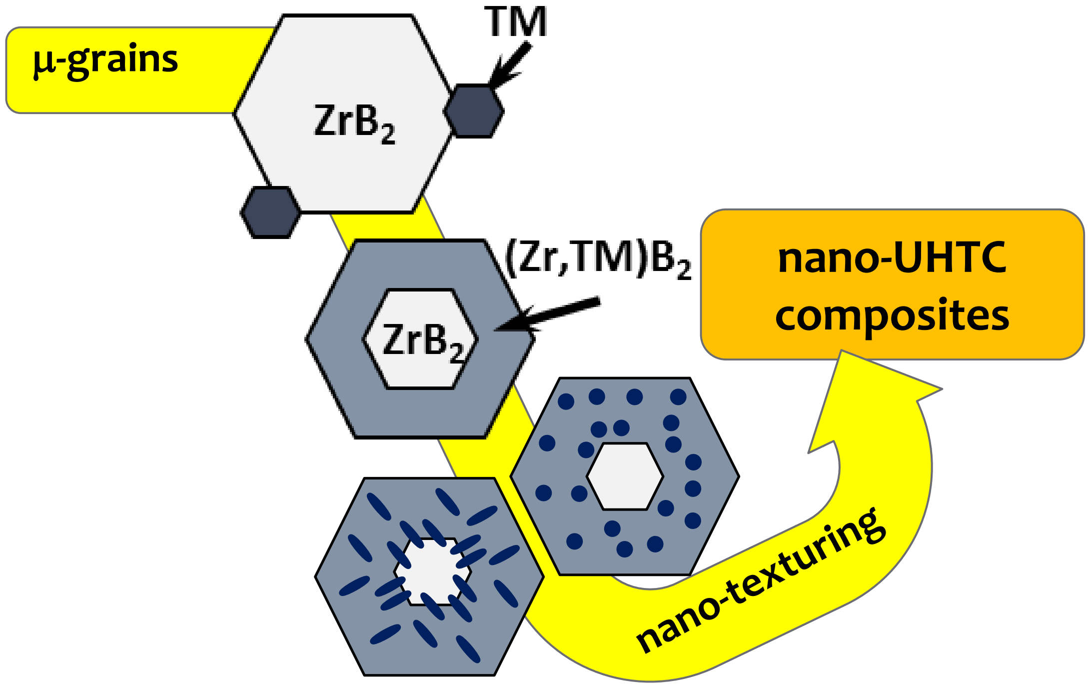
Goal & Approach

Multi-scale microstructure arrangement in ZrB_2 ceramics



1. Understanding basic phenomena

- CORE-SHELL formation by addition of transition metal (TM)
- How to SUPER-SATURATE the shell to precipitate nano-inclusions within μm-sized grain

2. Custom-making nano UHTC composites

- PHASE STABILITY DIAGRAMS define the partial pressure conditions within the sintering chamber that drive precipitation of nano-inclusions of variable nature.

Materials:

ZrB_2: refractoriness & ablation resistance

SiC or Silicide: formation of SiO_2

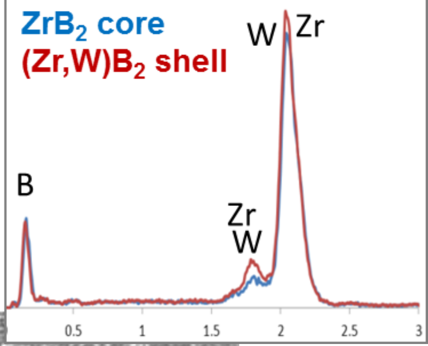
TM-compound: densification, refractoriness, oxidation & shell formation

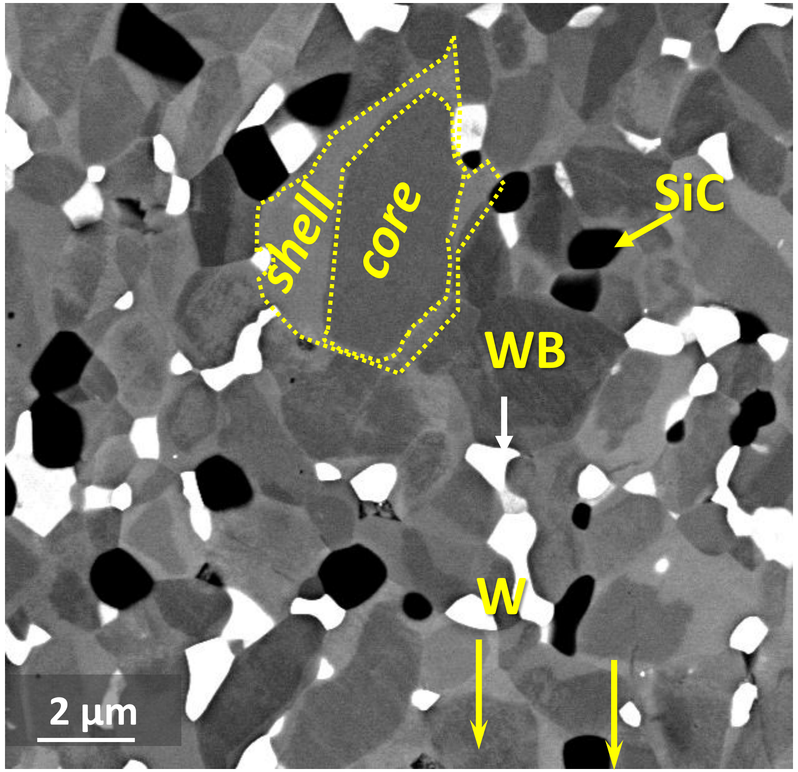
W: Low Solubility within ZrB_2 (~4 at%)

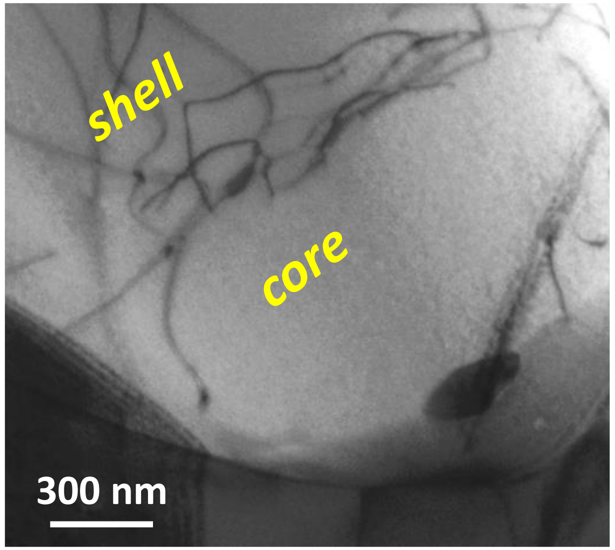
Ta: High Solubility within ZrB_2 (~15 at%)

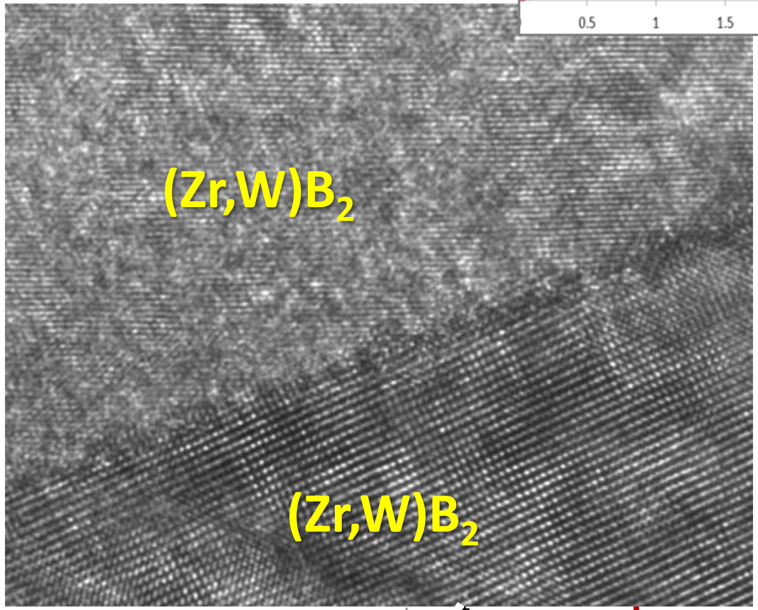
ZrB_2 – 3 SiC – 5 WC :

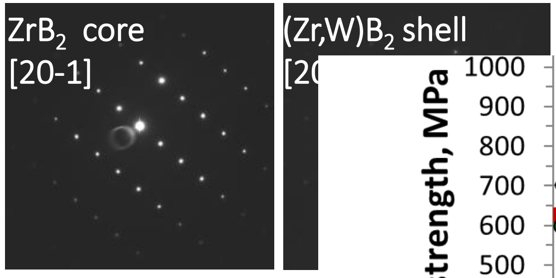
- Epitaxial $(Zr,W)B_2$ solid solution
- Dislocation accumulation at core/shell interface
- WC → WB
- Clean grain boundaries











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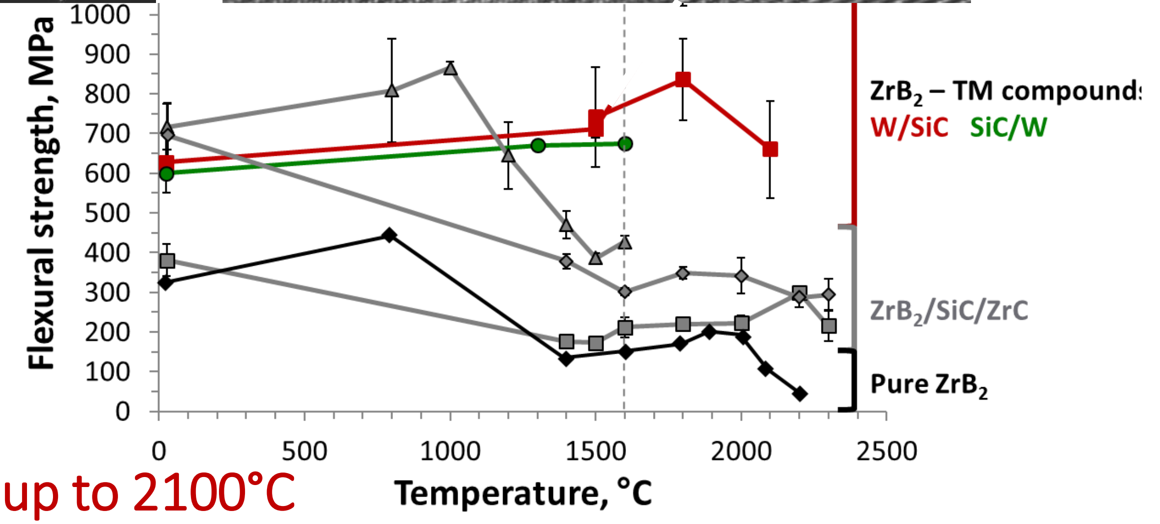
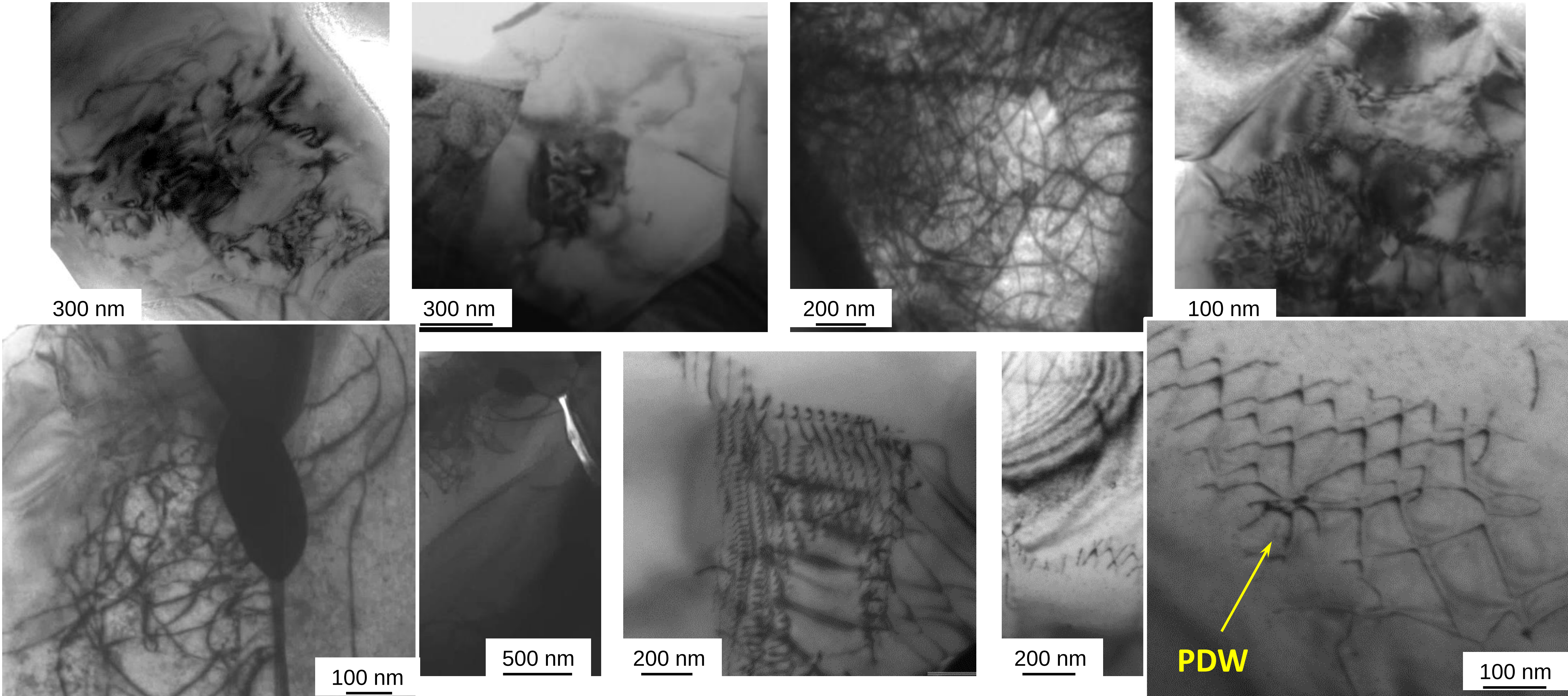


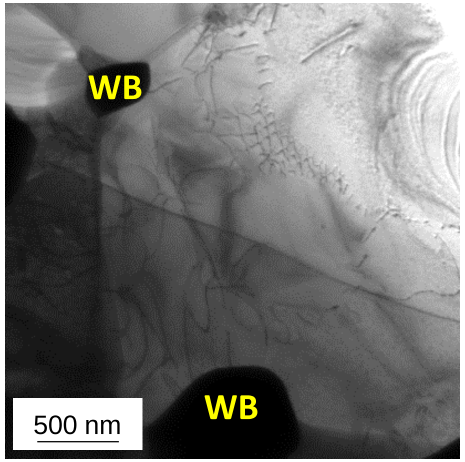
σ > 600 MPa up to 2100°C

ZSW upon σ1800, Ar: matrix

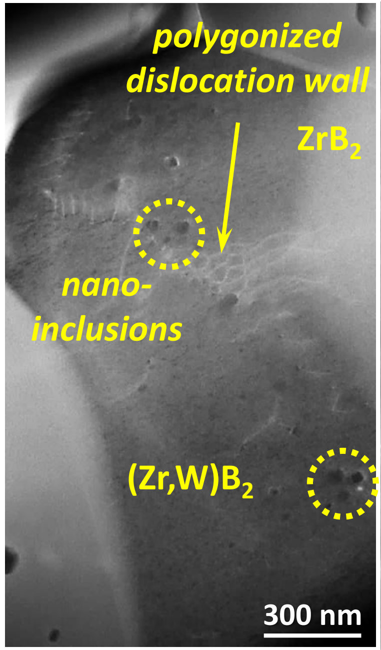
- Increased dislocations activity
- PDW at & across the core/shell boundary: grains refinement 2 μm→ 50 nm

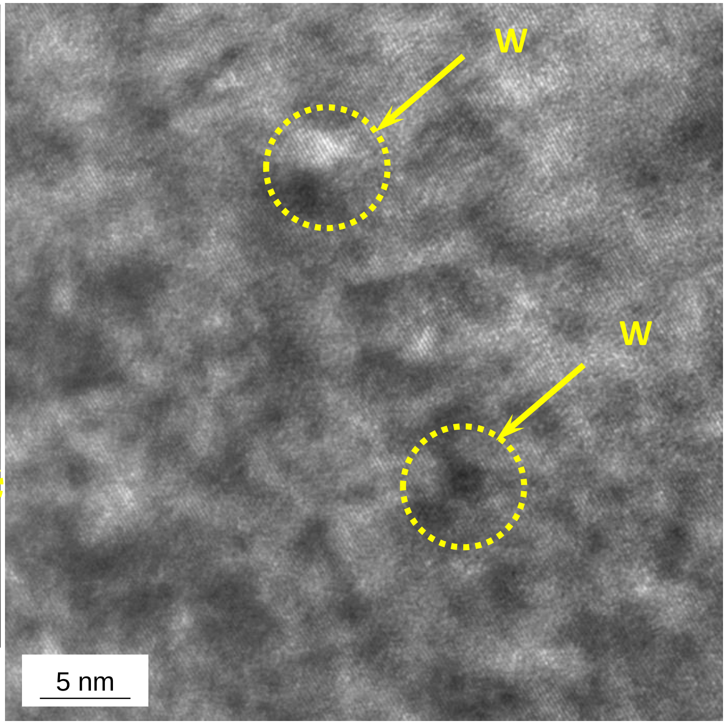


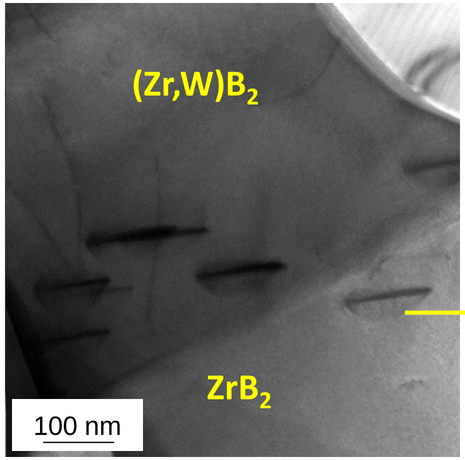
ZSW upon σ1800, Ar: core - shell

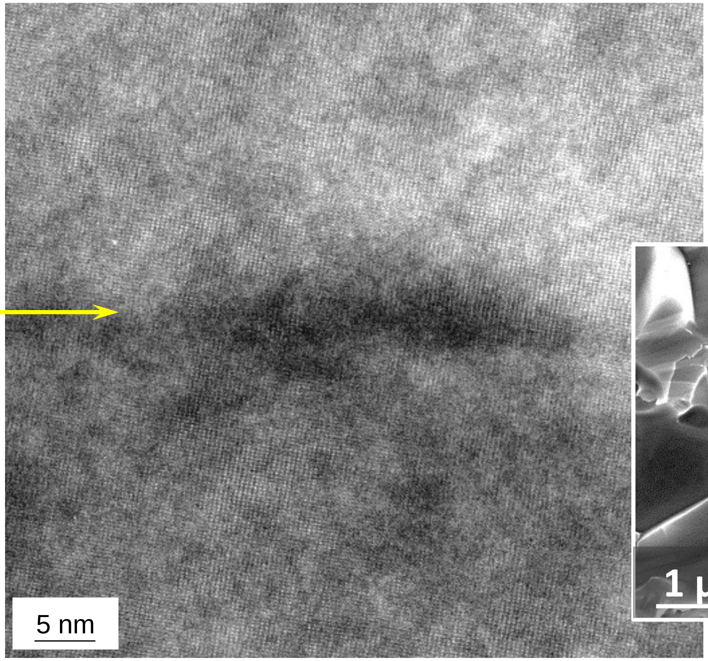


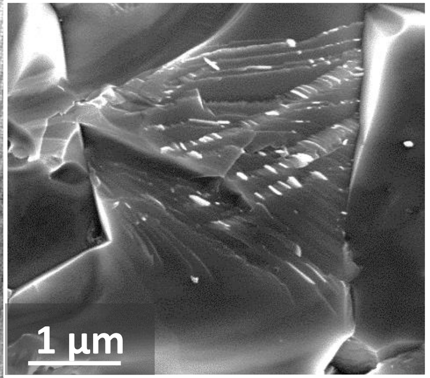
- Clean boride/boride interfaces
- Dislocations activity & crew
- W ppt at the core/shell boundary
- Bright W ppt on the fracture

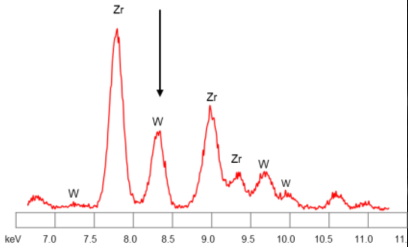


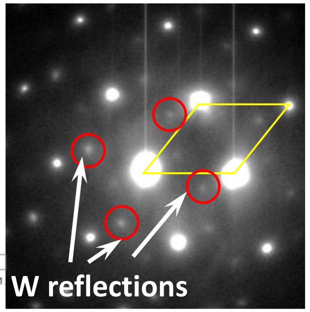




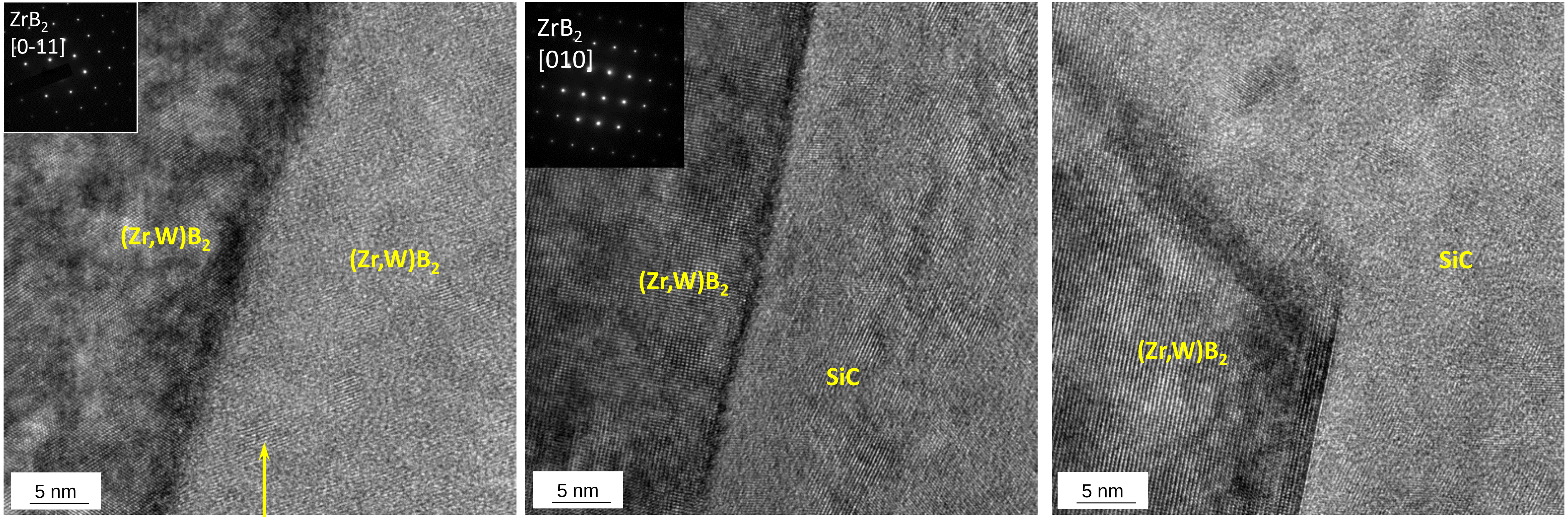


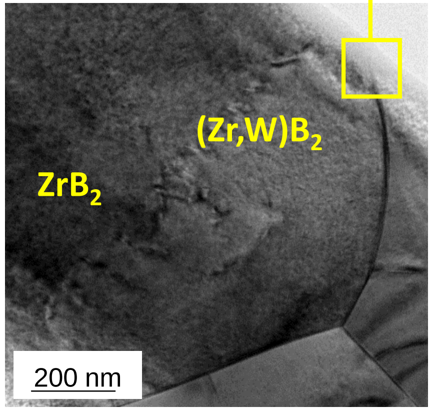






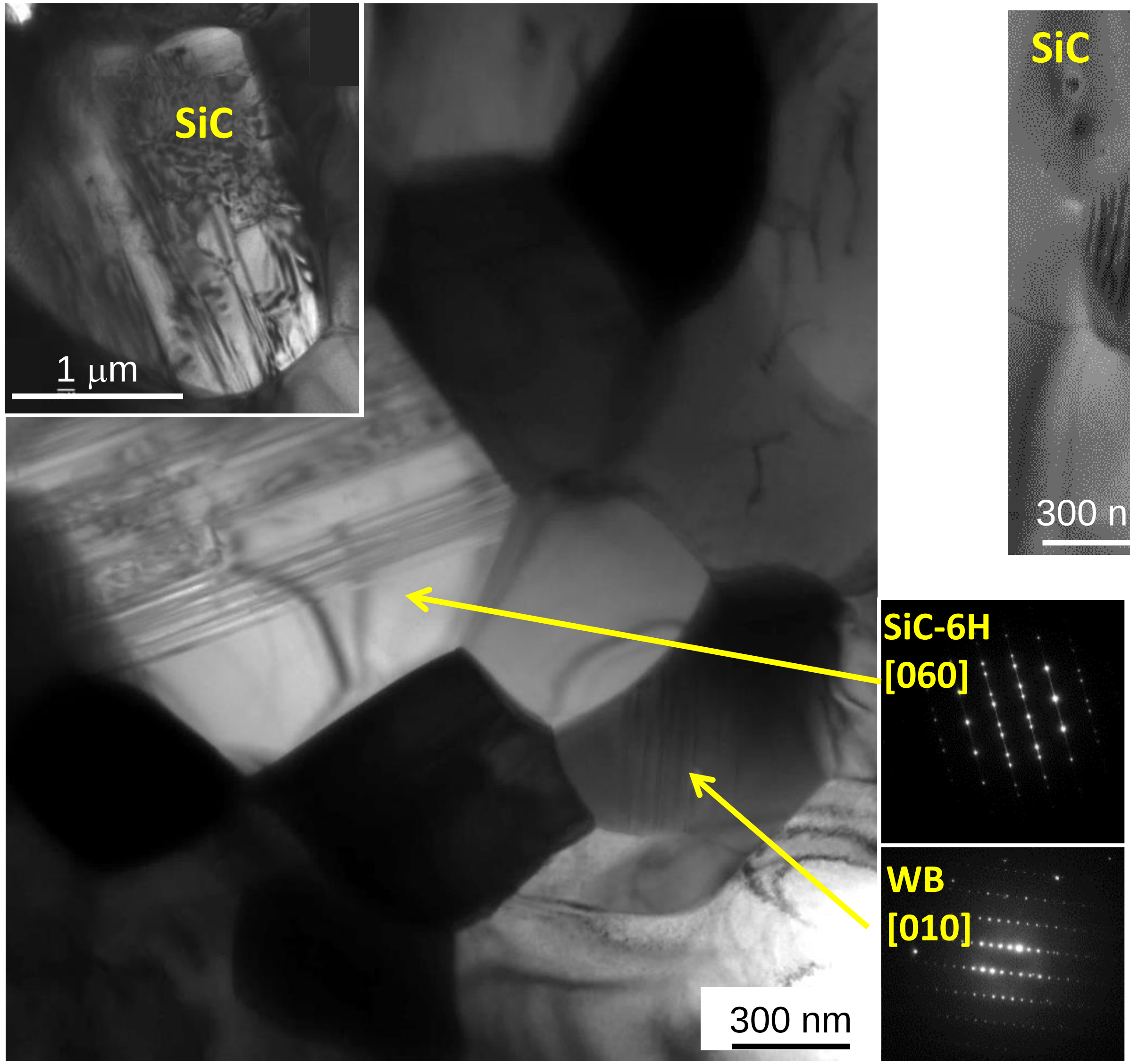
ZSW upon σ1800, Ar: grain boundaries

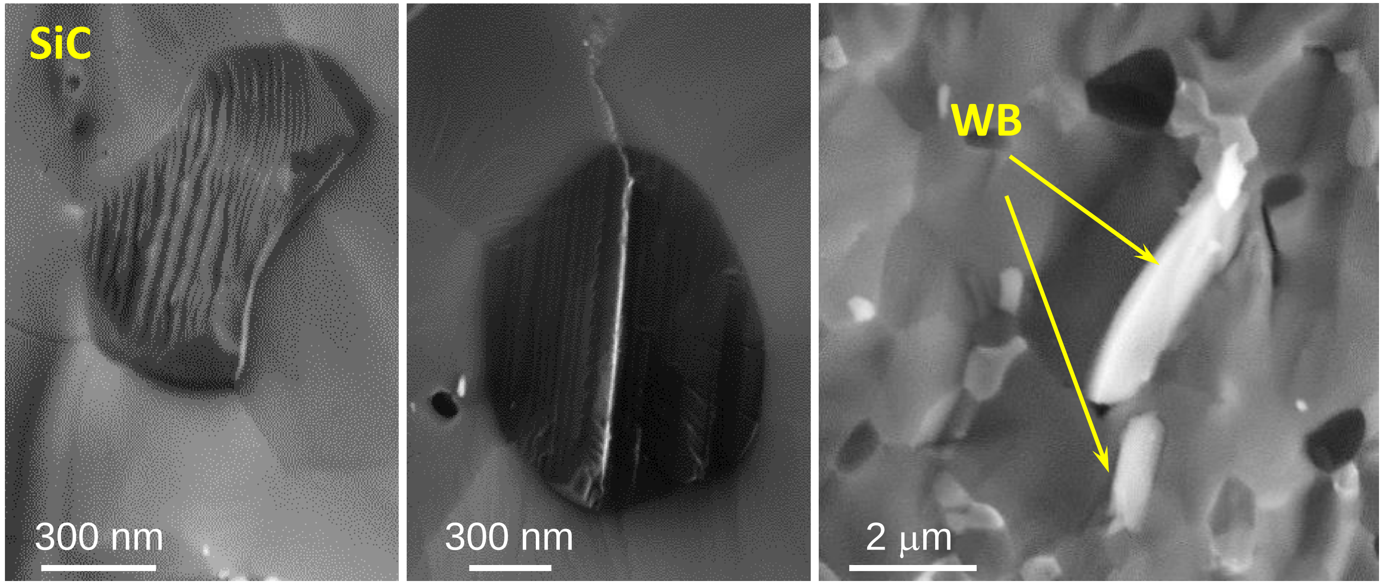




- Clean boride/boride interface
- Clean boride/SiC interface

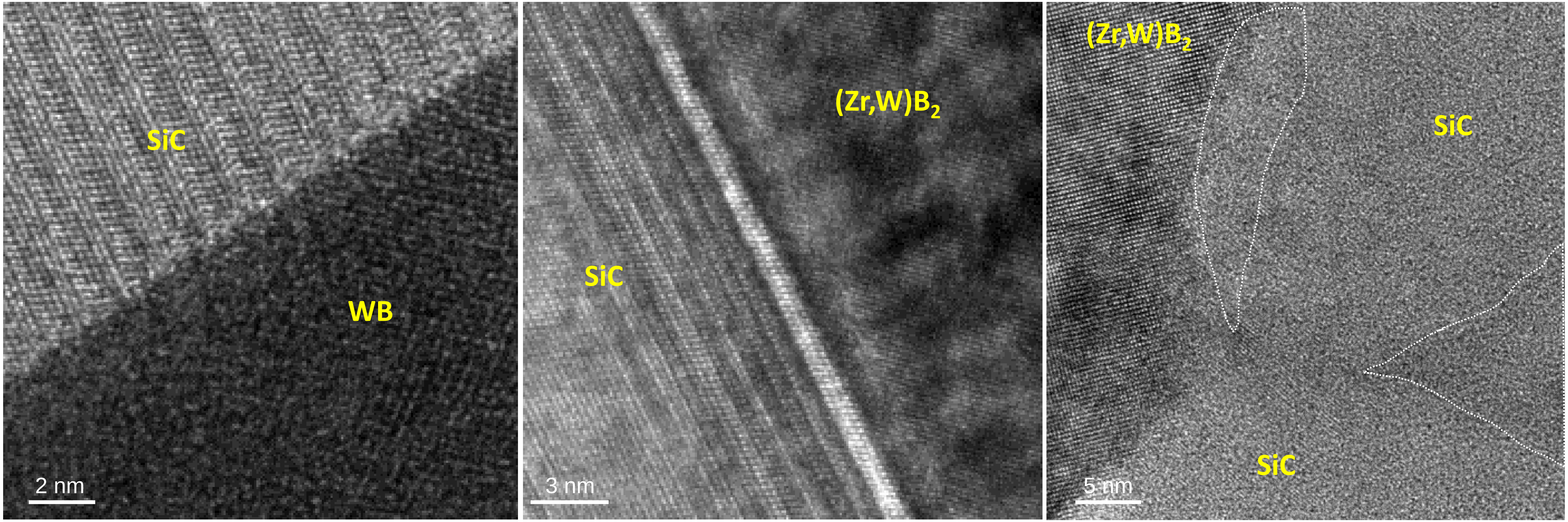
ZSW upon σ1800, Ar: second phases





- SiC, WB with stacking faults → pull-out, crack deflection

ZSW upon σ1800, Ar: second phases



- Wetted SiC/SiC interfaces → softening

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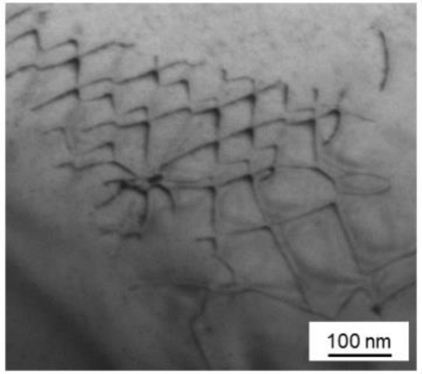
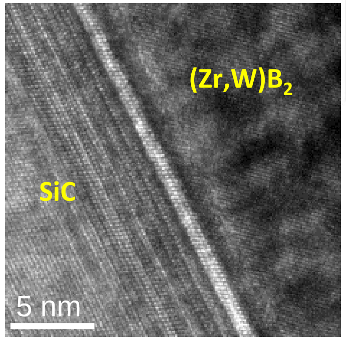
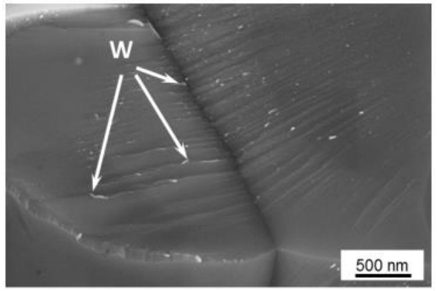
Strengthening at UHT

$\sigma = K_{Ic}/Y\sqrt{a}$

- ✓ Refractory phases ---- ZrB_2
- ✓ MGS preserved ---- grain refinement: dislocation movement and intersection, Petch-Hall hardening
- ✓ Clean grain boundaries --- WC
- ✗ Formation of a healing glassy layer --- test in Ar
- ✓ Reinforcing phases --- precipitation hardening & metal toughening (W is ductile and tough at HT)



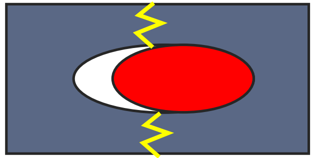




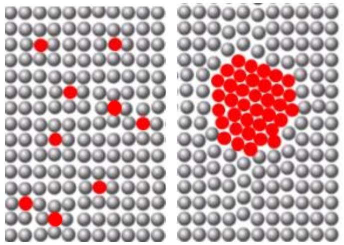
Local toughening at UHT

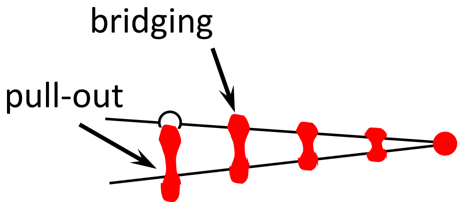
$\sigma = K_{Ic}/Y\sqrt{a}$

- SiC, WB platelets pull-out

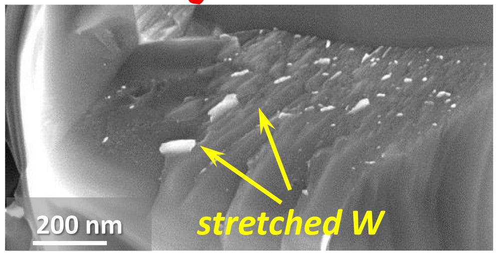


- W precipitation from the $(Zr,W)B_2$ solid solution

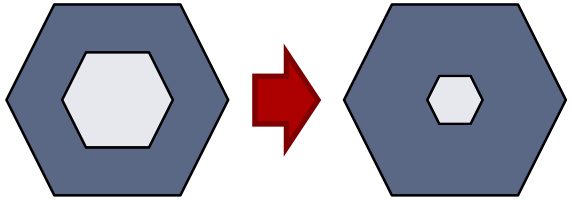




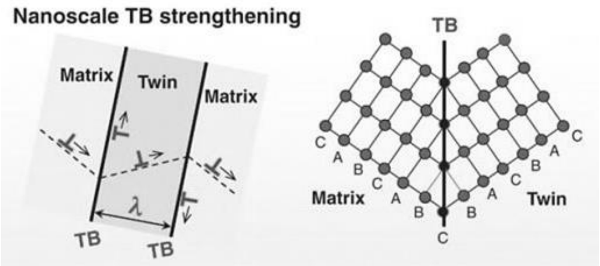
- W is ductile and tough at HT and absorbs fracture energy

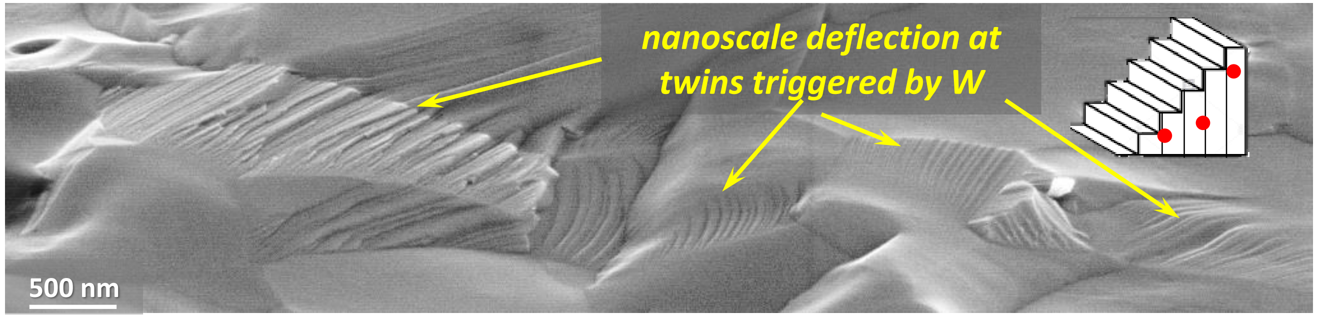


- M.g.s. is retained, but the shell region is enlarged



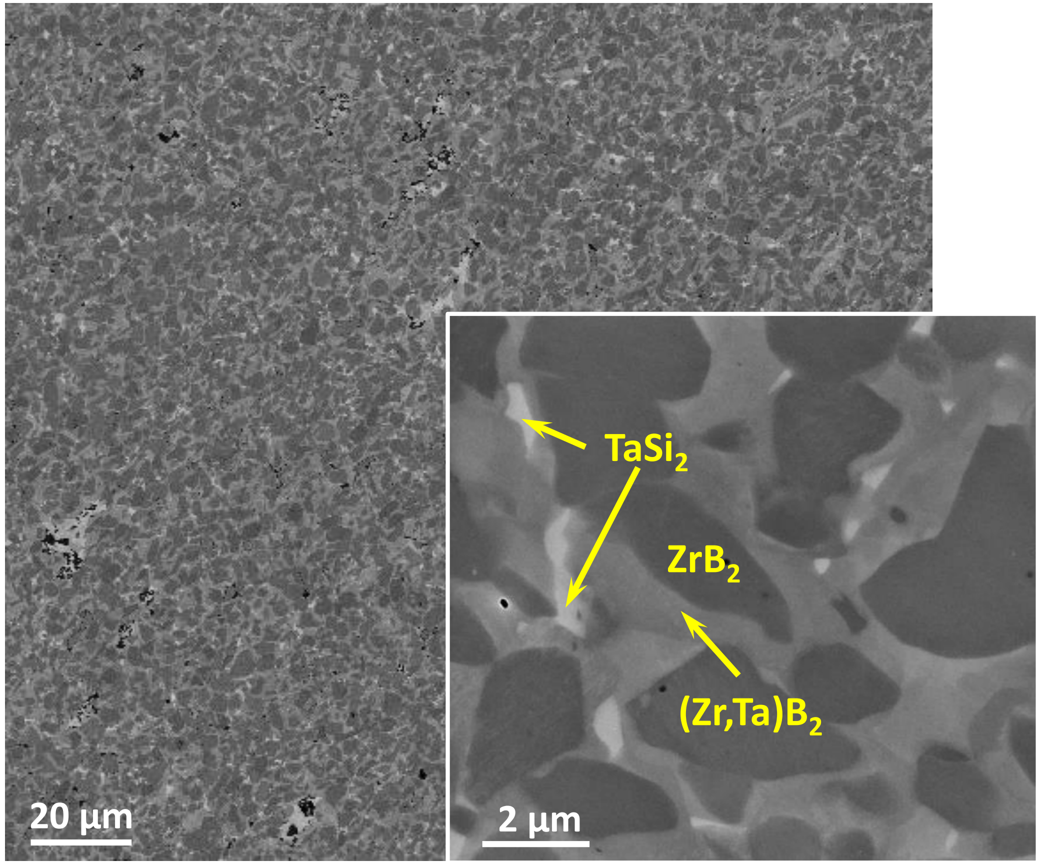
- Toughnening at nano-scale by twins and stacking faults





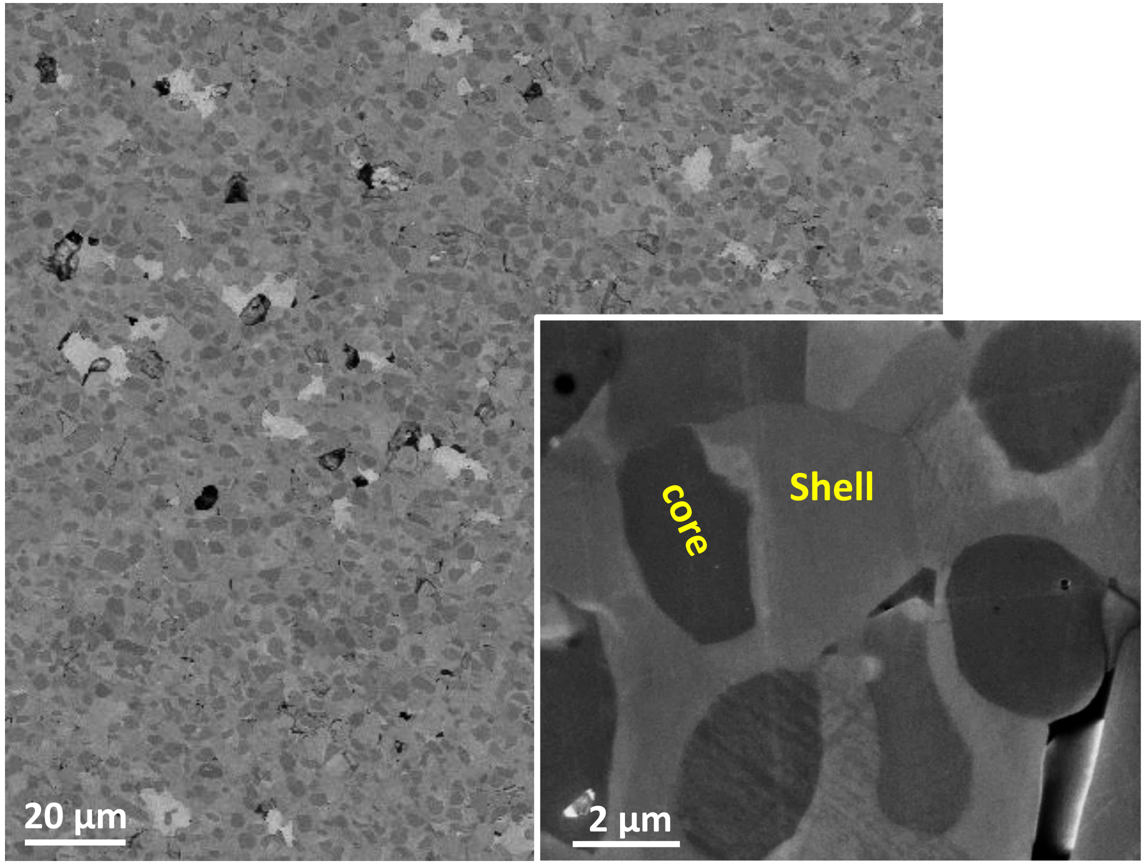
ZrB_2 - $TaSi_2$

As-sintered



- Formation of $(Zr,Ta)B_2$ shell (~40 vol%)
- Residual $TaSi_2$ and SiOC

Annealed



- Expansion of the shell (~60 vol%)
- SiOC conversion to SiC

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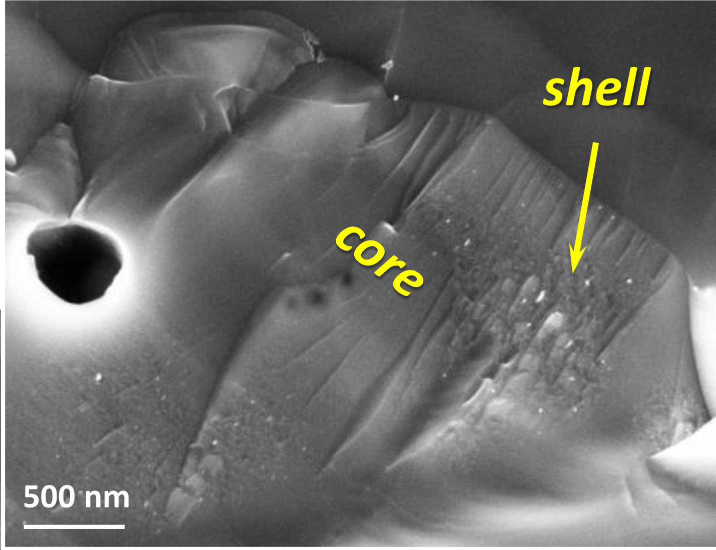
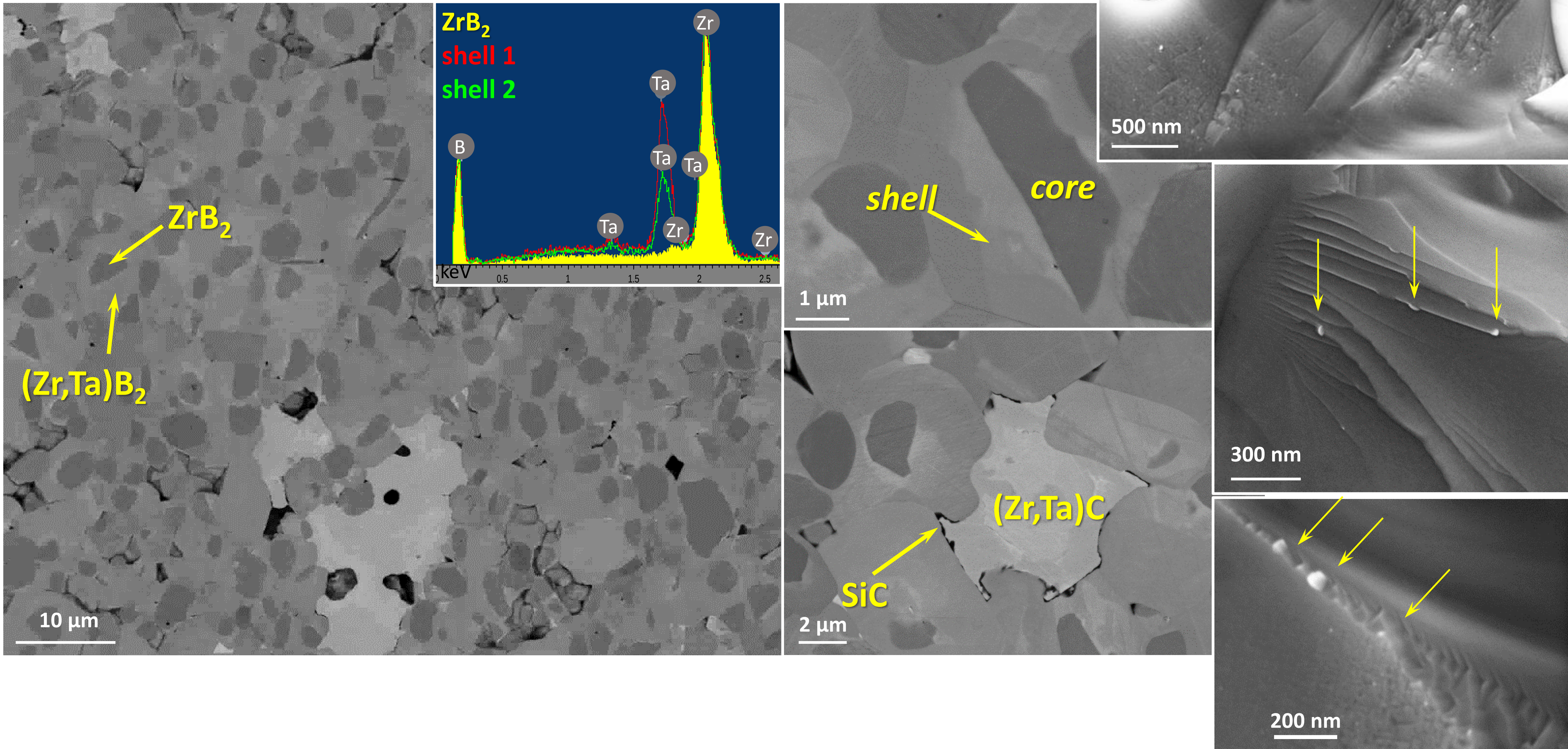
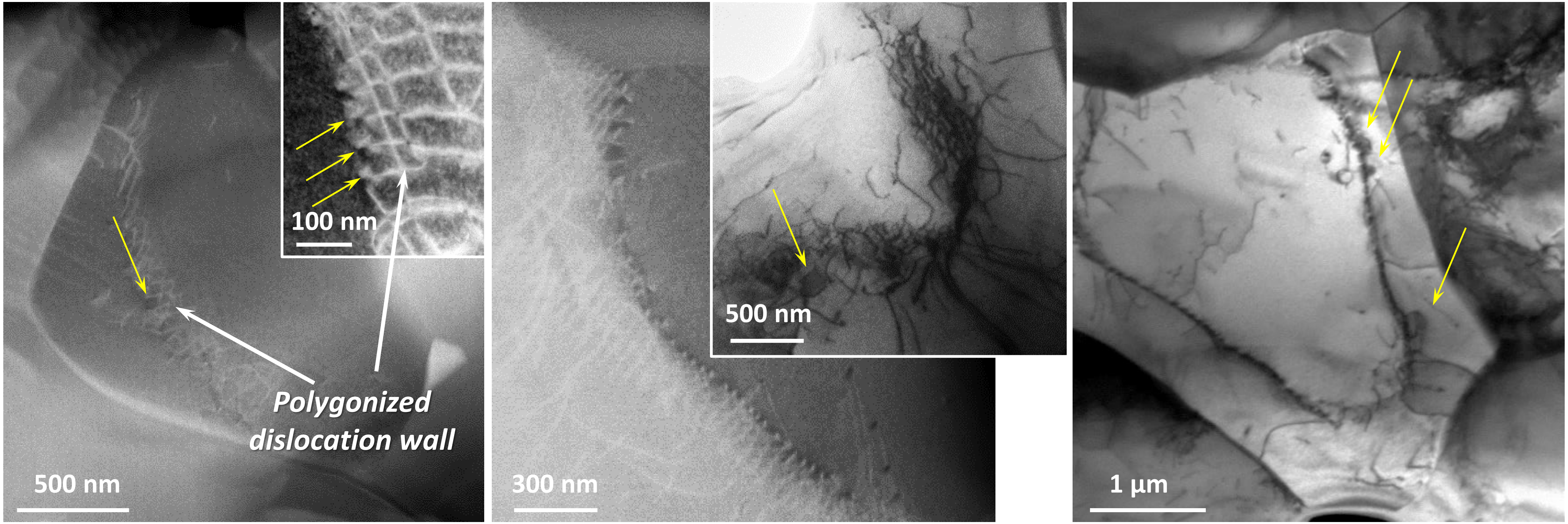
ZBT-ann

- (Zr,Ta)C second phase
- Smooth fracture in the core
- Zig-Zag fracture & nano-sized bright ppt in the shell





ZBT-ann: boride matrix



- Epitaxy between core and shell
- Intricate core-shell dislocation network
- Sharp core/shell interface, no clear definition between shell 1&2
- Dark inclusion at the core/shell interface

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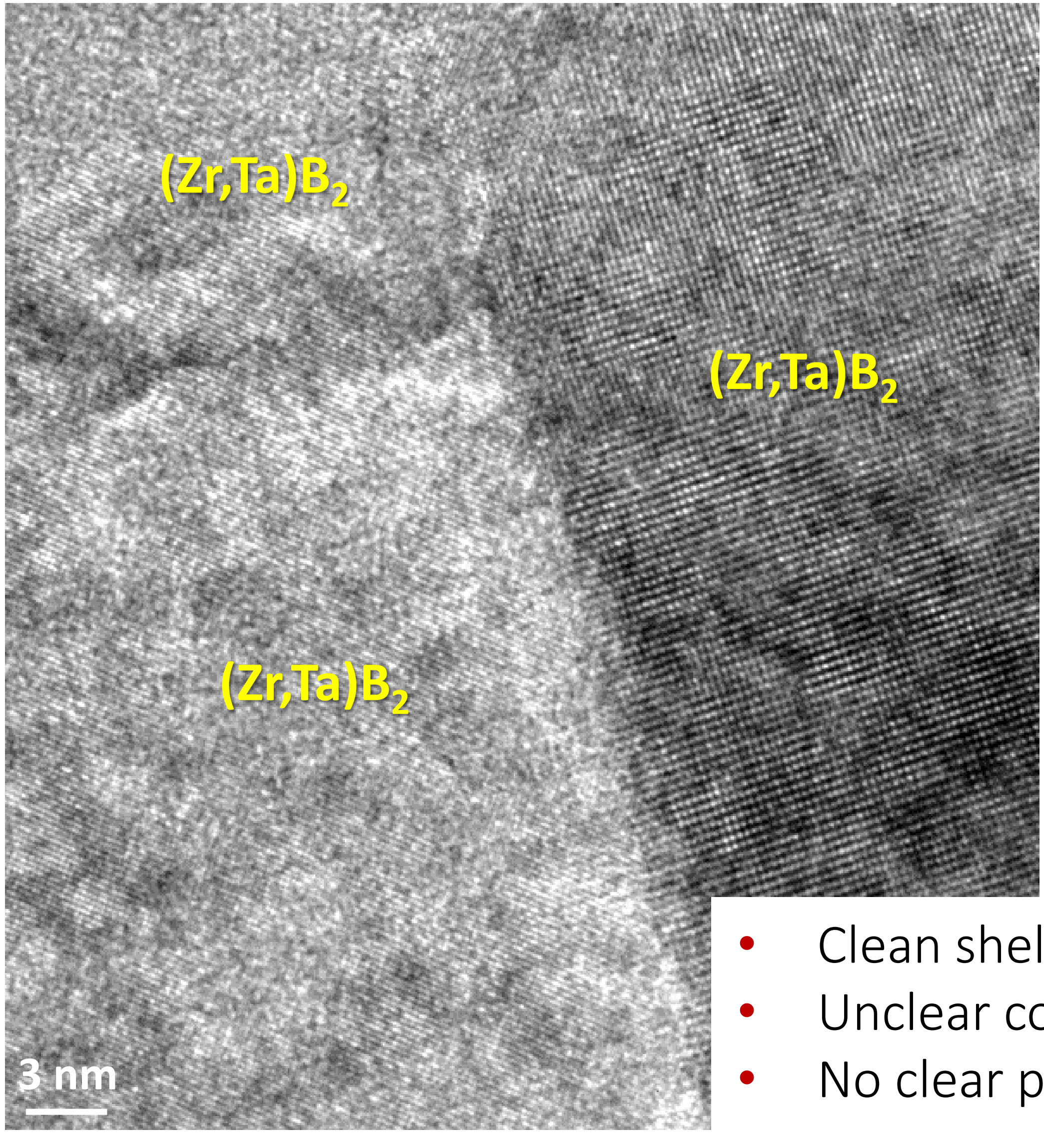
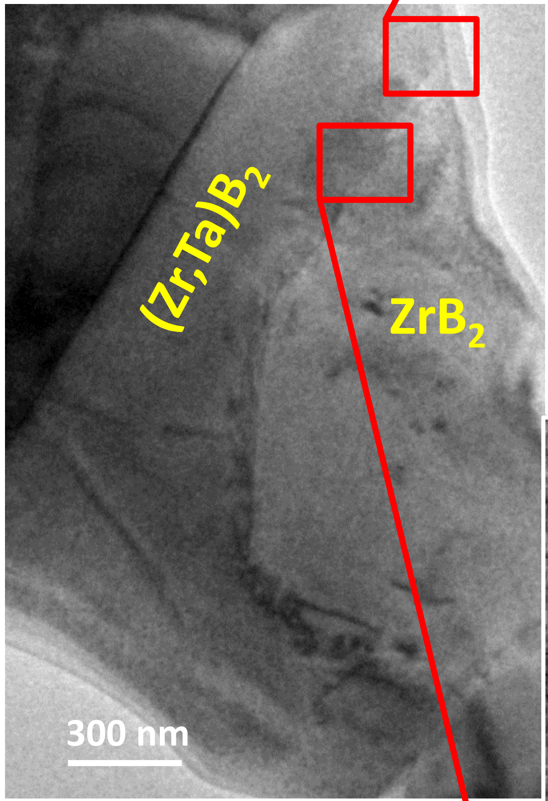
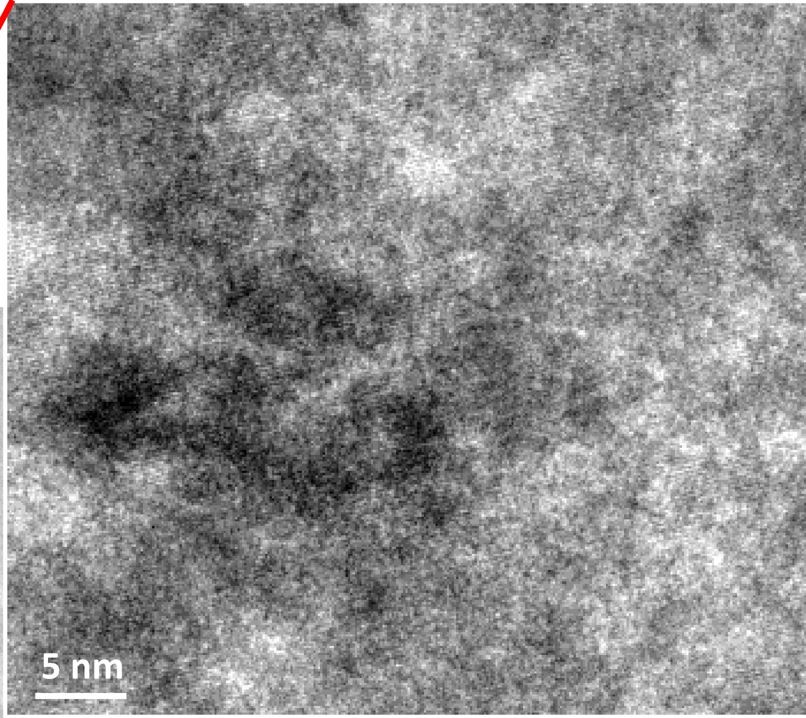
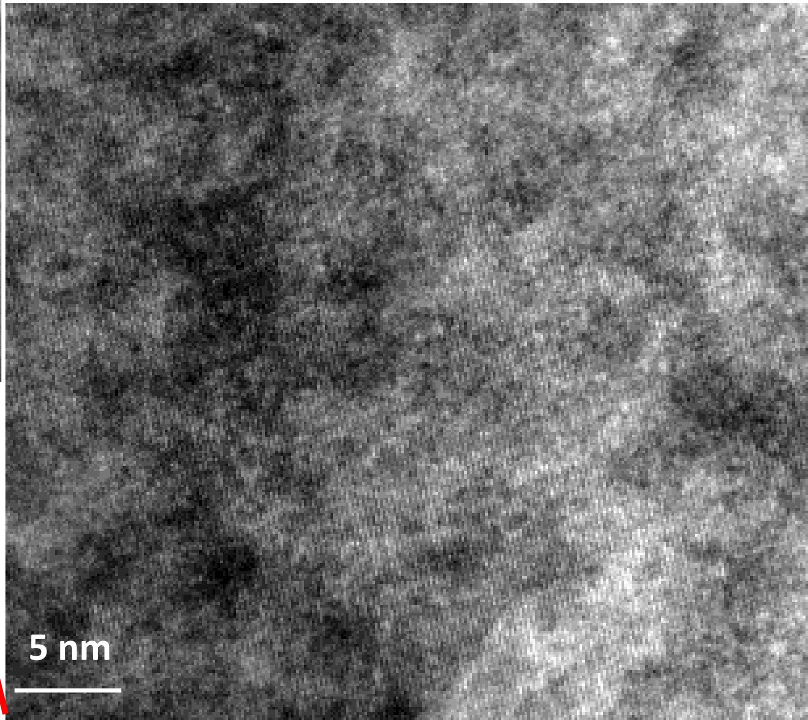
ZBT-ann: interfaces





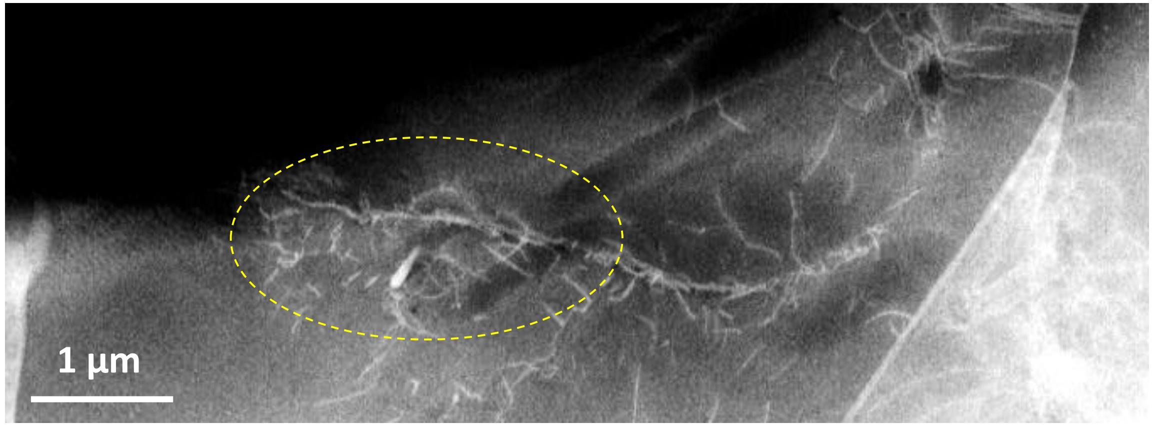


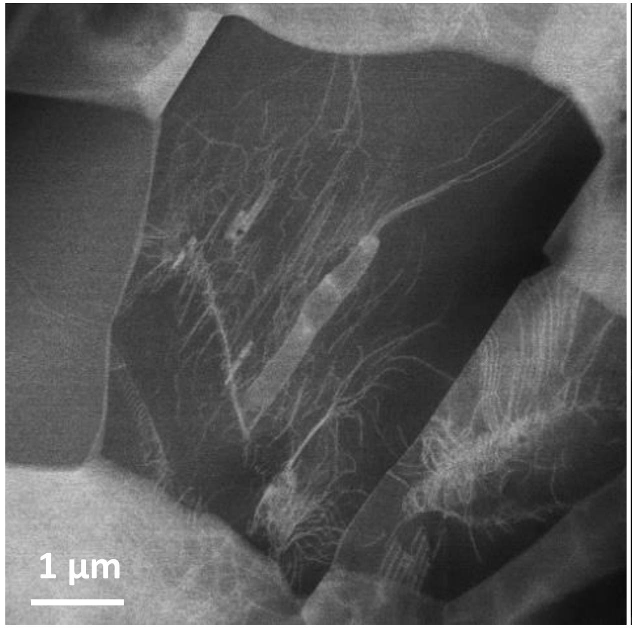


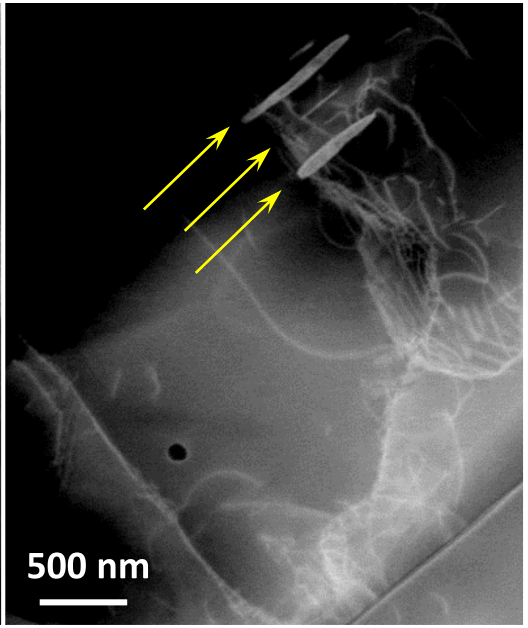
- Clean shell/shell gb
- Unclear core/shell boundary
- No clear ppt

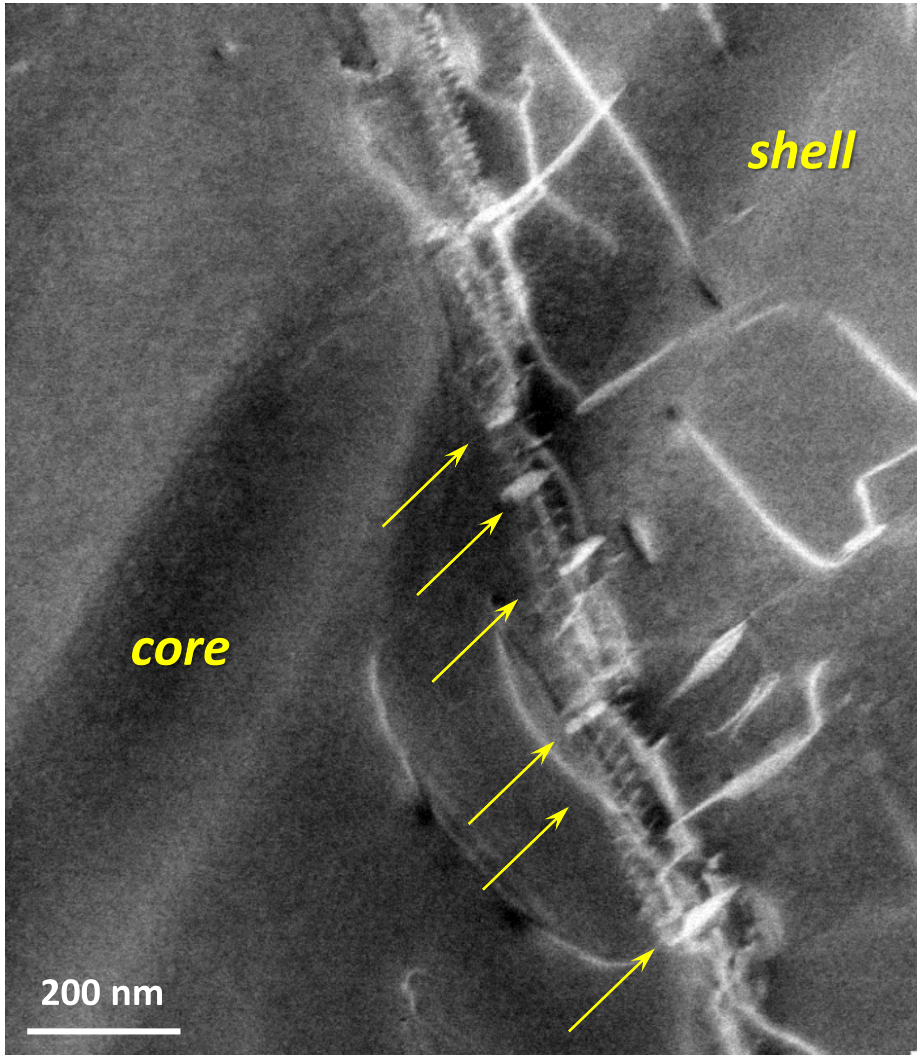
ZBT-ann: finally precipitates!

- Needles at core/shell interface

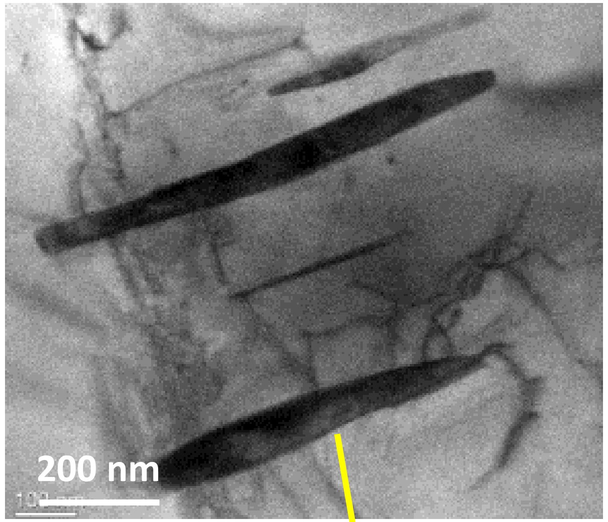


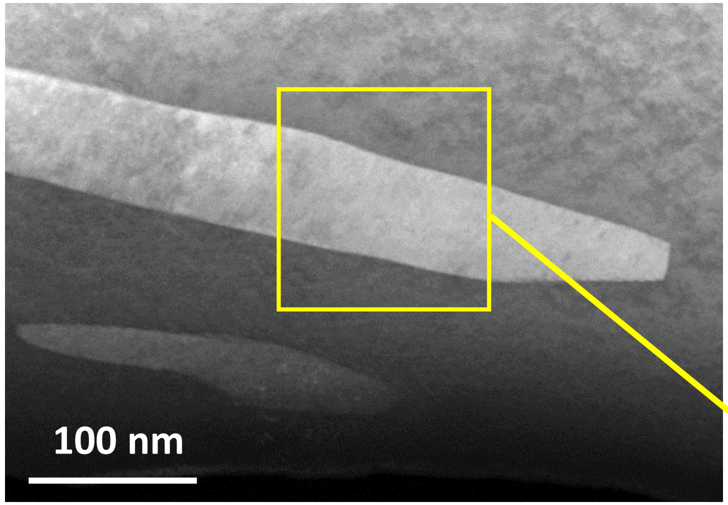


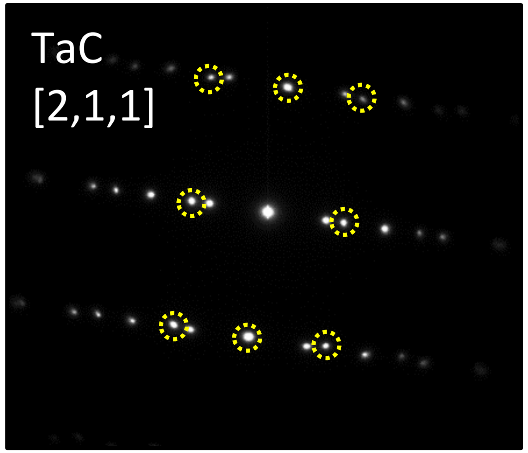


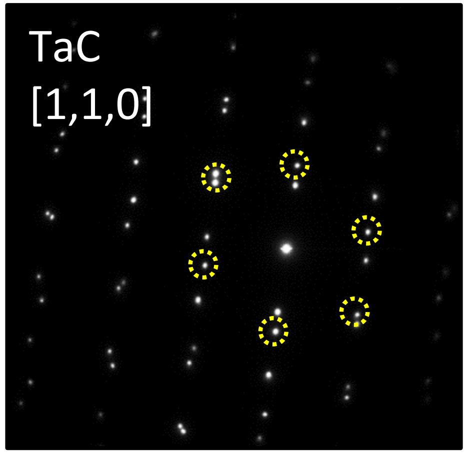


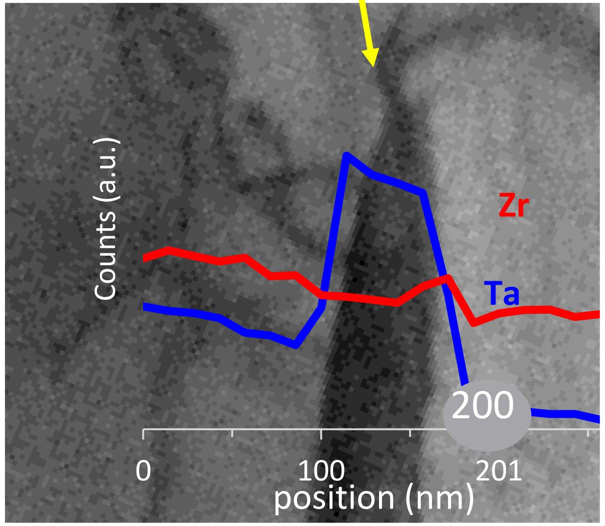
ZBT-ann: TaC needles

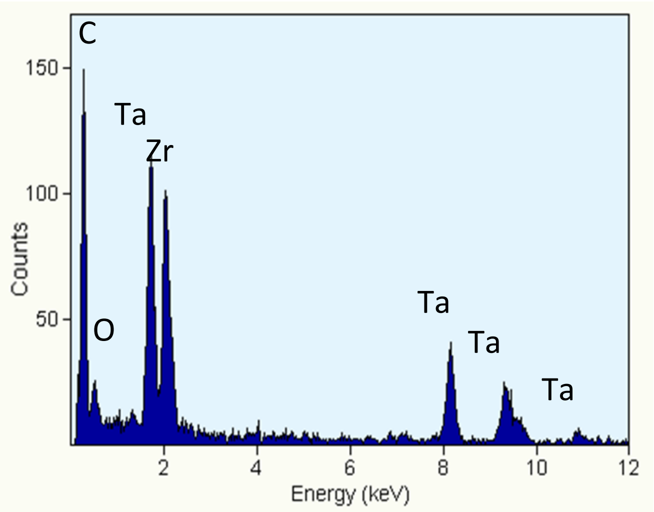


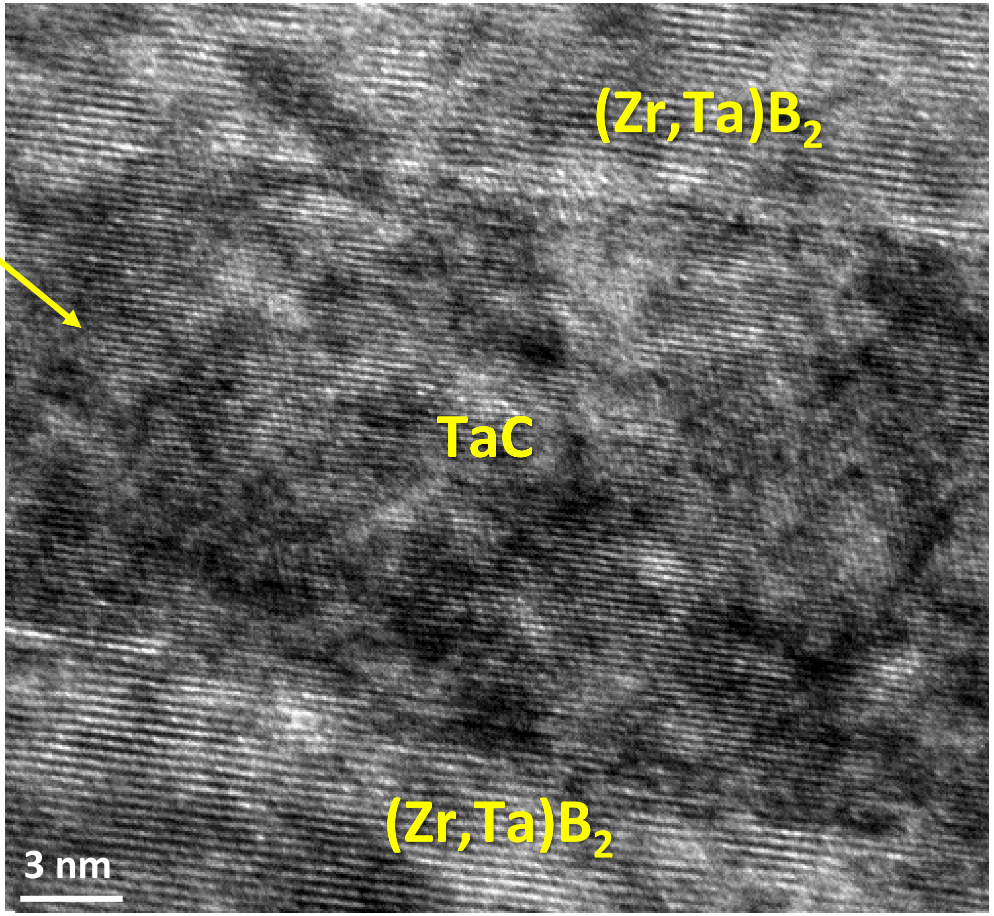












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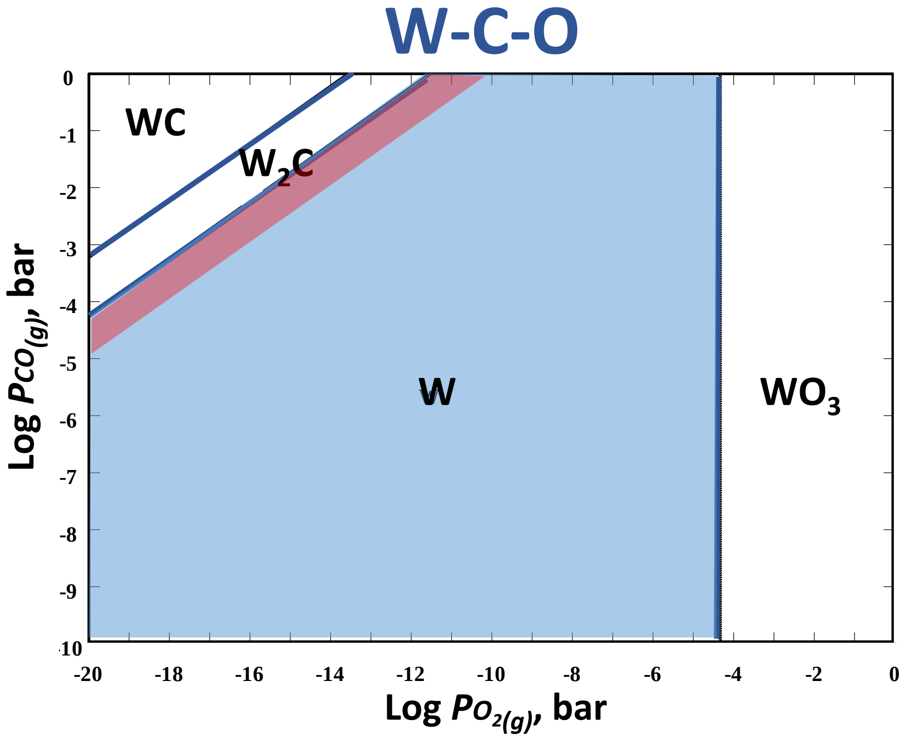
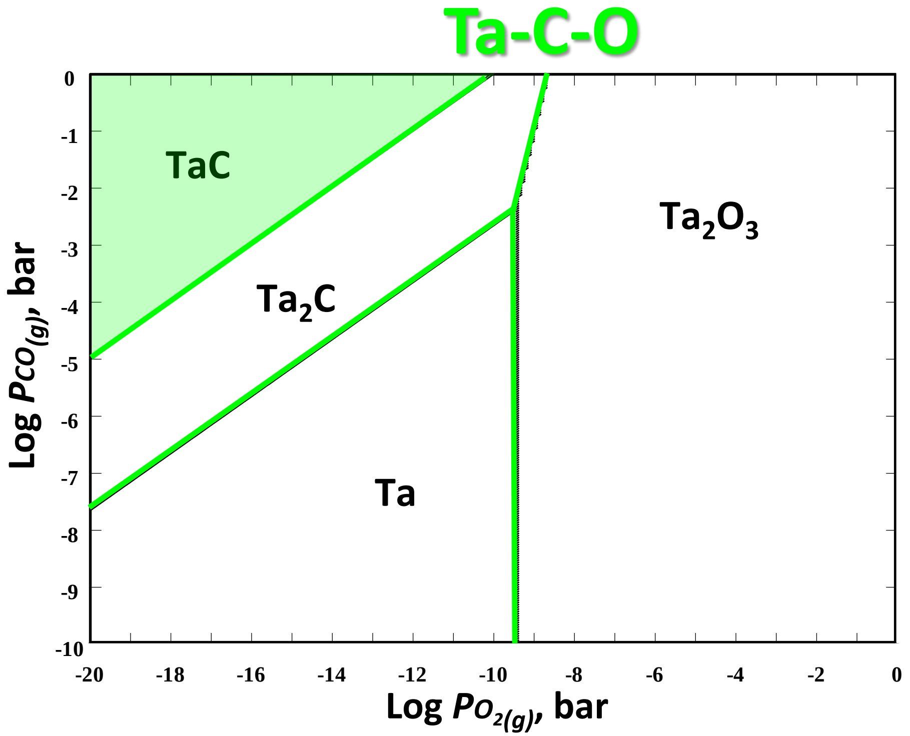
Nature of the precipitates

Type of inclusion VS benefit:

- **Metal**: + local toughness
- **Carbide**: + hardness & strength

- ZBW→ **$(Zr,W)B_2$** + rounded **metallic W** nano-precipitates
- ZBT → **$(Zr,Ta)B_2$** + elongated needle-like shaped **TaC** precipitates

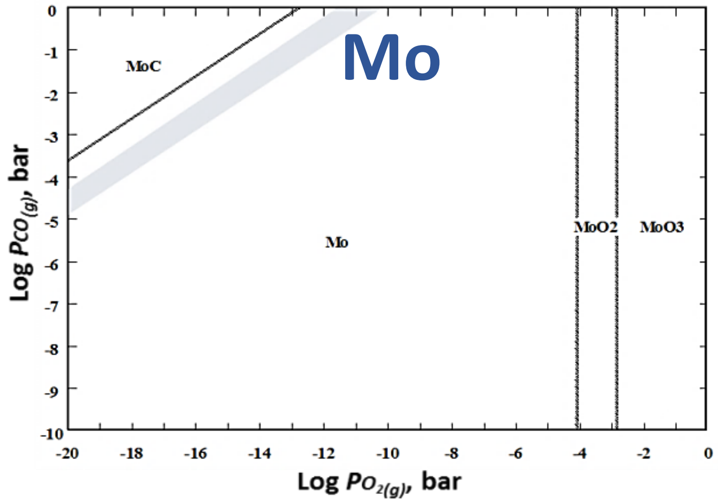


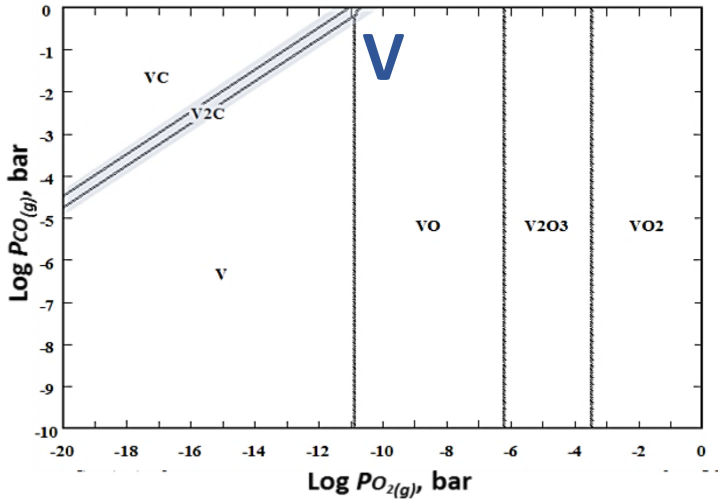


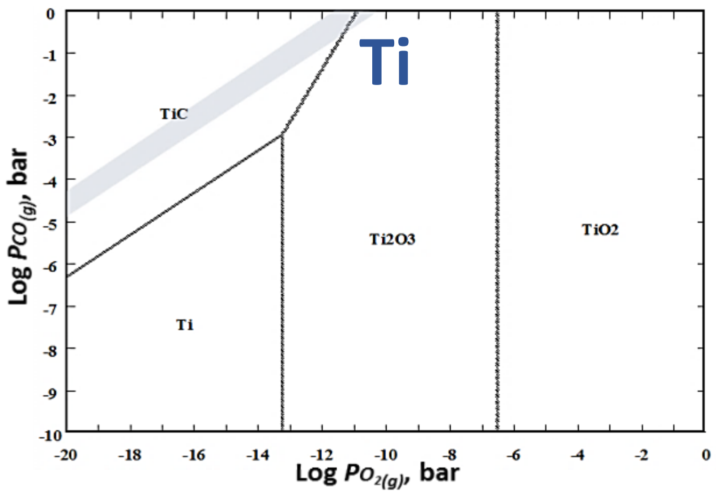
- Nature of the ppt dictated by HP CO/O_2 partial pressure
- By changing the sintering atmosphere (CO-rich or vacuum) we might tune the nature of the ppt

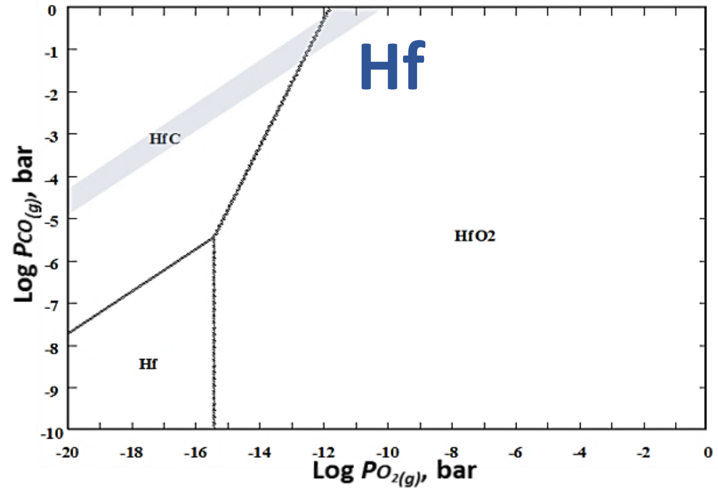
- Metal: Mo, Re, Os, Ir
- Carbide: Ti, Hf, Nb, Cr, V

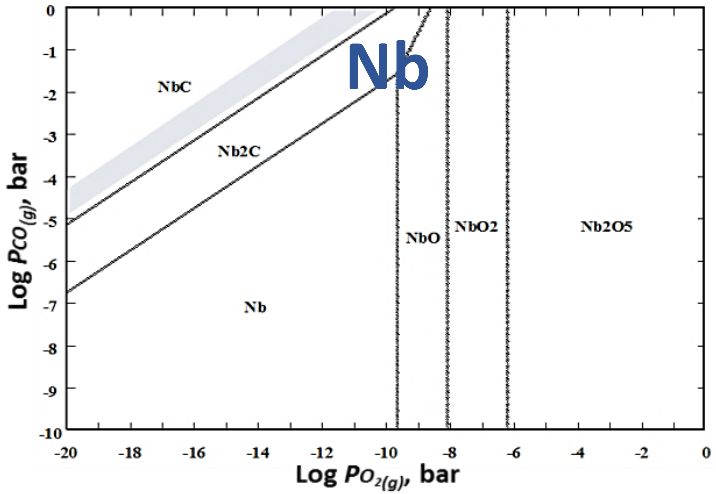
TM-C-O phase stability diagrams

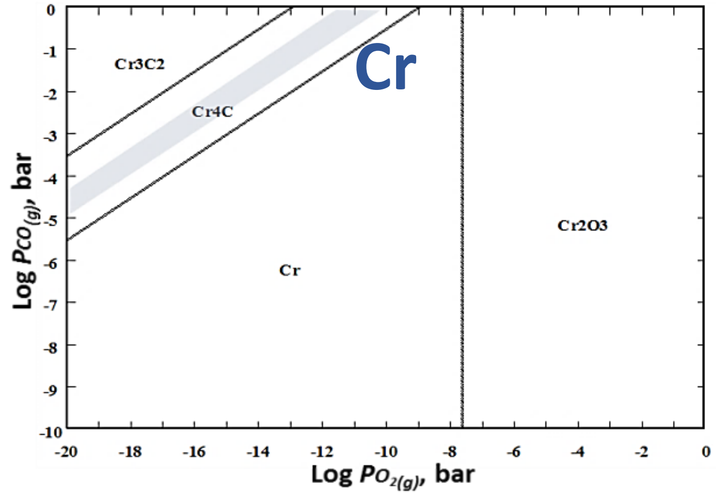












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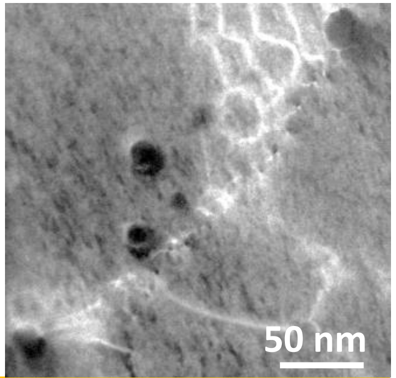
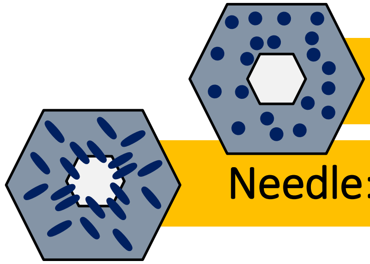
Shape & location of the precipitate

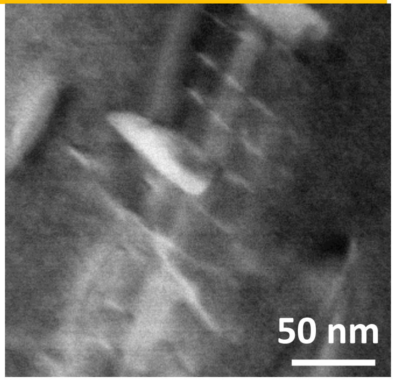
- Interface properties of solid solution and ppt
- Wettability between solid solution and ppt
- Plasticity of the novel formed phase
- Cooling rate?





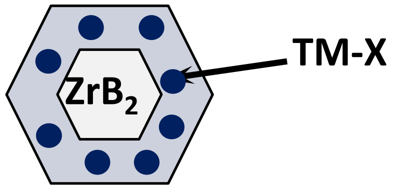
Sphere: isotropic energy, low wettability

Needle: anisotropic energy, growth rate controlled by mobility

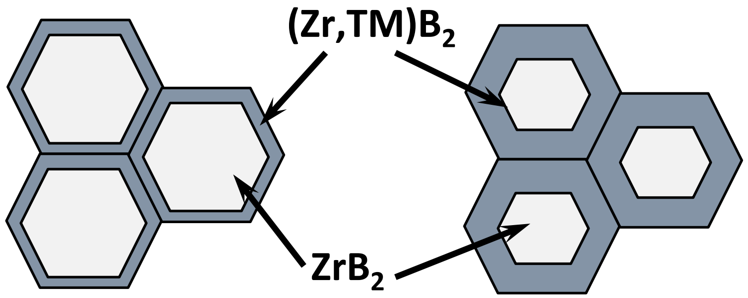


- Local TM enrichment /supersaturation
- Low energy sites with enhanced mobility for atomic attachment and precipitate growth (dislocations at the core-shell interface)

Amount of ppt



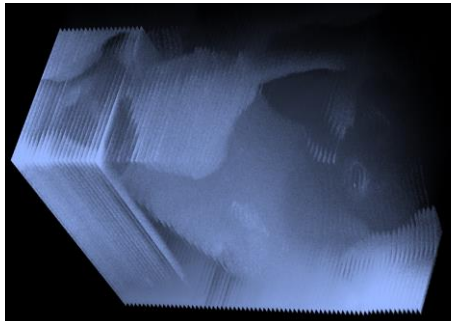
- **Solubility of the guest TM in the boride cell**
  - ➢ High solubility: Ta up to 15 at% → high amount of TM-additive to super-saturate the boride solid solution
  - ➢ Low solubility: W up to 4 at% → low amount of TM-additive to super-saturate the boride solid solution



- **Shell thickness**
  - ➢ can be manipulated by changing the **T & t** of the heat treatment
  - ➢ Is formation of a **homogeneous solid solution** desirable? elimination of one hierarchy grade →

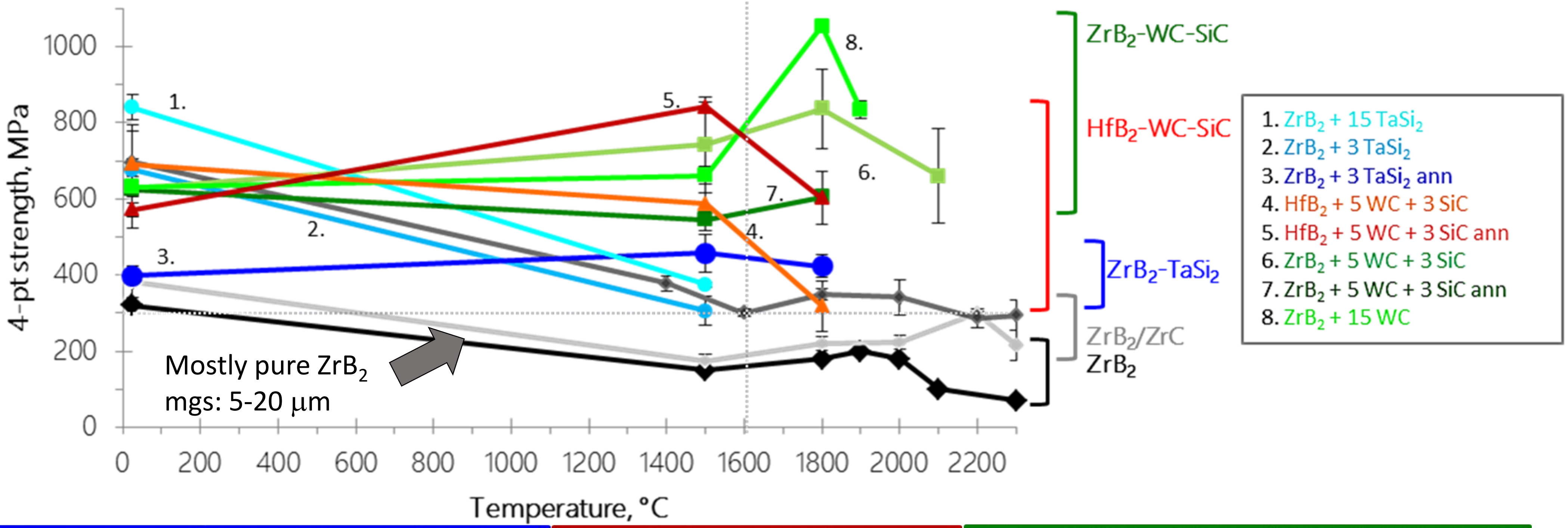
  Dislocations at the core-shell interface useful for:
  - grain refinement down to 30-50 nm
  - increased plasticity @UHT

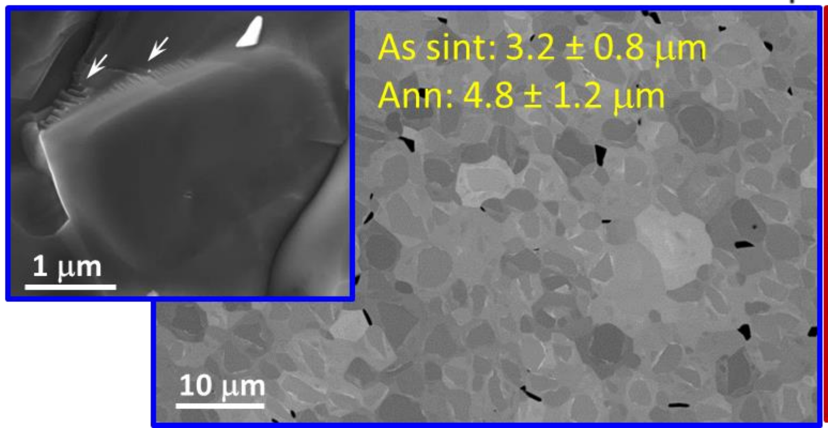
- **How to quantify** the ppt?
  - ➢ Ppt are difficult to image in TEM specimens
  - ➢ can only be observed on fracture surfaces by SEM
  - ➢ FIB slice and view ongoing

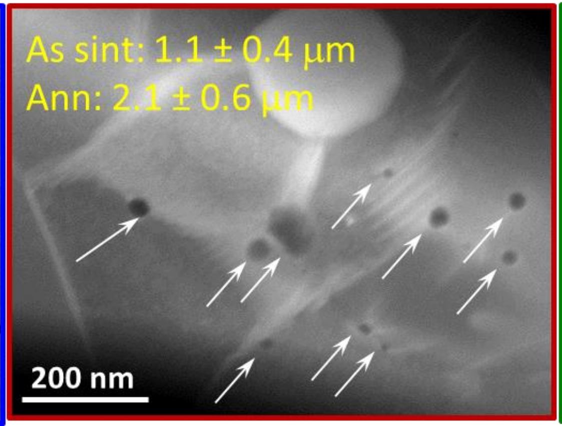


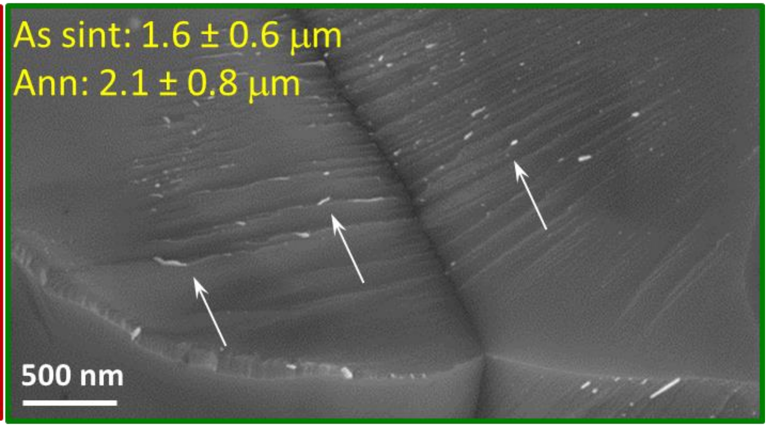
[Comp. B 226 (2021) 109344]

UHT strength



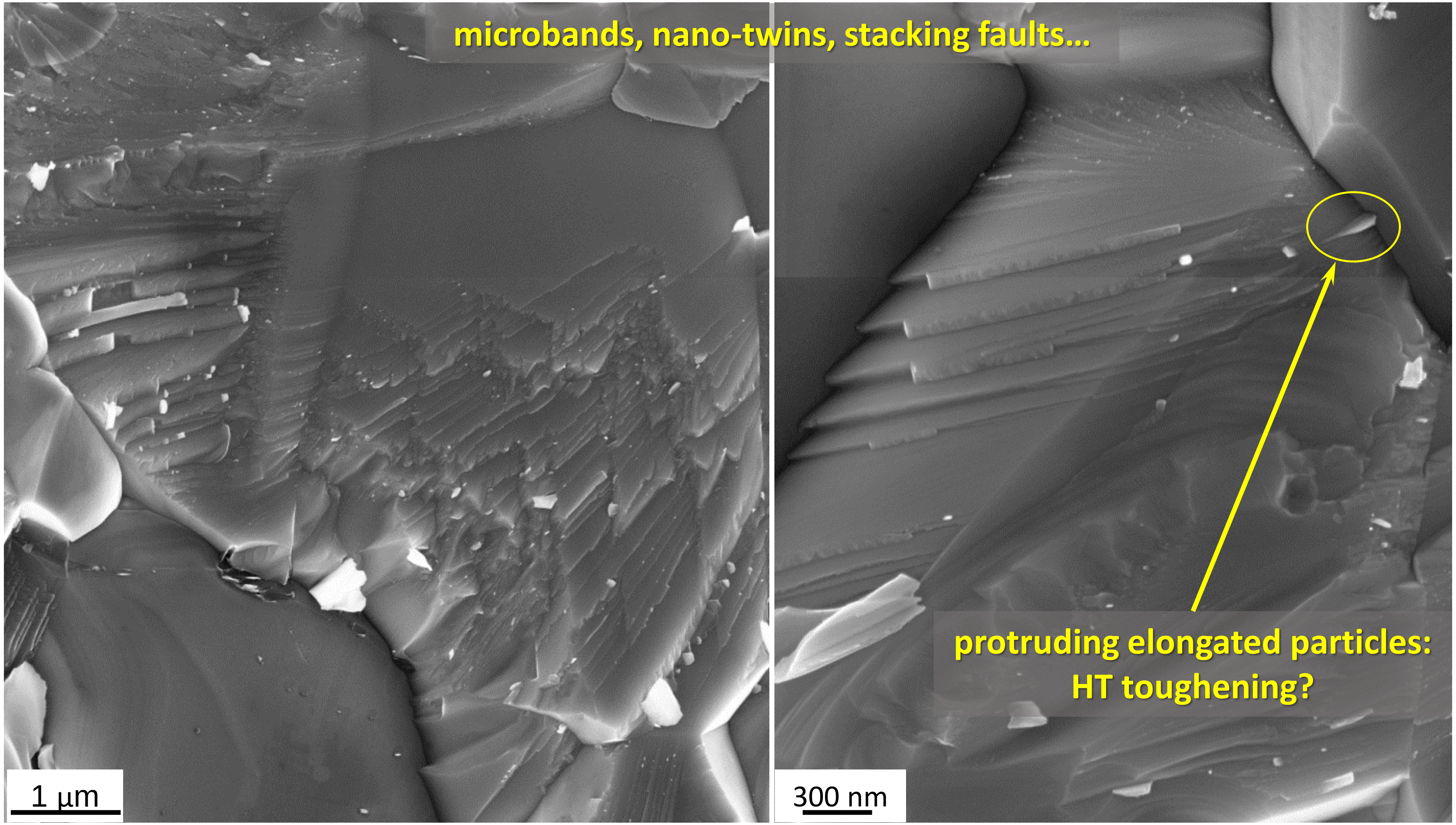






- Nanotexturing coarsening
- Dislocation structure relieve?

ZBW-ann



ZrB_2 + WC + SiC

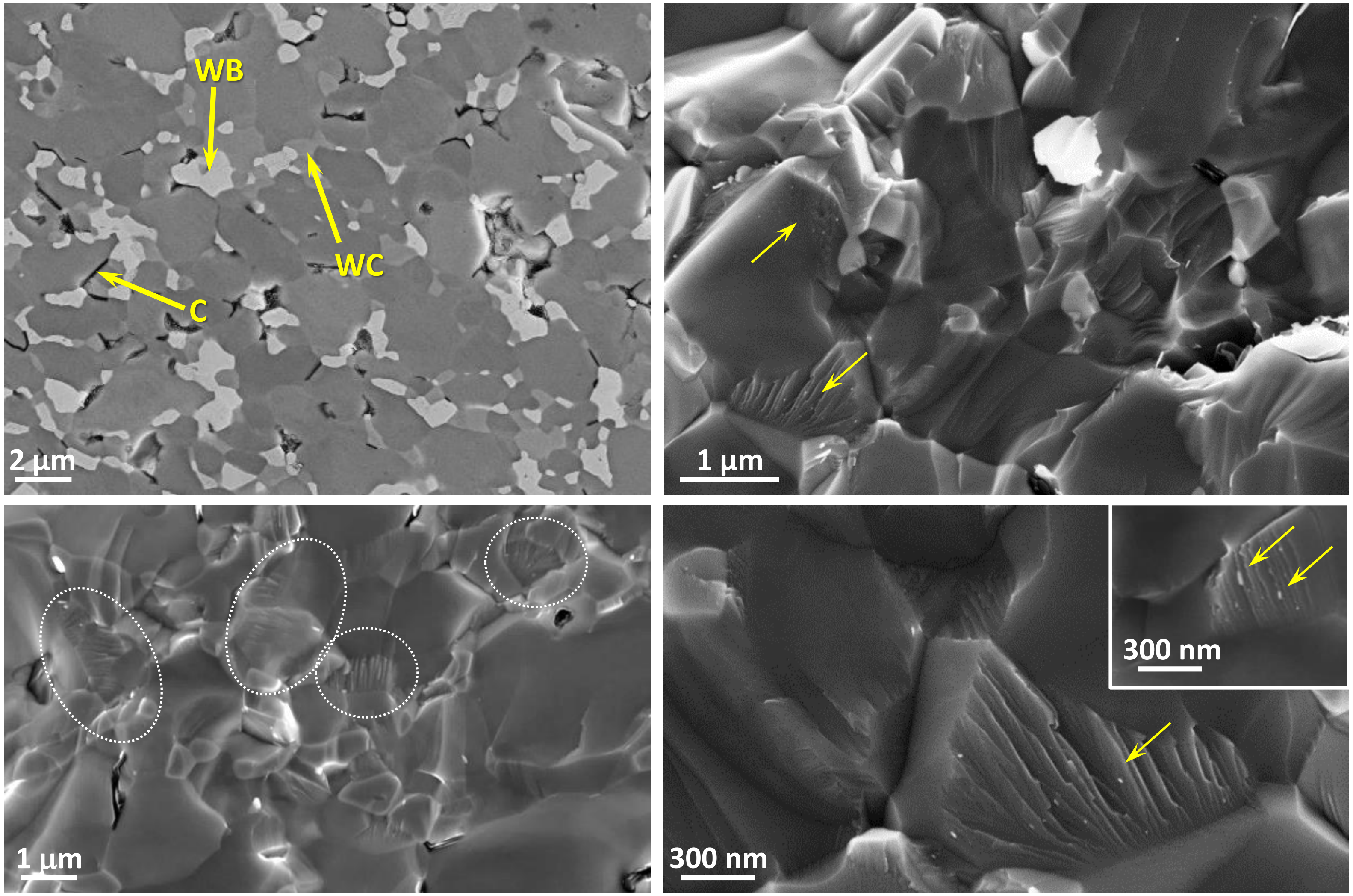
2.1 ± 0.8 μm
Core/shell
little WB

σRT: ~630 MPa
σ1800°C: ~**600 MPa**

(as-sintered material
σ1800°C: ~**800 MPa**)

UHT strength vs ductility

- Ductility of WB phase
- Approach to eutectic temperatures in the Zr–W–B–C system



ZrB_2 + 15 vol% WC

1.6 ± 0.4 µm
Core/shell
Residual WB

σ1800°C: ~1 GPa
σ1900°C: ~830 MPa
σ2000°C: bending

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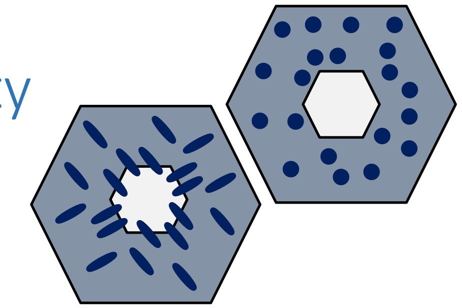
Conclusions

- ZrB_2 ceramics hot pressed in presence of **TM**
  - Core: ZrB_2
  - Shell: **(Zr,TM)B_2**
  - shell featured by precipitation of **nano-inclusions**

Material design through thermal treatment leads to **core/shell** structures with a **multi-scale nanostructured hierarchical** arrangement: is this the **X FACTOR for UHT strength** in boride-based ceramics?

- **Nano-inclusions**
  - Nature depends on the ***PCO/PO$_2$***
  - Shape depends on **interface properties**, wettability, ductility
  - Location: on **defects**
  - Amount depends on TM **solubility** within the shell

ZBT → TaC
ZBW → W



- **Strength >1 GPa @ 1800°C** and >600 MPa @2100°C:
  - Grain refinement by **dislocation intersection**
  - Local toughening by **ductile inclusions**

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Acknowledgements

EU-FP7

Super LIGHT-weight Thermal Protection System for space application (LIGHT TPS #607182)

NATO SPS

SUper Strong ceramics for Protection in harsh ENvironments and defenCE (SUSPENCE #G5767)

US AFOSR

NAnocomposite Core-Rim structures for Enhanced tOUghness and Strength at extreme temperatures (NACREOUS #FA9550-21-1-0399)

US ARMY ACC-APC-RTP & ONR

FunctiOnally graded fiber-Reinforced Ceramics for Extreme environments (FORCE #W911NF-19-2-0253)

Thank you!

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www.nature.com/scientificreports

SCIENTIFIC REPORTS

OPEN

Super-strong materials for temperatures exceeding 2000 °C

Laura Silvestroni[1], Hans-Joachim Kleebe[2], William G. Fahrenholtz[3] & Jeremy Watts[3]

Received: 04 November 2016
Accepted: 09 December 2016
Published: 19 January 2017

Ceramics based on group IV-V transition metal borides and carbides possess melting points above 3000 °C, are ablation resistant and are, therefore, candidates for the design of components of next generation space vehicles, rocket nozzle inserts, and nose cones or leading edges for hypersonic aerospace vehicles. As such, they will have to bear high thermo-mechanical loads, which makes strength at high temperature of great importance. While testing of these materials above 2000 °C is

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Composites Part B 226 (2021) 109344

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journal homepage: www.elsevier.com/locate/compositesb

ELSEVIER

Design of ultra-high temperature ceramic nano-composites from multi-scale length microstructure approach

Nicola Gilli[a,b], Jeremy Watts[c], William G. Fahrenholtz[c], Diletta Sciti[a], Laura Silvestroni[a,*]

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Journal of the European Ceramic Society 38 (2018) 2467–2476

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journal homepage: www.elsevier.com/locate/jeurceramsoc

ELSEVIER

Original Article

Method to improve the oxidation resistance of ZrB_2-based ceramics for reusable space systems

Laura Silvestroni[a,*], Simone Failla[a], Irina Neshpor[b], Oleg Grigoriev[b]

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October 2016 | Accepted: 14 December 2016

/jace.14738

ORIGINAL ARTICLE

Journal of the American Ceramic Society

Microstructure evolution of a W-doped ZrB_2 ceramic upon high-temperature oxidation

Laura Silvestroni[1] | Diletta Sciti[1] | Frédéric Monteverde[1] | Kerstin Stricker[2] | Hans-Joachim Kleebe[2]

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Journal of the European Ceramic Society 37 (2017) 1899–1908

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Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

ELSEVIER

Critical oxidation behavior of Ta-containing ZrB_2 composites in the 1500–1650 °C temperature range

CrossMark

Laura Silvestroni[a,*], Hans-Joachim Kleebe[b]

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Acta Materialia 151 (2018) 216–228

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Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

ELSEVIER

Full length article

Understanding the oxidation behavior of a ZrB_2–$MoSi_2$ composite at ultra-high temperatures

Laura Silvestroni[a,*], Kerstin Stricker[b], Diletta Sciti[a], Hans-Joachim Kleebe[b]

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Corrosion Science 159 (2019) 108125

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ELSEVIER

Effect of hypersonic flow chemical composition on the oxidation behavior of a super-strong UHTC

Laura Silvestroni[a,*], Stefano Mungiguerra[b], Diletta Sciti[a], Giuseppe D. Di Martino[b], Raffaele Savino[b]

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Scripta Materialia 160 (2019) 1–4

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Scripta Materialia

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ELSEVIER

Regular article

Core-shell structure: An effective feature for strengthening ZrB_2 ceramics

Laura Silvestroni[a,*], Simone Failla[a,b], Vladimir Vinokurov[c], Irina Neshpor[c], Oleg Grigoriev[c]

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Composites Part B 183 (2020) 107618

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journal homepage: www.elsevier.com/locate/compositesb

ELSEVIER

A simple route to fabricate strong boride hierarchical composites for use at ultra-high temperature

Laura Silvestroni[a,*], Nicola Gilli[a,b], Andrea Migliori[b], Diletta Sciti[a], Jeremy Watts[c], Greg E. Hilmas[c], William G. Fahrenholtz[c]

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