Deformation-Resistant Multipurpose Ultra-High Temperature Ceramic with Superior Hardness, Toughness, and Flexural Strength

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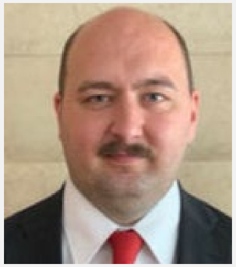
Keynote Talk October 15, 2024, T14 High Temperature Materials

My main collaborators:



Demirskyi Dmytro

Sepehri-Amin Hossein

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Sakka Yoshio

Badica Petre

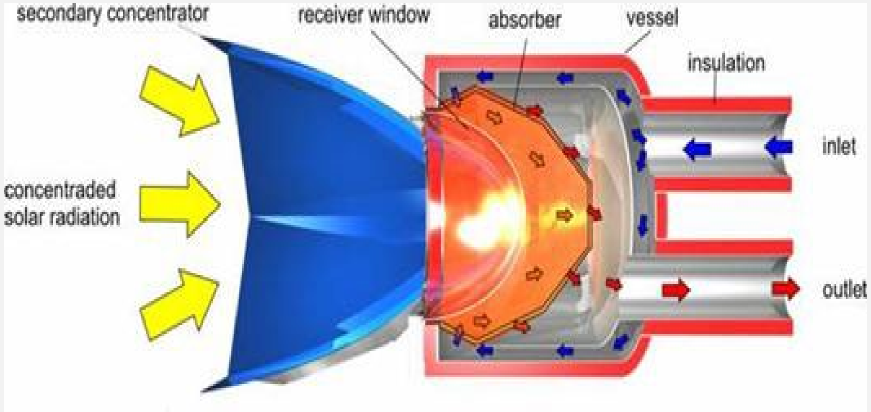
Borodianska Hanna

Nishimura Toshiyuki

Yoshimi Kyosuke

Why do we need high-temperature ultra-ceramics? Materials for extreme environments

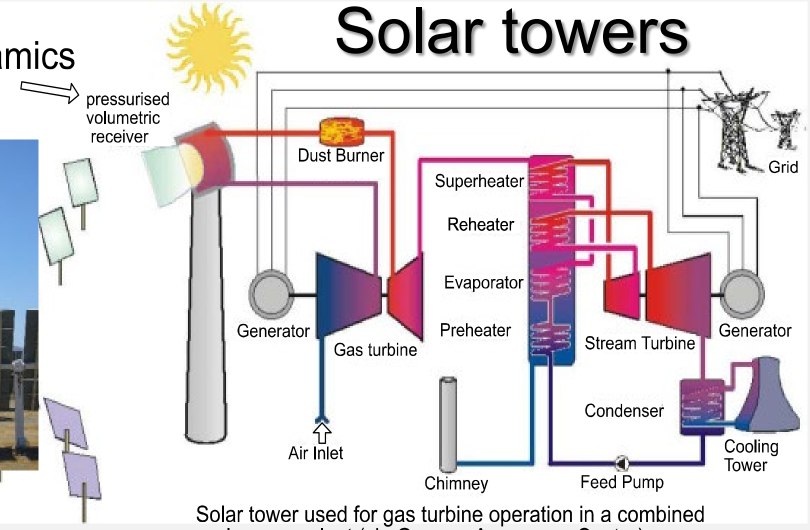
Ceramics with high thermal conductivity, operation temperature unacceptable for metallic alloys due to creep, oxidation, & ablation processes…



Leading edge components for aerospace

The solar tower power plant on the Plataforma Solar in Almería

Solar towers



Solar tower used for gas turbine operation in a combined cycle power plant (via German Aerospace Center)

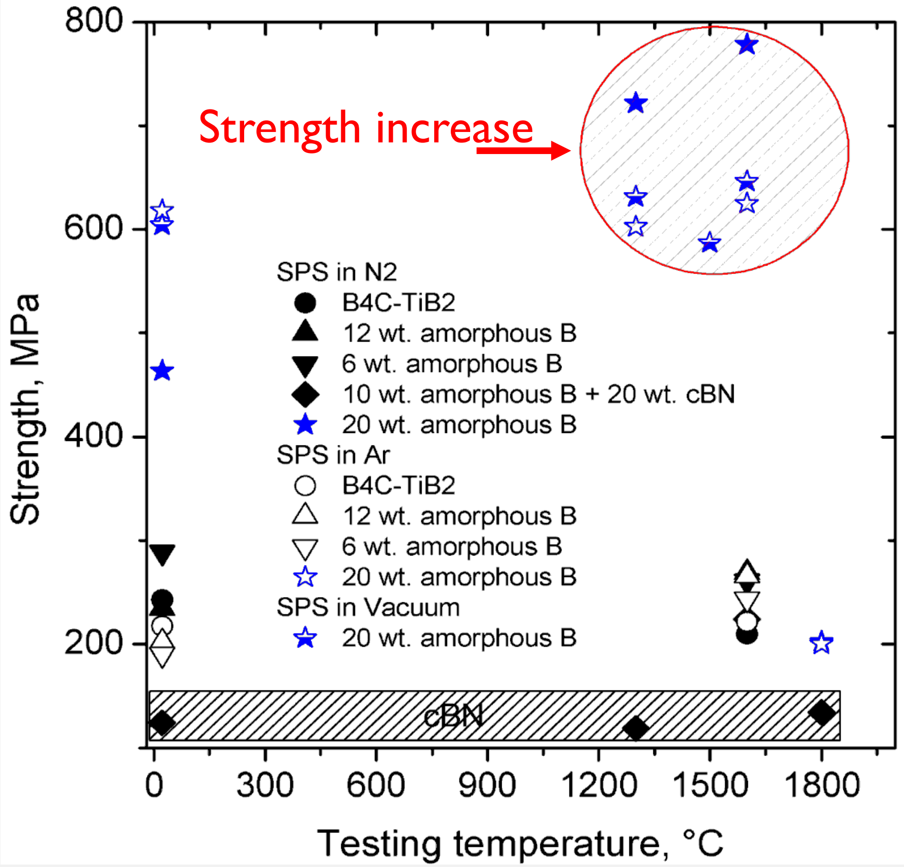
Gas turbine operation

Grids, superheaters, reheaters, evaporators, steam turbines, condensers, and chimneys

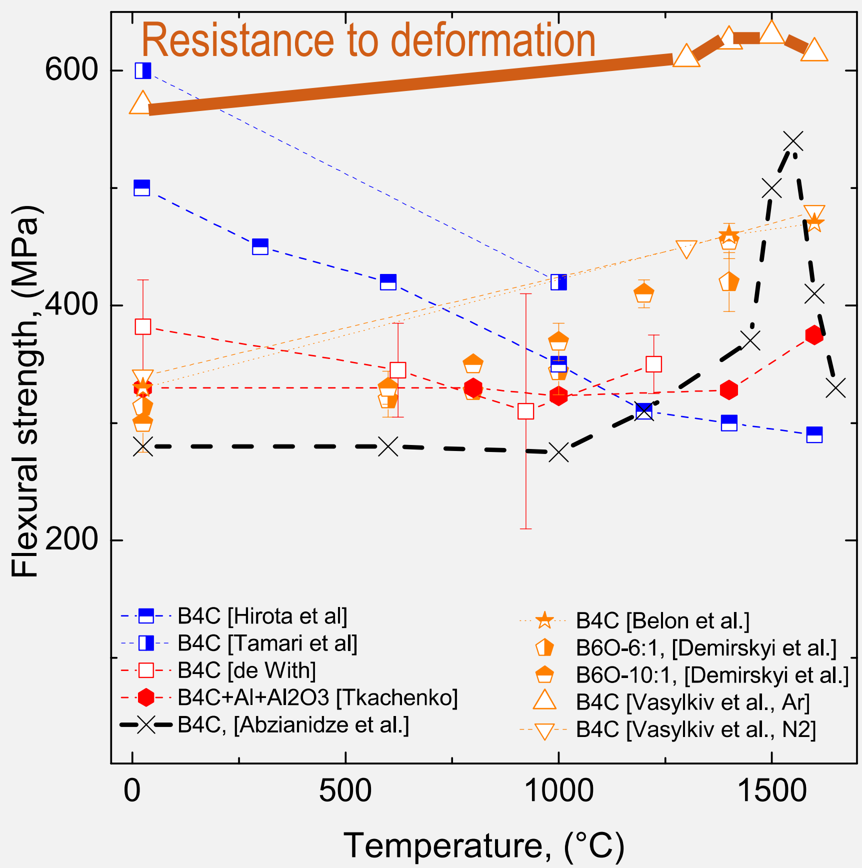
Mechanical strength can be improved by controlling composition and deformation mechanism from the originally brittle to ductile by adjusting its nano-structure.

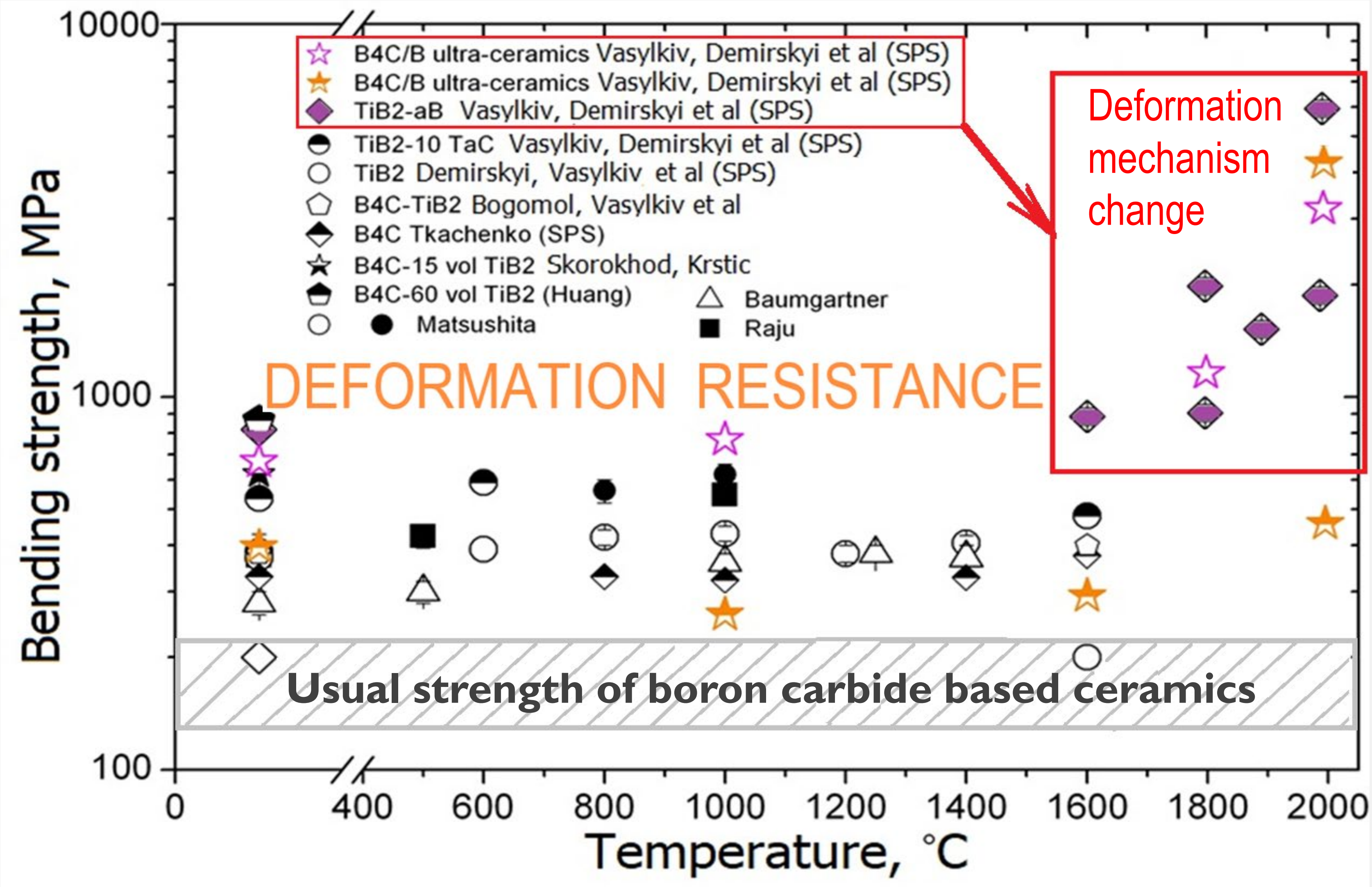
Boron carbide

Manipulating by B to C ratio in boron carbide, and GB modification

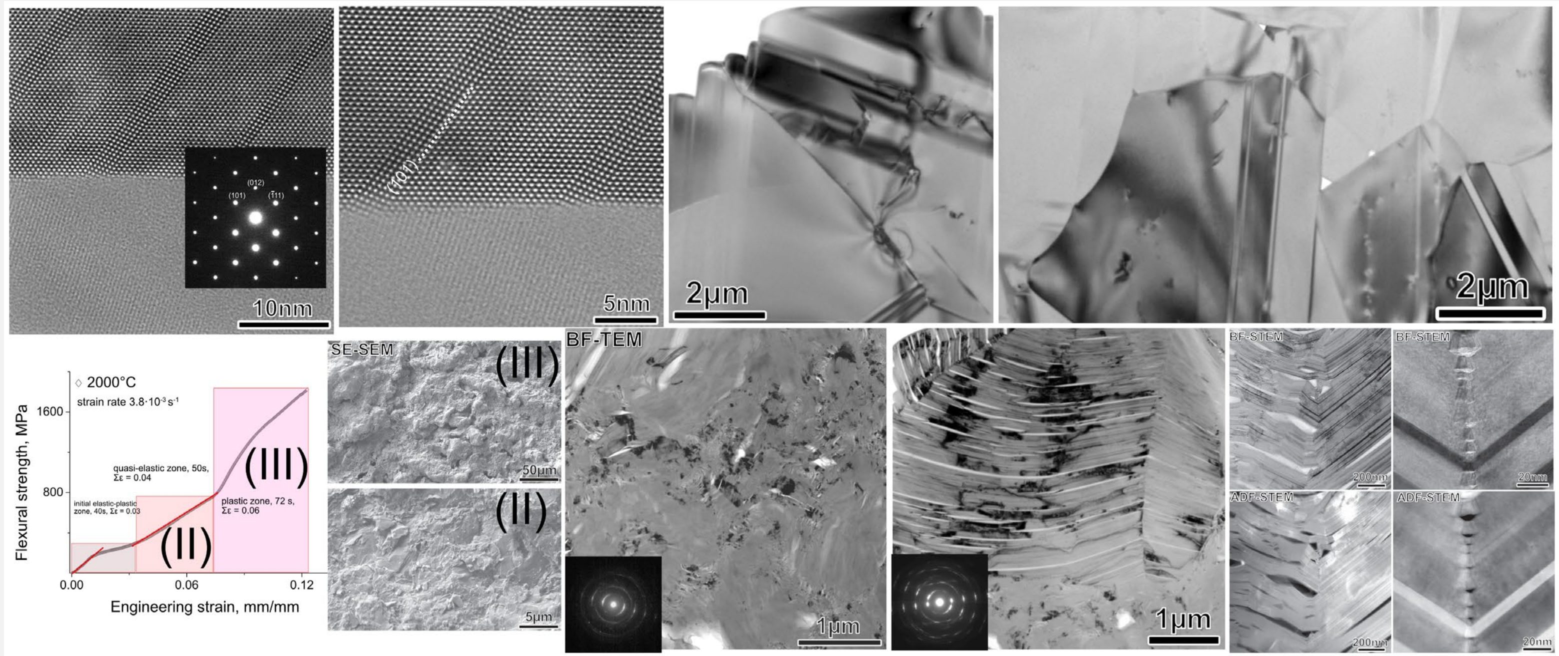


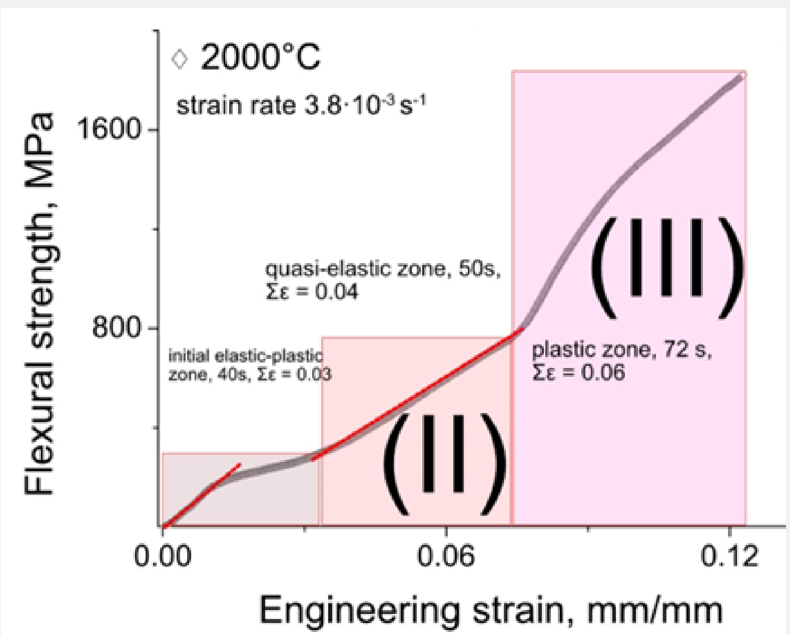
Boron rich ceramics and strength behavior at **elevated** temperatures





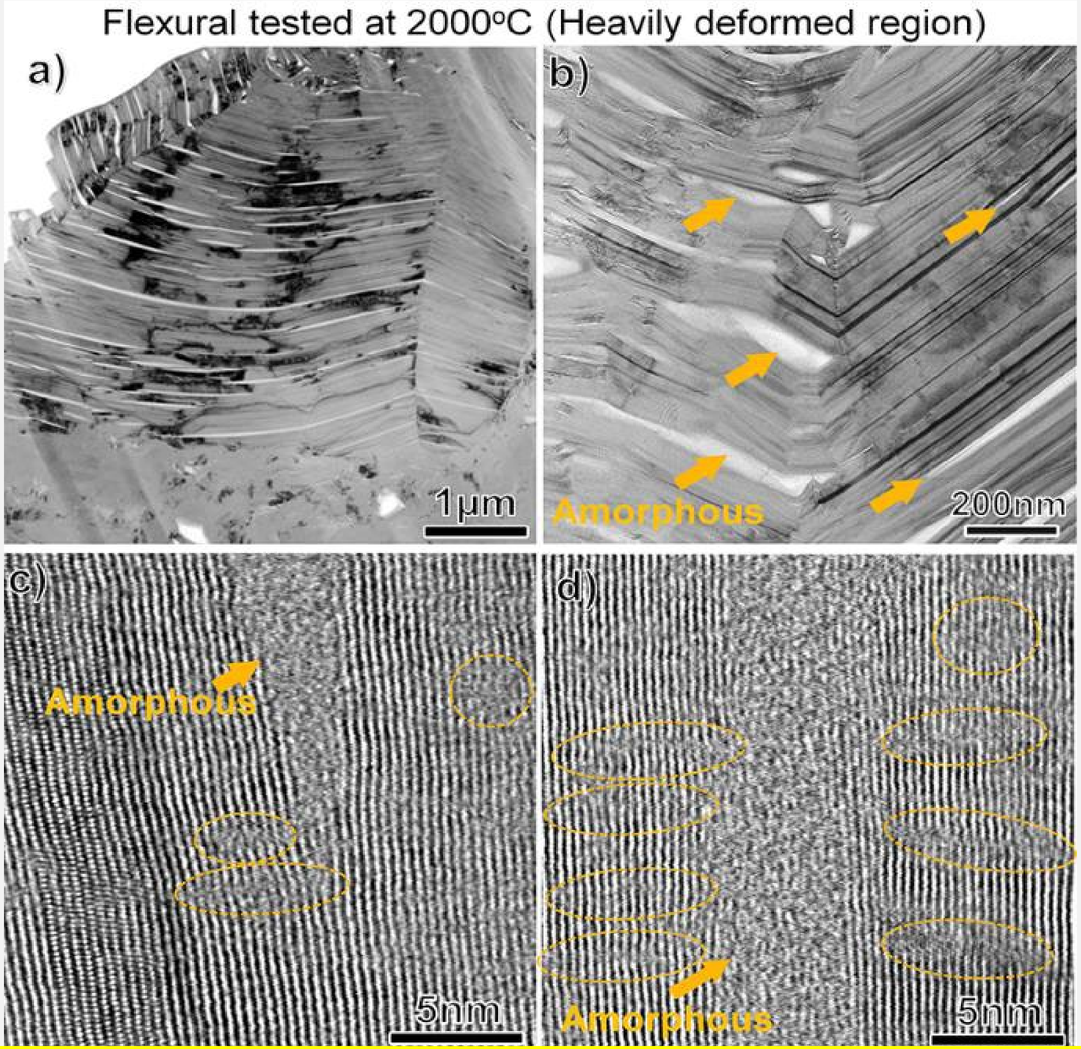
With RT to 1800 °C mean strength of 650 MPa, boron carbide exhibits ultra-high strength far exceeding 1000 MPa accompanied by change in the deformation mechanism from brittle fracture to plastic deformation at 1800 – 2000 °C


10nm
5nm
2μm
2μm
◇ 2000°C
strain rate 3.8·10-3 s-1
Flexural strength, MPa
1600
800
quasi-elastic zone, 50s, Σε = 0.04
initial elastic-plastic zone, 40s, Σε = 0.03
plastic zone, 72 s, Σε = 0.06
(III)
(II)
0.00
0.06
0.12
Engineering strain, mm/mm
SE-SEM
(III)
50μm
(II)
5μm
BF-TEM
1μm
1μm
BF-STEM
200nm
BF-STEM
20nm
ADF-STEM
200nm
ADF-STEM
20nm


◇ 2000°C
strain rate 3.8·10-3 s-1
Flexural strength, MPa
1600
800
quasi-elastic zone, 50s,
Σε = 0.04
initial elastic-plastic
zone, 40s, Σε = 0.03
plastic zone, 72 s,
Σε = 0.06
(III)
(II)
0.00
0.06
0.12
Engineering strain, mm/mm

UHT flexure and strain driven amorphization in polycrystalline boron carbide

Structure and amorphous zone formation inside severely deformed grains
(a,b) low & (c,d) high magnification BF-STEM images from heavily deformed region



Nucleation and propagation of amorphous region inside of the grains pointed out with broken lines and yellow arrows in (c,d).

Scripta Materialia **210** 15 Mar *(2022) 114487* https://doi.org/10.1016/j.scriptamat.2021.114487

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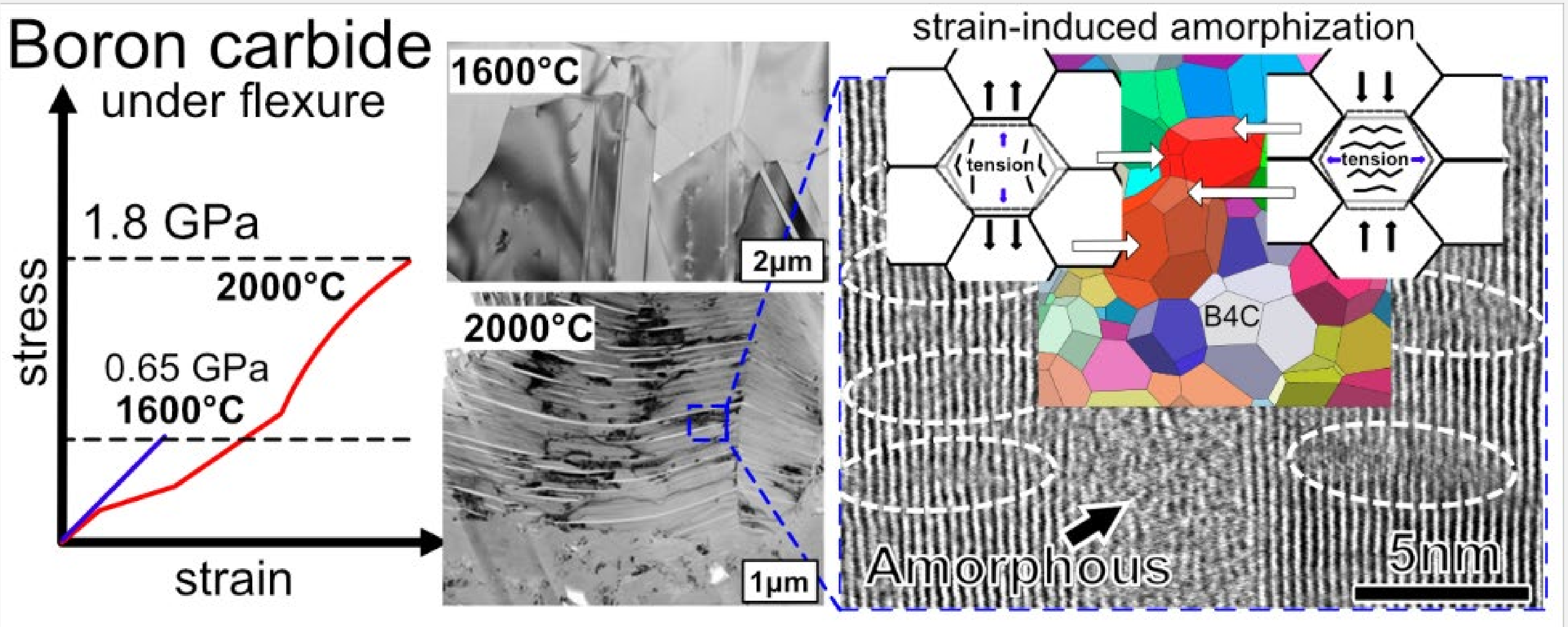
UHT flexure and strain driven amorphization in polycrystalline boron carbide



- ✓ UHT flexure driven amorphization in boron-reach boron carbide was accompanied with strength of up to 8.4 GPa at 2000 °C.
- ✓ The initiation of amorphization under ultra-high temperature flexure conditions occurs inside of the severely deformed grains.
- ✓ Magnitude of tensile stresses imposed on boron carbide grains during deformation in flexure & total strain transferred to ceramic during deformation process play the dominant role.

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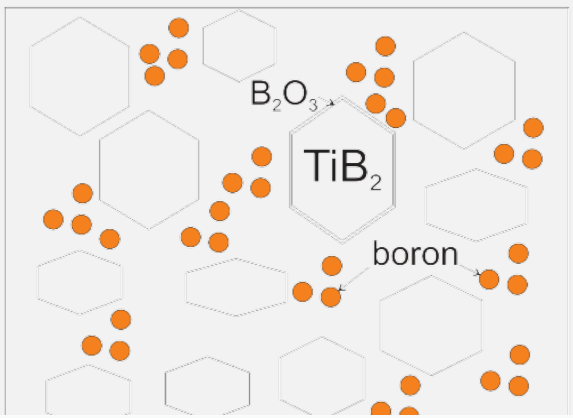
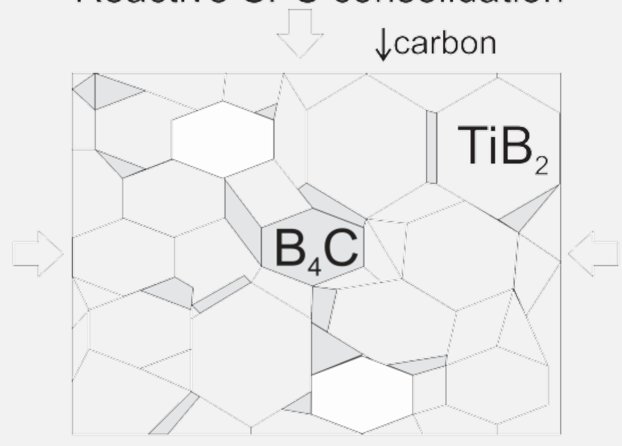
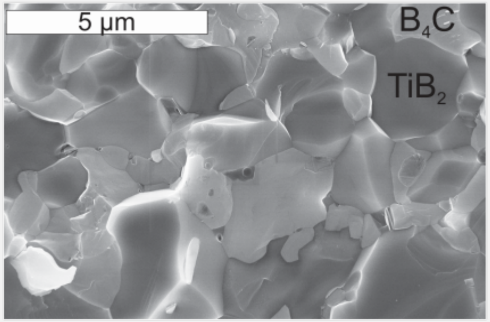
Structure formation during reactive SPS of TiB_2 – B ceramics

Materials and Method TiB_2 (.0–2.4 µm) and **amorphous B** (0.1–1.0 µm) from Wako Pure Chemicals, Osaka, Japan. **TiB_2 + 10-30 wt.% aB** by mixing in alcohol. RD-SPS using the 'Dr. Sinter' Sumitomo, Japan.

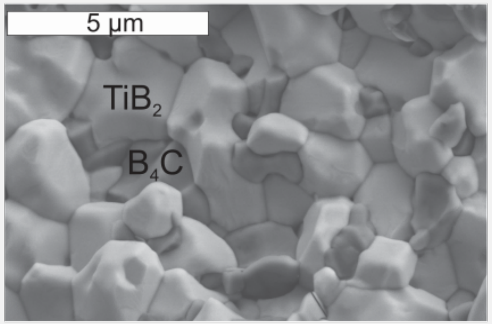




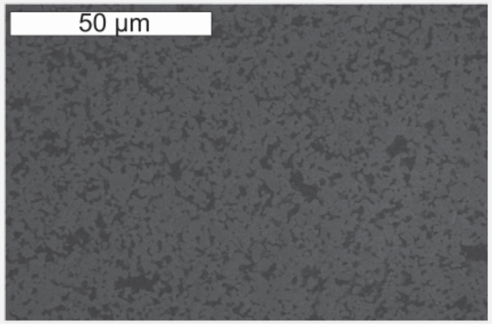
Newly formed grains locate at grain junctions & triple point of TiB2 grains, forming a covalent and stiff skeleton of B4C



Secondary electrons +
low angle back scattered electrons



Secondary electrons



High angle back scattered electrons

TiB_2 served either as matrix and reinforcement phase with stiff grain-boundary covalent skeleton of boron carbide.

***J. Euro. Ceram. Soc.**, 37 [1] Jan. 393-397 (2017),* https://doi.org/10.1016/j.jeurceramsoc.2016.08.009

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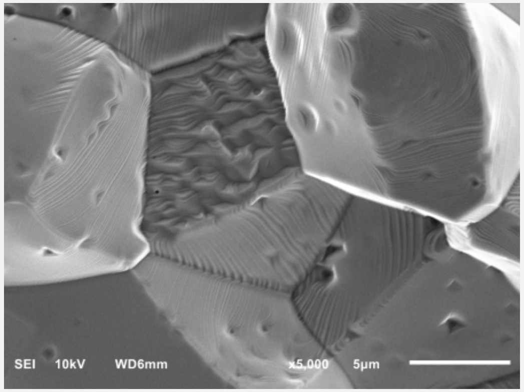
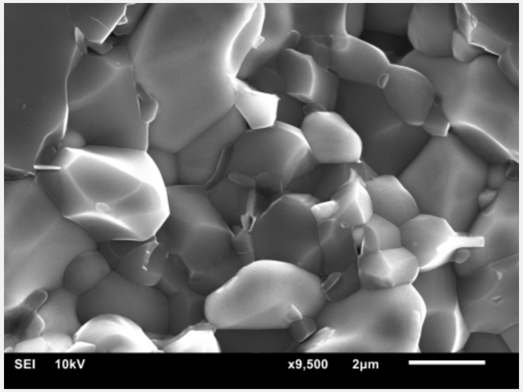
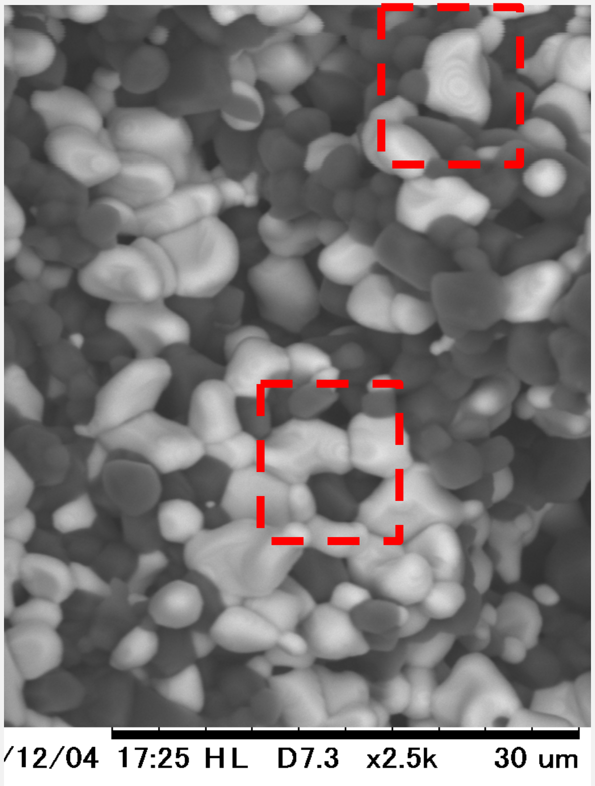
High-temperature strength of tailored B_4C/TiB_2 ceramic composites

Pre-modified TiB_2 ceramics after 2000 C bending strength test



B_4C-TiB_2 ceramics after 1600 C bending strength test





Three reasons for GPa strength:

(i) Complex composite structure with uniform distribution of newly formed secondary boron carbide phase;

(ii) Interfacial micro-cracking as result of large difference in the linear thermal expansion between TiB2matrix and B4C inclusion.

(iii) Finally, small value of the grain size, which corresponds to the initial particle size of raw TiB2powder (i.e. 2–5 μm).

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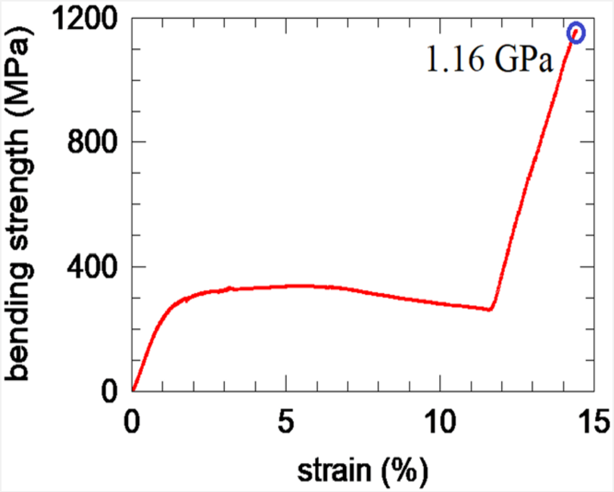
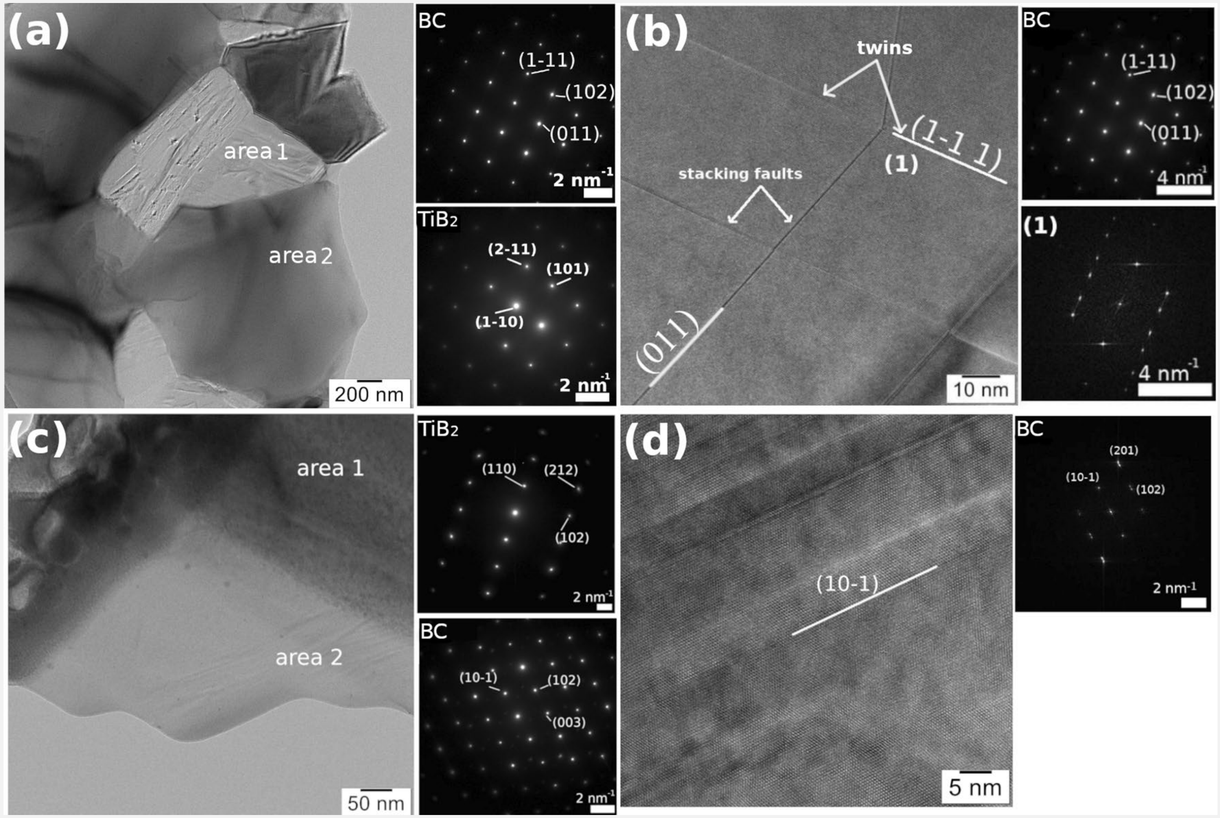
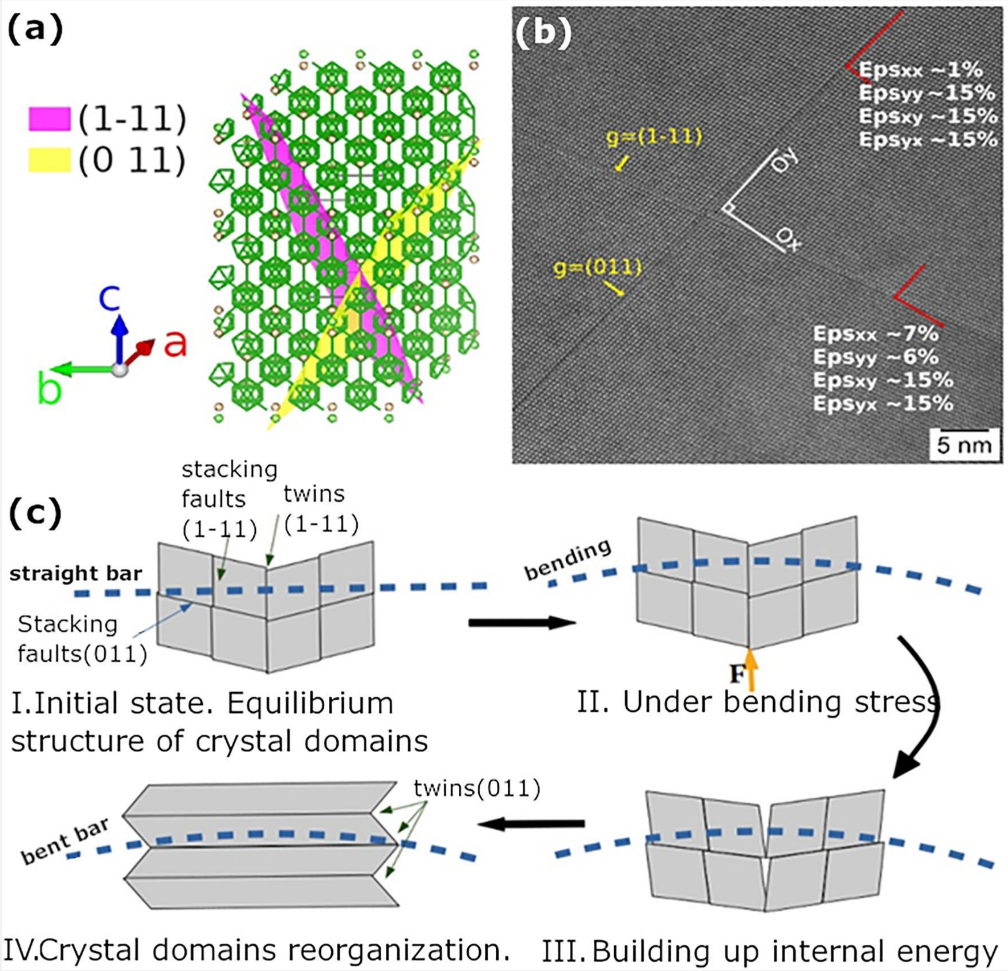
RD-SPSed TiB-B_4C (70/30 vol%) exhibits mean flexural strength of 1.1 GPa for up to 1800 °C. The strength–strain curve presents a peculiar shape composed of three regions where elastic and plastic deformations are active with different weights.





(a) CTEM and SAED images of area 1 = BC and area 2 = TiB2;
(b) HRTEM and SAED images showing stacking faults and twins (1) in the BC grain
(c) CTEM and SAED images where area 1 = TiB2 and area 2 = BC grains;
(d) HRTEM and SAED images showing nano-twins in BC.

***Scientific Report*, 13** (2023) 6915 *https://doi.org/10.1038/s41598-023-33135-w*



(a) Boron carbide crystal representation by VESTA software showing equivalent planes (1-11) and (011);

(b) HRTEM image taken on sample E showing strain components with Oy being parallel to (011) planes;

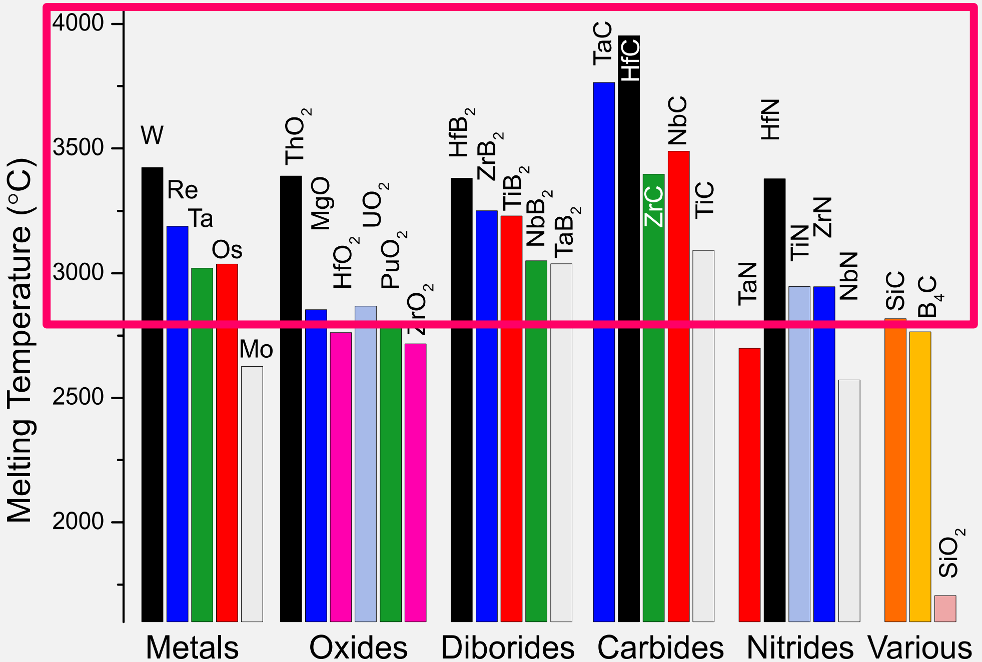
(c) Schematics of the transition under bending load between twinned and stacking faulted structure as in sample E to nano-twinned one as in sample F.

Based on TEM observations we propose process of mechanical energy absorption driven by shear stress in the boron carbide crystals: stacking faults with (1-11) **and** (011) **stacking planes and twins with** (1-11) **twinning plane rearrange into nano-twins** with (10-1) twinning planes, orthogonal but equivalent to the initial ones.

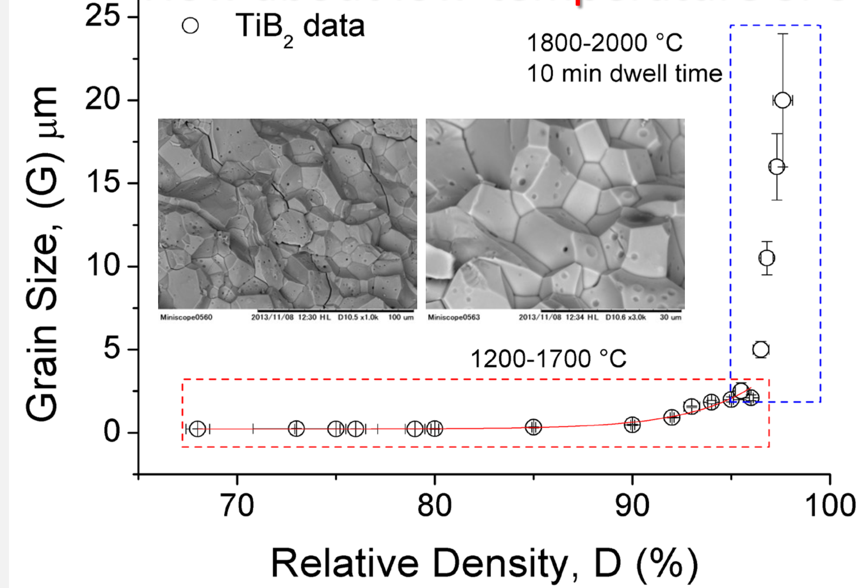
This rearrangement mechanism provides in the first instance a plastic signature but further contributes to strengthening.

Scientific Report, **13** (2023) 6915 https://doi.org/10.1038/s41598-023-33135-w

Densification and grain growth of UHT carbides & borides



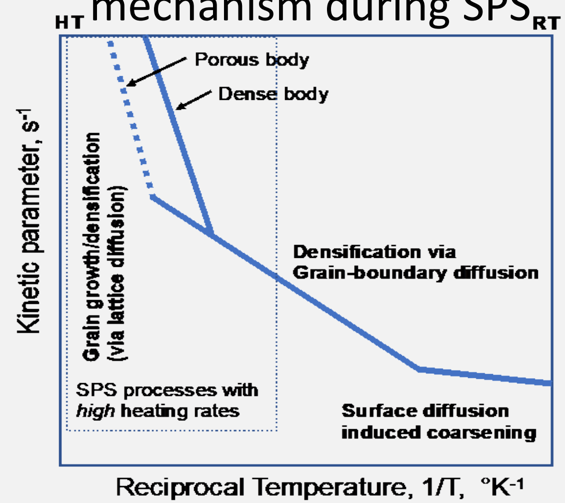
How about low-temperature SPS?



Monolithic carbide or boride without additives are required

For example: HfC, TaC, and their solid solutions are among the compounds with the highest melting points reported.
Using the 0.7 Tm treatment will yield 2500°C?
This suggests that temperatures over 2200°C should be used for densification, even using SPS.

Heating rate effect on consolidation mechanism during SPS



Try SPS using high heating rates

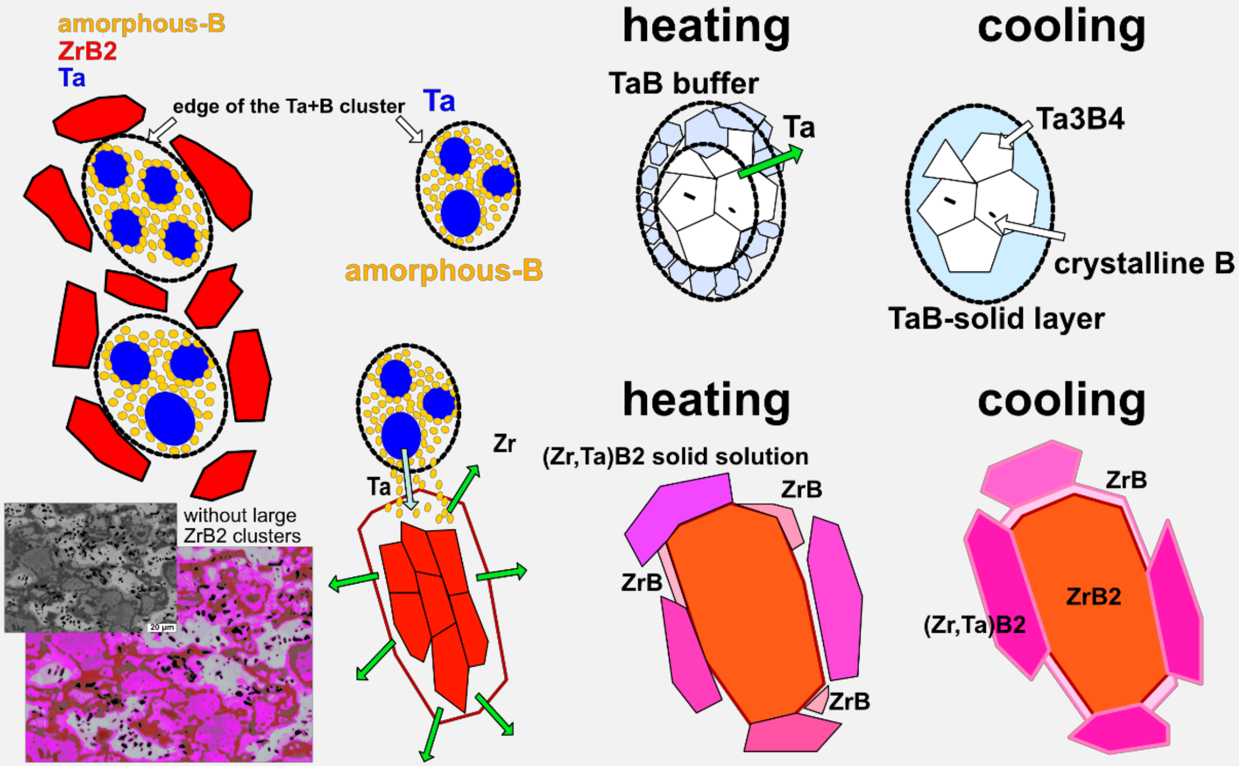
Engineered Zr-Ta multiboride ceramic with a supercomposite structure

Starting materials:

ZrB_2 (High-Purity Chemicals, Japan), amorphous B (Wako Pure Chemical Industries, Japan), Ta (Micronmetals, USA) powders.

Ta-B mixture was prepared, then the ZrB_2 was added to the mixture.

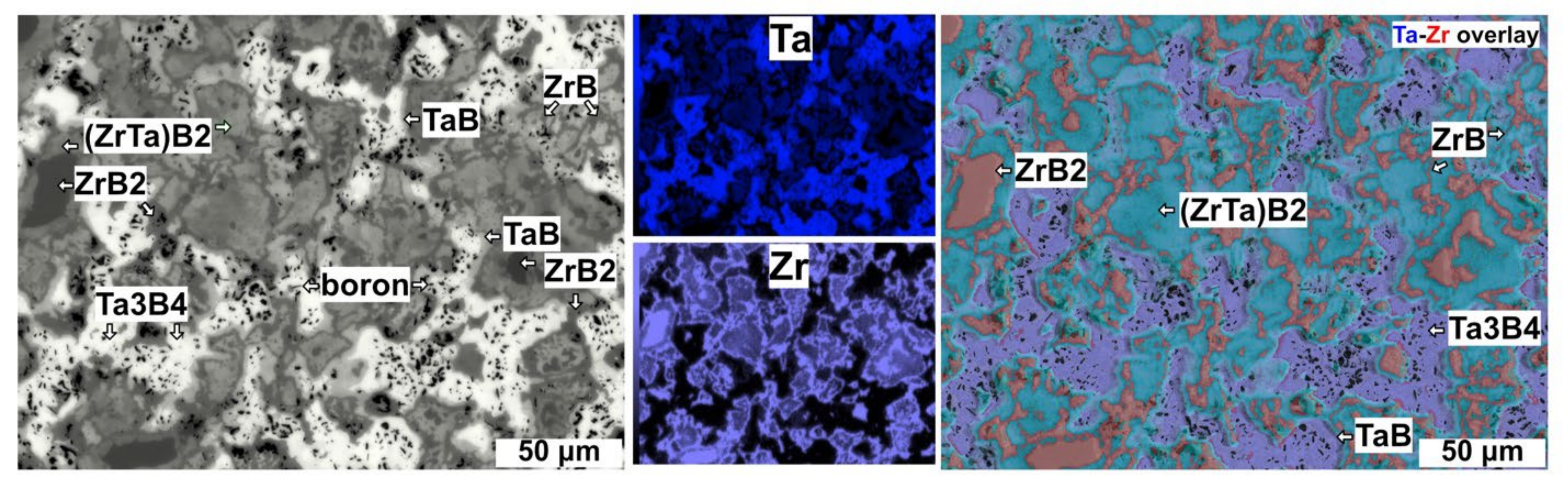
Formation of phases during the reaction and cooling stages of SPS



Areas where the TaZrB phase is being formed, while the main phase is the diboride solid-solution.

J. Am. Ceram. Soc., **105** [11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653

Engineered Zr-Ta multiboride ceramic with a supercomposite structure



- ✓ Ta_3B_4 ~ 10 µm clusters have an entrapped crystallized boron self-assemble into the short-rod grains.
- ✓ TaB serves as a porous interlayer during the high-temperature range, but similar to ZrB it forms dense ~2–5 µm layer covering the Ta_3B_4-B clusters.
- ✓ Ta_3B_4 and two binary $(Zr,Ta)B_2$ solid-solutions act as a composite matrix, whereas the fine ZrB/ZrB_2 quasi-continuous fibrils act as a reinforcing phase

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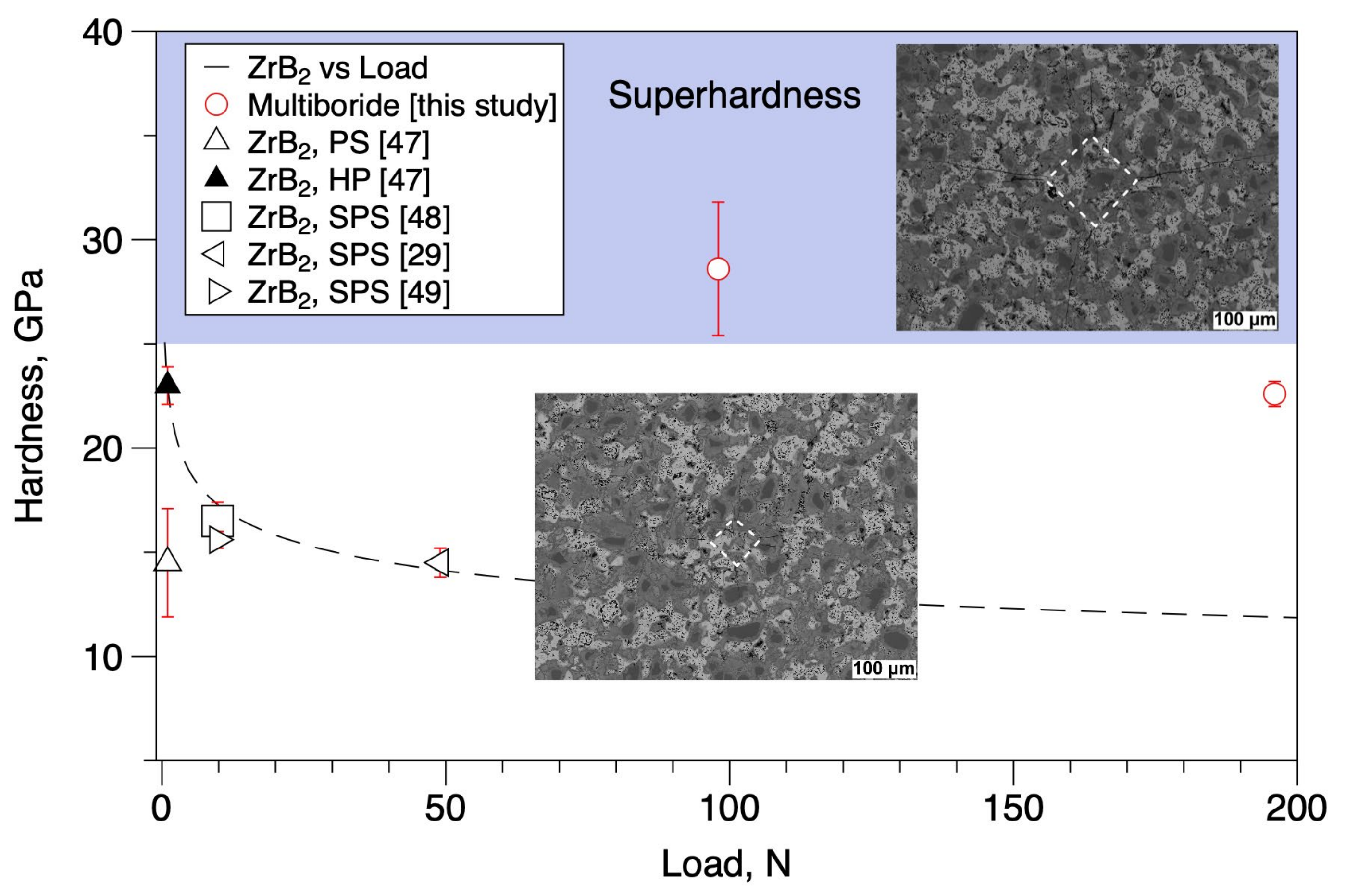
J. Am. Ceram. Soc., ***105*** *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

Engineered Zr-Ta multiboride ceramic with a supercomposite structure



Hardness of Zr-Ta multiboride supercomposite exceeding 30 GPa (load 98 N), and 22.6±0.6 GPa (load 196 N). Increase in hardness for multiboride Ta-Zr ceramic is due to (1) the continuous Ta_3B_4 phase, and/or (2) solid-solutions formed between the zirconium & tantalum diborides. The toughness was 4.6±0.4 MPa $m^{1/2}$

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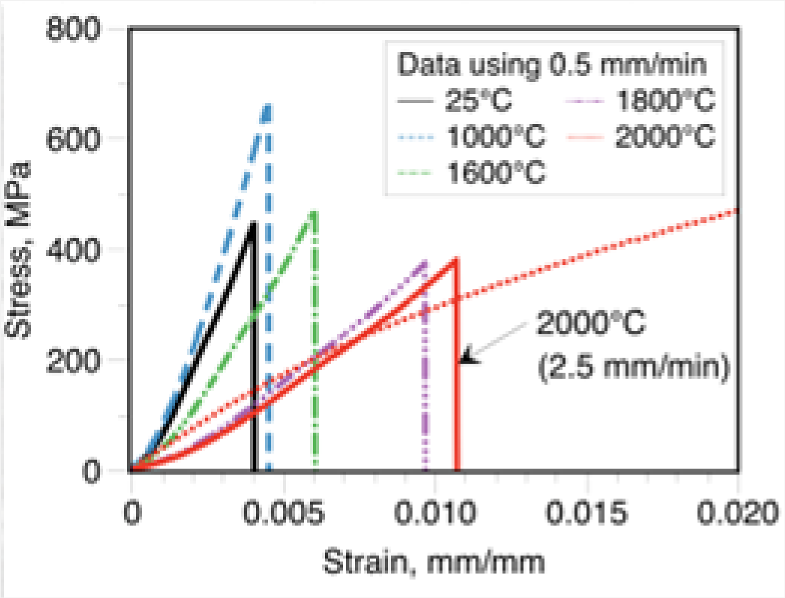
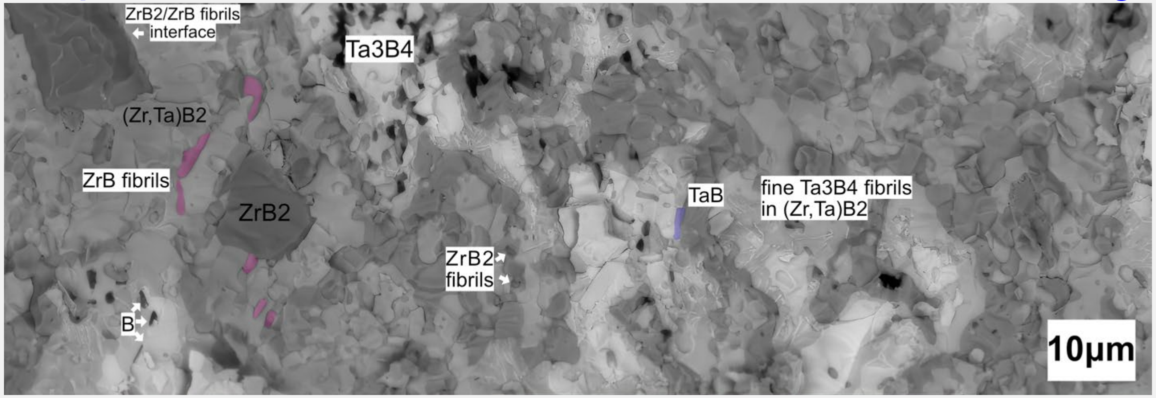
Engineered Zr-Ta multiboride ceramic with a supercomposite structure



At 2000 °C, multiboride composite showed a strength 400 MPa & fractured in an elastic manner at the loading rate of 2.5 mm/min. This level of strength is usual for the bulk zirconium diboride at room temperature.

Representative fracture of the multiboride during the flexure at 1800 °C



There were some quasi-lamella sub-grains mainly at the interface of the Ta_3B_4 phase.

Fracture at 1800 °C revealed only the presence of fine Ta_3B_4 fibrils.

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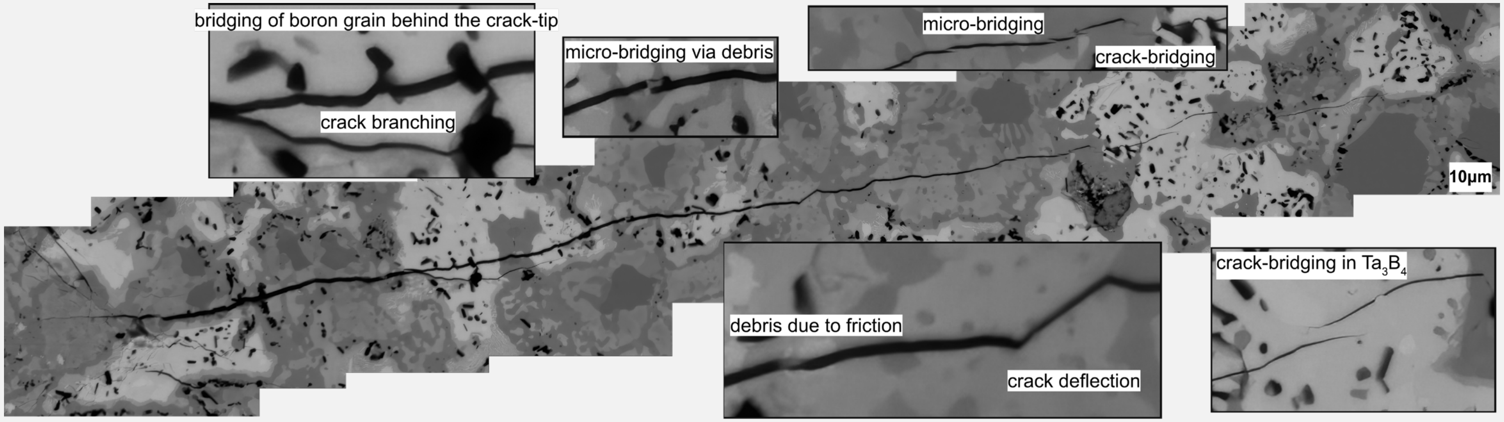
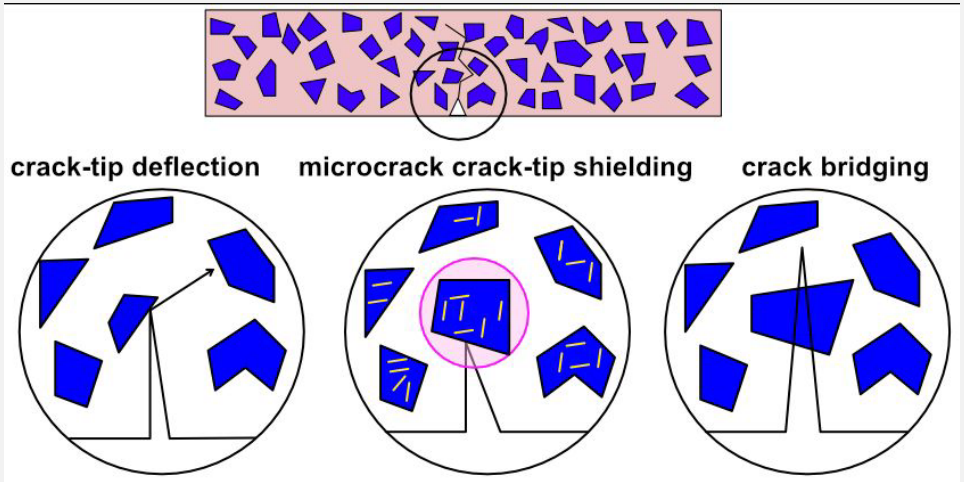
Engineered Zr-Ta multiboride ceramic with a supercomposite structure



Fracture details and effect of the loading rate on the flexure of the Zr-Ta multiboride ceramic composite at 2000 °C.

Strengthening/toughening mechanisms in multi-boride composite



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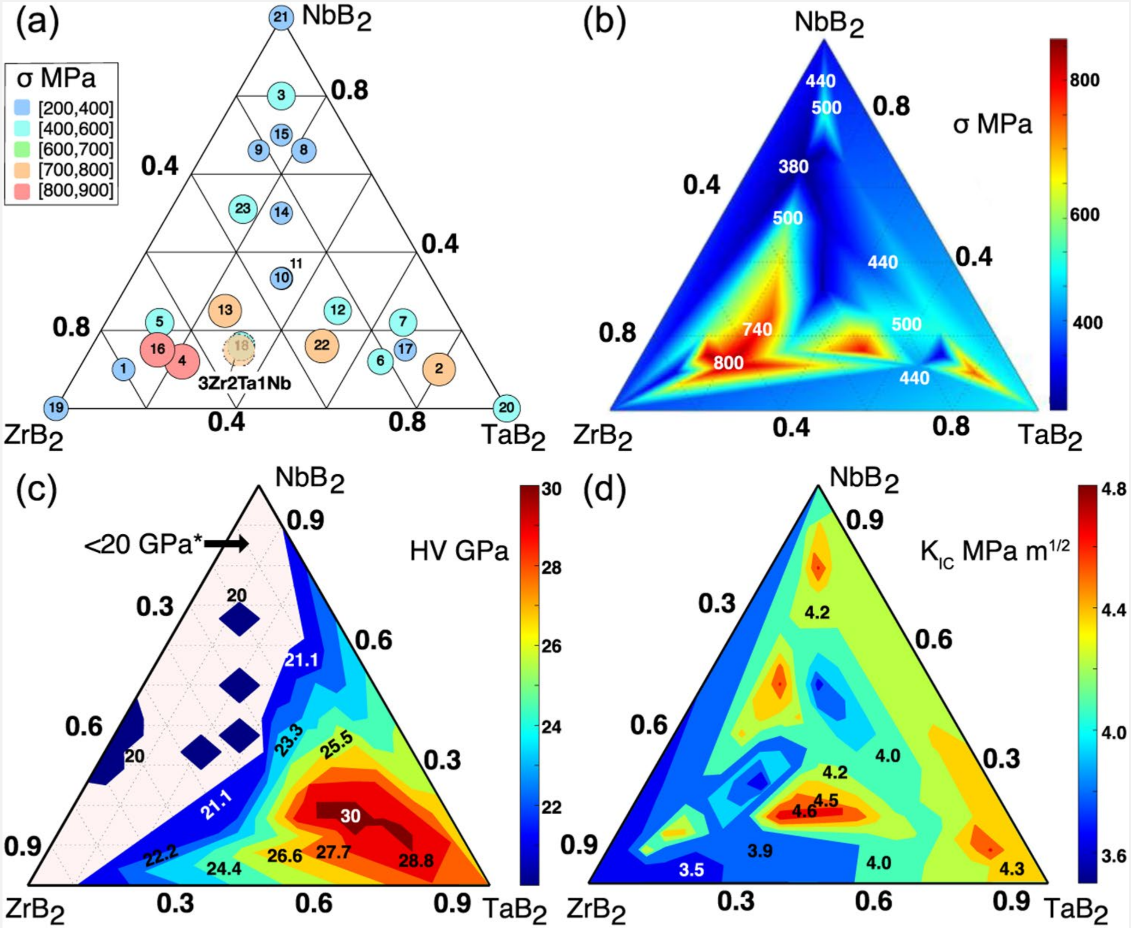
High-strength, medium entropy Zr-Ta-Nb diboride ceramics

Exploring ternary medium-entropy (Zr, Ta, Nb)B_2 system allows to create solid-solution of diborides to improve the set of properties at elevated temperatures…

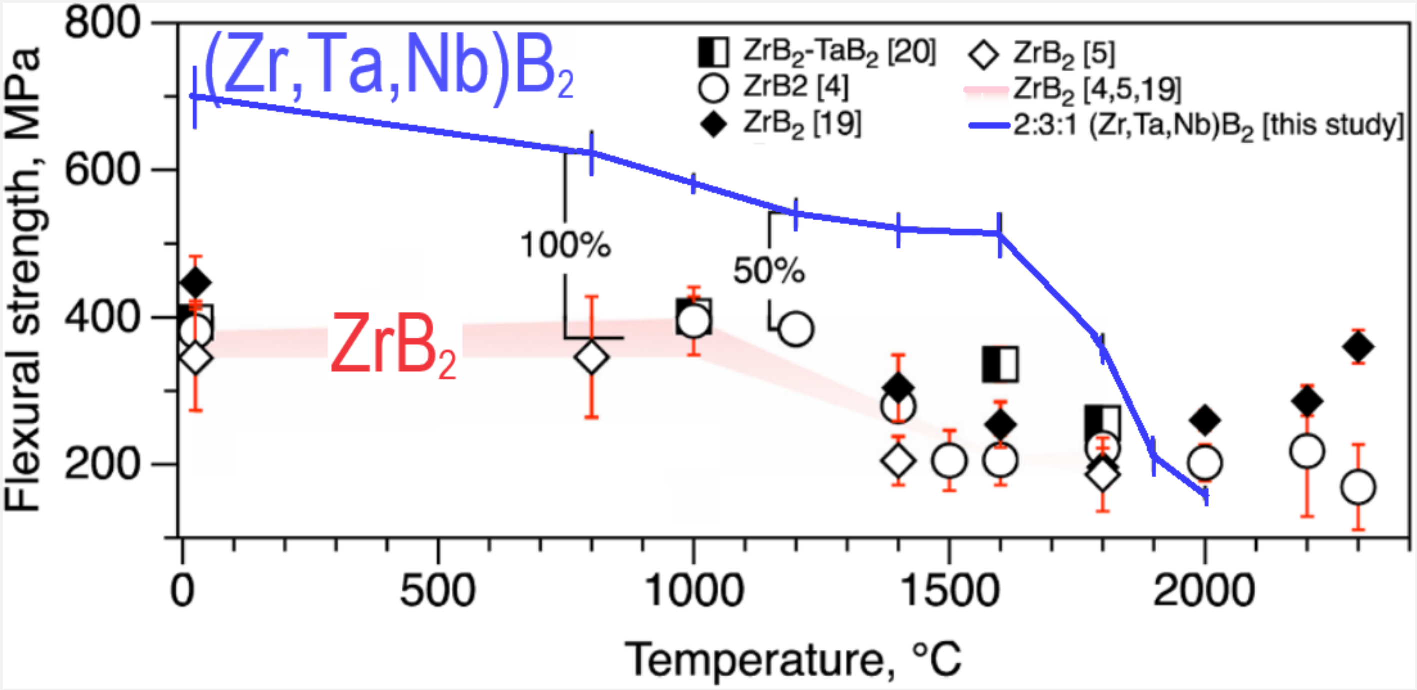


After close inspection of the data, it was decided that the ZTN diboride with a 3:2:1 composition should be evaluated as it had a strength above 800 MPa & one of the finest grain sizes after SPS at 2000 °C 8 ± 2 µm.

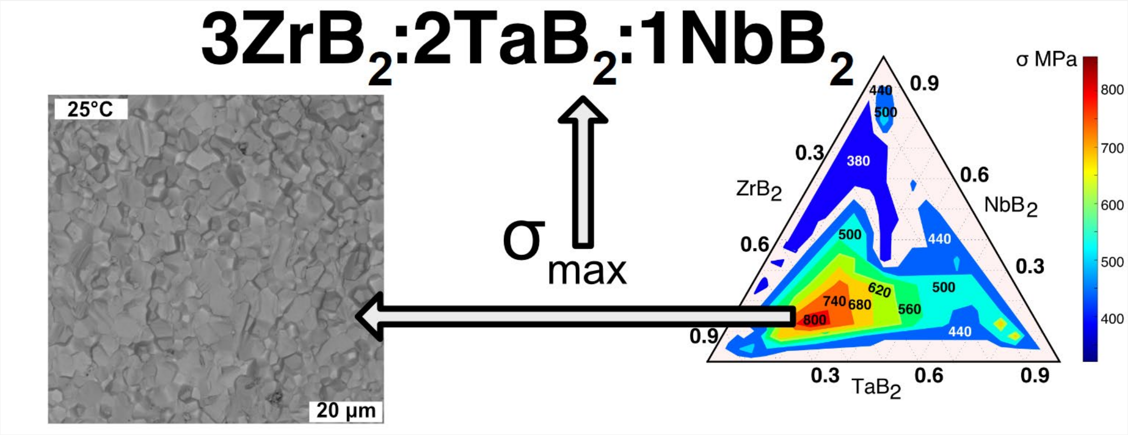
Scripta Materialia **225** 1 Mar *(2023)* 115170 https://doi.org/10.1016/j.scriptamat.2022.115170

High-strength, medium entropy Zr-Ta-Nb diboride ceramics

ZTN diboride with a 3:2:1 composition had a strength above 800 MPa and had one of the finest grain sizes after the SPS at 2000 °C (8 ± 2 µm).



The optimum mechanical properties do not essentially correspond to the equimolar composition - widely used for medium- or high-entropy ceramics



***Scripta Materialia* 225** 1 Mar *(2023)* 115170 https://doi.org/10.1016/j.scriptamat.2022.115170