Scripta Materialia

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

--Manuscript Draft--

| | |
|---|---|
| **Manuscript Number:** | SMM-22-1629R2 |
| **Article Type:** | Regular article |
| **Keywords:** | Diborides, High Temperature Strength, High-Entropy Ceramic, Reactive SPS |
| **Corresponding Author:** | Oleg O. Vasylkiv, ScD /Dr. Habil./, PhD<br>National Institute for Materials Science Research Center for Functional Materials: Busshitsu Zairyo Kenkyu Kiko Kinosei Zairyo Kenkyu Kyoten<br>Tsukuba, JAPAN |
| **First Author:** | Dmytro Demirskyi |
| **Order of Authors:** | Dmytro Demirskyi |
| | Toshiyuki Nishimura |
| | Kyosuke Yoshimi |
| | Oleg O. Vasylkiv, ScD /Dr. Habil./, PhD |
| **Abstract:** | Reactive consolidation of medium entropy diboride in the ZrB2–TaB2–NbB2 system was performed by spark plasma sintering of diboride powders at 2000 °C. The 3:2:1 ratio between Zr, Ta, and Nb showed the highest specific strength at room temperature during the initial screening of the mechanical properties. The flexural strength gradually decreased from 700±42 MPa at RT to 518±30 MPa at 1600 °C with the Weibull parameter exceeding 15. Diborides with an equimolar composition did not show a maximum in their strength, fracture toughness or hardness. |

Dear Editor of Scripta Materialia Prof. Nitin P. Padture,

We would like to submit the revised version (R2) of the manuscript entitled “High-strength, medium entropy Zr-Ta-Nb diboride ceramics” by Dmytro Demirskyi, Toshiyuki Nishimura, Kyousuke Yoshimi and Oleg Vasylkiv for publication in the Scripta Materialia.

First, we want to express our gratitude for the comments that were asked for this submission. Second, the text was highlighted with a green background in the revised copy (r2) of the manuscript.

Reviewer #1:

English should be polished, for instance, page 5 line 13, two "using".

Thank you. We hope we improved the main issues with language in the revised copy.

If the chemical composition would affect the element distribution or even form different core-rim or core-shell structure, the discussion on the fracture mode or strength would become different.

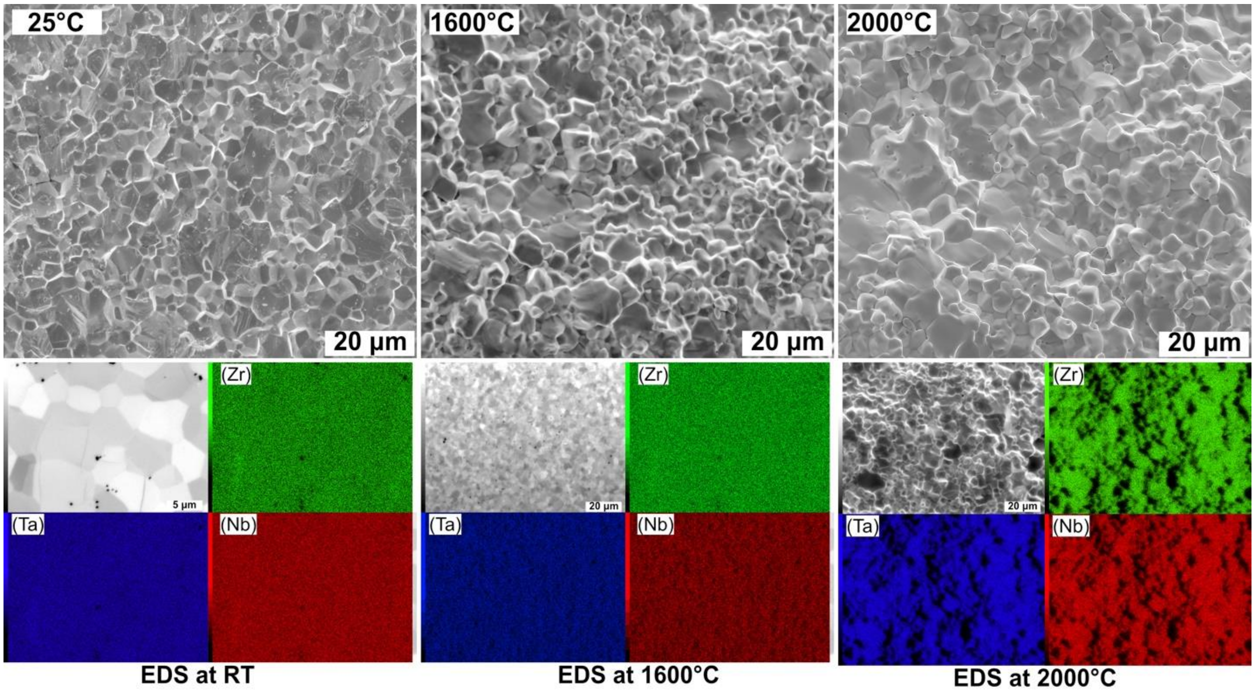
And

In Fig. 4, EDS maps from fractured surface can not provide accurate information on the element distributions, and those from polished surface are needed.

Thank you. The concerns are mutual. In this study, the core-rim structure was observed during processing at lower temperatures or due to the inappropriate mixing of powders. Nevertheless, if these being present in the specimens, we can detect these using the XRD. And only specimens with a single-phase XRD were selected for further strength/hardness/toughness testing. In other words, these issues were resolved using 2000°C/5 min configuration before the publication.

The polished probing was not so distinctive as for fractured surface, please kindly see the revised copy of the Figure 4. It was reorganized to show the EDS probes at

RT (polished), 1600 °C (thermally etched polished), and 2000 °C fracture (as it was in r1).



The EDS map for polished surface (EDS at RT) seems to have a core-rim-like structure, however the local probing shows an unchanged ratio. The other probe from the polished surface after the 1600 °C test indicates that there is no particular segregation of the metal in the individual grain i.e., homogeneous solid solution. Hopefully this interpretation will be acceptable for the publication. Alternatively, we can present the overlay of the probing lines for the polished specimens (as these may be clearer than the map right now). Also, all three of these EDS maps were acquired and analyzed using identical probing procedures and the same JEOL software.

All authors have seen and approved the revised manuscript for submission to Scripta Materialia.

On behalf of the authors,
Oleg Vasylkiv

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

D. Demirskyi (a,b,c)†, T. Nishimura(b), K. Yoshimi (c), and O. Vasylkiv (b)†

(a) WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan
(b) National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
(c) Department of Materials Science and Engineering, Tohoku University, 6-6-02 Aramaki Aza Aoba, Sendai, 980-8579, Japan

Reactive consolidation of medium entropy diboride in the $ZrB_2$–$TaB_2$–$NbB_2$ system was performed by spark plasma sintering of diboride powders at 2000 °C. The 3:2:1 ratio between Zr, Ta, and Nb showed the highest specific strength at room temperature during the initial screening of the mechanical properties. The flexural strength gradually decreased from 700±42 MPa at RT to 518±30 MPa at 1600 °C with the Weibull parameter exceeding 15. Diborides with an equimolar composition did not show a maximum in their strength, fracture toughness or hardness.

Borides of transition metals, such as $ZrB_2$ or $TaB_2$, are being widely used for a variety of applications including thermal protection systems, cutting tools, etc. [1]. These diborides belong to the ultra-high-temperature ceramics (UHTCs) family and are capable of withstanding high temperatures and high external loads in severe or extreme environments [2].

The consolidation of diborides requires a relatively high consolidation temperature due to the presence of metal-covalent, covalent-ionic bonds in the diboride crystal cell [1,2]. Second, the raw powder may have a surface oxide layer, which will slow down the densification or will result in the formation of a considerable amount of the oxide [3]. Finally, the strength of the bulk $ZrB_2$ has been extensively studied, but

---

† Authors to whom correspondence should be addressed, Dmytro Demirskyi, demirskyi.dmytro.e2@tohoku.ac.jp, Oleg Vasylkiv oleg.vasylkiv@nims.go.jp

still requires improvement [4,5]. The solid-solution diborides have received considerable attention [6–9] in order to improve their strength. Recently, considerable attention has focused on medium- or high-entropy diboride ceramics [8]. For these compounds [10–12], an equimolar contribution of the principal transition metal is widely used and it is widely anticipated that effects characteristic for high-entropy alloys, such as ‘sluggish diffusion’, should lead to the higher strength or creep resistance at elevated temperatures [12].

Nevertheless, for the binary solid-solutions [13], the optimum in the creep resistance sometimes lies outside an equimolar composition and, in general, there is a limited number of studies that focus on finding the optimum composition for the required set of material properties.

Considering these observations within the present study, we investigated a ternary medium-entropy diboride system based on $ZrB_2$, $TaB_2$ and $NbB_2$. Exploring this system allows one 1) to obtain information about the lattice parameters; 2) to create a solid-solution between the diborides in order to explore if the solid-solution strengthening will improve the strength at elevated temperatures, and 3) to find the optimum composition for the room-temperature strength which was also studied up to 2000 °C. To fulfill these ideas, we applied a reactive sintering approach using commercial $ZrB_2$, $TaB_2$ and $NbB_2$ which have a mean particle size below 4 μm, acquired from Wako Pure Chemicals. The concentration of the secondary elements in the $ZrB_2$ powder was as follows: Fe 50 ppm, Hf $\leq$ 120 ppm, C< 0.5 wt.%, N $\leq$ 0.5 wt.%, and O <0.7 wt.%. For $NbB_2$ and $TaB_2$ oxygen content was within 0.5 wt.%, while the concentration of Ta or Nb impurities were up to 300 ppm. The $NbB_2$ and $ZrB_2$ powders used in this study were also used in the [7] and [9], respectively.

The received untreated powders were mixed using the Intelli-Mixer RM-2M (ELMI, Latvia) mixer. This procedure excludes using solvents or grinding the materials as mixing occurs due to fast vibrations in a relatively small volume (50 ml). The SPS experiments were conducted using the ‘Dr. Sinter’ 1050 (Sumitomo, Japan) unit with a 30-mm die and an inner Ta-foil to control the carbon diffusion [14] and argon as the atmosphere.

The schedule for the specimens prepared in this study had the following major steps: (1) heating to 700 °C in four minutes followed by (2) a 200 °C/min heating to the densification temperature of 2000 °C. At 2000 °C (3) a dwell of 5 min was used as a homogenizing step. (4) cooling to 600 °C at the rate of 20 °C/min was then performed. The pressure of 45 MPa was maintained during the heating, consolidation and cooling stages.

In order to produce the ceramic with the maximum performance the first step was determining the composition for which the diboride shows the highest strength. For this step, twenty three original mixtures were prepared, while the strengths for the monolithic $ZrB_2$ [5], $TaB_2$ [14] and $NbB_2$ [15] ceramics were from the previous studies. After completing the sintering, the specimens were polished by diamond abrasives to 0.5 μm. The XRD data were then collected using a D8 Advance (Bruker) and if the specimen was a single-phase diboride, these specimens underwent cutting and flexural tests. Based on the XRD data, the theoretical X-ray density was estimated which was used to evaluate the relative density of the medium entropy diboride. For each composition, two tests were performed at room temperature using the three-point flexural strength (16 mm span) and a single-test using the four-point flexural strength in a 20/10 mm configuration. Tests were performed using a modified Shimadzu set up that was previously described in detail [16]. The lowest values from these three tests were analyzed by a linear regression [17] using a custom code in MatLab.

The indentation fracture toughness was calculated based on the half-length of the crack $c$ formed around the corners of the indentations at the load $P$ of 196 N using the following equation [18]: $K_{IC} = 0.0725\ (P/c^{3/2})$. The hardness was determined by a Vickers hardness tester (Akashi, AVK-A, Japan) using a load of 196 N with a dwell time of 15 s following the standard procedure (ASTM C 1327–15). Similar to the strength, the hardness and toughness were analyzed for their maxima; however, the strength was the main factor under consideration.

**Figure 1** shows the contours for the (b) room-temperature strength for the diborides in the Zr-Ta-Nb system. After close inspection of the data, it was decided that the ZTN diboride with a 3:2:1 composition should be further evaluated as this diboride had a strength above 800 MPa and had one of the finest grain sizes after the SPS at 2000 °C (8±2 μm). The lattice parameter for the 3:2:1 composition was estimated as *a* = 3.138(5) Å and *c* = 3.447(0) Å.

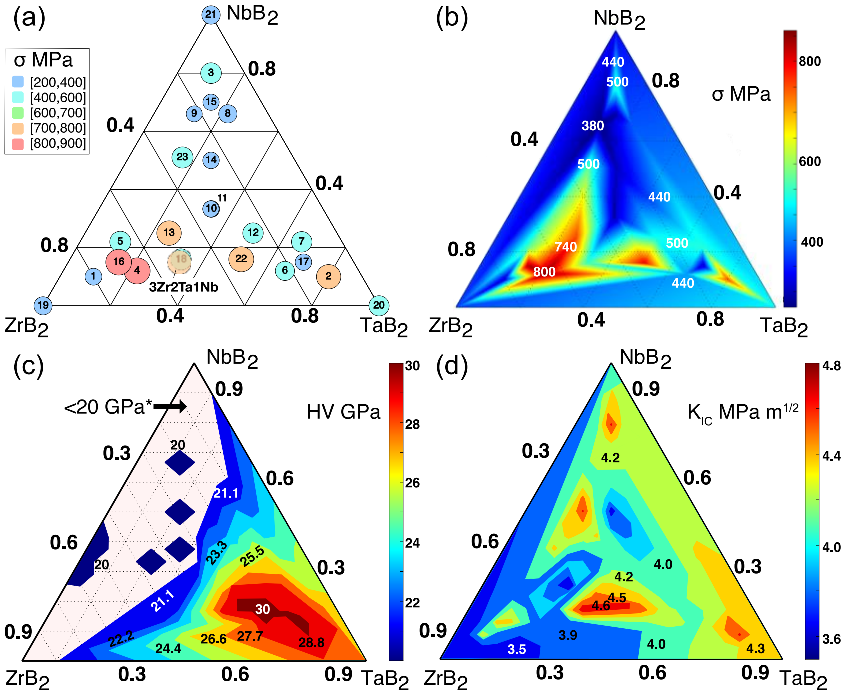


**Figure 1**. Mechanical properties as a function of the composition for the ternary $ZrB_2$– $TaB_2$–$NbB_2$ system. (a) compositions used in the screening process and their individual strength, surface projections of (b) strength at room temperature, (c) hardness and (d) indentation fracture toughness.

* More data points are needed for correct approximation.

In order to further evaluate the properties of the 3:2:1 ZTN diboride, we prepared four specimens using the identical SPS schedule that was used for the three-point flexural tests (ASTM C1211−13, configuration B). A total of 16 tests were performed at room temperature and 12 tests at 1600 °C. The tests at 1600 °C were carried out using two separate batches of six specimens. Tests at the other temperatures averaged 3 tests per temperature.

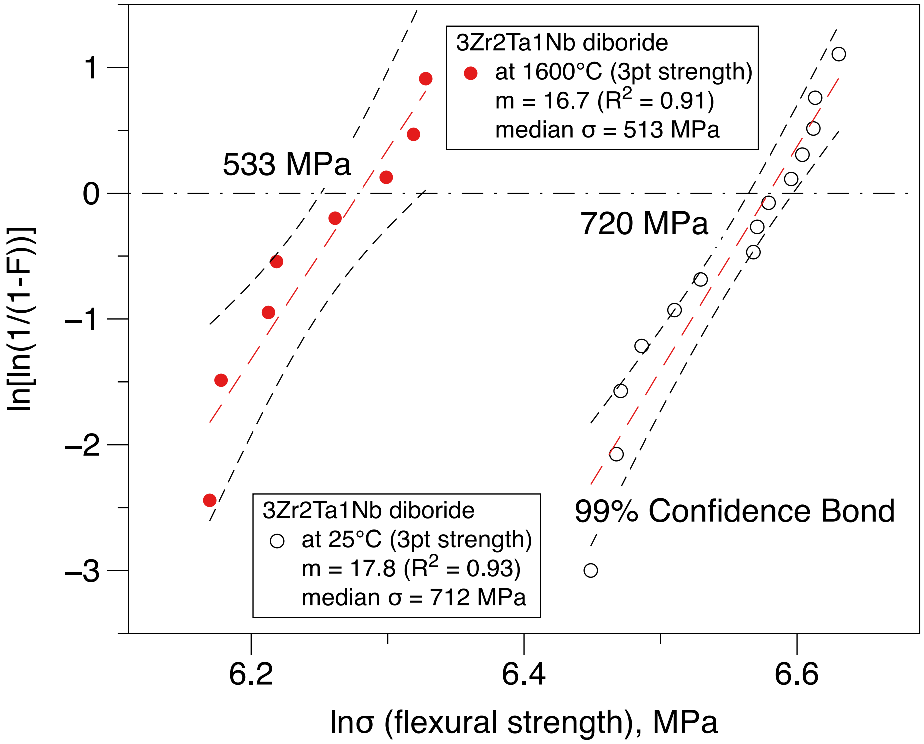


**Figure 2**. Statistical variation in flexural strength of ZTN diboride with a 3:2:1 ratio at room temperature and at 1600°C.

The Weibull analysis was used as a method of determining the reliability of the strength tests for the room temperature and 1600°C data. **Figure 2** shows the statistical variation of the attempted flexural tests. In both cases, a relatively high Weibull exponent *m* of above 15 was obtained. The exponent reported here cannot be used for the engineering purposes, as at least 30 tests are required according to the ASTM C1161-13. Nevertheless, the number of tests used in this study was sufficient to estimate the average/median strength. The median strengths for the tests at 25°C and 1600°C were 712 MPa and 513 MPa, respectively. The value for the room temperature strength is in acceptable agreement with the data presented in **Fig. 1**, however, one can expect slightly different results if all the compositions were tested using a statistically acceptable number of tests (i.e., above 10 according to ASTM C1161-13).

**Figure 3** provides a summary for the flexural strength data of the $ZrB_2$, $ZrB_2$-$TaB_2$ composite and 3:2:1 ZTN diboride ceramic [4,5,19,20]. The $ZrB_2$-$TaB_2$ composite was a two-phase diboride ceramic consolidated by non-reactive spark plasma sintering at 2300 °C [20]. There were no solid-solution detected between diborides owing to a short dwell and a special loading procedure. Hence, plastic failure of $ZrB_2$-$TaB_2$ was observed only at 1800°C. During the present investigation, the flexural strength slowly decreased up to 1600°C, followed by a rapid decrease in strength above 1800 °C (362±16 MPa). Noticeably, at 800 °C or 1000 °C, the flexural strength for the selected ZTN diboride was from 100% to 50% higher than that reported in [4] and [5]. For clarity, the $ZrB_2$ data using refs [4,5,19] are illustrated by the pale background color in **Fig. 3**.

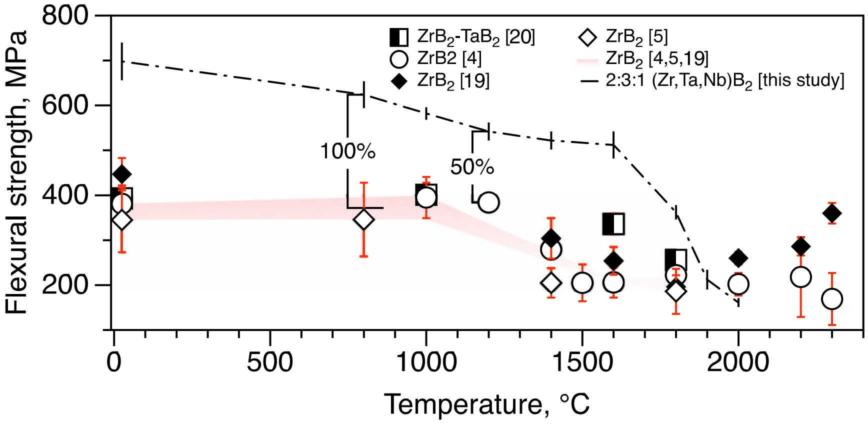


**Figure 3**. Temperature dependence of the flexural strength of the bulk $ZrB_2$ [4,5,19], $ZrB_2$–$TaB_2$ [20], and ZTN diboride ceramics.

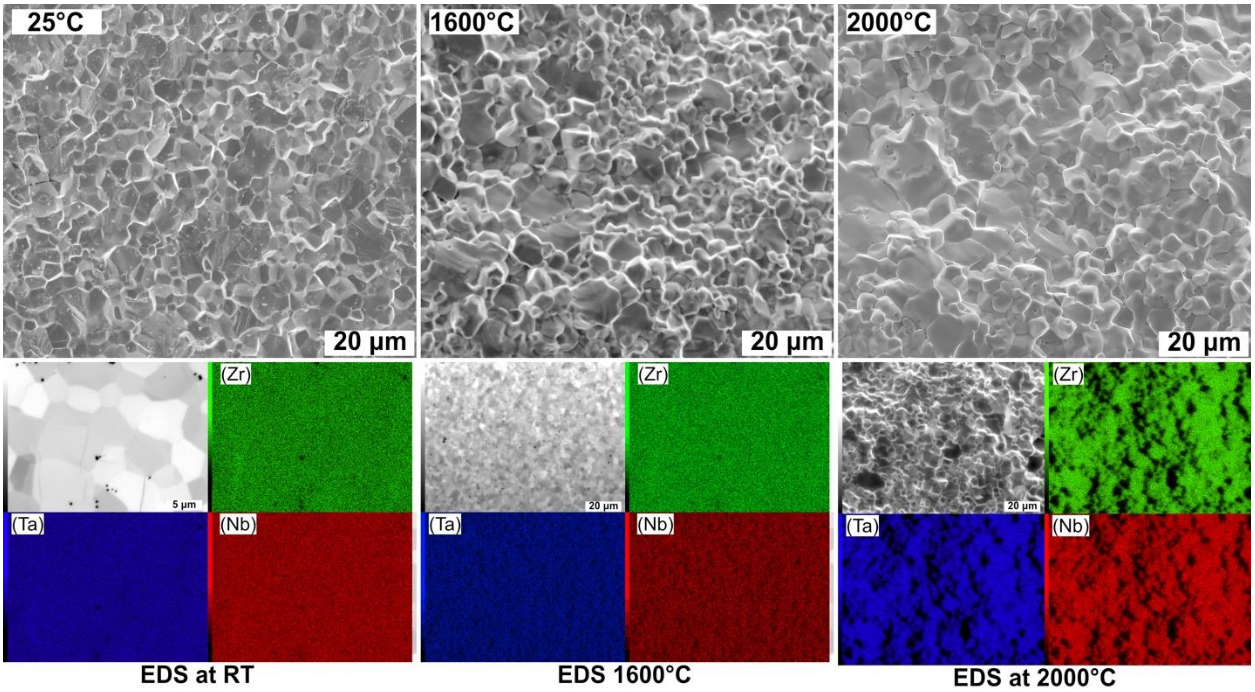


**Figure 4.** Typical fracture of the 3:2:1 ZTN diboride at selected temperatures. The fracture was acquired in the SE mode. EDS for polished surfaces was taken from the upper side of a specimen after testing at room temperature or at 1600 °C.

The gradual decrease in strength seems to follow the linear decrease in Youngs' modulus with the temperature [13]. The deviation from this quasi-linear decrease can be observed if (i) annealing was performed or (ii) existing surface flaws healed; while the rapid decrease in strength should correspond to (iii) generation of new flaws during the reheating process due to thermal expansion or elastic modulus anisotropy [13]. The rapid decrease in strength observed above 1800 °C can be explained by the increase in the dislocation generation or at higher temperatures by the fast dislocation movement as noted by Wang for the $ZrB_2$ after high-temperature indentation tests [21]. Furthermore, once the macroscopic plastic deformation will be activated, the majority of the ceramics will possess a strength of ~200 MPa while any increase in strength is due to (a) loading rate [22] or (b) relief of the stress before the crack tip [7,13,15]. In addition, at these temperatures, the fracture changes to intergranular as evidenced by **Fig. 4** for the 321 ZTN diboride. One can presume that the high-temperature strength especially above 1800 °C can be optimized as in **Fig. 1**. At present, these tests are being conducted and analyzed. The effects of the composition on the resulting structures and properties will be subsequently reported.

In summary, within this, study the 3:2:1 ratio between Zr, Ta, and Nb showed the highest specific strength at room temperature during the initial screening of the mechanical properties within the Zr-Ta-Nb-B system. For the medium entropy diboride, the lattice parameter for the 3:2:1 composition was estimated as $a = 3.138(5)$ Å and $c = 3.447(0)$ Å. The strength of the ZTN SPSed ceramics gradually decreased from 700±42 MPa at RT to 518±30 MPa at 1600 °C. Above 1800 °C, the strength decreased to 200 MPa which is consistent with the data for $ZrB_2$ and is caused by the ongoing plastic deformation. Finally, the proposed quick method for the properties evaluation indicated that the optimum mechanical properties do not essentially correspond to the equimolar composition that is being widely used for medium- or high-entropy ceramics.

D.D. was supported by the Core Research Cluster for Materials Science, Tohoku University, Japan.

[1] G.V. Samsonov, T.I. Serebryakova, V.A. Neronov, Borides. Atomizdat, Moscow, 1975. [in Russian].

[2] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium. J. Am. Ceram. Soc. 90[5] (2007) 1347–1364. https://doi.org/10.1111/j.1551-2916.2007.01583.x.

[3] M. Brochu, B.D. Gauntt, L. Boyer, R.E. Loehman, Pressureless reactive sintering of $ZrB_2$ ceramic. J. Eur. Ceram. Soc. 29[8] (2009) 1493–1499. https://doi.org/10.1016/j.jeurceramsoc.2008.08.032.

[4] E.W. Neuman, G.E. Hilmas, W.G. Fahrenholtz, Strength of zirconium diboride to 2300°C. J. Am. Ceram. Soc. 96[1] (2013) 47–50. https://doi.org/10.1111/jace.12114.

[5] D. Kalish, E.V. Clougherty, K. Kreder, Strength, fracture mode, and thermal stress resistance of $HfB_2$ and $ZrB_2$. J. Am. Ceram. Soc. 52[1] (1969) 30–36. https://doi.org/10.1111/j.1151-2916.1969.tb12655.x.

[6] C. Mroz, Processing TiZrC and $TiZrB_2$. Am. Ceram. Soc. Bull. 73[4] (1994) 78–81.

[7] D. Demirskyi, I. Solodkyi, T. Nishimura, O. Vasylkiv, Fracture and property relationships in the double diboride ceramic composites by spark plasma sintering of $TiB_2$ and $NbB_2$ J. Am. Ceram. Soc. 102[7] (2019) 4259–4271. https://doi.org/10.1111/jace.16276.

[8] J.-X. Liu, X.-Q. Shen, Y. Wu, F. Li, Y. Liang, G.-J. Zhang, Mechanical properties of hot-pressed high-entropy diboride-based ceramics. J. Adv. Ceram. 9 (2020) 503–510. https://doi.org/10.1007/s40145-020-0383-8.

[9] D. Demirskyi, T.S. Suzuki, K. Yoshimi, O. Vasylkiv, Synthesis of medium-entropy $(Zr_{1/3}Hf_{1/3}Ta_{1/3})B_2$ using the spark plasma consolidation of diboride powders. J. Ceram. Soc. Jpn. 128[11] (2020) 977–980. https://doi.org/10.2109/jcersj2.20151.

[10] L. He, J. Zhang, Z. Li, N. Lin, B. Liu, S. Zhao, K. Jin, H. Chen, H. Yan, F. Peng, Y. Ma, Z. Wu, Toughening (NbTaZrW)C high-entropy carbide ceramic through Mo doping, J Am Ceram Soc. 105[8] (2022) 5395-5407. https://doi.org/10.1111/jace.18474.

[11] W. Lu, L. Chen, W. Zhang, W. Su, Y. Wang, Y. Fu, Y. Zhou, Single-phase formation and mechanical properties of (TiZrNbTaMo)C high-entropy ceramics: First-principles prediction and experimental study, Journal of the European Ceramic Society 42 (2022) 2021-2027. https://doi.org/10.1016/j.jeurceramsoc.2021.12.058.

[12] Q. Yang, X. Wang, W. Bao, P. Wu, X. Wang, X. Guo, C. Zhang, D. Jiang, Influence of equiatomic Zr/(Ti,Nb) substitution on microstructure and ultra-high strength of (Ti,Zr,Nb)C medium-entropy ceramics at 1900 ℃, Journal of Advanced Ceramics 2022, 11(9): 1457-1465. https://doi.org/10.1007/s40145-022-0623-1.

[13] R.A. Andrievski, I.I. Spivak, Strength of Refractory Compounds. Metallurgiya, Chelyabinsk, 1989. [in Russian].

[14] D. Demirskyi, O. Vasylkiv, Consolidation and grain growth of tantalum diboride during spark plasma sintering. Ceram. Int. 42[14] (2016) 16396–16400. https://doi.org/10.1016/j.ceramint.2016.07.059.

[15] D. Demirskyi, I. Solodkyi, T. Nishimura, Y. Sakka, O. Vasylkiv, High-temperature strength and plastic deformation behavior of niobium diboride consolidated by spark plasma sintering. J. Am. Ceram. Soc. 100[11] (2017) 5295–5305. https://doi.org/10.1111/jace.15048.

[16] D. Demirskyi, O. Vasylkiv, Analysis of the high-temperature flexural strength behavior of $B_4C$–$TaB_2$ eutectic composites produced by in situ spark plasma sintering. Mater. Sci. Eng. A 697 (2017) 71–78. https://doi.org/10.1016/j.msea.2017.04.093.

[17] F.C. Leone, N.L. Johnson, Statistics and Experimental Design In Engineering and the Physical Sciences, Vol 2, John Wiley and Sons, N.Y., 1964.

[18] B.R. Lawn, E.R. Fuller, Equilibrium penny-like cracks in indentation fracture. J. Mater. Sci. 10 (1975) 2016–2024. https://doi.org/10.1007/BF00557479.

[19] A.C. Murchie, J.L. Watts, W.G. Fahrenholtz, G.E. Hilmas, Mechanical properties of borothermally synthesized zirconium diboride at elevated

temperatures. Int. J. Appl. Ceram. Technol. 18[4] (2021) 1235–1243. https://doi.org/10.1111/ijac.13755.

[20] D. Demirskyi, O. Vasylkiv, Flexural strength behavior of a $ZrB_2$–$TaB_2$ composite consolidated by non-reactive spark plasma sintering at 2300°C. Int. J. Refract. Met. H. 66 (2017) 31–35. https://doi.org/10.1016/j.ijrmhm.2017.02.003.

[21] Wang Jianye, "Processing and Deformation of ZrB2," (2012). Doctoral Dissertation. (http://hdl.handle.net/10044/1/11179).

[22] H.J. Frost, M.F. Ashby, Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics, Pargamon Press, Oxford, 1982.

Dear Reviewers,

First, we want to express our gratitude for the comments that were asked for this submission. Second, the text was highlighted with a green background in the revised copy (r2) of the manuscript.

Reviewer #1:

English should be polished, for instance, page 5 line 13, two "using".

Thank you. We hope we improved the main issues with language in the revised copy.

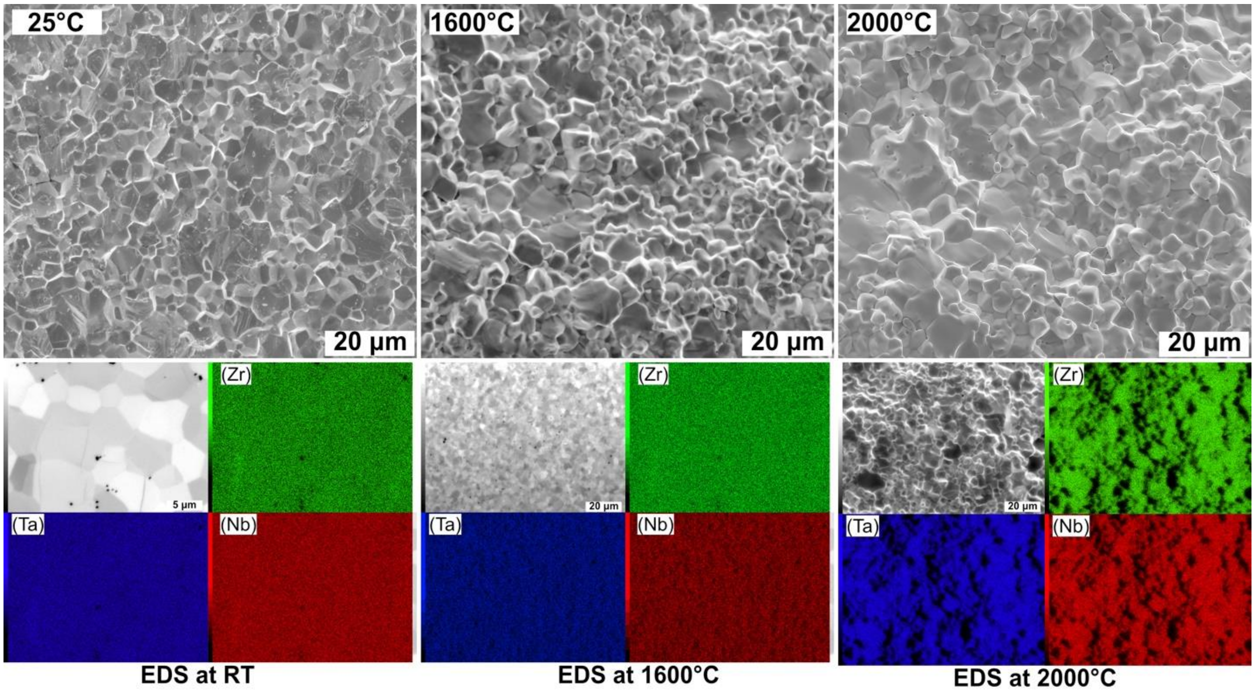
If the chemical composition would affect the element distribution or even form different core-rim or core-shell structure, the discussion on the fracture mode or strength would become different.

And

In Fig. 4, EDS maps from fractured surface can not provide accurate information on the element distributions, and those from polished surface are needed.

Thank you. The concerns are mutual. In this study, the core-rim structure was observed during processing at lower temperatures or due to the inappropriate mixing of powders. Nevertheless, if these being present in the specimens, we can detect these using the XRD. And only specimens with a single-phase XRD were selected for further strength/hardness/toughness testing. In other words, these issues were resolved using 2000°C/5 min configuration before the publication.

The polished probing was not so distinctive as for fractured surface, please kindly see the revised copy of the Figure 4. It was reorganized to show the EDS probes at RT (polished), 1600 °C (thermally etched polished), and 2000 °C fracture (as it was in r1).

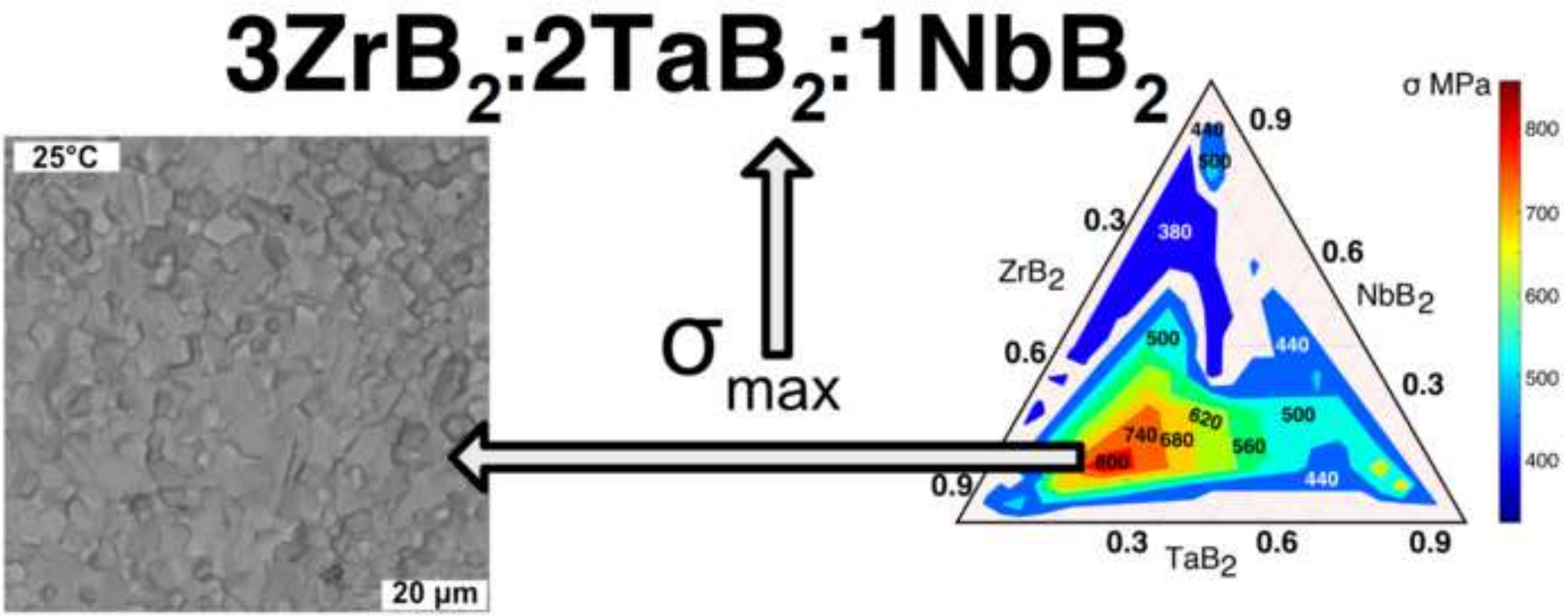


EDS at RT EDS at 1600°C EDS at 2000°C

The EDS map for polished surface (EDS at RT) seems to have a core-rim-like structure, however the local probing shows an unchanged ratio. The other probe from the polished surface after the 1600 °C test indicates that there is no particular segregation of the metal in the individual grain i.e., homogeneous solid solution. Hopefully this interpretation will be acceptable for the publication. Alternatively, we can present the overlay of the probing lines for the polished specimens (as these may be clearer than the map right now). Also, all three of these EDS maps were acquired and analyzed using identical probing procedures and the same JEOL software.

On behalf of the authors,
O. Vasylkiv

Graphical abstract



## Compliance with Ethical Standards

The authors declare that they have no conflict of interest.