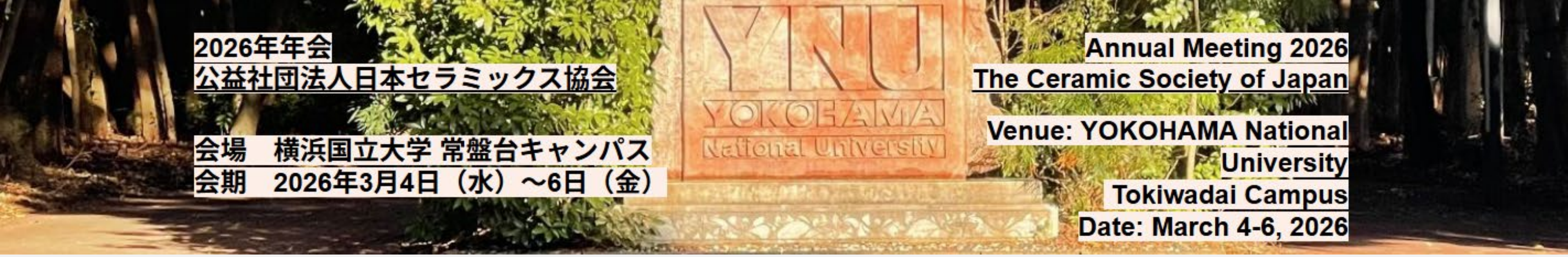


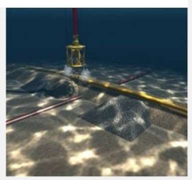
Ultra-High-Temperature Deformation Resistivity in SPS-Consolidated Transition Metal Diborides

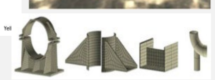
Vasylkiv Oleg
National Institute for Materials Science

3K02 March 6, 2026, Symposium: 01. Engineering ceramics

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

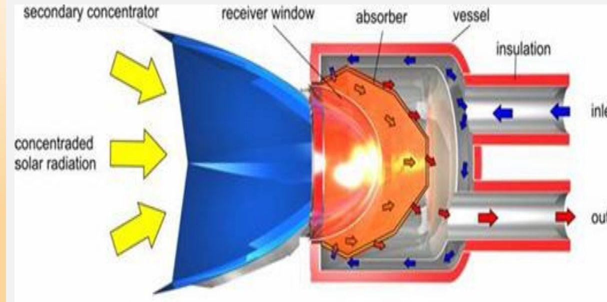
Leading-edge components for aerospace



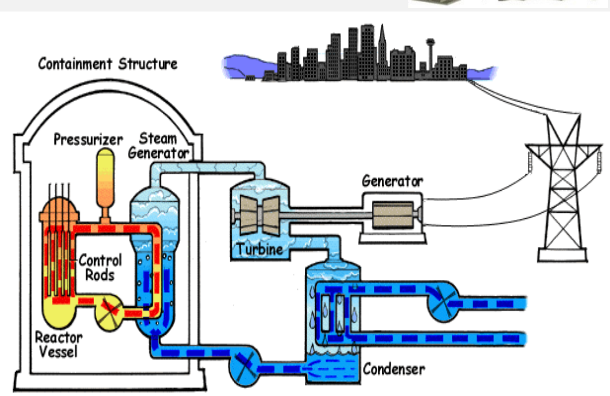


UHT ceramics are crucial for aerospace, energy, & power systems, where maintaining mechanical integrity under extreme thermal conditions is vital.

Gas turbine operation



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

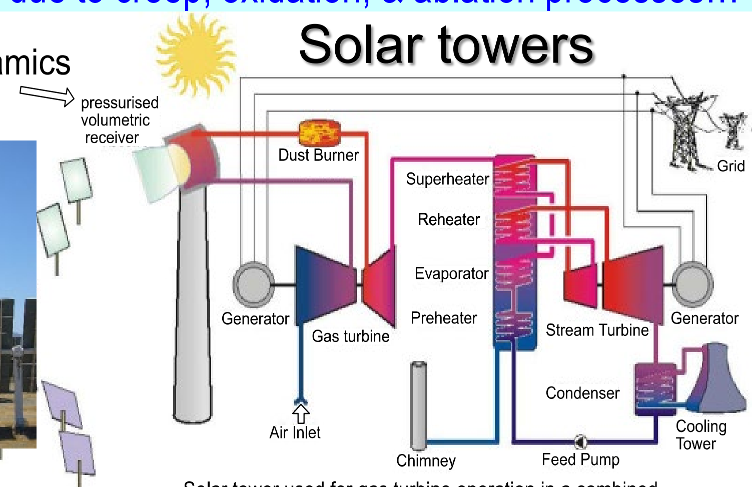


Plasma facing parts

HT Carbide ceramics

Solar towers

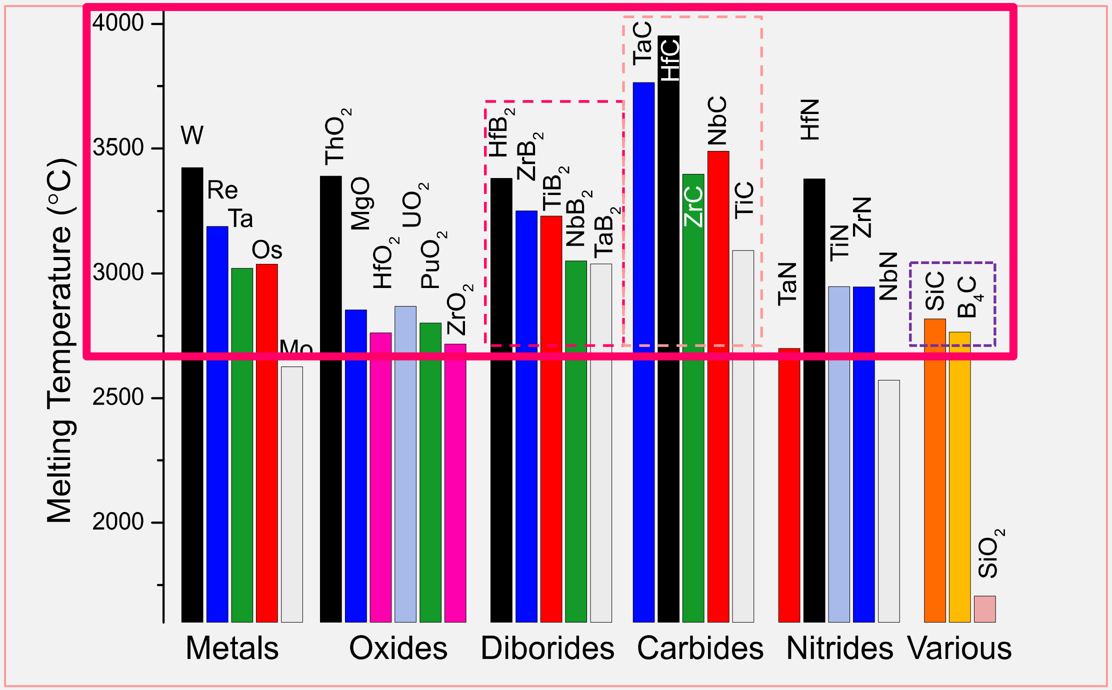
The solar tower power plant on the Plataforma Solar in Almería



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

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

Creation of bulk UHTC: densification & grain growth of transition-metal carbides & borides



- ✓ Monolithic carbides & borides **without additives** are required
- ✓ **Most borides, carbides**, and their solid solutions are among the compounds with the highest reported melting points
- ✓ The 0.7 Tm treatment results in a temperature of 2500°C
- ✓ This suggests that SPS temperatures over 2200°C are often required.

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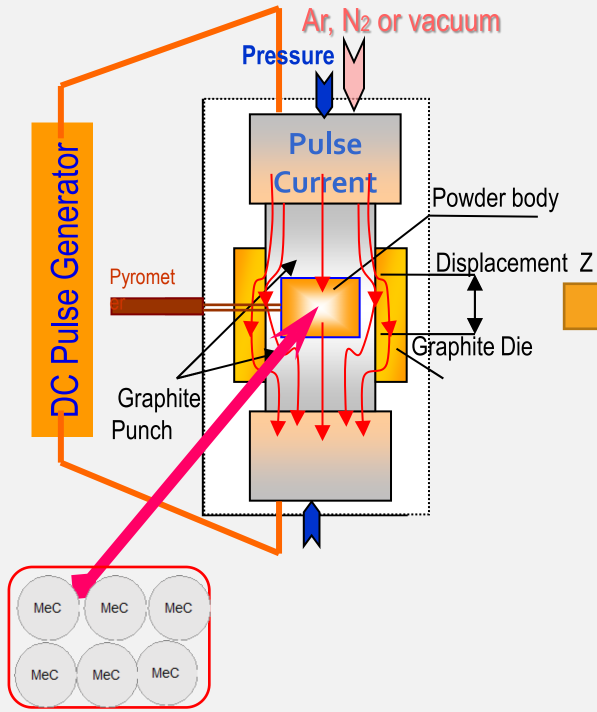
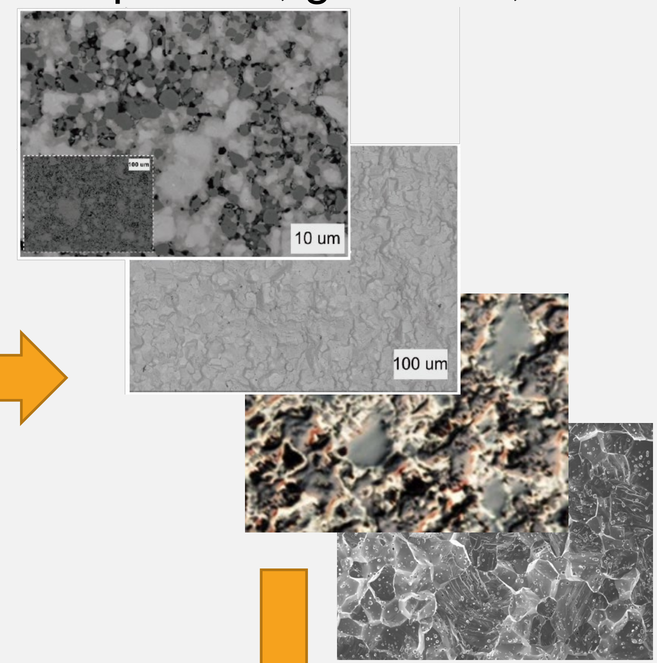
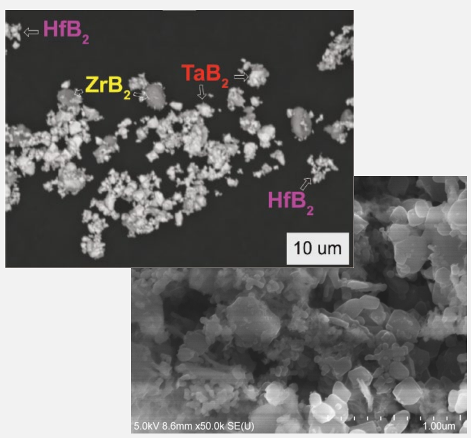
Processing – composition/structure – properties



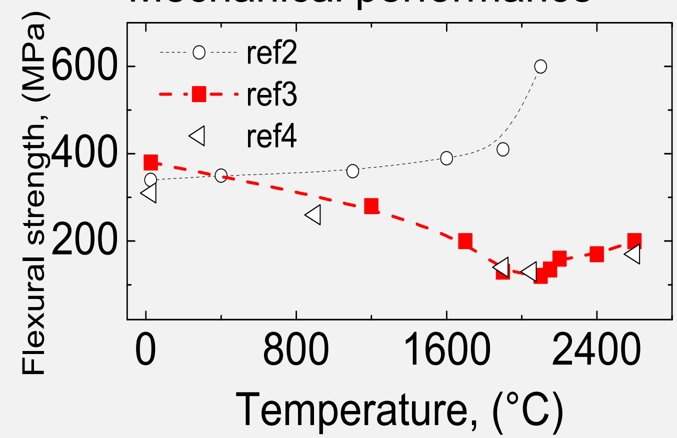
Composition, grain size, etc.



Starting powders/mixtures

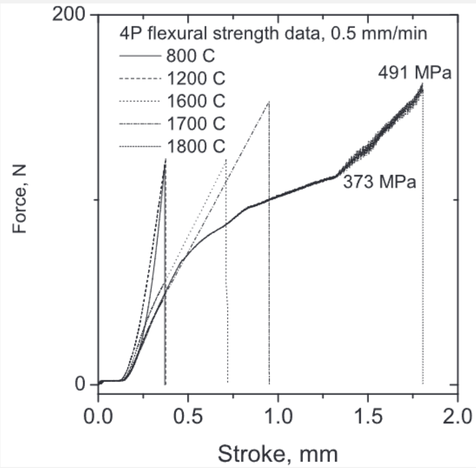


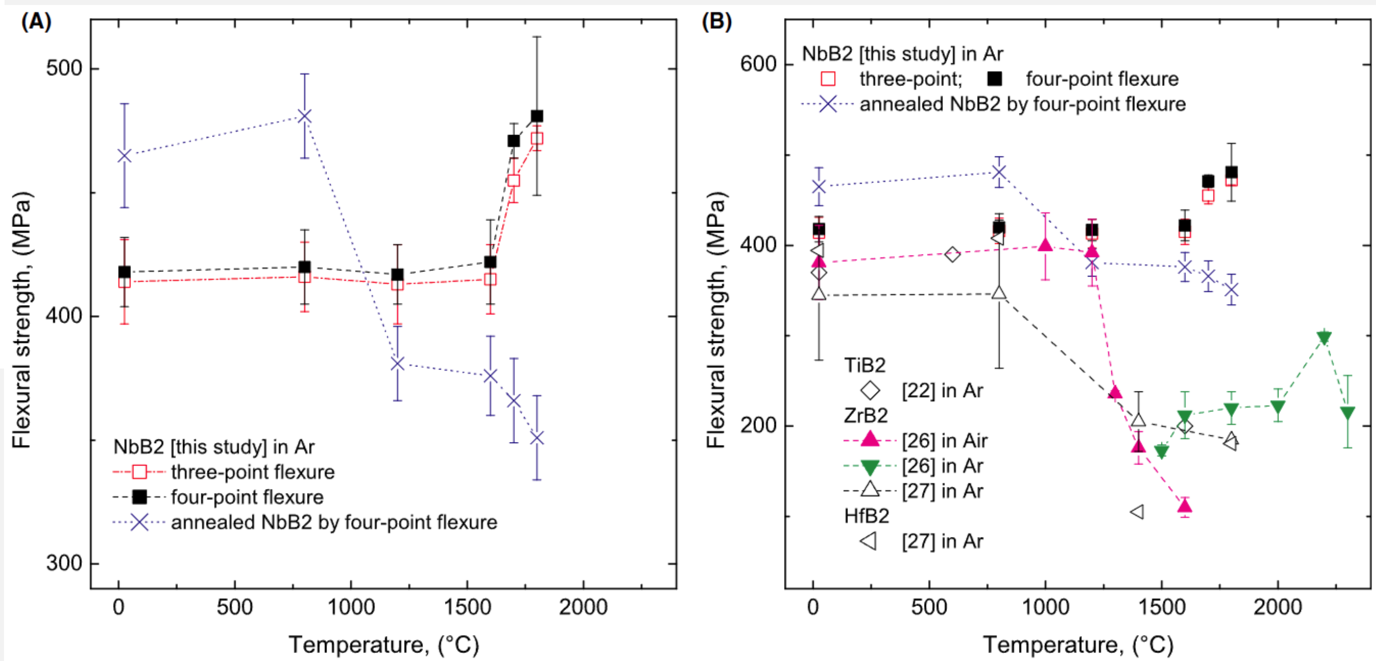
Mechanical performance



High-temperature strength and plastic deformation behavior of niobium diboride consolidated by SPS

Bulk niobium diboride SPSed (**NbB_2 1.0-2.4 μm powder** from Wako Pure Chemical Industries, Ltd., Osaka, Japan), at 1900°C with a **density of 98%** and a **mean grain size of 6 μm**.





- The **RT strength was 420 MPa & remained constant up to 1600°C**.
- **At 1700°C, it increased to 450 MPa, and at 1800°C, signs of plastic deformation appeared.**
- Fractographic analysis showed etching pits & step-like surfaces, indicating HT deformation.
- **This was abnormal behavior (2016) compared with the bulk diborides of Ti, Zr, and Hf.**

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***J. Am. Ceram. Soc.* 100** [11] Nov. 5295-5305 (2017), *https://doi.org/10.1111/jace.15048*

Deformation resistance of UHTC and sensitivity of flexural strength to loading rate at elevated temperatures.

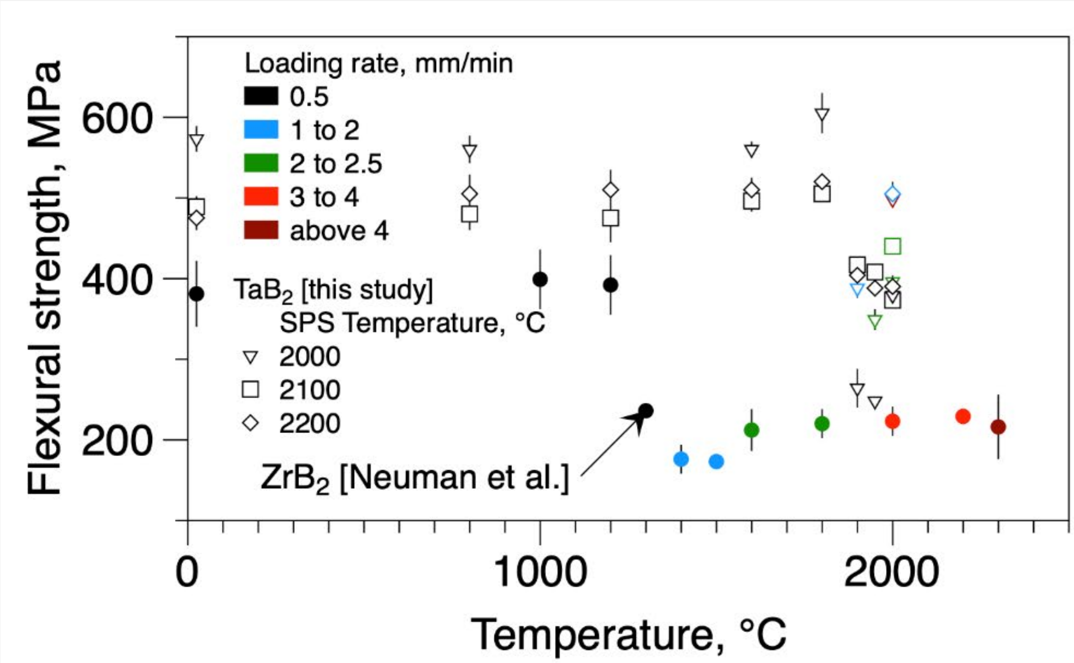
- Dense TaB_2 with a grain size of 3 - 7 µm SPSed at 2000 - 2200°C.
- Three-point flexural strength measured as a function of temperature up to 2000°C in an Ar atmosphere.
- Strength exhibited deformation resistivity from room temperature to 1800°C.
- Above 1900°C, the strength became sensitive to the applied loading rate.
- TaB_2 demonstrated further resistance to deformation, with flexural strength increasing to 400±20 MPa at 1900°C.
- In comparison, ZrB_2 exhibited strengths of 220±18 MPa at 1800°C and 223±18 MPa at 2000°C.

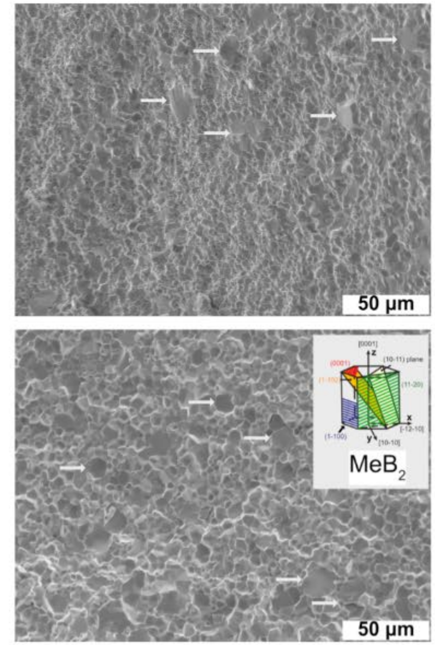
Flexural strength for TaB2 and ZrB2 ceramics at room & elevated temperatures.

Temperature, °C	SPS Temperature, °C	Crosshead rate (mm/min)	Strength, MPa	Loading curve
25	2000	0.5	573 ± 16	Elastic
25	2100	0.5	489 ± 13	Elastic
25	2200	0.5	475 ± 15	Elastic
1900	2000	0.5	264 ± 24	Plastic
		1.5	388 ± 12	Elastic
1900	2100	0.5	417 ± 9	Elastic
1900	2200	0.5	404 ± 16	Elastic
1950	2000	0.5	248 ± 4	Plastic
		2.0	349 ± 13	Elastic
1950	2100	0.5	408 ± 6	Elastic
1950	2200	0.5	388 ± 8	Elastic
2000	2000	0.5	389 ± 5	Plastic
		2	396 ± 8	Plastic
		4	498 ± 10	Elastic
2000	2100	0.5	373 ± 7	Plastic
		2	440 ± 10	Elastic
2000	2200	0.5	390 ± 10	Plastic
		1.0	505 ± 15	Elastic
1800	ZrB_2[9]	2.5	220 ± 18	Elastic
2000	ZrB_2[9]	3.0	223 ± 18	Elastic
2200	ZrB_2[9]	3.5	299 ± 5	Elastic

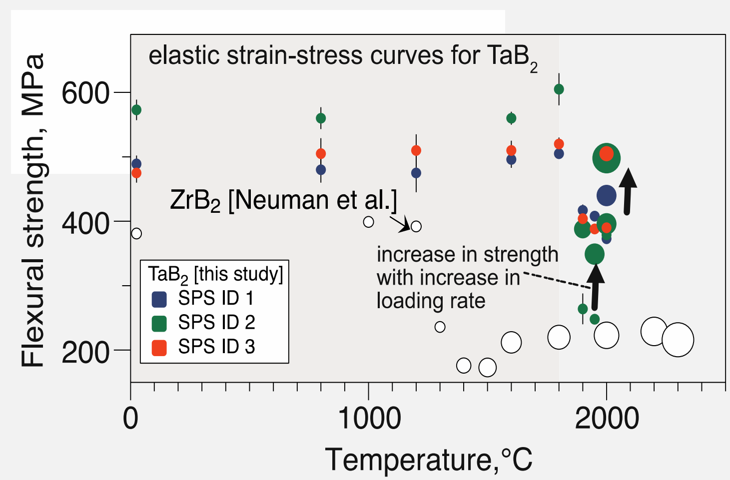
NIMS *J. Am. Ceram. Soc., 106 [11] 6385-6389 (2023)* https://doi.org/10.1111/jace.19307

High-temperature strength behavior of tantalum diboride to 2000°C





- Strength exhibited a variation of approximately 50 MPa between RT and 1800°C, with temperature behavior dependent on the consolidation temperature.
- Above 1900°C, the strength became sensitive to the applied loading rate. TaB_2 demonstrated resistance to deformation as the flexural strength gradually increased to 400±20 MPa at 1900°C.



J. Am. Ceram. Soc., ***106*** *[11] 6385-6389 (2023)* https://doi.org/10.1111/jace.19307

High-temperature strength behavior of tantalum diboride to 2000°C

- The difficulty in processing tantalum diboride ceramics to full density appears to correlate with the high strength and elastic fracture up to 1900°C.
- In this case, once a ceramic with a certain density/grain size is formed, it becomes difficult to further deform it unless higher temperatures are used.
- The resistance to deformation at elevated temperatures can be attributed to factors such as stress, local bonding, and grain size.
- Coarse grains may enhance strength through grain-boundary sliding. In such cases, stress concentrations can be relieved, resulting in premature failure and allowing higher applied stresses to be reached before fracture.
- The significant increase in flexural strength with increasing loading rate suggests that fracture behavior is partially influenced by creep-like mechanisms.

J. Am. Ceram. Soc., 106 *[11] 6385-6389 (2023)* *https://doi.org/10.1111/jace.19307*

Reactive consolidation of tough, deformation resistant tantalum monoboride

TaB specimens (30-mm diameter, 6-mm thickness) by reactive SPS, using TaB_2, Ta, B (Wako Pure Chemicals)

Two approaches were used:

(A) Mixture of Ta and B

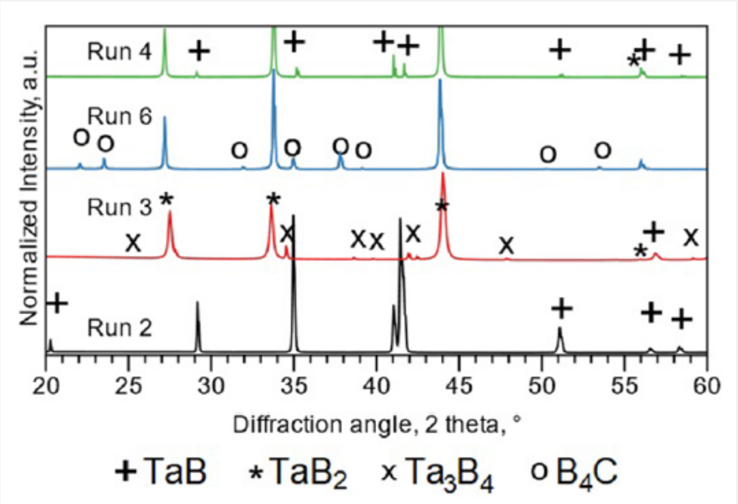
(B) Reaction between the TaB_2 powder and Ta

- ❑ Untreated powders mixed using the Intelli-Mixer RM-2M (ELMI, Latvia) mixer.
- ❑ The SPS 'Dr. Sinter' 1050, Sumitomo, Japan, 30-mm die, Ta-foil to control C diffusion, Ar atm.
- ❑ The SPS schedule: heating to 1000 °C, 50 °C/min heating to **1900 and 2200 °C**; homogenizing dwell

Table 1
Summary of spark plasma sintering experiments.

SPS run ID	Mixture type	Temperature, °C	Final phases	Porosity, %
4	A-TaB	1900	TaB, TaB_2	4.5 ± 0.6
6	A-TaB	2000	TaB_2, B_4C	3.2 ± 0.4
7	A-TaB	2050	TaB_2, B_4C	1.6 ± 0.2
5	A-TaB	2100	TaB_2, B/B_4C	1.8 ± 0.5
3	B-TaB	1900	TaB_2, Ta_3B_4, B/B_4C	4.4 ± 1.1
1	B-TaB	2000	TaB, TaB_2, boron	3.8 ± 1.5
2	B-TaB	2150	TaB, traces of boron	1.3 ± 0.5
8	B-TaB	2200	TaB, TaB_2, boron	1.8 ± 0.6

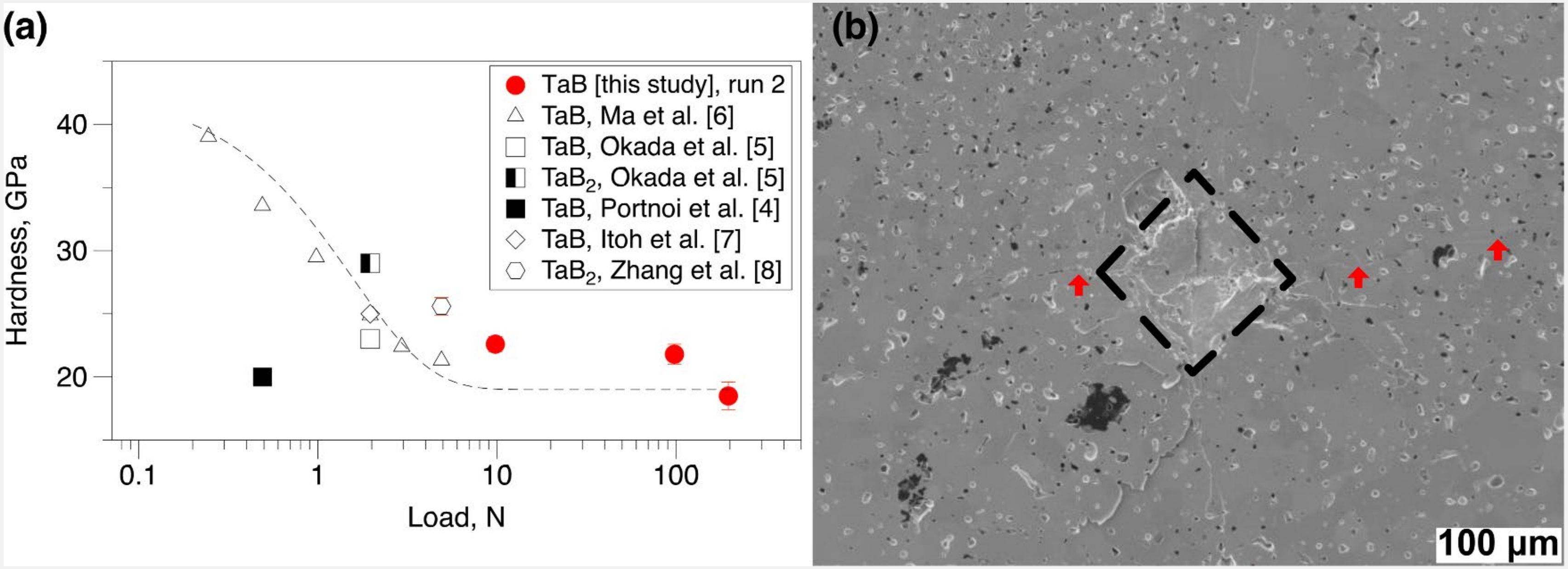
X-ray diffraction patterns for the sintered ceramics using SPS conditions 2,3,4, and 6



Single-phase **TaB (orthorhombic *Cmcm* cell** with the lattice parameters *a* = 3.28(1) Å, *b* = 8.67(2) Å, *c* = 3.15(7) Å), with up to 3 vol.% of boron as a residual phase

Scripta Materialia **229** May (2023) 115383 https://doi.org/10.1016/j.scriptamat.2023.115383

Mechanical performance of TaB studied using samples prepared under the Run 2 conditions.

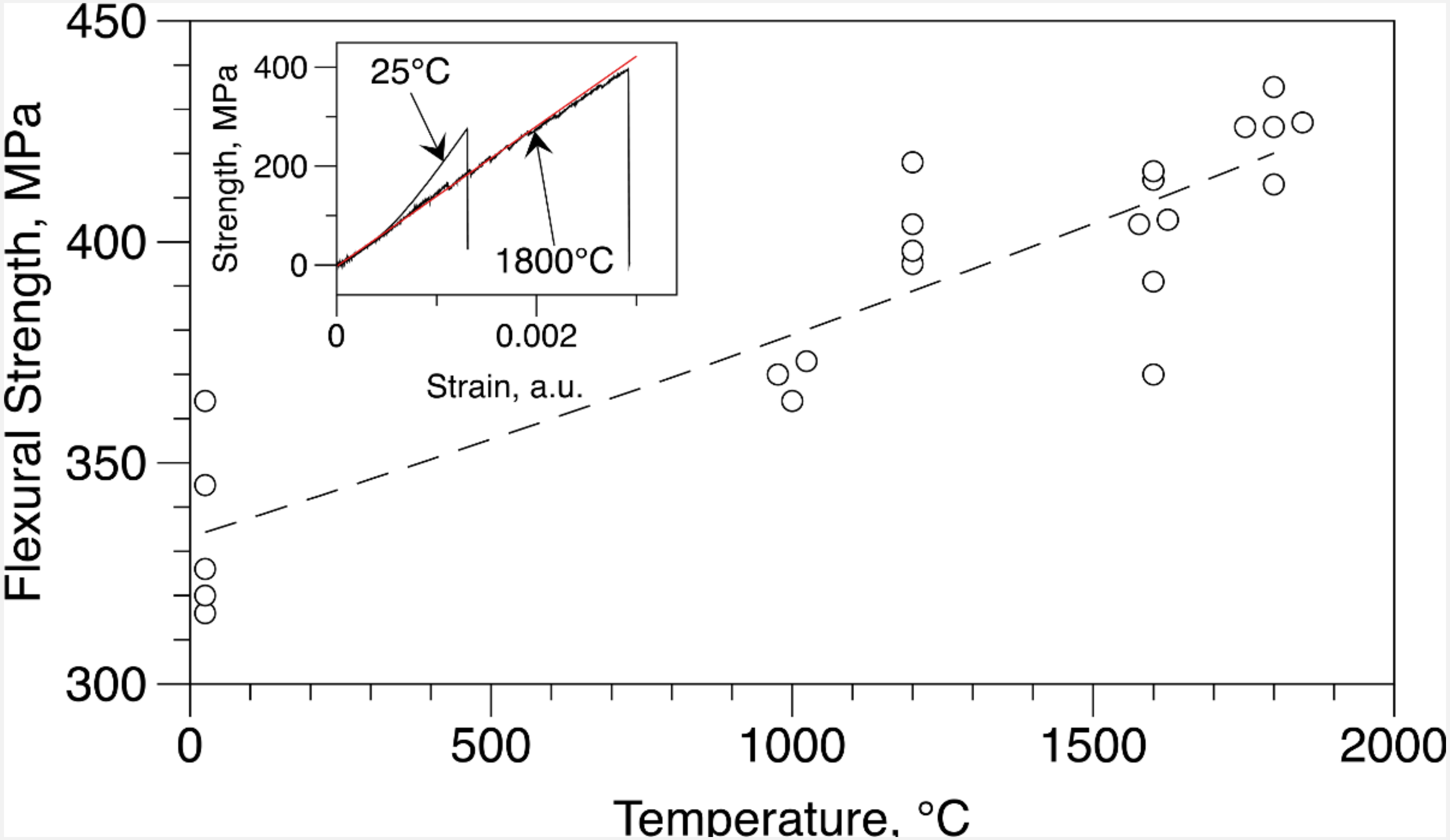


(a) hardness of TaB and TaB2 as a function of load; (b) shows typical indent using 196 N load

The **indentation fracture toughness was within 9.8** ± 0.4 MPa $m^{1/2}$ – an **unusually high value** compared to 4.5 MPa $m^{1/2}$ reported for TaB_2

Scripta Materialia **229** May (2023) 115383 https://doi.org/10.1016/j.scriptamat.2023.115383

Flexural strength of TaB gradualy increase with an increase in temperature.



Only at 1800 °C TaB had loading curves exhibited nonlinear characteristics associated with (i) flaw healing or (ii) plasticity (micro-plasticity) contribution. This indicates that test above 1800 °C will result in plastic deformation.

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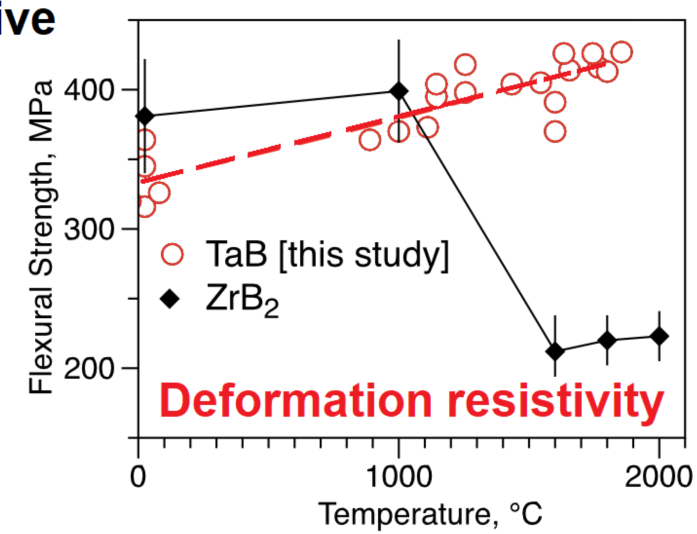
***Scripta Materialia* 229** May *(2023) 115383* https://doi.org/10.1016/j.scriptamat.2023.115383

In summary:

- ✓ This was the first study to report reactive synthesis/consolidation and strength of TaB bulks. Despite using the 1:1 molar ratio between reagents, monoboride formed only at 2150 °C from a mixture of tantalum and tantalum diboride.
- ✓ TaB had fairly elongated grains of 30 – 100 μm and showed excellent macroscopic hardness of 18.5 ± 0.2 GPa (at 196 N load) and **exceptionally high indentation fracture toughness** of 9.8 ± 0.4MPa $m^{1/2}$.
- ✓ TaB showed RT strength lower than reported for TaB_2, i.e., 330 vs 550 MPa.
- ✓ However, **with increasing temperature, TaB exhibited resistance to deformation, with flexural strength gradually increasing to 425±7 MPa at 1800 °C**.

Tantalum monoboride via reactive SPS of TaB_2 and Ta mixture

- Hardness 18.5 GPa
- Toughness 9.8±0.4 MPa $m^{1/2}$
- Strength at RT 320 MPa
- HT strength increases up to 1800°C



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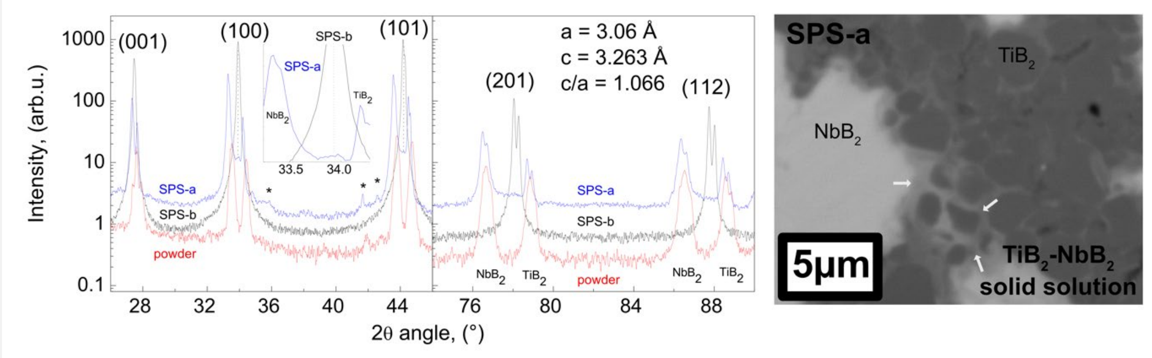
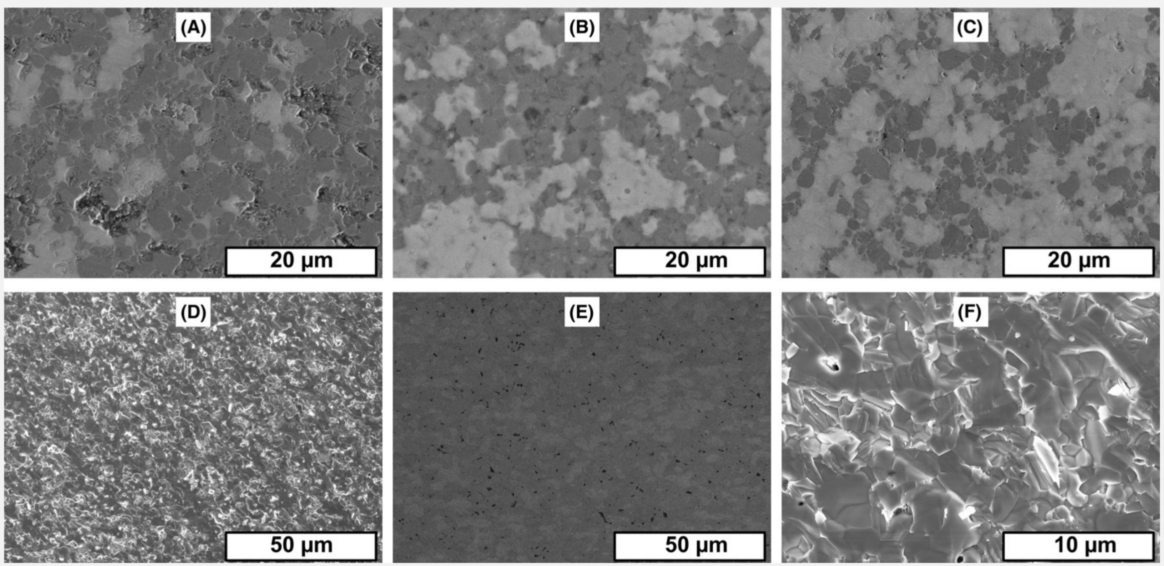
Fracture and property relationships in double diboride composites by SPS of TiB_2 and NbB_2



XRD patterns for TiB_2–NbB_2 composites 1:1 mole ratio after SPS 10 min at 2000 °C (SPS-a) and 30 min at 2100 °C (SPS-b). In both cases SPS pressure of 60 kN was applied throughout the consolidation cycle.

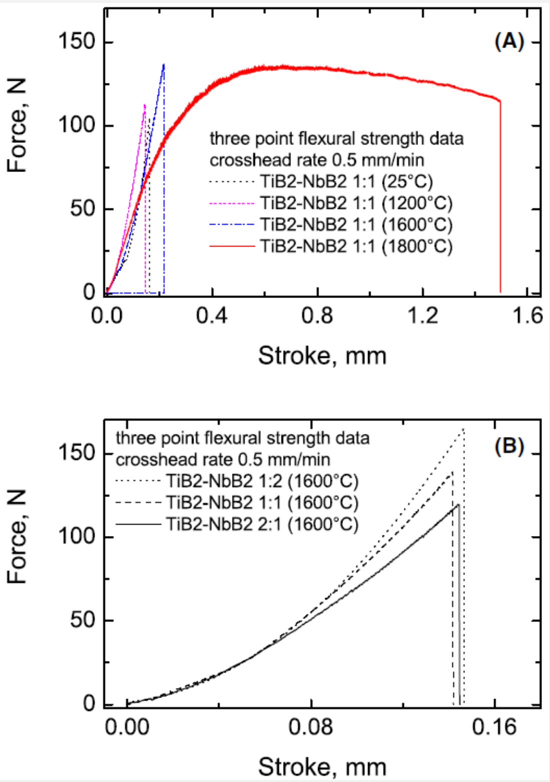
Three mixtures with 2:1, 1:1, and 1:2: TiB_2 (0.7-2.2 μm) and NbB2 (1.0-2.4 μm) (Wako Pure Chemicals, Osaka, Japan) were used in this study. TiB_2–NbB_2 ceramic composites SPSed at 1950 °C, achieving >98% theoretical density and a bimodal 1–10 μm grain structure. Controlled application and release of pressure produced a stable two-phase microstructure.



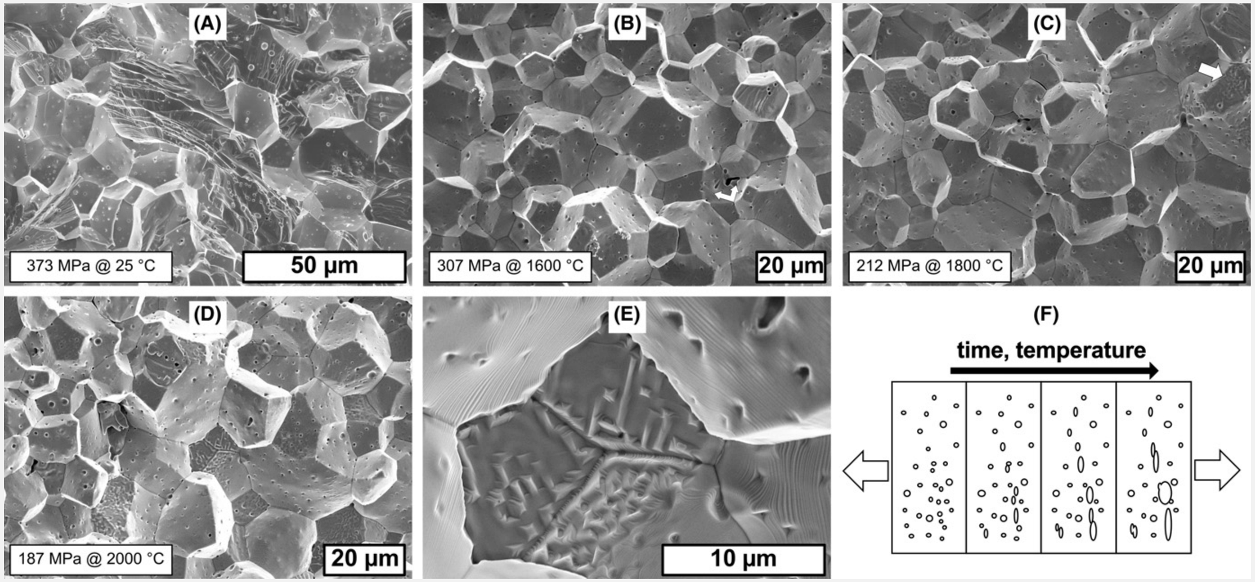
(A-C) and fractured surfaces of TiB2–NbB2 ceramics following flexural test at room temperature (D-F).
(A, D)—2:1; (B, D–F) 1:1 and (C) 1:2. Microstructures for (A-C) were obtained in BSE mode, (D-F)—secondary electrons, whereas (E) was acquired using high-angle BSE filter. Black areas in (E) indicate pores and grain pullouts.

J. Am. Ceram. Soc. **102** [7] Jul. 4259-4271 (2019), https://doi.org/10.1111/jace.16276

Fracture and property relationships in double diboride composites by SPS of TiB_2 and NbB_2



Loading diagrams of TiB2–NbB2 ceramic composites tested at RT and elevated temperatures by three-point flexural strength test. B - effect of composition on the flexural strength at 1600°C



Specimens after flexural tests at (A) RT, (B) at 1600°C, (C) at 1800°C. An arrow in (C) shows an area of the creep-induced fracture/sliding, or alternatively, by the void coalescence process (F), which can also be observed in (B). Mind, the typical pore size for this specimen was ~ 1 µm; thus, a significant number of voids were formed during fracture at HT. (D) and (E) show that for specimens tested at 2000°C, the number of grain faces affected by high-temperature deformation is increased. A loading rate was 0.5 mm/min. (E) - schematic representation for the formation of the structure observed by void coalescence (ie, a mechanism associated with plastic metal-like deformation), pores that are inherited from SPS processing have a larger size.

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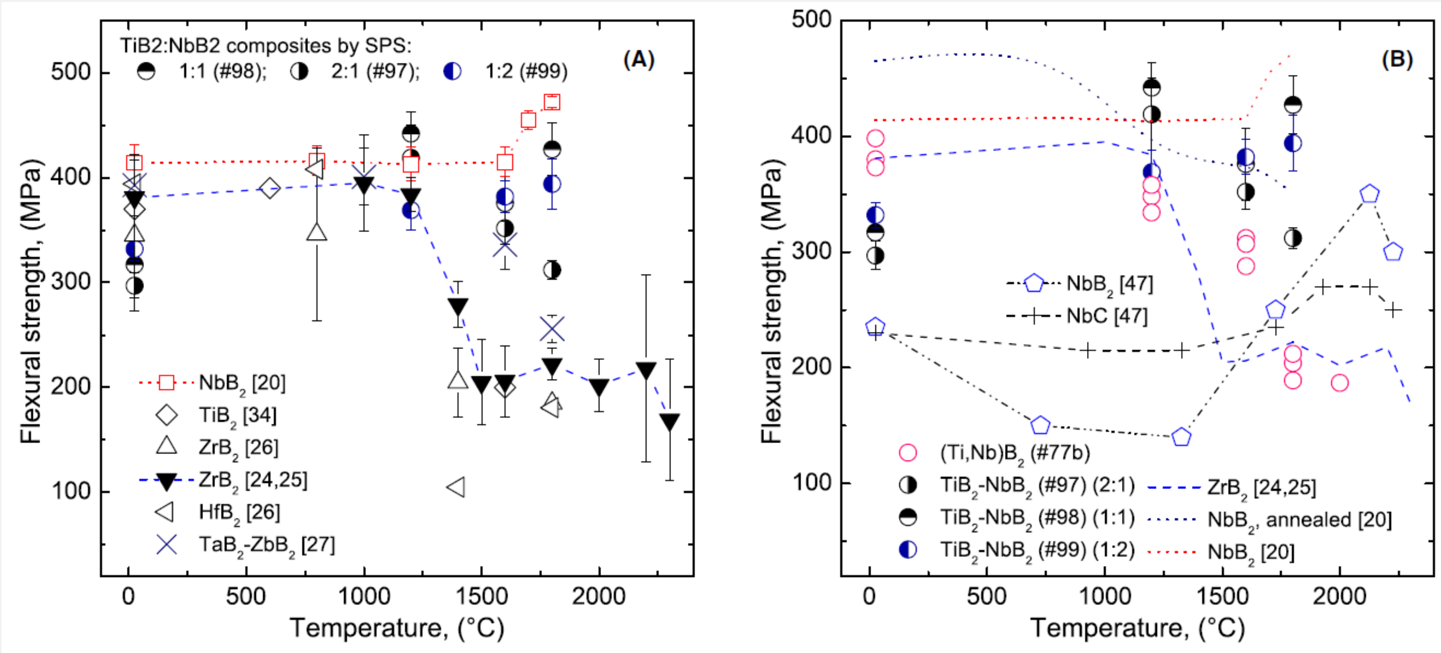
J. Am. Ceram. Soc. **102** [7] Jul. 4259-4271 (2019), https://doi.org/10.1111/jace.16276

Fracture and property relationships in double diboride composites by SPS of TiB_2 and NbB_2



Effect of temperature on the flexural strength of transition-metal diborides and double diboride ceramic composites (DDCCs).

- The RT 300–330 MPa with increasing to 400 MPa at 1200–1600 °C.
- HT deformation induced needle-shaped NbB_2 subgrains, indicating active plasticity. The mechanical response transitioned from elastic loading at 1600 °C to predominantly plastic fracture at 1800 °C, with strengths of 300–450 MPa.
- Comparison with a $(Ti, Nb)B_2$ solid-solution specimen highlights the distinct high-temperature behavior arising from the two–phase TiB_2–NbB_2 architecture.

J. Am. Ceram. Soc. **102** [7] Jul. 4259-4271 (2019), https://doi.org/10.1111/jace.16276

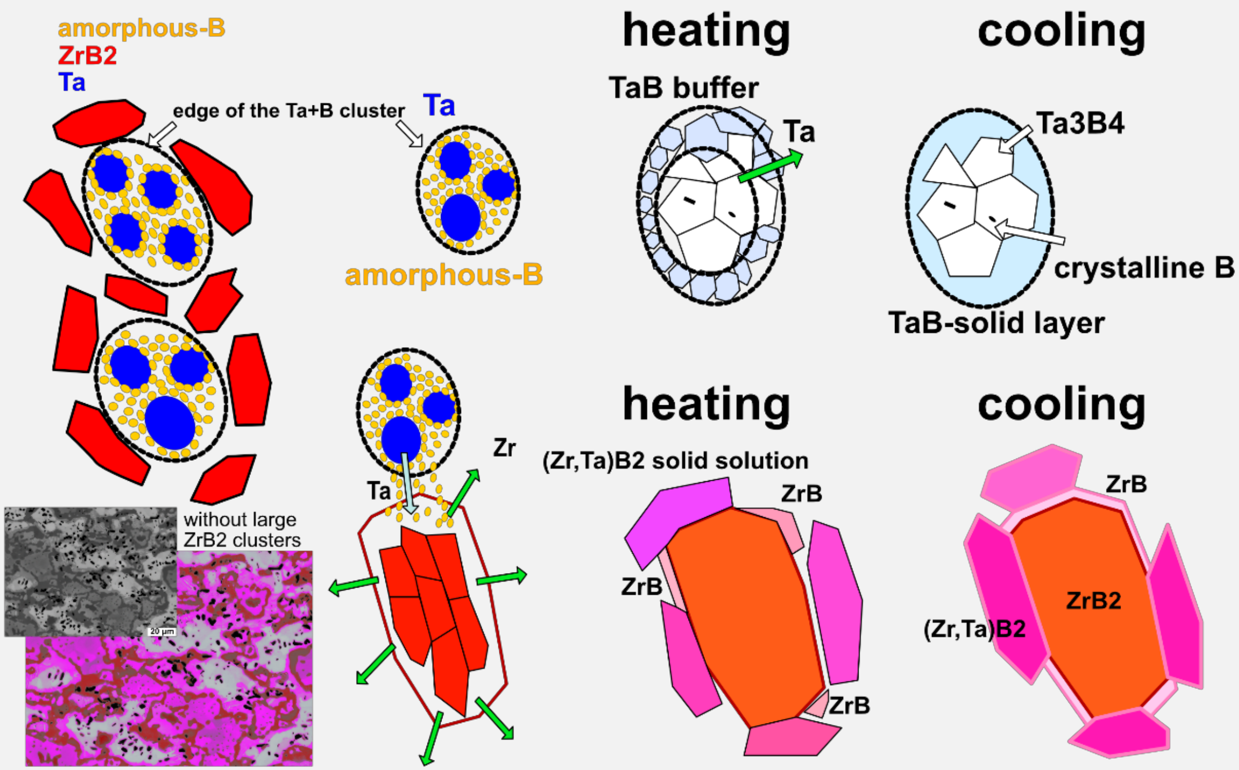
Engineered Zr-Ta multiboride ceramic with a supercomposite structure

<u>Starting materials:</u>

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.

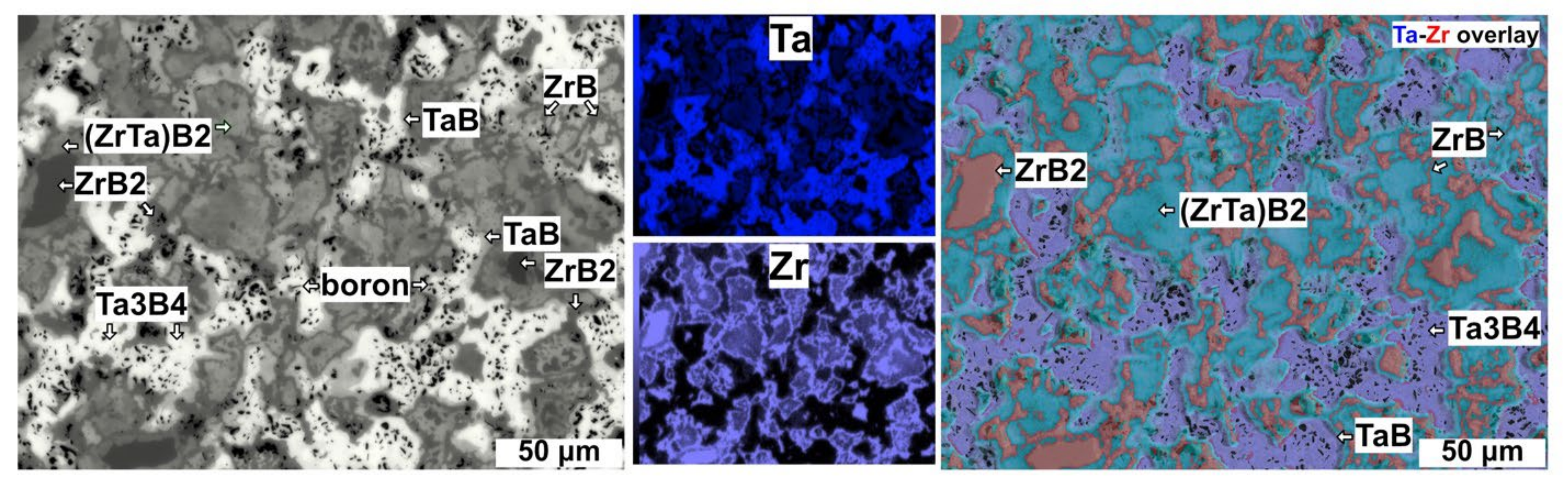
J. Am. Ceram. Soc., ***105*** *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

Engineered Zr-Ta multiboride ceramic with a supercomposite structure

After SPS at 1900 °C, ceramic had a distinctive **supercomposite microstructure** with fairly high reproducibility of the structural elements.

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

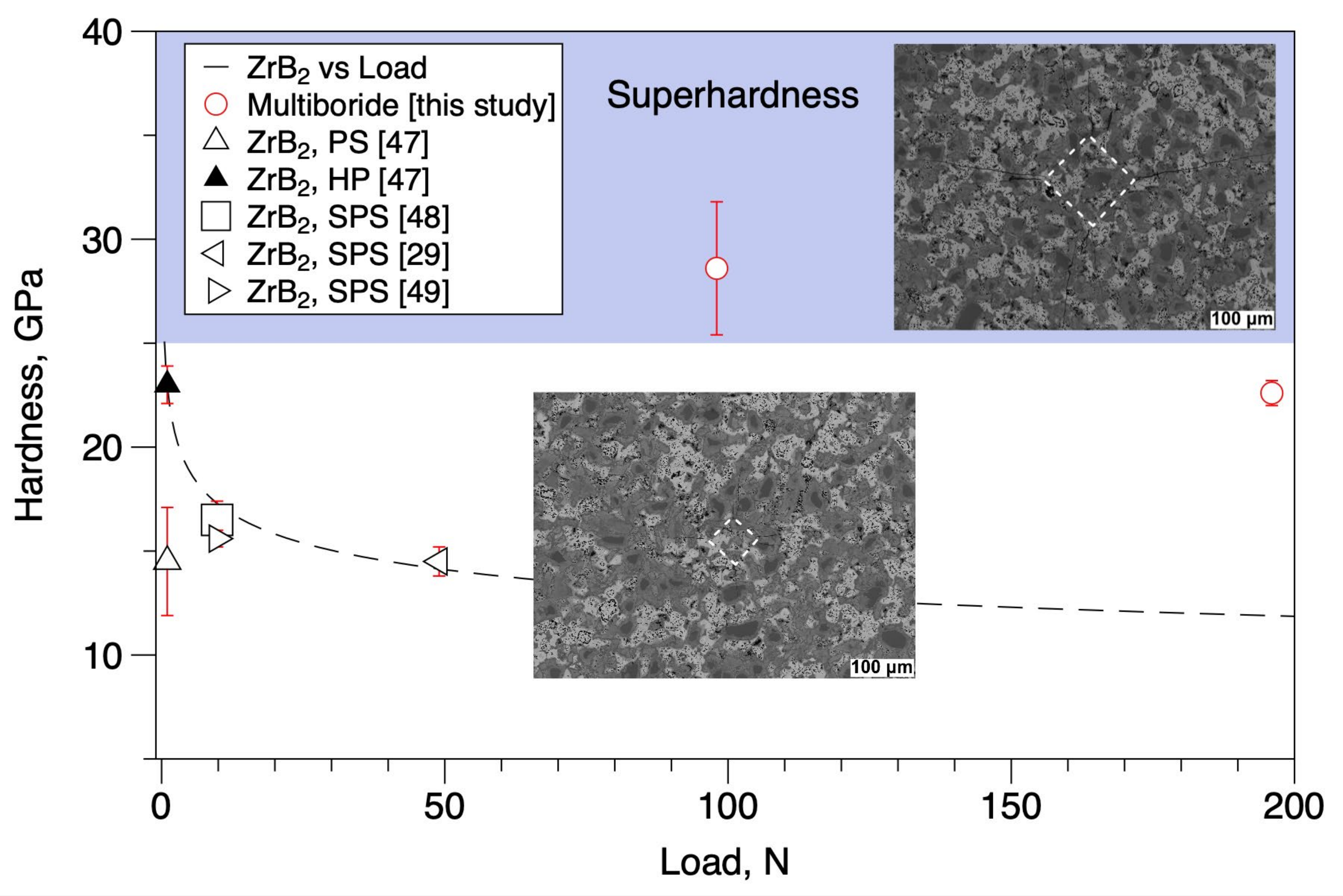
Engineered Zr-Ta multiboride ceramic with a supercomposite structure



- ✓ Ta_3B_4 ~ 10 µm clusters with an entrapped crystallized boron (**Ta_3B_4-B**) 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

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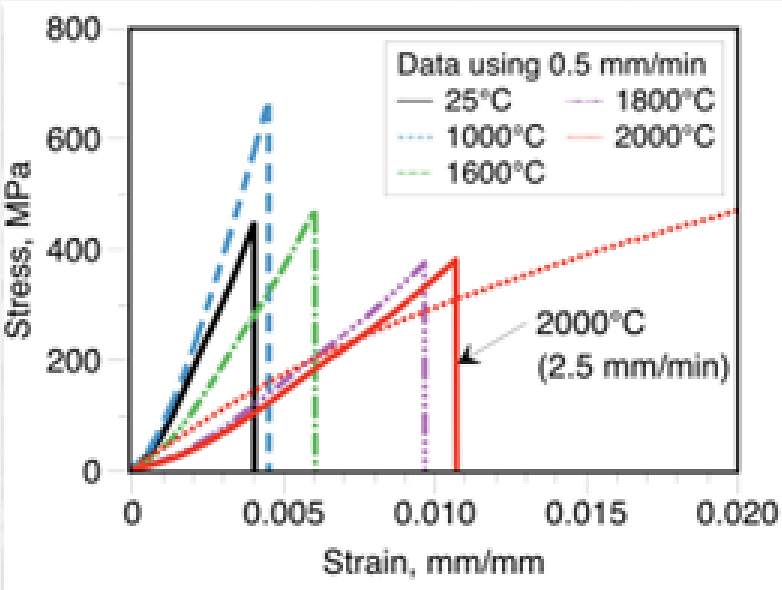
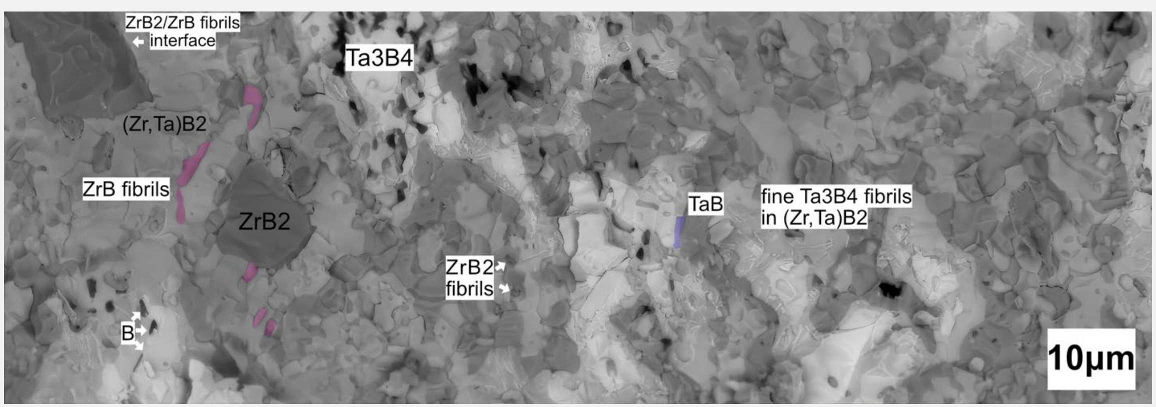
***J. Am. Ceram. Soc.*, 105** *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

Engineered Zr-Ta multiboride ceramic with a supercomposite structure



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

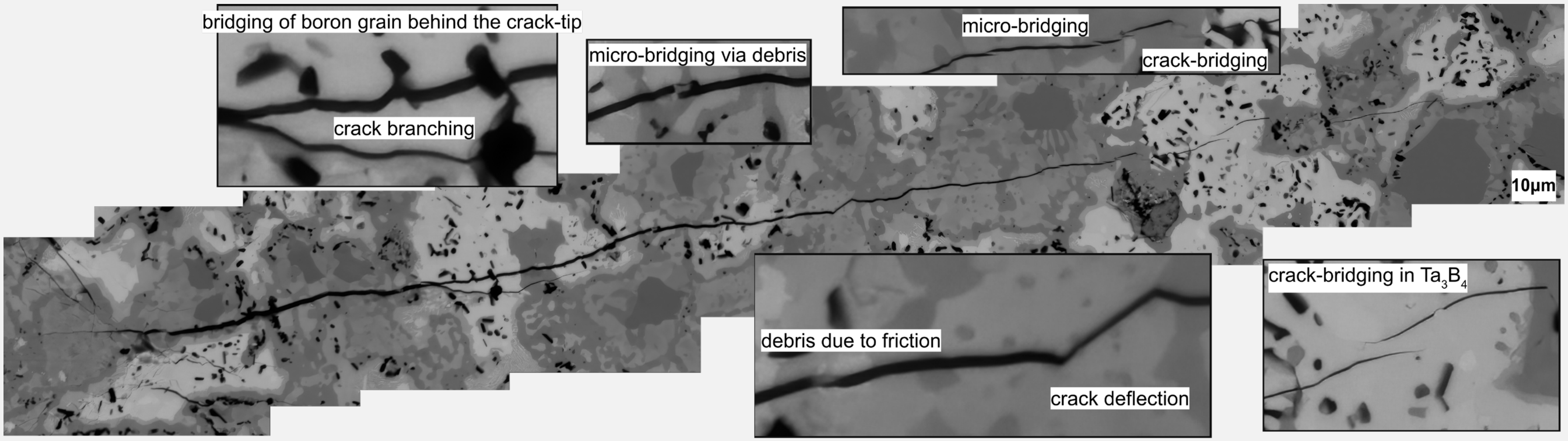


There were some quasi-lamella sub-grains mainly at the interface of the Ta_3B_4 phase.

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

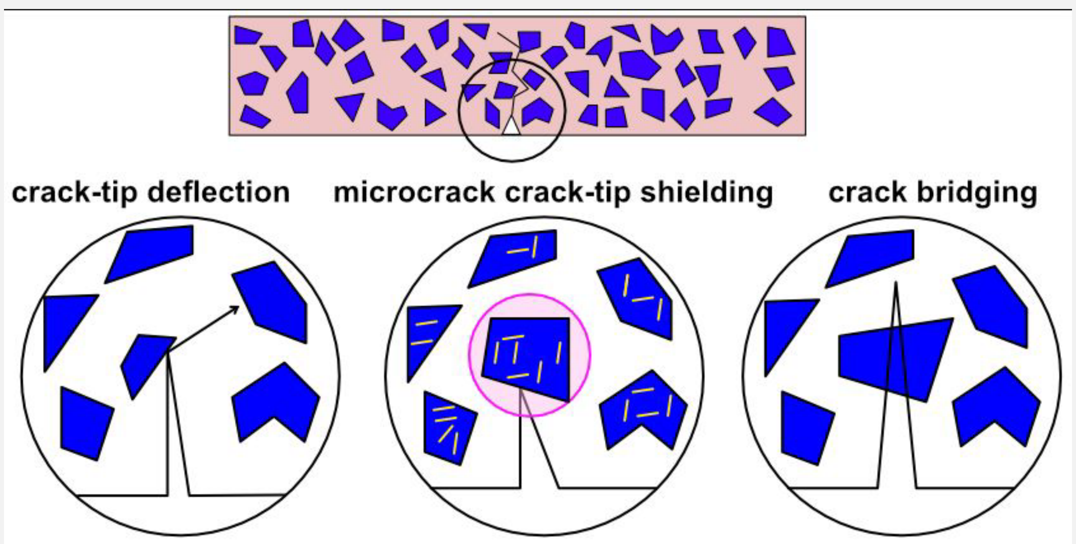
J. Am. Ceram. Soc., ***105*** *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

Engineered Zr-Ta multiboride ceramic with a supercomposite structure



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



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

- Ultra-high-temperature ceramics are crucial for aerospace, energy, and power systems, where maintaining mechanical **integrity under extreme thermal conditions is vital**.
- This study shows that transition-metal borides consolidated by spark plasma sintering (SPS) — including NbB_2, TaB_2, TaB, TiB_2–NbB_2 composites, and Zr–Ta multiborides — exhibit **excellent deformation resistance**, maintaining nearly the same flexural strength from room temperature to 1800–2000 °C
- Across all systems, the defining feature is **temperature-independent flexural strength** from room temperature to 1800–2000 °C, which sets these transition metal borides apart from conventional ceramics and underscores their promise for extreme-environment technologies.

Main collaborators: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Nishimura T.


Yoshimi K.


Demirskyi D.

I truly appreciate your attention & time!
Thank you for being here!