IXth International Materials Science Conference
HighMatTech-2025
October 6-10, 2025 Kyiv, Ukraine

Deformation-Resistant Ultra-High Temperature Borides

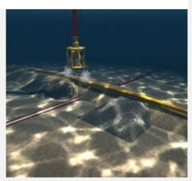
Vasylkiv Oleg
National Institute for Materials Science

October 7, 2025, Symposium: Advanced Ceramics and Glasses

Why do we need high-temperature ultra-ceramics?

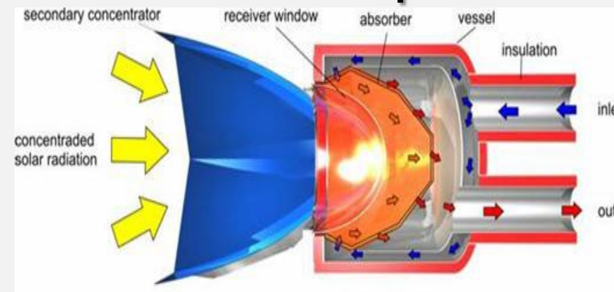
Materials for extreme environments

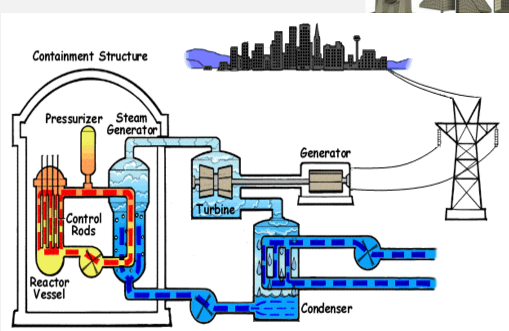
Leading edge components for aerospace



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

Gas turbine operation



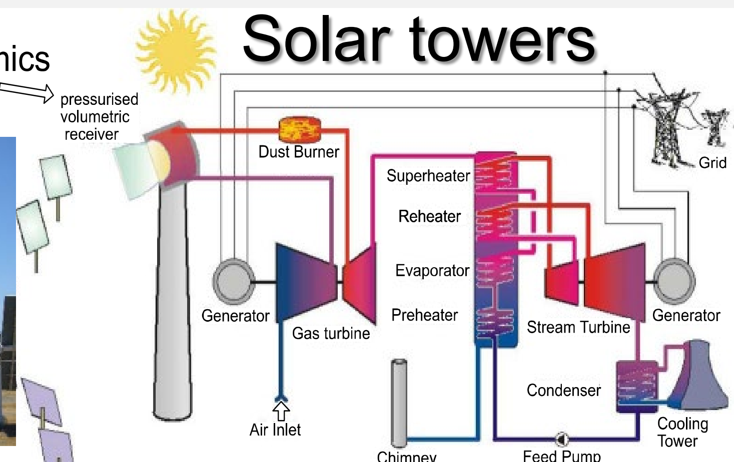


Plasma facing parts

Solar towers

HT Carbide ceramics

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

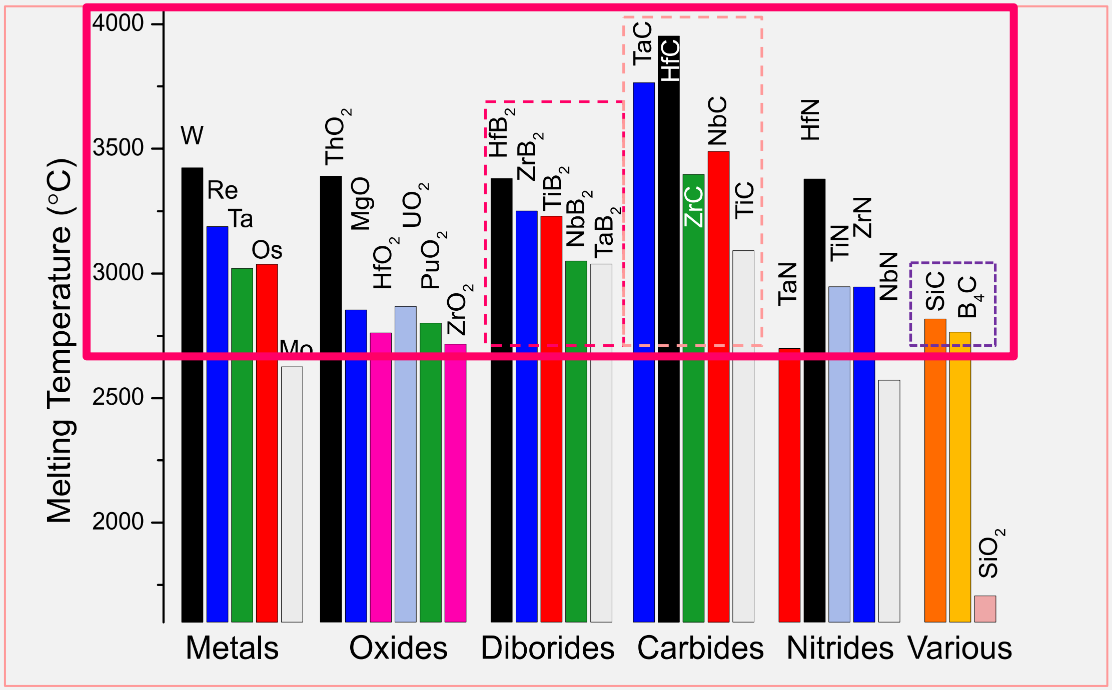
The demand for new ultra-high-temperature ceramics is rising, particularly those that are multipurpose, deformation-resistant, and offer specialized protection for engines and vehicles.

Thus, there is a global need for a new ceramic composite class with an exceptional, well-balanced combination of strength, toughness, hardness, and modulus.

Today, I will discuss the preparation and resistance to deformation of Zr-Ta multi-boride, TaB, TaB_2, Nb ZrB_2, and medium-entropy (Zr, Ta, Nb)B_2

NIMS

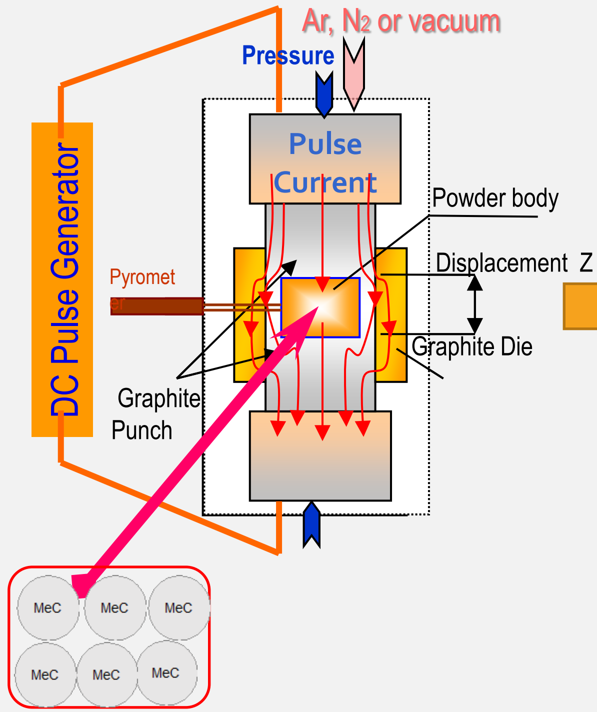
Densification and grain growth of UHT carbides & borides



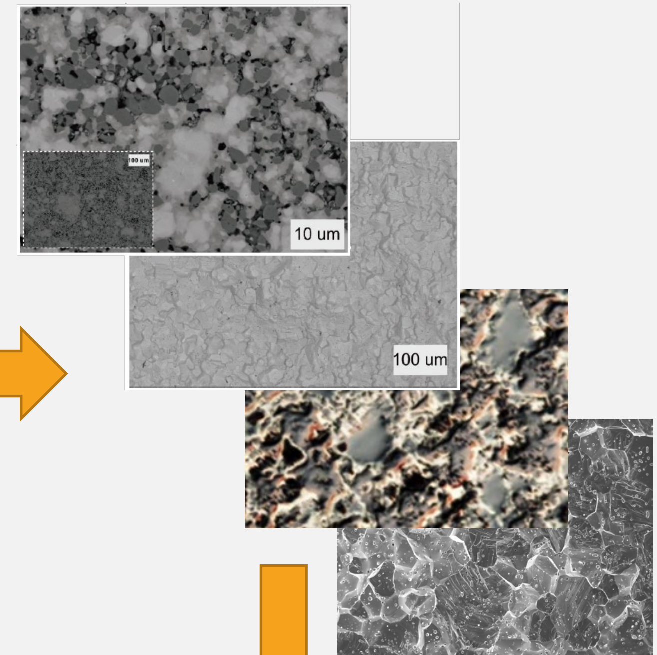
- ✓ **Monolithic carbides & borides without additives are required**
- ✓ Most borides, carbides, and their solid solutions are among the compounds with the highest reported melting points
- ✓ The 0.7 Tm treatment results in a temperature of 2500°C
- ✓ This suggests that SPS temperatures over 2200°C are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

NIMS

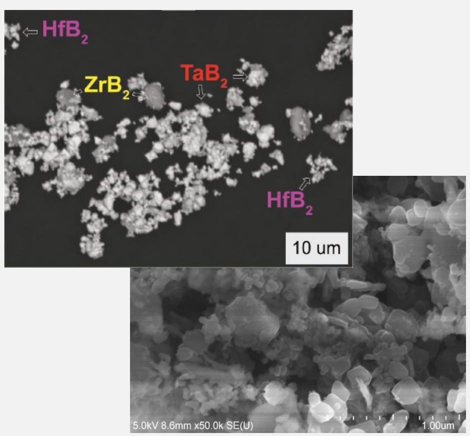
Processing – composition/structure – properties



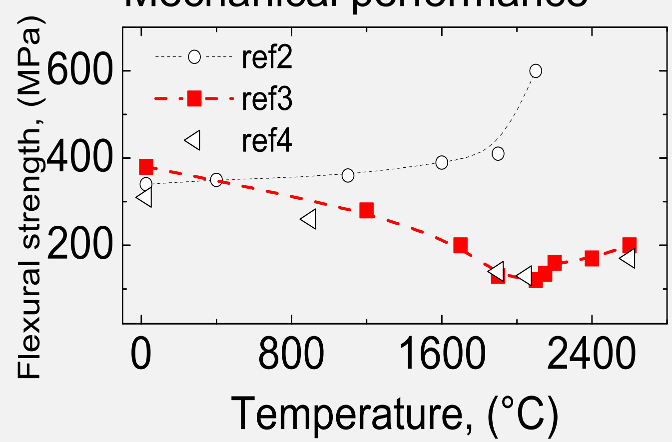
Composition, grain size, etc.



Starting powders/mixtures



Mechanical performance



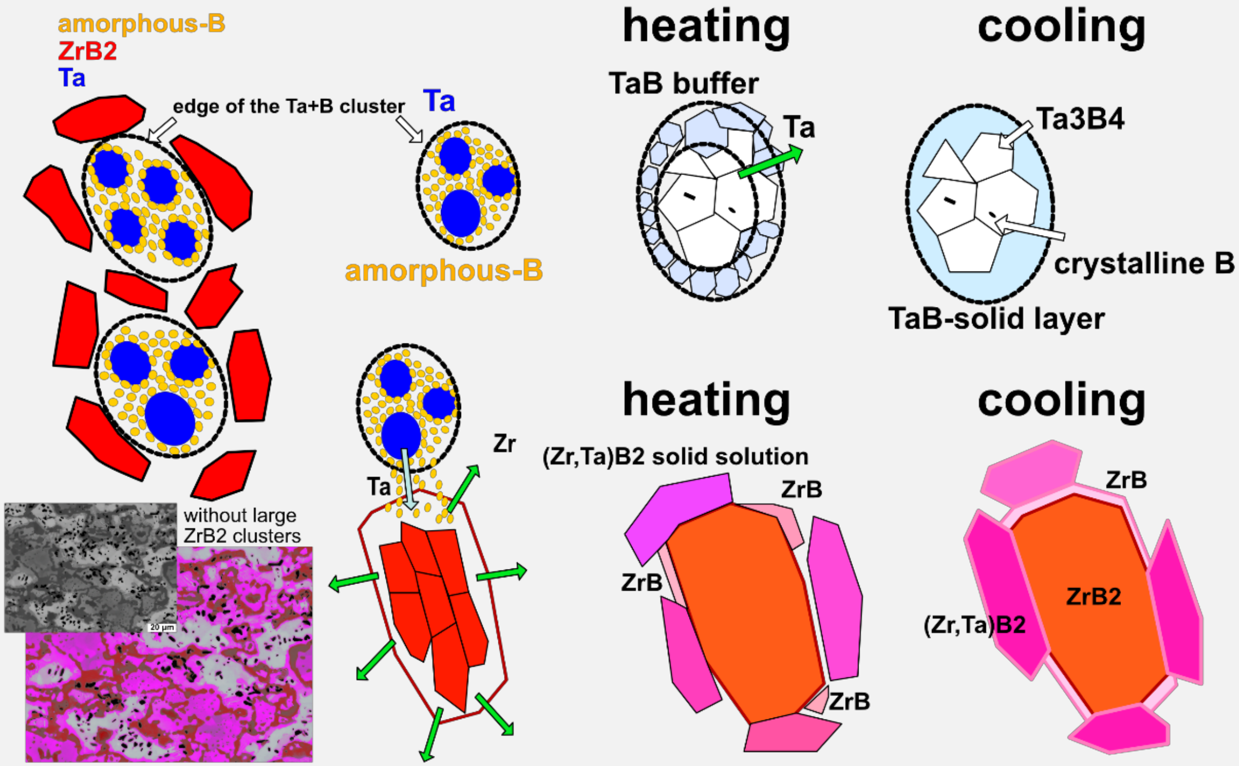
Engineered Zr-Ta multiboride ceramic with a supercomposite structure

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.

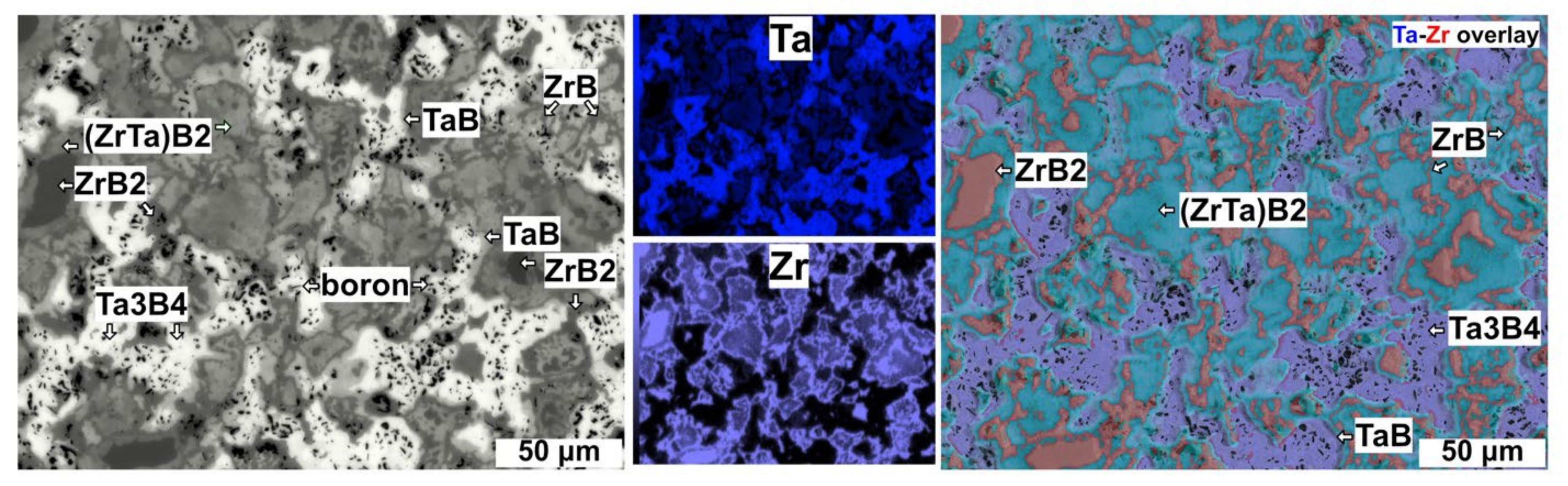
J. Am. Ceram. Soc., ***105*** *[11] Nov. 6989-7002 (2022)* https://doi.org/10.1111/jace.18653

Engineered Zr-Ta multiboride ceramic with a supercomposite structure

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*

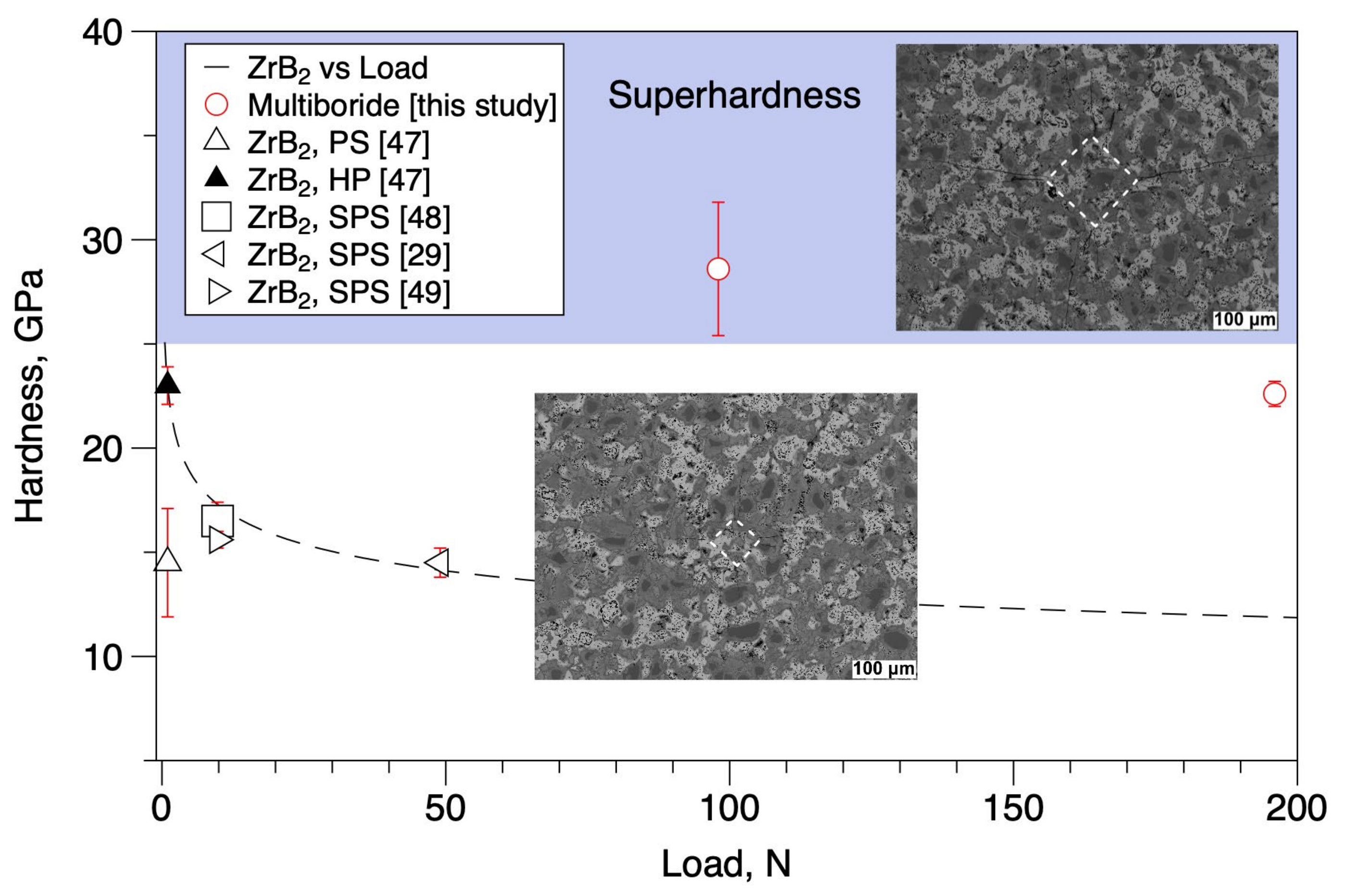
Engineered Zr-Ta multiboride ceramic with a supercomposite structure



- ✓ 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

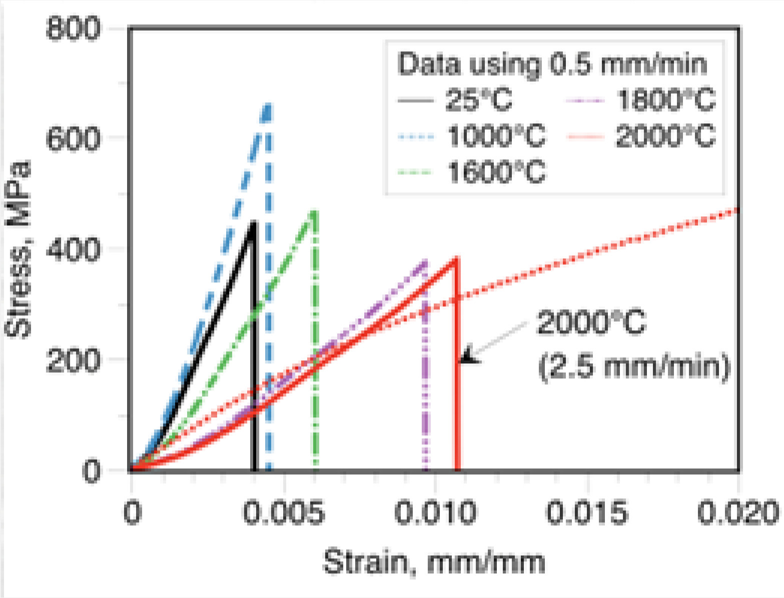
Engineered Zr-Ta multiboride ceramic with a supercomposite structure



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 $m^{1/2}$

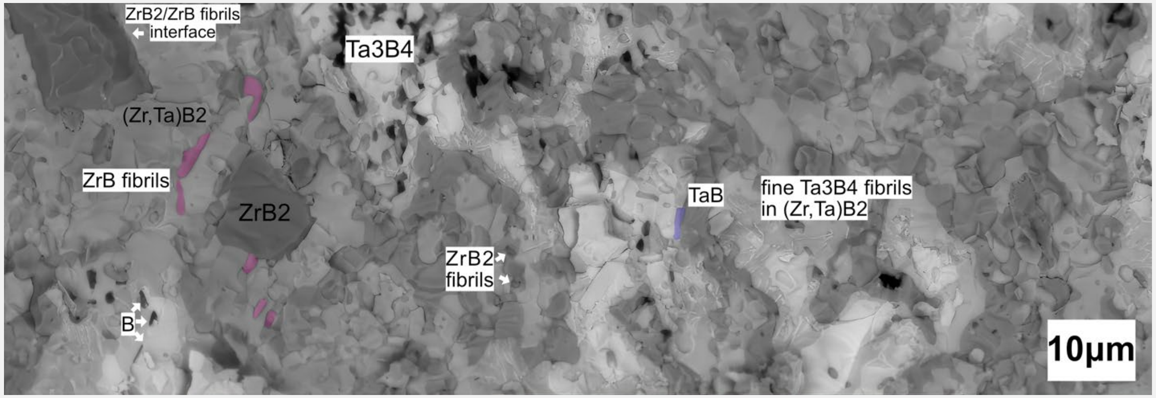
J. Am. Ceram. Soc.*, *105 *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

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

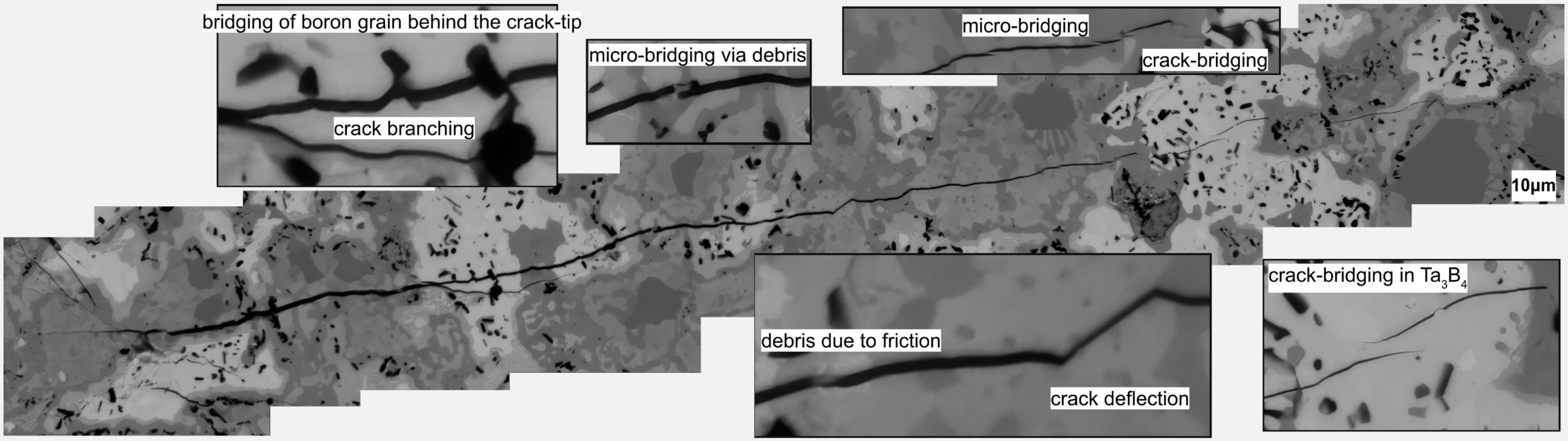


There were some quasi-lamella sub-grains mainly at the interface of the Ta_3B_4 phase.

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

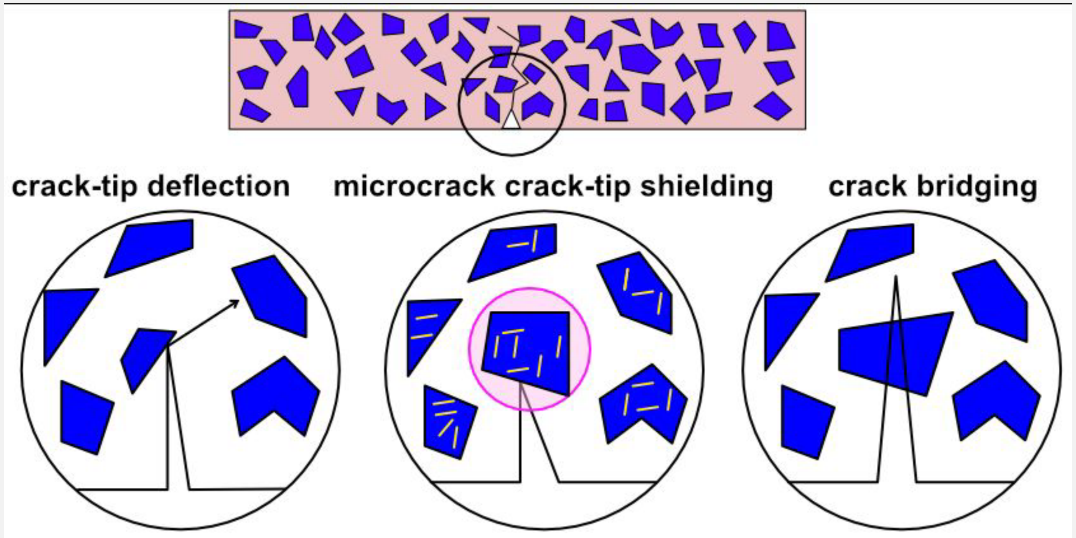
J. Am. Ceram. Soc.*, *105 *[11] Nov. 6989-7002 (2022) https://doi.org/10.1111/jace.18653*

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*

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

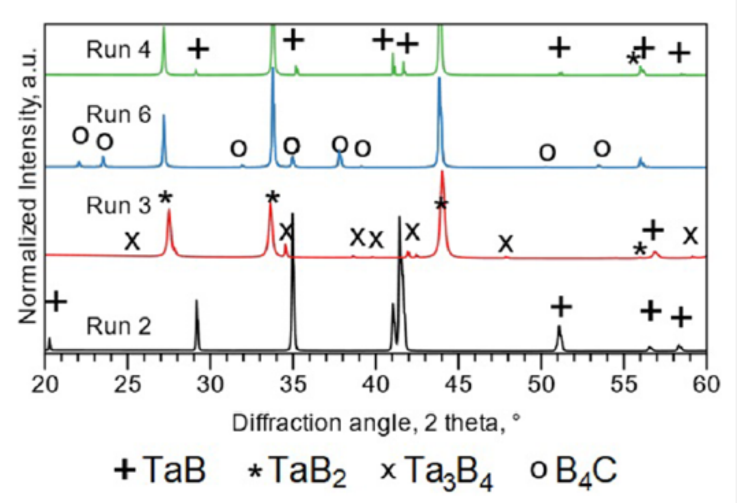
(B) Reaction between the TaB_2 powder and Ta

- 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

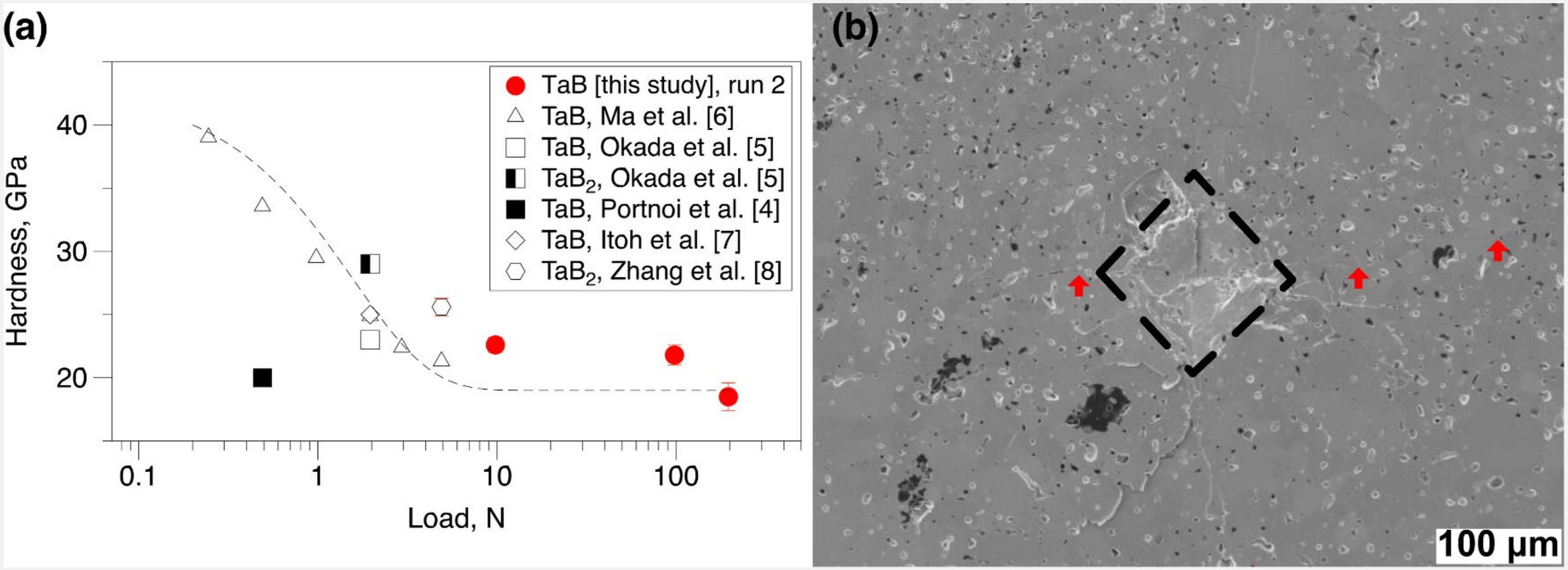


Single-phase **TaB (orthorhombic *Cmcm* cell** with the lattice parameters a = 3.28(1) Å, b = 8.67(2) Å, c = 3.15(7) Å), with up to 3 vol.% of boron as a residual phase

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

Reactive consolidation of tough, deformation resistant tantalum monoboride

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

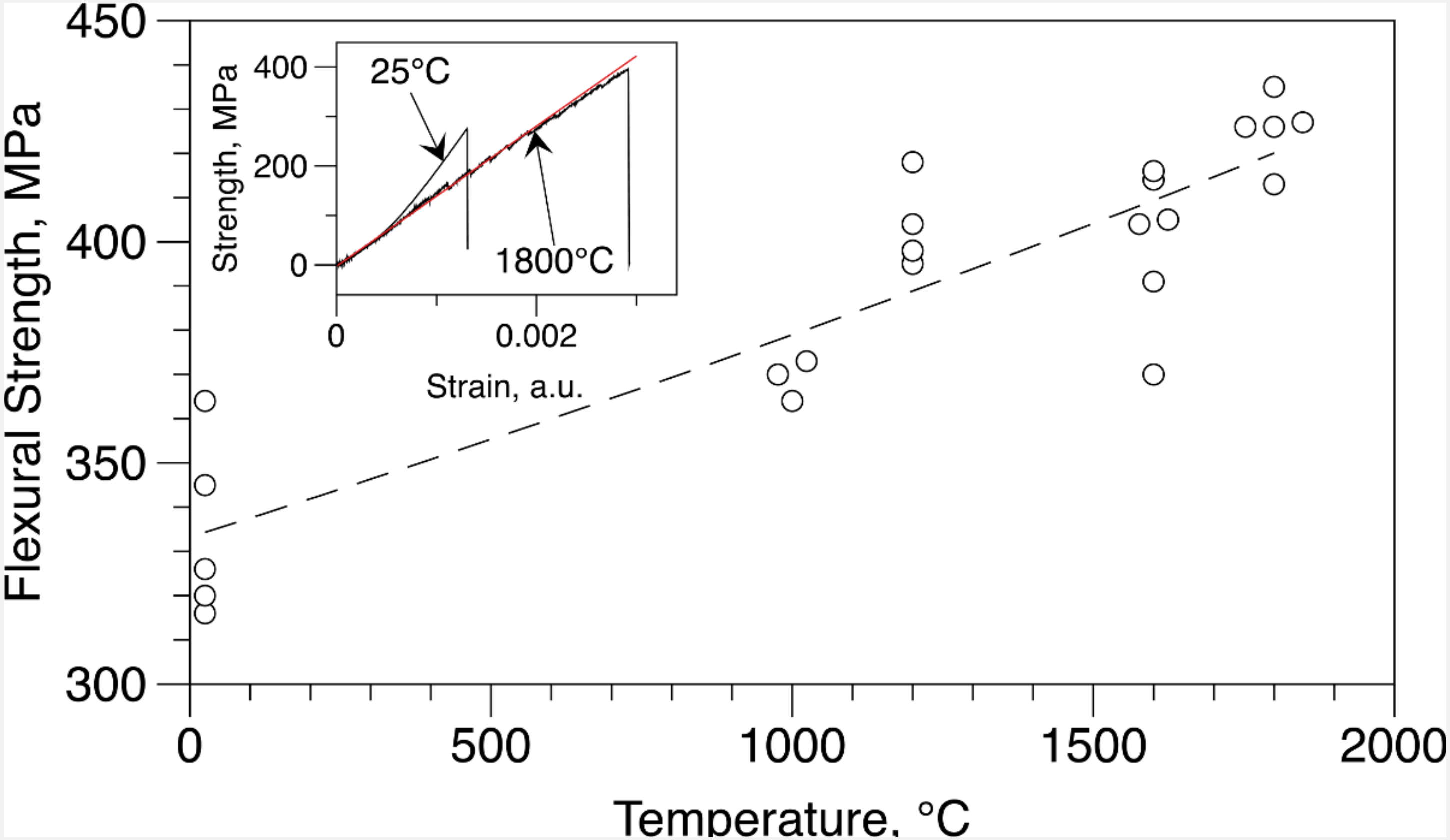


(a) hardness of TaB and TaB2 as a function of load; (b) shows typical indent using 196 N load

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.

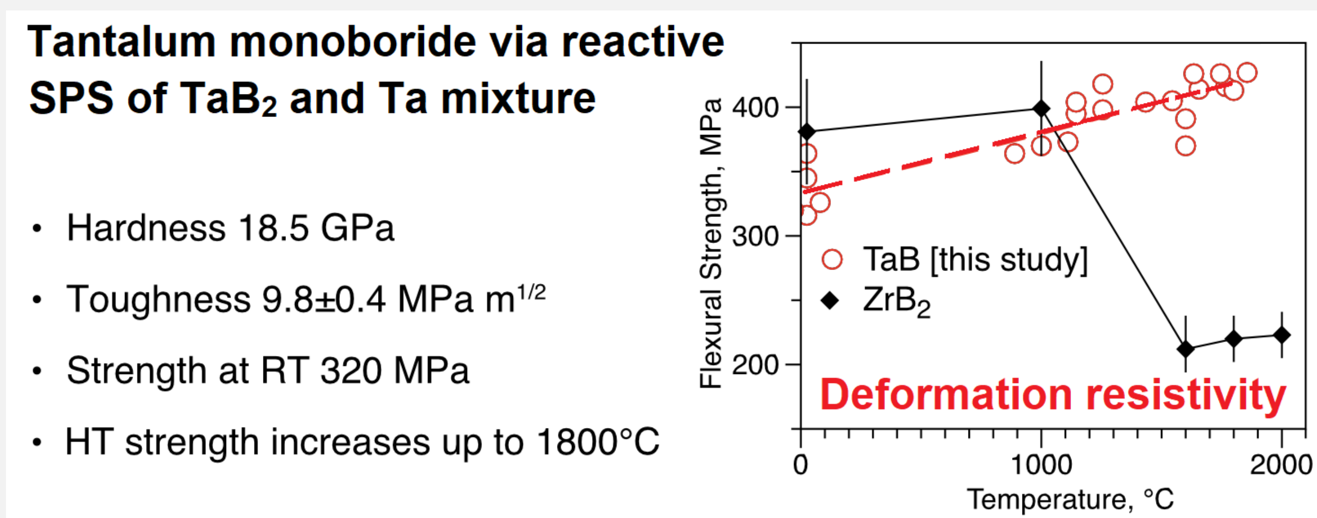


Only at 1800 °C TaB had loading curves exhibited nonlinear characteristics associated with (i) flaw healing or (ii) plasticity (micro-plasticity) contribution. This indicates that test above 1800 °C will result in plastic deformation.

***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, the formation of the monoboride was observed only when processing at 2150 °C using 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 $m^{1/2}$.
- ✓ At room temperature, TaB showed strength lower than reported for TaB2 (330 vs 550 MPa). However, with an increase in temperature, TaB showed **resistance to deformation** as the flexural strength gradually increased to 425±7 MPa at 1800 °C, while, for instance, ZrB_2 has only 220±18 MPa strength at 1800 °C.



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

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

Flexural strength for TaB_2 and ZrB_2 ceramics at room and elevated temperatures.

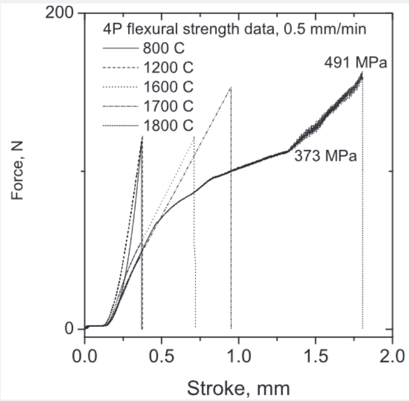
Temperature, °C	SPS Temperature, °C	Crosshead rate (mm/min)	Strength, MPa	Loading curve
25	2000	0.5	573 ± 16	Elastic
25	2100	0.5	489 ± 13	Elastic
25	2200	0.5	475 ± 15	Elastic
1900	2000	0.5	264 ± 24	Plastic
		1.5	388 ± 12	Elastic
1900	2100	0.5	417 ± 9	Elastic
1900	2200	0.5	404 ± 16	Elastic
1950	2000	0.5	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

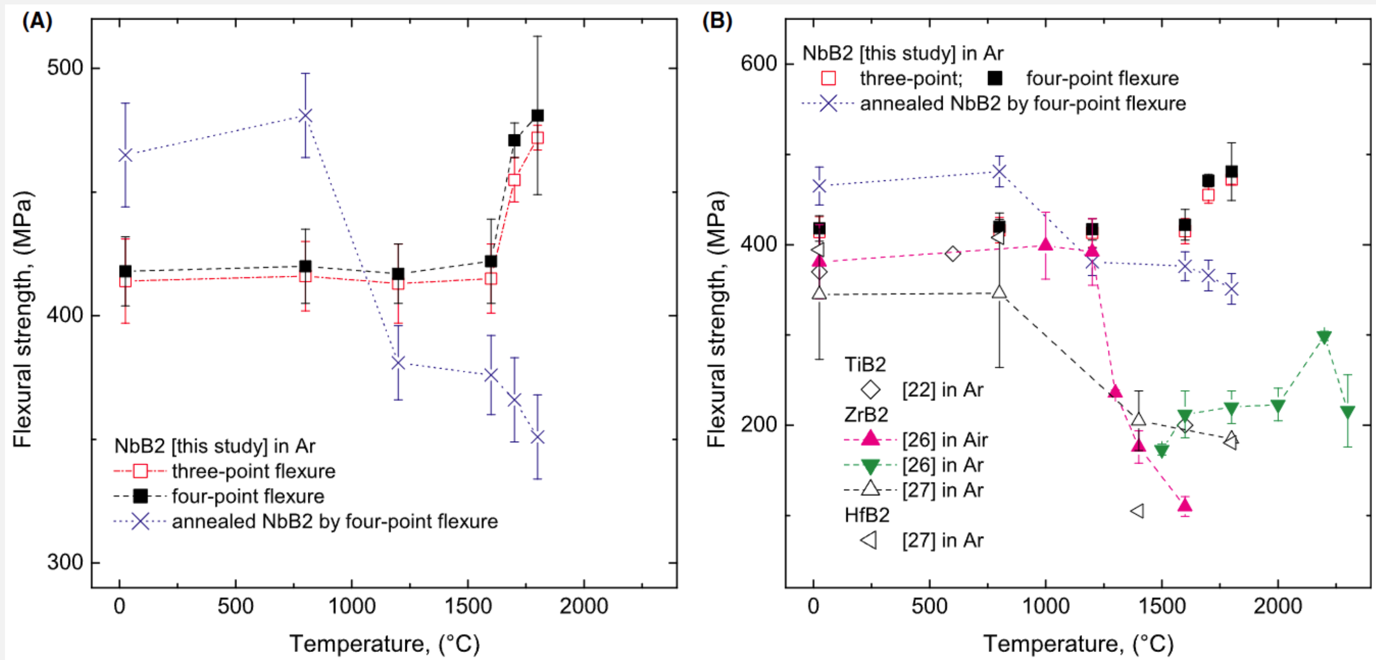
Dense TaB_2 with a grain size ranging from 3 to 7 µm was SPSed at 2000 - 2200°C. The three-point flexural strength was measured as a function of temperature up to 2000°C in an Ar atmosphere. The strength exhibited deformation resistivity from room temperature to 1800°C. Above 1900°C, the strength became sensitive to the applied loading rate. TaB_2 demonstrated further resistance to deformation as the flexural strength gradually increased 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.

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

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.





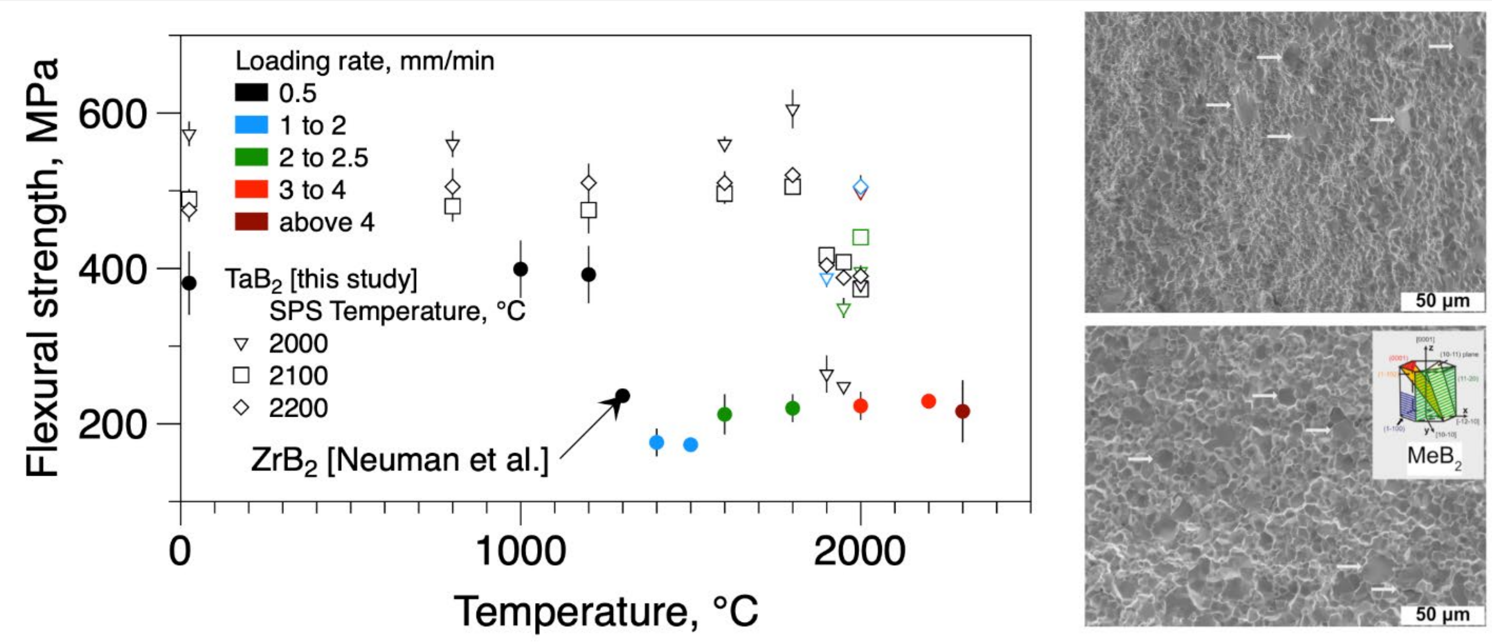
The room temperature (RT) strength was 420 MPa and remained constant up to 1600°C. At 1700°C, it increased to 450 MPa, and at 1800°C, signs of plastic deformation appeared. Fractographic analysis showed etching pits and step-like surfaces, indicating high-temperature deformation.

This was abnormal behavior (2016) compared with the bulk diborides of Ti, Zr, and Hf.

NIMS

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

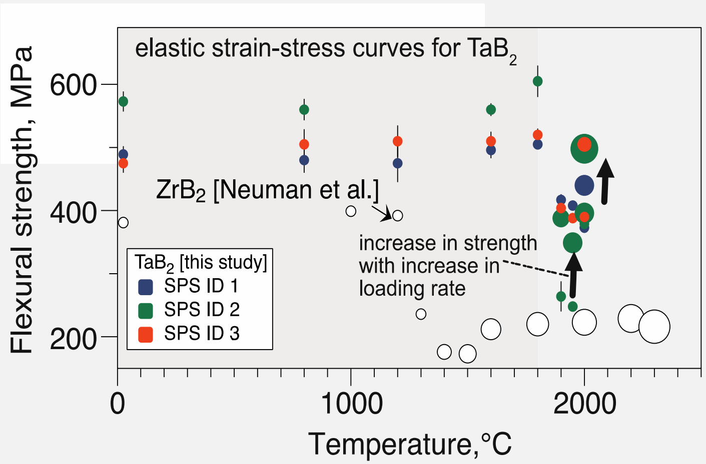
High-temperature strength behavior of tantalum diboride to 2000°C



The strength exhibited a variation of approximately 50 MPa between room temperature and 1800°C with the temperature behavior of the strength being 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.

In comparison, ZrB_2 exhibited strengths of 220±18 MPa at 1800°C and 223±18 MPa at 2000°C.



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

High (Medium)-entropy diborides generally exhibit higher strength compared to high-entropy carbides due to several factors:

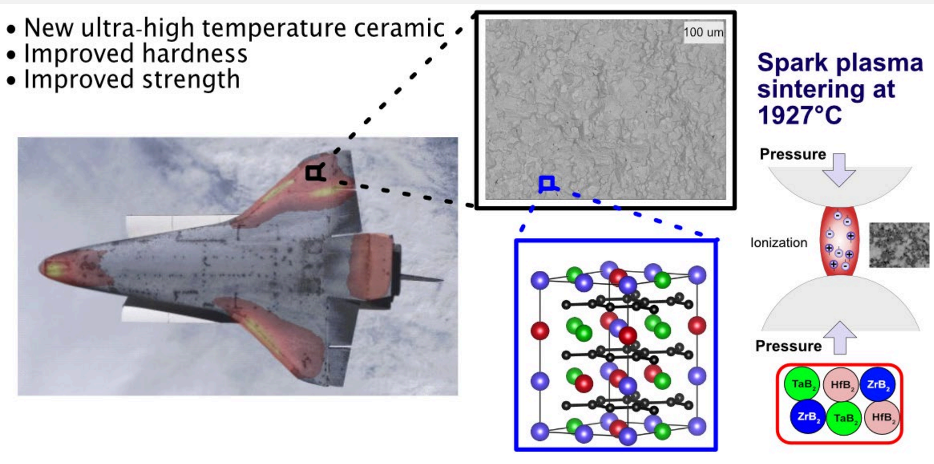
1. **Bonding Characteristics**: Diborides have strong covalent bonds between boron atoms, which contribute to their exceptional hardness and strength. The boron-boron bonding in HEBs is more robust than the carbon-carbon bonding in HECs.
2. **Lattice Distortion**: The severe local lattice distortion in HEBs, caused by the disordered arrangement of transition metal atoms, enhances their mechanical properties. This distortion strengthens the boron-boron bonds, contributing to higher hardness.
3. **Electron Work Function (EWF)**: HEBs have optimized electronic structures that result in higher bonding charge density. This results in stronger metallic layers and enhanced mechanical strength.
4. **Grain Refinement**: The grain size in HEBs is often smaller, which contributes to their higher hardness and strength through the grain boundary strengthening mechanism.

Bonding Characteristics Unique to High (Medium)-Entropy Diborides

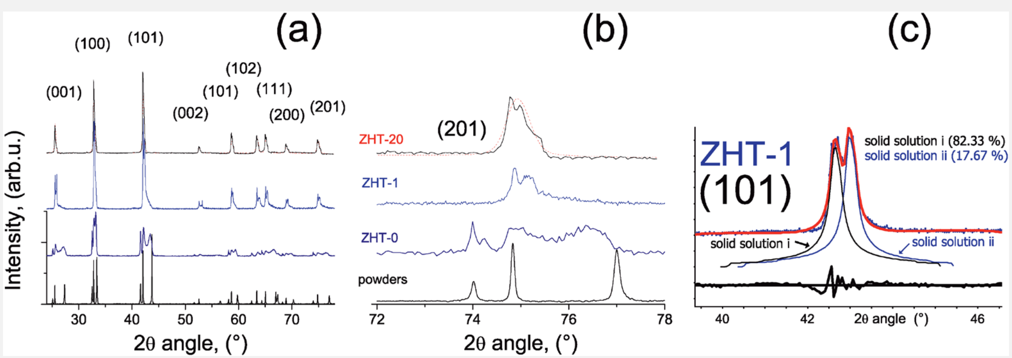
- **Bonding Disorder**: High-entropy diborides consist of multiple principal metal elements, leading to random distribution and local lattice distortion. This disorder modifies the bonding environment, enhancing the material's toughness and hardness.
- **Strong Boron Framework**: The boron layers are highly rigid due to the covalent bonding network. This makes the material resistant to shearing and deformation.
- **High Charge Density**: The bonding electrons are concentrated around the boron and metal atoms, creating a dense and robust bonding framework. This increases the material's hardness and thermal stability.

The interplay of these bonding types results in a combination of extreme hardness, high strength, and thermal resistance, making HEBs suitable for demanding applications.

Synthesis of medium-entropy $(Zr_{1/3}Hf_{1/3}Ta_{1/3})B_2$ by SPS consolidation of diborides



This research presents a practical and straightforward method for creating a ternary solid solution of diborides, specifically a medium-entropy $Zr_{1/3}Hf_{1/3}Ta_{1/3}B_2$. Using commercially available diboride powders in equal proportions and conducting spark plasma consolidation at 1927 ° C demonstrates that a single-phase high-entropy ceramic can be consolidated in just one hour. The flexural strength and fracture toughness at room temperature were measured at 318 ± 14 MPa and 2.9 MPa1/2, respectively.



XRD patterns for ZHT ceramic after spark plasma consolidation. (b) shows the evolution of the (201) peak. (c) shows a refinement procedure performed by Topas for the (101) peak. For the ZHT1, the lattice parameters for two solid solutions were: (i) a = 3.137¡ and c = 3.467¡ and (ii) a = 3.107¡ and c = 3.415¡. For reference, lattice parameters of hafnium diboride were evaluated as a = 3.139¡ and c = 3.474¡. The red dashed line for the ZHT20 provides a fitting using refined lattice parameters.

NIMS

***J. Ceram. Soc. Japan*, 128** *[11] 977-980 (2020)* http://doi.org/10.2109/jcersj2.20151

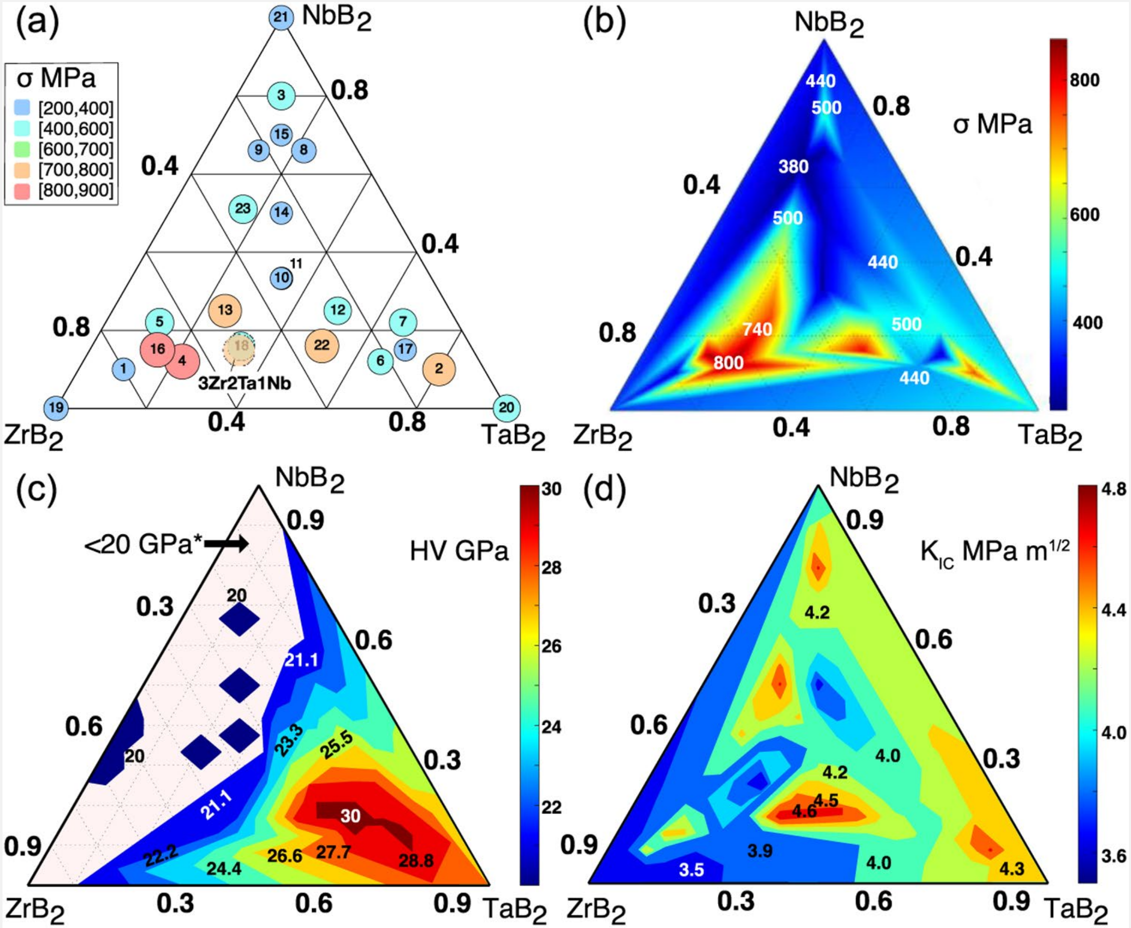
- ✓ Optimum creep resistance in binary solid solutions always outside an equimolar composition!
- ✓ Rare studies focus on finding an optimum composition with the required set of material properties!
- ✓ To evaluate the properties of the 3:2:1 ZTN diboride, we prepared four specimens using the identical SPS schedule for the three-point flexural tests.

NIMS

***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

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…

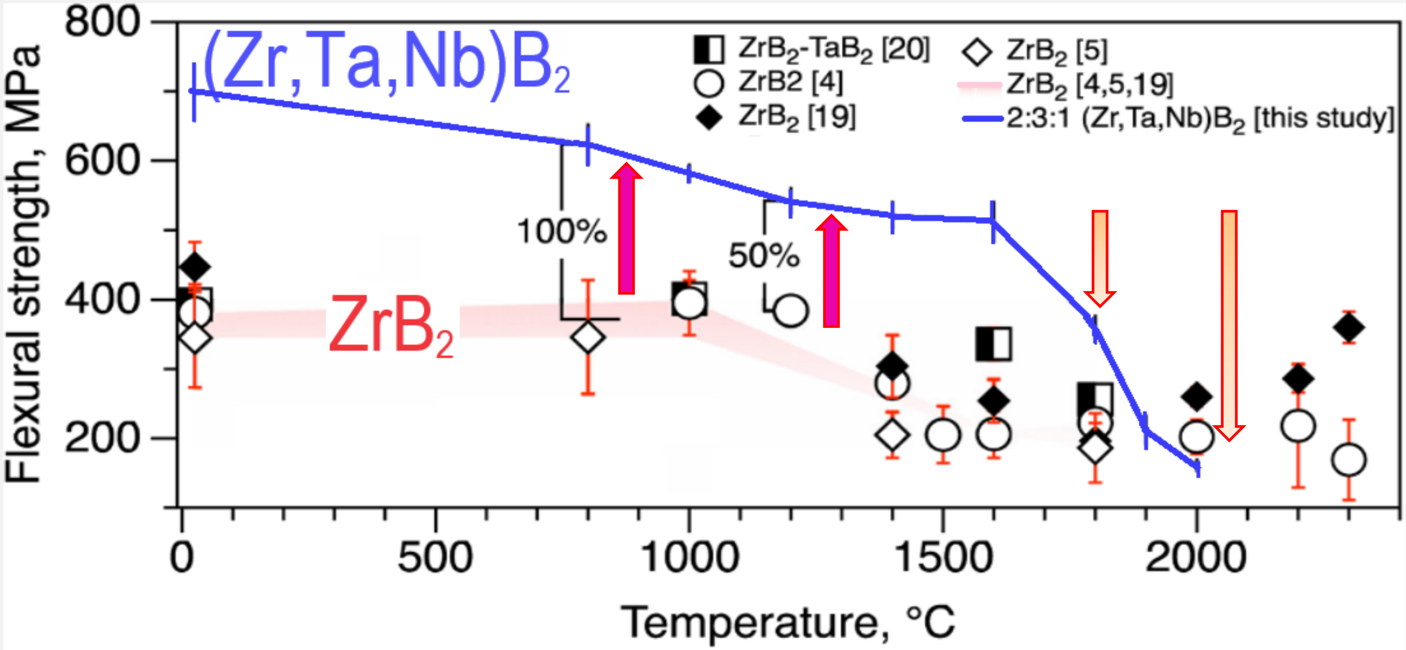


After close inspection of the data, it was decided that the ZTN diboride with a 3:2:1 composition should be evaluated as it had a strength above 800 MPa and one of the finest grain sizes 8 ± 2 µm after SPS at 2000 °C.

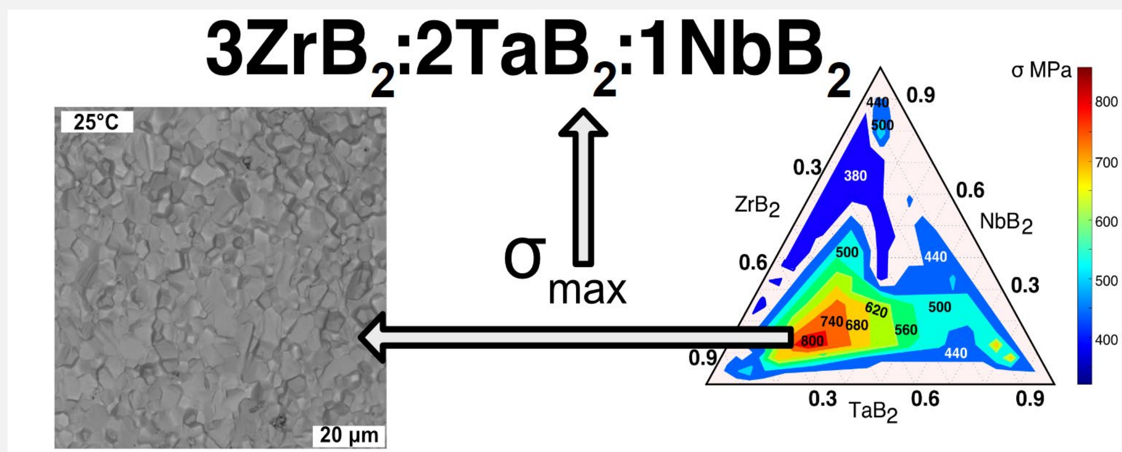
Scripta Materialia **225** 1 Mar *(2023)* 115170 https://doi.org/10.1016/j.scriptamat.2022.115170

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

Temperature dependence of flexural strength of bulk ZrB2, ZrB2–TaB2, and ZTN diboride



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

Main collaborators:

Suzuki Tohru S.

Nishimura Toshiyuki

Yoshimi Kyosuke

Demirskyi Dmytro

Thank you for your attention!