National Research Council of Italy

DSCTM
Department of Chemical Sciences and Materials Technology

Young Investigator Award 2018

ADVANCED MATERIALS

Ceramic Materials for Extreme Environments

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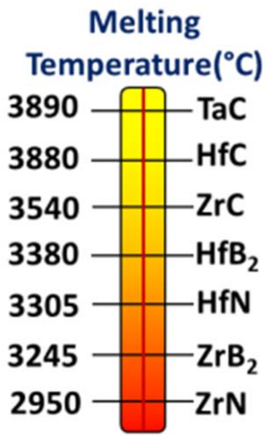
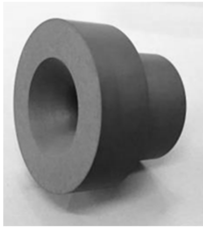
Ultra-High Temperature Ceramics





Aim:

Design materials for extreme environments → UHTCs with increased strength, toughness, oxidation resistance

Approaches:

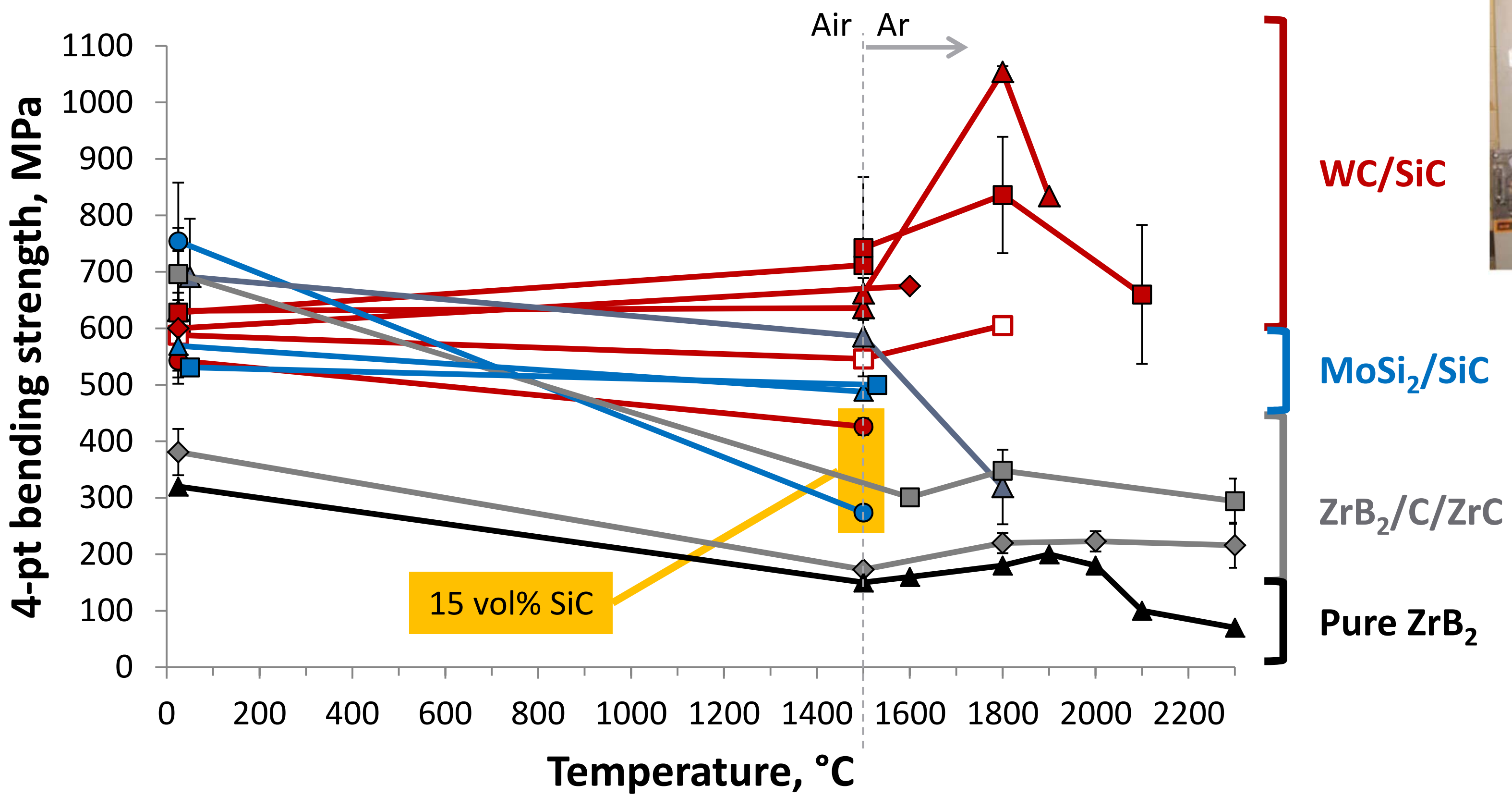
- Addition of refractory secondary phases: TM alloying
- Thermal treatment to trigger toughening mechanisms (pull-out, crack deflection)
- Combination of phases able to provide oxidation protection over a wide T range

In this talk:

A. Flexural strength up to UHT
B. Fracture toughness
C. Oxidation behavior

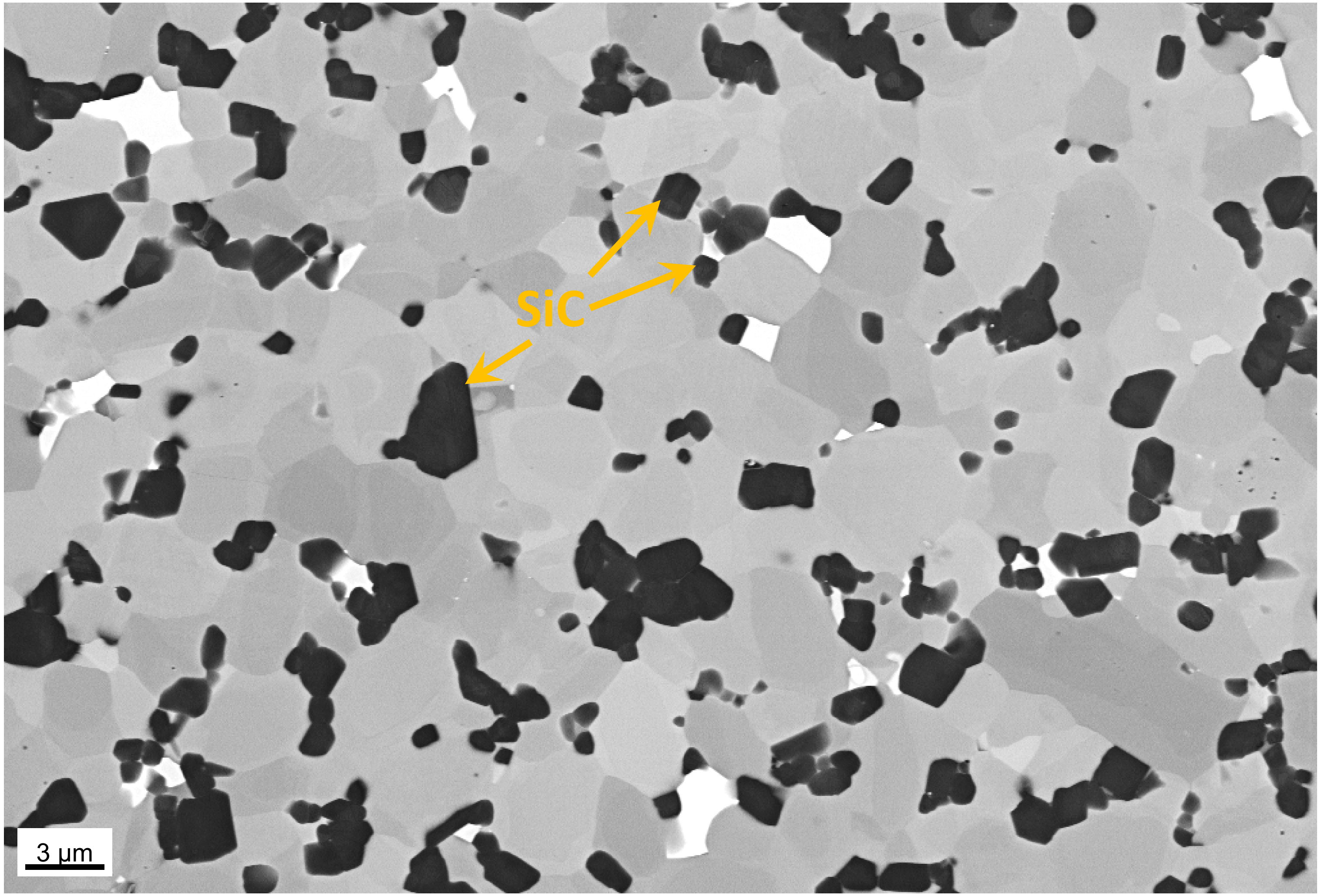
ZrB_2 + SiC + WC

A. Flexural strength



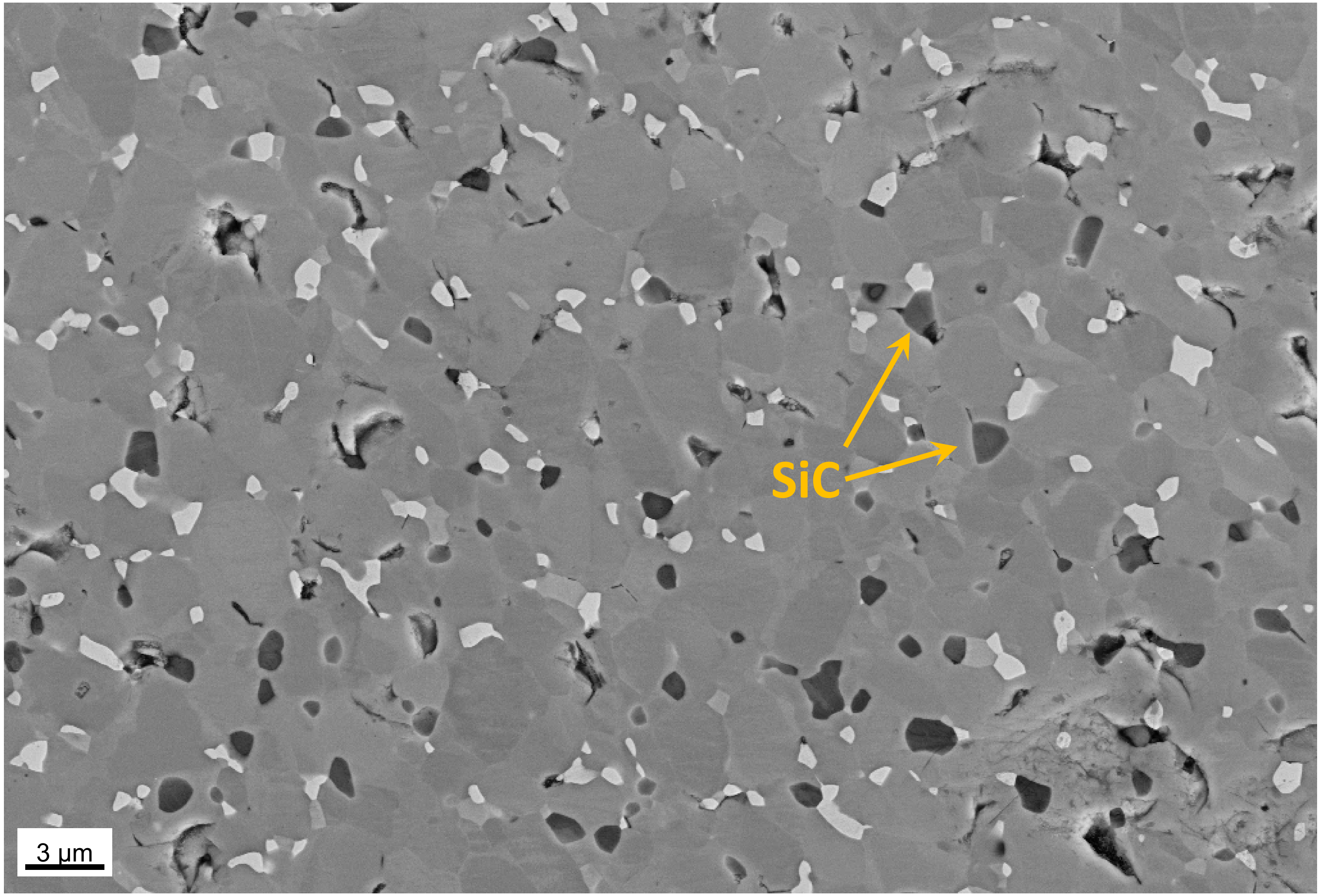
- C/ZrC results in clean ZrB_2 boundaries allowing for stable HT strength at ~350 MPa
- TM additives maintain and even increase the HT strength
- Exceptional HT strength for composites containing no or low SiC amount
- ***WC: strength > 1GPa*** at 1800°C, fully retained at 2100°C

The baseline: ZrB_2 + 15 vol% SiC + WC



- SiC particles form an interconnected network.
- Above 1500°C SiO_2 forms → grain boundary sliding, strength decay

The good one: ZrB_2 + 0/5 vol% SiC + WC



- Isolated SiC particles
- strength not hampered by SiO_2 glass at the grain boundaries, no grain boundary sliding

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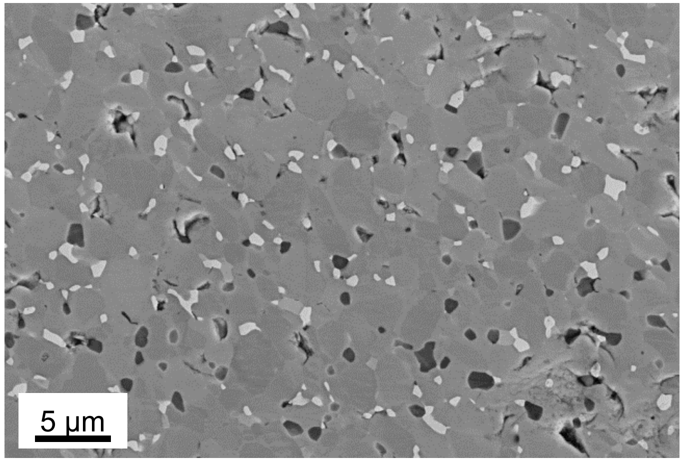
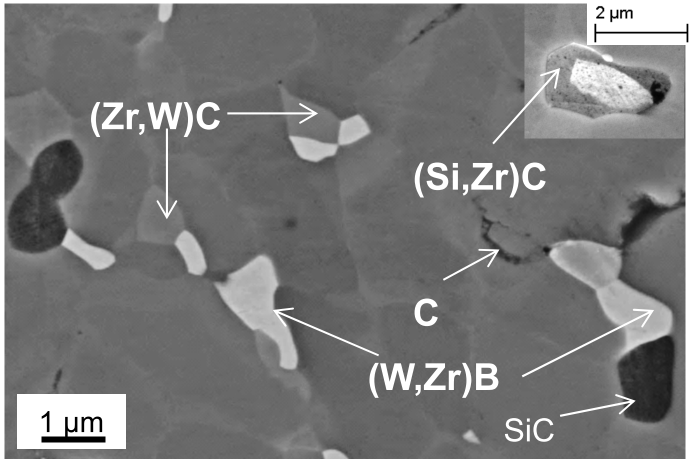
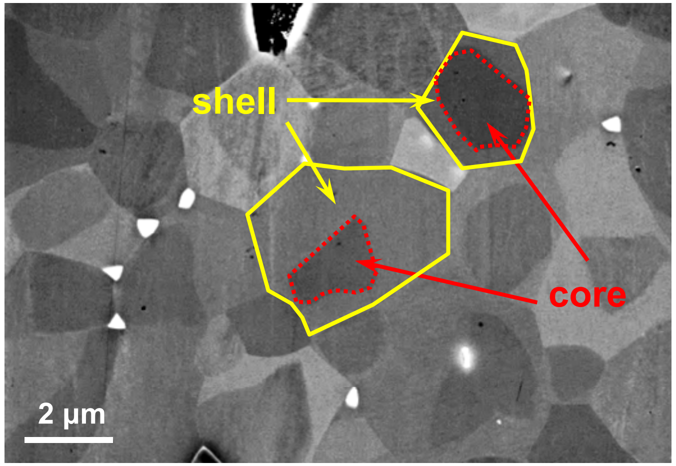
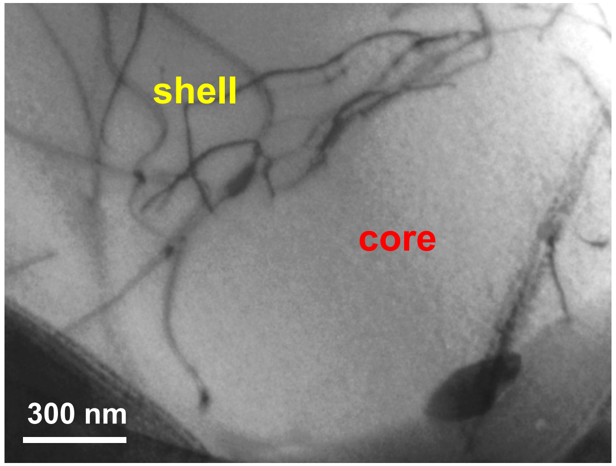
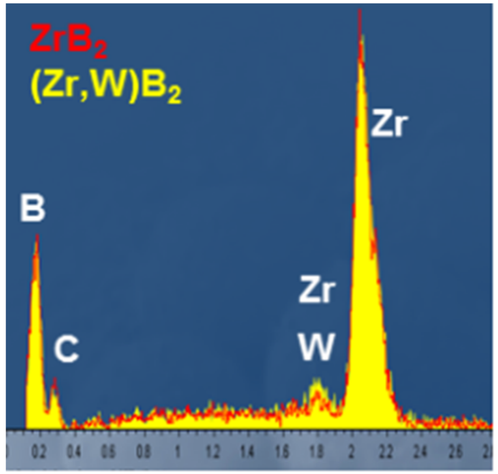
As sintered microstructure







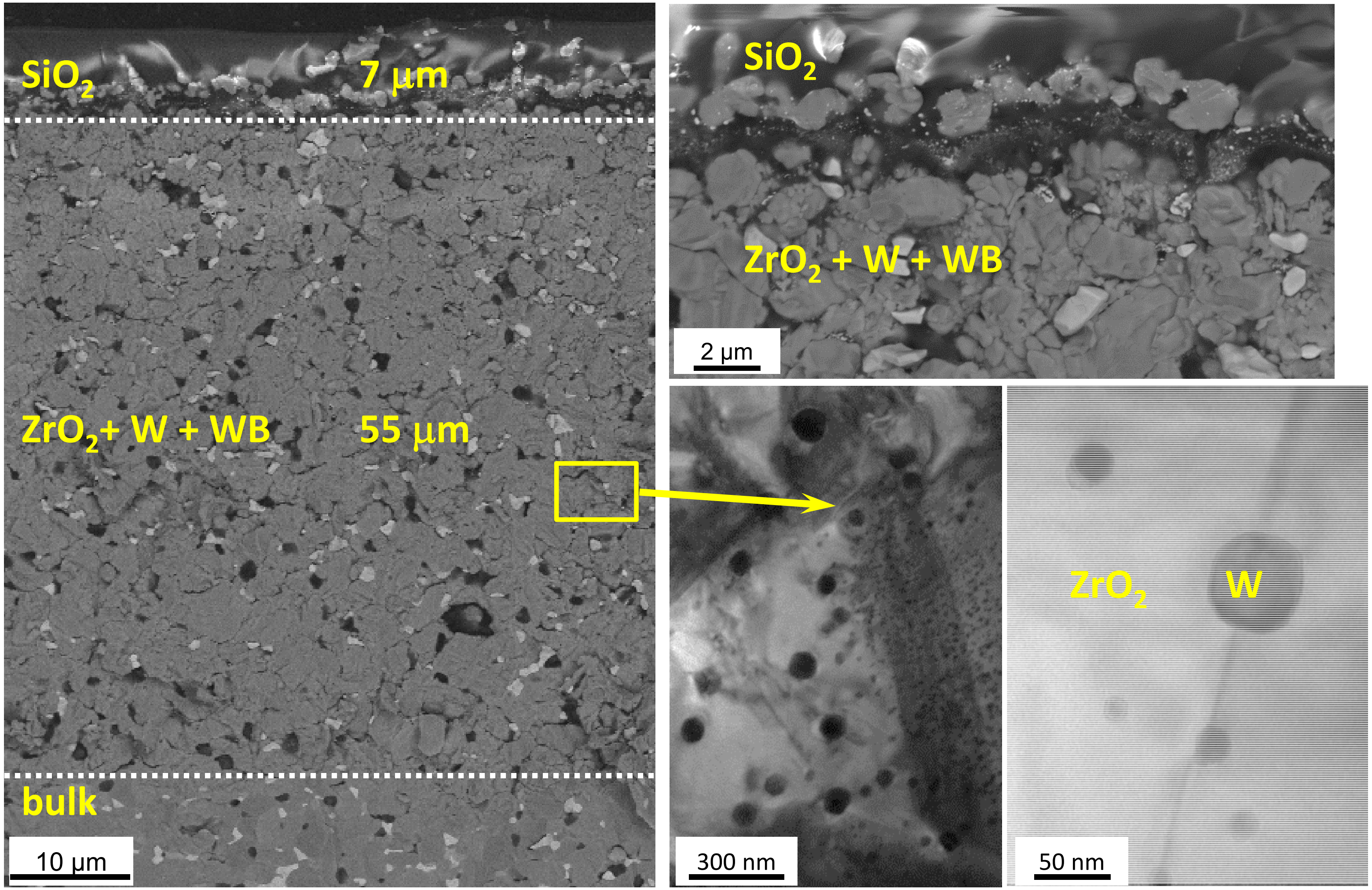




- Fully dense
- Core-shell matrix grain: $(Zr,Wr)B_2$ on ZrB_2 core: shell=70:30 vol%
- New mixed phases: WB, Zr-W-C
- Clean grain boundaries

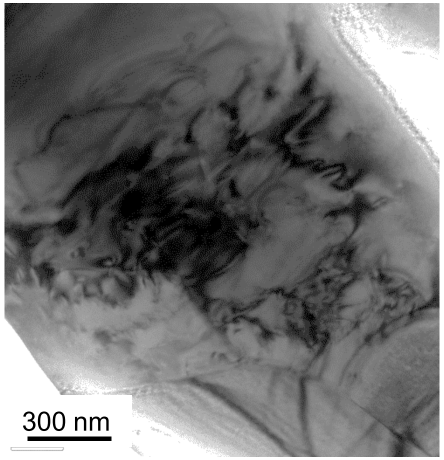
Modified scale

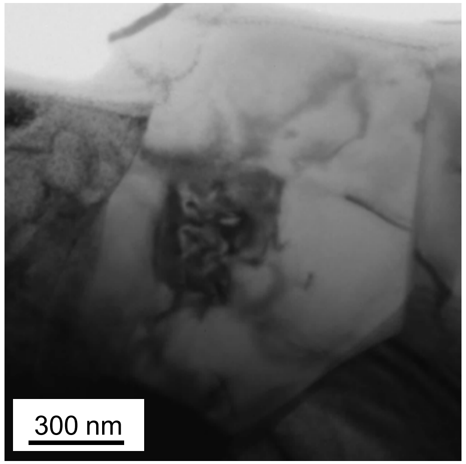
Fractography after σ1500, air

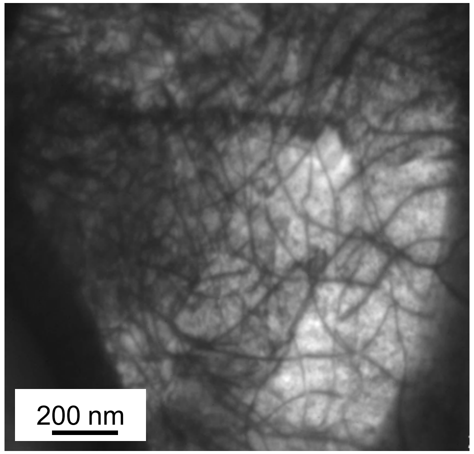


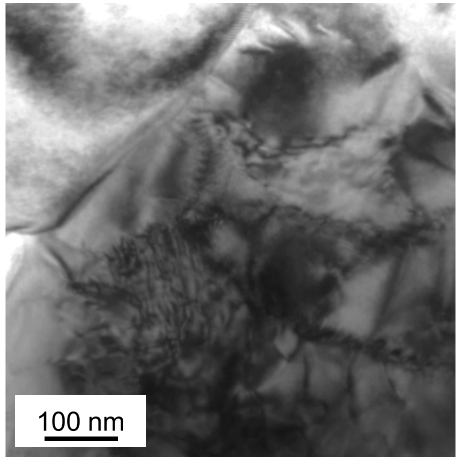
- ~ 62 μm modified thickness → 11 vol% modified material
- Outermost SiO_2 glass → flaws healer
- W droplets encased in ZrO_2 → intrinsic ZrO_2 toughening by metallic nanoparticles

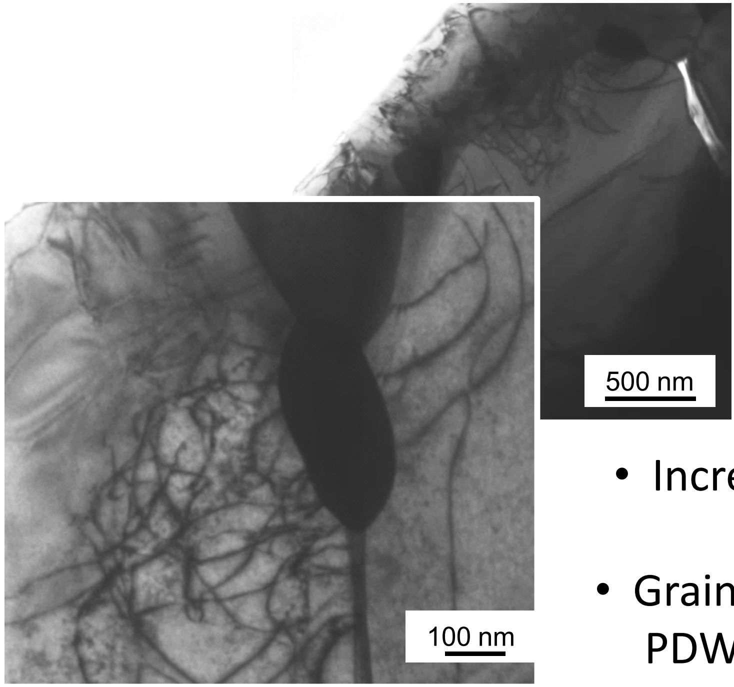
TEM analysis after σ1500, air

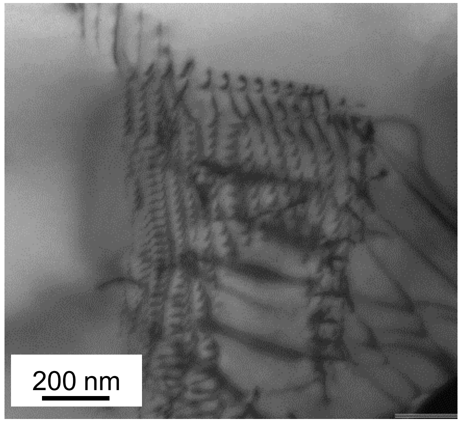


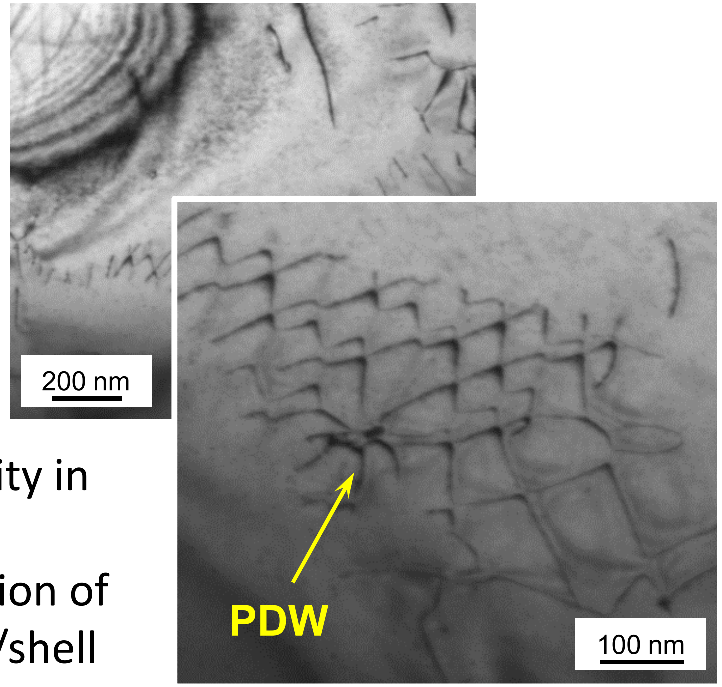






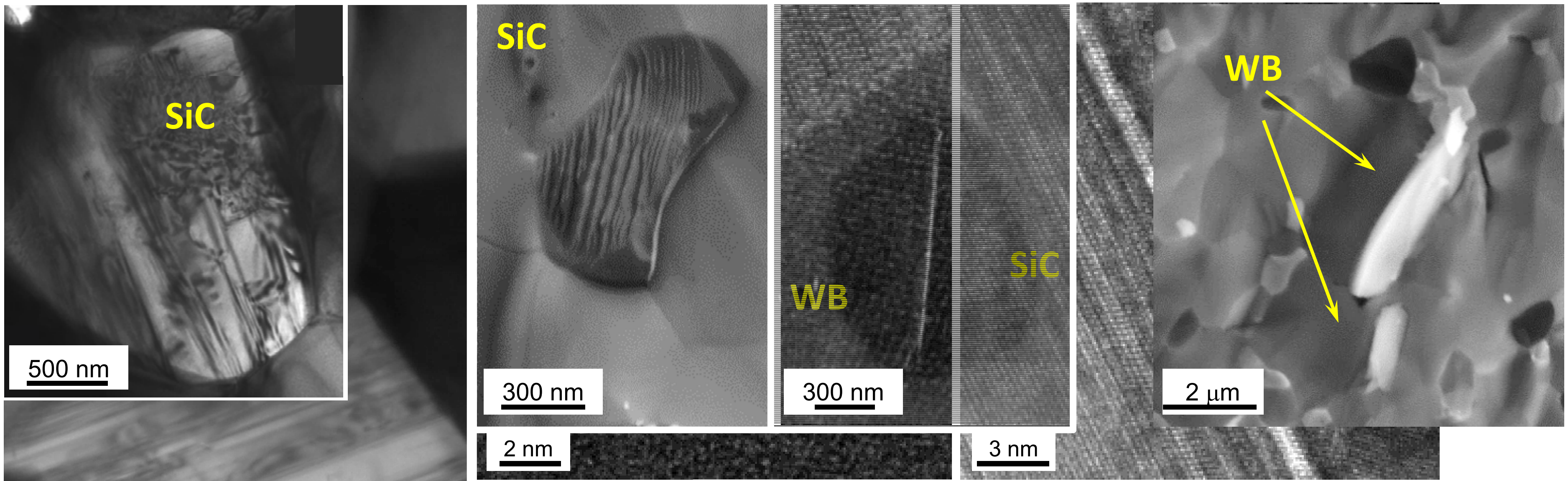


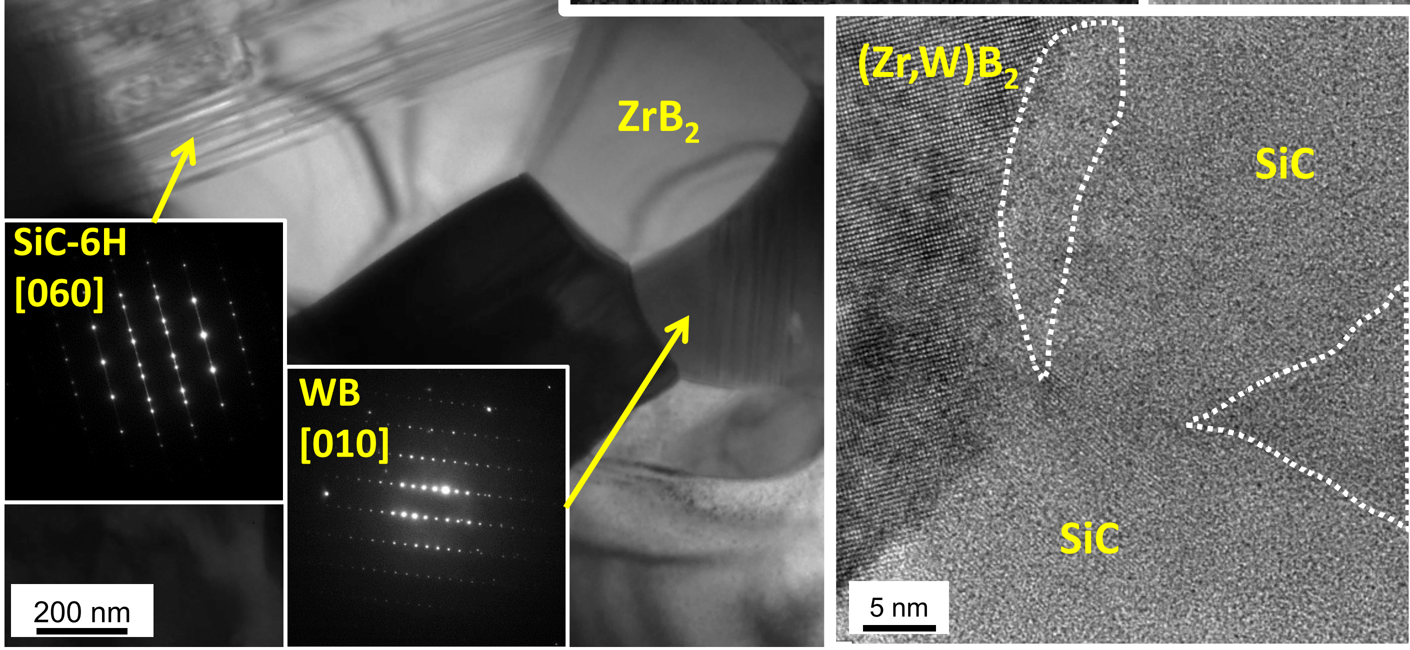




- Increased dislocations activity in boride grains
- Grains refinement by formation of PDW at and across the core/shell boundary (2 μm→ 50 nm)

TEM analysis after σ1500, air

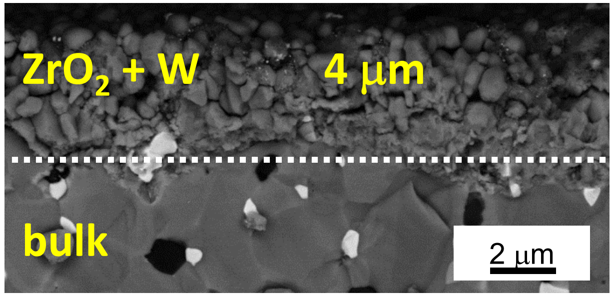




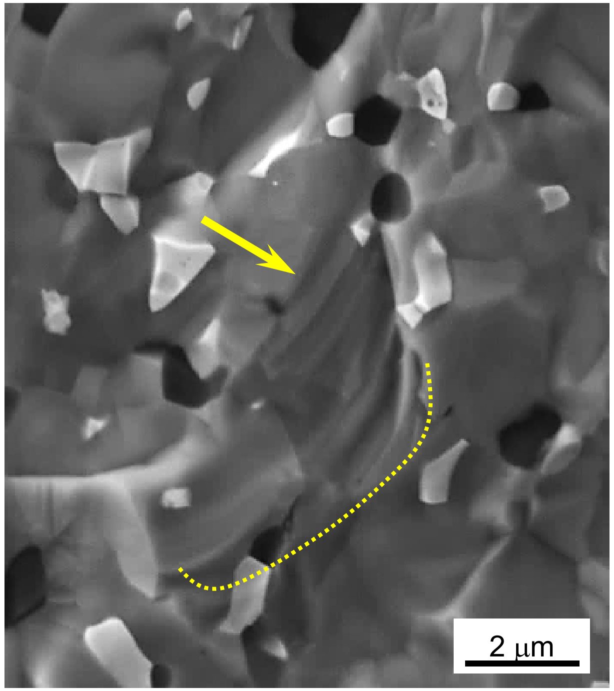
- Phases with stacking faults: SiC, WB → pull-out, crack deflection
- GB: all clean, BUT SiC/SiC → softening

Fractography after σUHT, Ar

Modified scale & bulk



- No SiO_2 healing layer
- ~ 4 μm modified thickness (1500-2100°C) → 2 vol% modified material

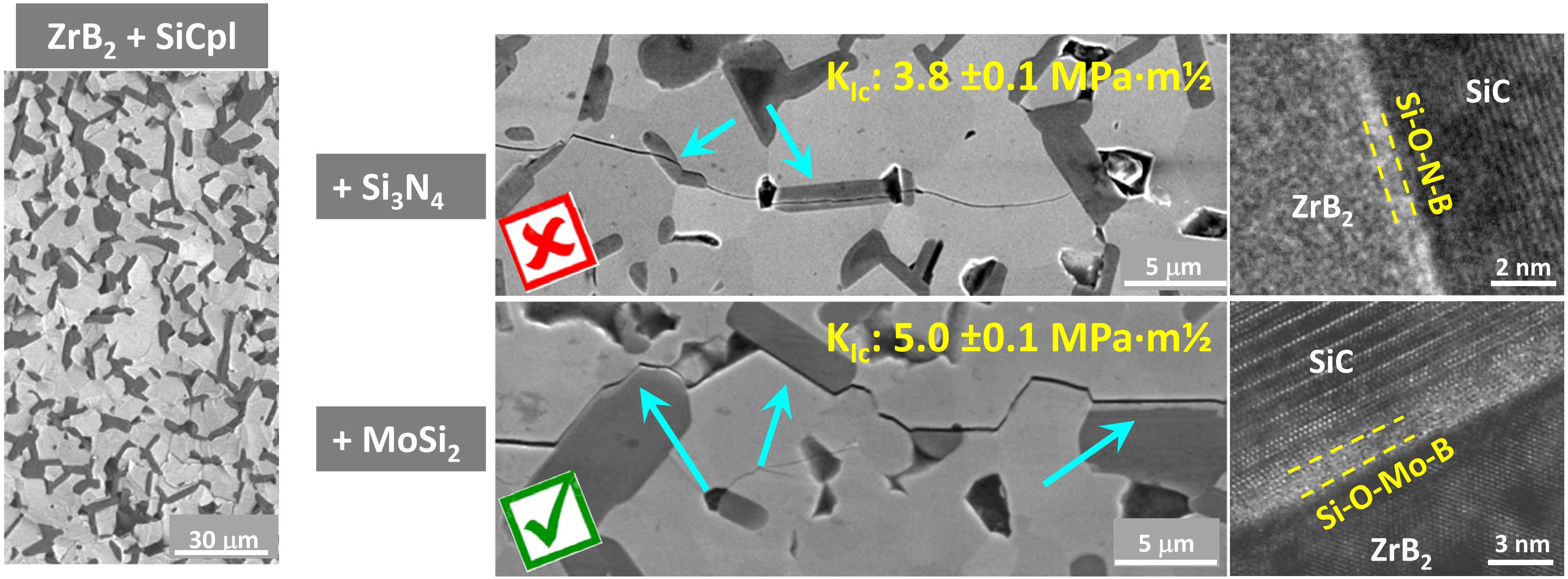


- Plastic deformation in the boride at 2100°C

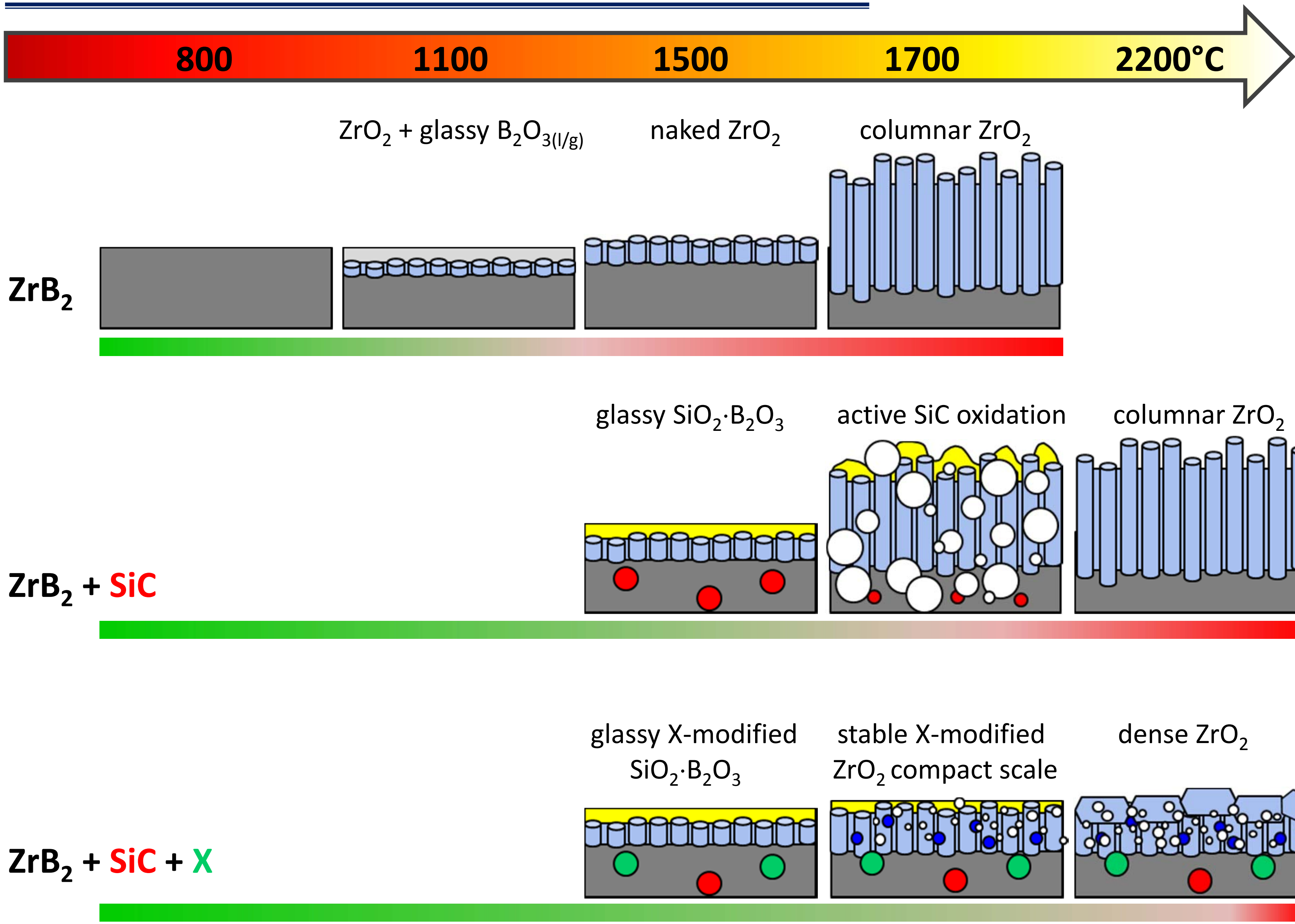
B. Fracture toughness

Introduction of secondary phases:

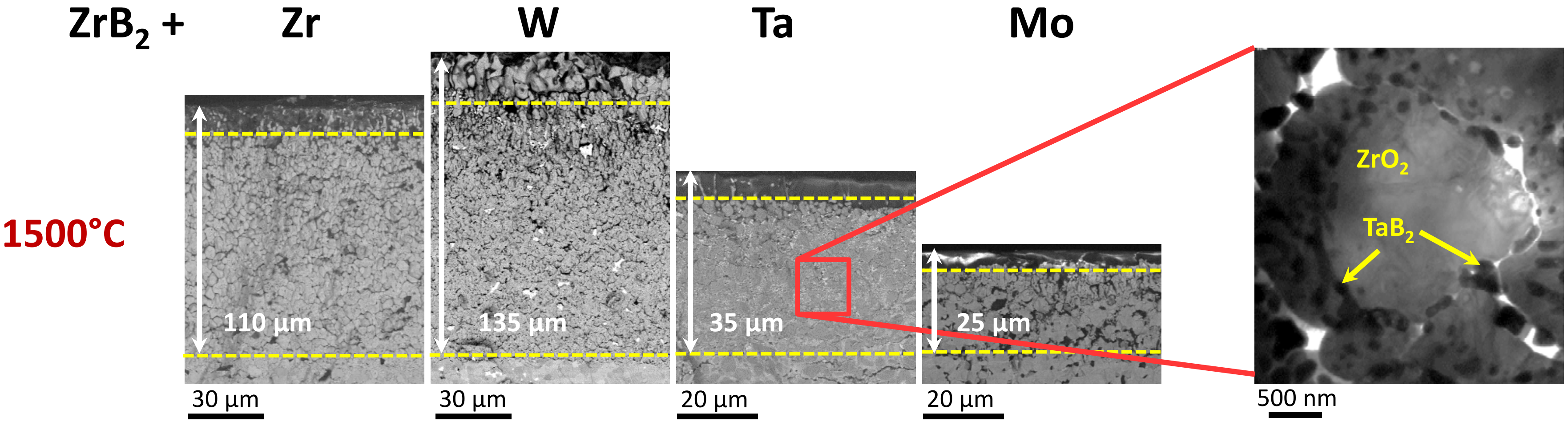
- Whiskers, nanotubes, graphene → critical handling, do not survive the sintering T
- Short/long fiber → K_{Ic} up to 7 MPa·m½, BUT σRT-1500: 300-120 MPa, oxidation, costs
- SiC platelets → K_{Ic} up to 5 MPa·m½, BUT control of the grain boundaries

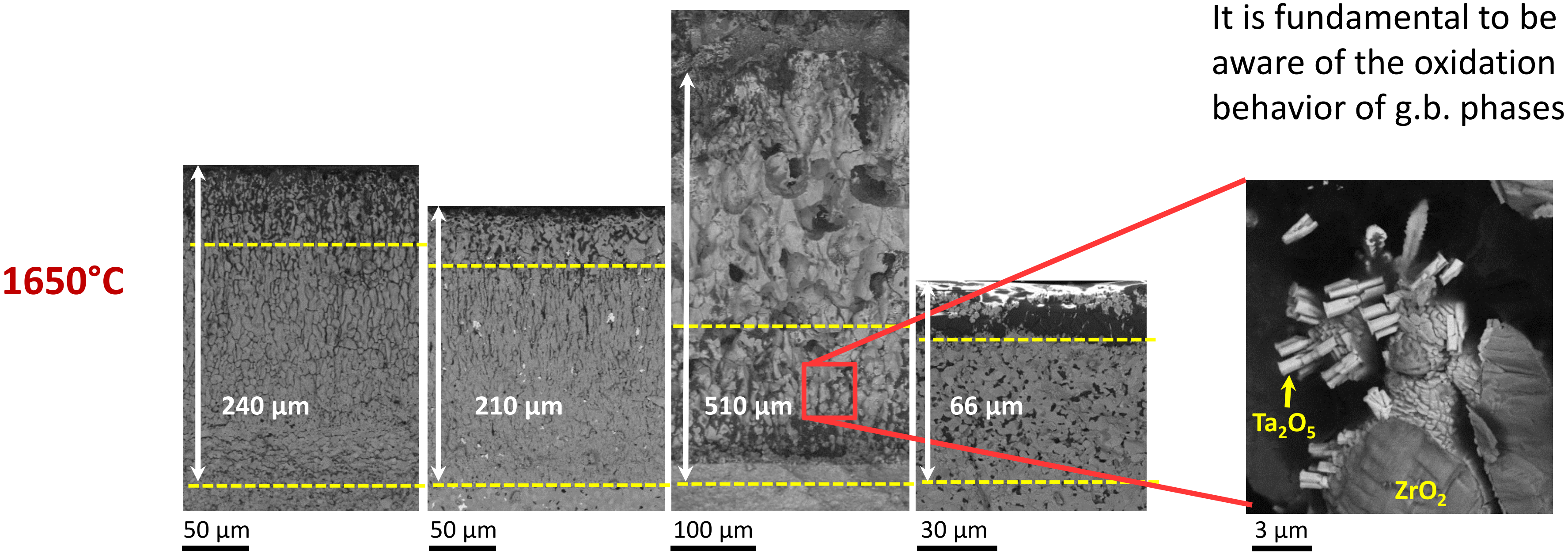


C. Oxidation behavior



TM effect on the oxidation





It is fundamental to be aware of the oxidation behavior of g.b. phases

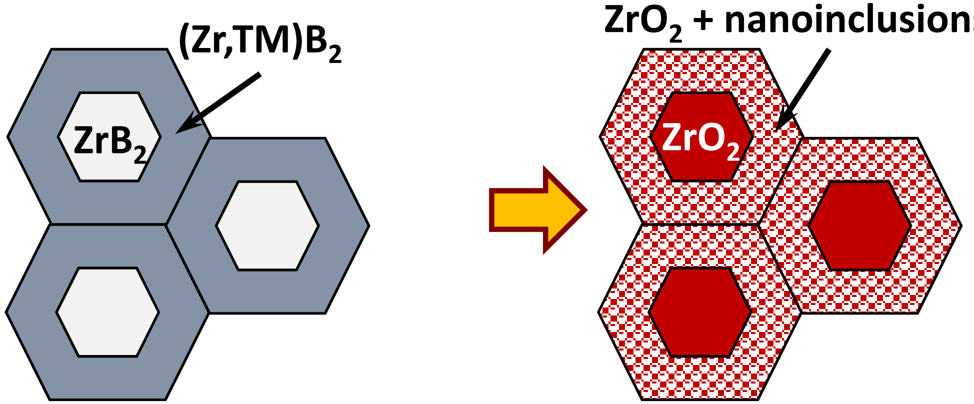
TM effect on the oxidation

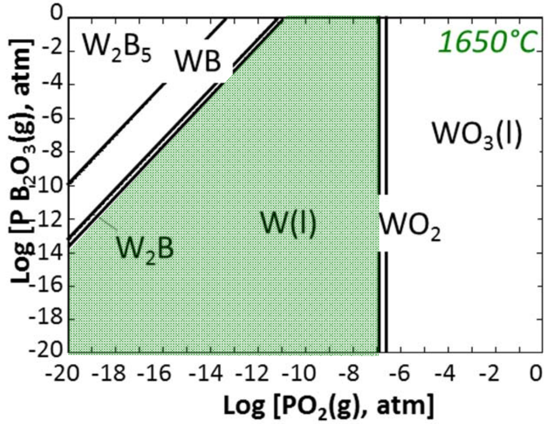
ZrB_2 + TM → (Zr,TM)B_2

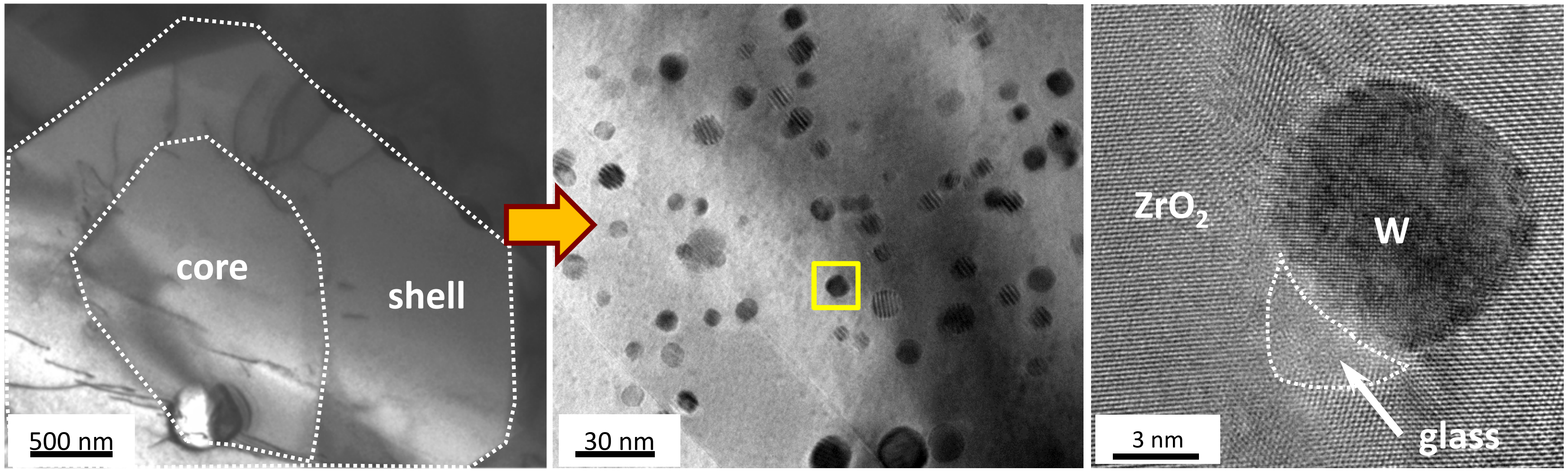
(Zr,TM)B_2 + O_2 → ZrO_2 + TM*

*depending on P_{O_2} vs $P_{B_2O_3}$

TM	inclusion	oxide
Mo	MoB	MoO_3
Ta	TaB_2	Ta_2O_5 (+Δvol)
W	W	WO_3







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Concluding remarks

- **UHT zone** still rather unexplored
- **Super strong borides** with strength peaks of 1 GPa @ 1800°C and above 600 MPa @ 2100°C
- **Strength at UHT** increases by grain refinement upon dislocation intersection, plastic deformation and by ductile-phase toughening by W nanoparticles expelled by the solid solution
- **SiC** amount has to be carefully controlled: too much leads to creep, too little does not offer protection to oxidation.
- **Solid solutions** are beneficial as they provide a diffused source of guest cation → benefits on HT strength, toughness and oxidation.
- **Oxidation** behavior at UHT can be improved by functionalization of the oxide scale.
- **W** is a kind of magic!!! Benefits on HT properties and easy to track by imaging.

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Acknowledgements

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- **EU H2020 Project** C3HARME # 685594

Thank you for your attention!