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Reactive consolidation of tough, deformation resistant tantalum monoboride

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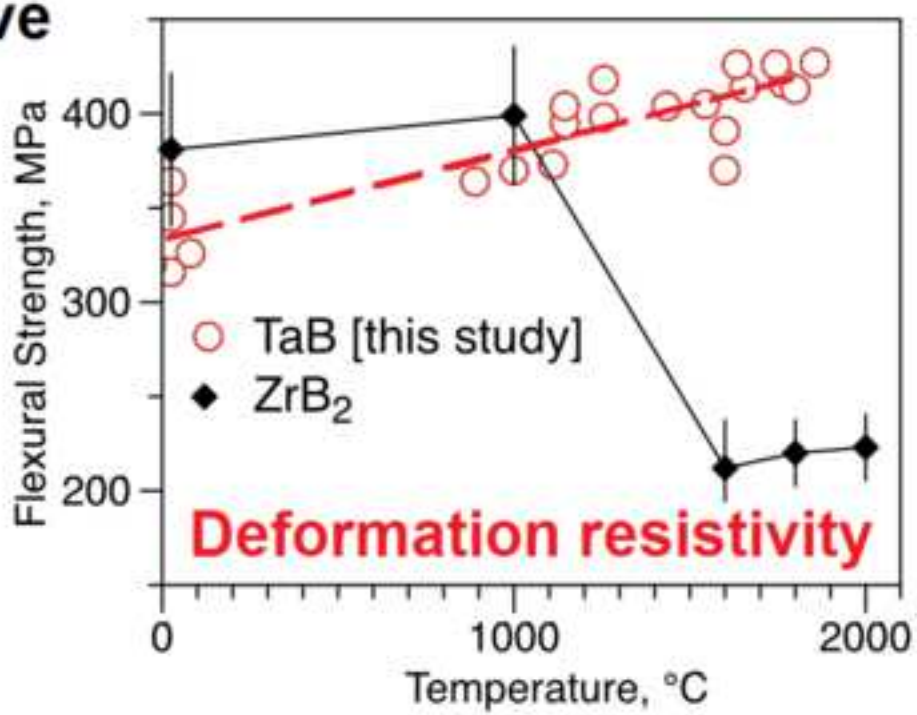
Graphical Abstract

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



Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

Reactive consolidation of tough, deformation resistant tantalum monoboride

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(c) Department of Materials Science and Engineering, Tohoku University, 6-6-02 Aramaki Aza Aoba, Sendai, 980-8579, Japan

Reactive consolidation of tantalum monoboride (TaB) was performed by spark plasma sintering at 2150 °C. The TaB ceramic had elongated grains with a length/width ratio between 2.4 and 4.8 and a length between 30 and 100 μm. Up to 3 vol.% of residual non-reacted boron was also present. The hardness, indentation fracture toughness and room-temperature strength of the TaB were 18.5±0.2 GPa, 9.8±0.4 MPa $m^{1/2}$, and 320 MPa, respectively. The TaB showed resistance to high-temperature deformation as its flexural strength gradually increased from 370 MPa at 1000 °C to 425±7 MPa at 1800 °C.

The diborides of tantalum, zirconium and hafnium with the hexagonal AlB_2-type structure 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 [1]. In the case of tantalum, there are other diborides with a tetragonal (Ta_2B) or orthorhombic structure (Ta_3B_4 and TaB) [2–7]. The latter phase was estimated to have a melting point of least 2500 °C [2], while an analysis by

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Leitnaker et al. [3] suggested that this boride should have a melting point of at least 2800 °C, which is consistent with the data of Portnoi et al. [4] (3090±20 °C), and it is on the same level as the melting point of tantalum diboride (3040±30 °C).

According to Okada et al. [5], tantalum monoboride single-crystals showed a microhardness lower than tantalum diboride (23 GPa vs 29 GPa), and Ma et al. [6] reported a superhardness with a load of only 25 g·f (38.8 GPa), while loads of 500 g·f resulted in a microhardness of 21.3 GPa, which is comparable to [4] or [5].

Up to now, the strength or toughness of tantalum monoboride has not been reported, while TaB_2 usually has the toughness and strength of 4.5 MPa $m^{1/2}$ and 555±103 MPa, respectively [8]. Recent studies of the complex multiboride [9] composites or high-entropy monoboride [10] indicated that the research on monoborides may lead to the development of ceramics with improved mechanical properties.

Based on this information, in the present study, we prepared the tantalum monoboride specimens with a 30-mm diameter and 6-mm thickness by spark plasma sintering. This allowed us to: 1) obtain data on the macroscopic mechanical properties such as hardness, toughness and strength; and 2) find the temperature dependence of the flexural strength up to 1800 °C. To fulfill these objectives, we applied a reactive sintering approach using commercial TaB_2, Ta, and B powders from Wako Pure Chemicals.

Two approaches were used. The first one involved a mixture of tantalum and boron similar to Ma et al. [6], while the second one relied on the reaction between the diboride powder and tantalum. The latter case was similar to Leitnaker et al. [3], as such approaches minimize a temperature rise associated with the synthesis. The specimens obtained by these approaches were labeled as A-TaB and B-TaB, respectively (see **Table 1**).

The received untreated powders were mixed using the Intelli-Mixer RM-2M (ELMI, Latvia) mixer, as previously used in [9]. 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 [11] and argon as the atmosphere.

The schedule for the specimens prepared in this study had the following major steps: (1) heating to 1000 °C in four minutes followed by (2) a 50 °C/min heating to the densification temperature between 1900 and 2200 °C; (3) a dwell of 5 min was used as a homogenizing step at the densification temperature, and (4) cooling to 600 °C at the rate of 20 °C/min was then performed. The pressure of 40 MPa was maintained during the heating, consolidation and cooling stages.

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

After completing the sintering, the specimens were polished by diamond abrasives to 0.5 μm. The XRD data were then obtained using a D8 Advance (Bruker), and if the specimen was a single-phase monoboride, these specimens underwent cutting and flexural tests. For each composition, eight tests were performed at room temperature using the three-point flexural strength (16 mm span) and four tests at selected temperatures. The tests were performed using a modified Shimadzu machine [12].

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 [13]: $K_{IC} = 0.0725\ (P/c^{3/2})$. The hardness was determined by a Vickers hardness tester (Akashi, AVK-A, Japan) using a load of 9.8 to 196 N with a dwell time of 15 s following the standard procedure (ASTM C 1327–15).

Despite using the proper molar ratio between the reagents, none of the attempted SPS runs resulted in 100% TaB. Run 2 using the B-TaB mixture was the closest to monolithic tantalum monoboride (i.e. XRD single phase pattern, and below 5 vol.% of the secondary phases by SEM). XRD suggested that this was a 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), however, up to 3 vol.% of the boron was observed as a residual phase (B 99 mol.%, C+O ≳1 mol.%) by SEM. For instance, run 4 resulted in TaB_2/TaB composite, where the diboride was detected by the XRD, while boron or boron carbide was not detected (**Fig. 1**).

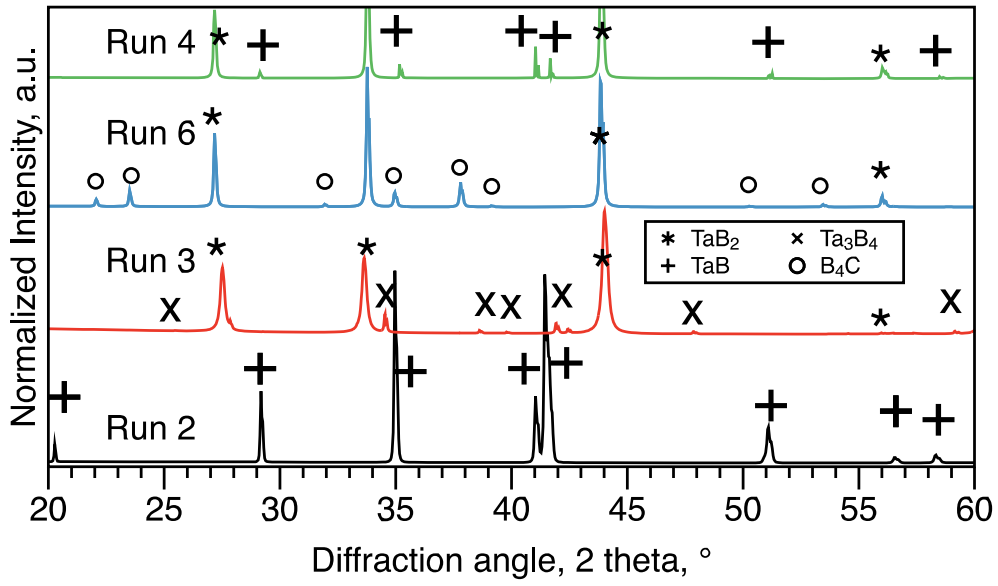

Figure 1. X-ray diffraction patterns for the sintered ceramics using SPS conditions 2,3,4, and 6.

For the Run 2, the numerous EDS probes suggested the 50:50 ratio between, the tantalum and boron (maximum ±1% deviation), and up to 4 mol.% of C. The carbon seems to originate from the TaB_2 powder as it roughly satisfies the 0.5 wt.% of C. Alternatively, carbon diffusion from the SPS dies via CO/CO_2 can be expected, as direct contact of the Ta foil with the outer graphite foil resulted in the 50–60 μm TaC film. The latter is consistent with the observation in [14]. The tantalum foil used during SPS seems to cause the appearance of the boron grains as it causes a shift from the 1:1 Ta:B ratio at the surface of the specimen. Preliminary trials suggested that the addition of excess of Ta to the mixture will result in formation of TaB_2/Ta_2B which is consistent with the observation in [3].

Furthermore, fairly large 100-μm needled-shaped grains were observed after sintering above 2100 °C. The microstructure of the sintered compacts consists mostly of TaB elongated grains, with average aspect ratios between 2.4 and 4.8 uniformly distributed in the matrix of equiaxed or slightly elongated TaB grains mixed with up to 3 vol.% boron grains. A study of the grain growth of tantalum diboride during the spark plasma sintering suggested that one can obtain ~50-μm TaB_2 grains using a 20-min dwell at 2000 °C [11]. While the analysis for the crystal growth performed in [9] suggested that orthorhombic TaB crystals may form crystals with a plate-like morphology as well as needle-like grains. Okada et al. [5] reported the formation of plate-like prisms. These observations suggested that the elongated crystal shape can be due to (i) preferable growth in *c*-axis direction or (ii) due to the pressure applied during the spark plasma sintering process.

Mechanical performance of the tantalum monoboride was investigated using samples prepared under the Run 2 conditions (**Table 1**). The hardness was between 18 and 21 GPa, and decreased with an increase in the load (**Fig. 2**) [4–8].

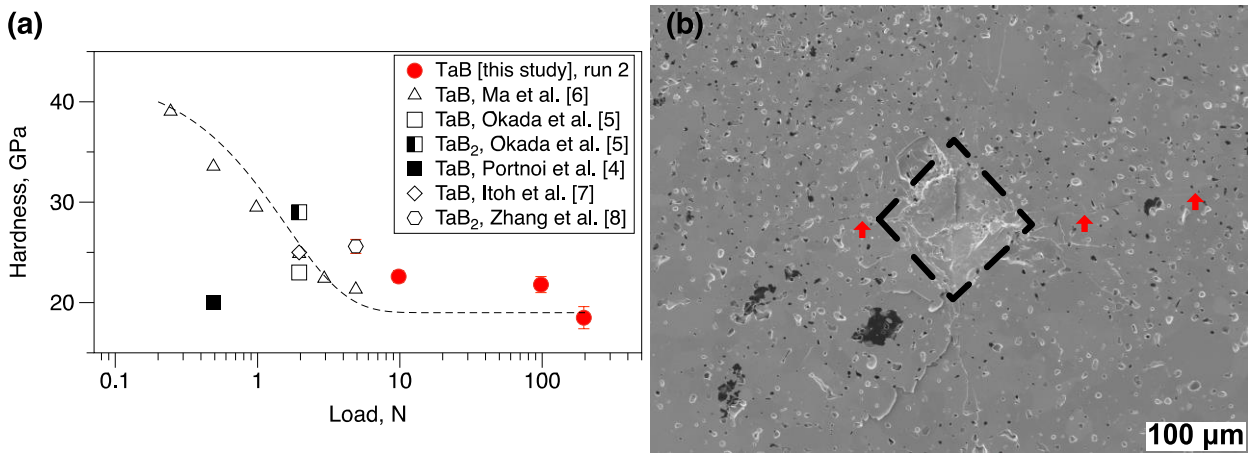

Fig. 2. The hardness of TaB [4–7] and TaB_2 [8] as a function of load. (b) shows typical indent using 196 N load for the specimen prepared under Run 2 conditions (**Table 1**). Black areas here are pores and residual boron. Red arrows in (b) indicate the crack deflection.

The indentation fracture toughness was within 9.8±0.4 MPa $m^{1/2}$ which is an unusually high value compared to 4.5 MPa $m^{1/2}$ reported for TaB_2 in [8,15]. Residual boron may contribute to the increase in toughness, however, observations of the crack propagation suggested that crack deflection will most likely occur at the TaB/TaB interfaces suggesting that tests using the notch method may provide an additional clarification for the observed toughness.

Figure 3 provides a summary for the flexural strength data of the TaB. There is a tendency for the gradual increase in strength with an increase in temperature. The inset in **Fig. 3** illustrates that only at 1800 °C TaB had loading curves that exhibited nonlinear characteristics. This indicates that test above 1800 °C will result in plastic deformation. As a rule, AlB_2-type diborides, such as ZrB_2 [1], will have an unchanged strength up to 1000 °C (~400 MPa), and a 40% decrease in strength at 1600 °C. Data for the high temperature strength data for TaB_2 were not previously published, while the TaB_2–B_6O or TaB_2–B_4C composites showed a gradual increase

in strength up to 1800 °C [12,16]. At room temperature, TaB_2 shows a strength of 555±103 MPa [8], which is higher than that for the TaB (330±25 MPa).

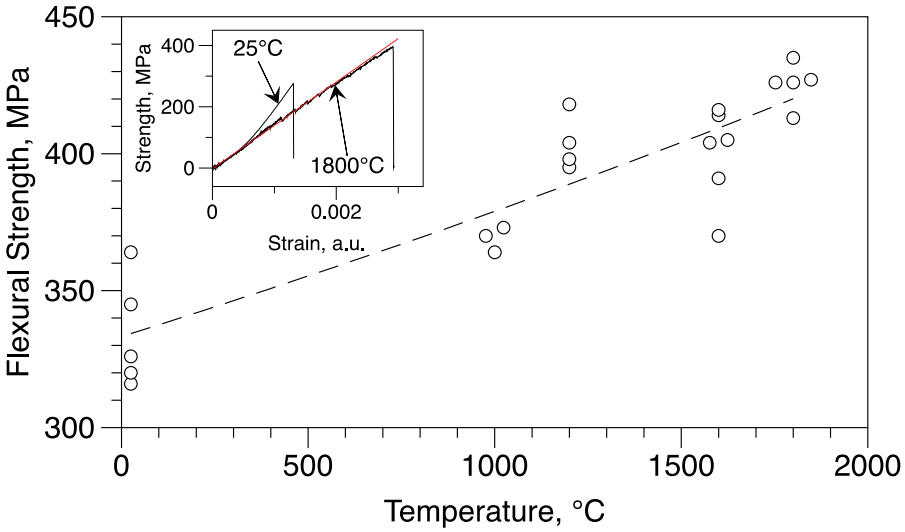

Figure 3. Temperature dependence of the flexural strength of the bulk TaB prepared under Run 2 conditions (see **Table 1**).

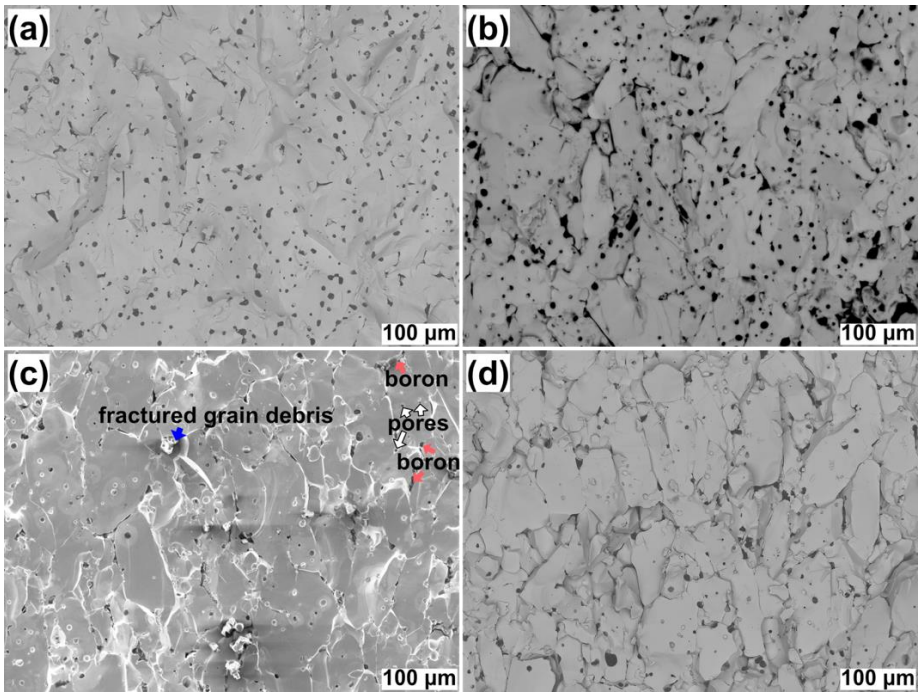

Figure 4. Effect of temperature of the flexural test on the fracture behavior of the tantalum monoboride (SPS run ID #2): a) 25 °C, b) 1200 °C, c) 1600 °C, and d) 1800 °C.

The fracture behavior did not change with an increase in the temperature (**Fig. 4**), while it was easier to observe the grain morphology above 1600 °C. At all temperatures, a fairly large amount of debris from the fractured grains were observed, suggesting that the transgranular fracture mechanism was active despite that intergranular fracture being the dominant fracture mechanism. Loading curves using a 0.5 mm/min loading rate showed that there was a slight deviation from the linearity at 1800 °C (i.e., plastic end of the loading curve). The increase in the strength at 1800 °C can be associated with (i) flaw healing or (ii) plasticity (micro-plasticity) contribution [12]. The latter seem to be the reasonable explanation when one considers the large size of the TaB grains, and according to the fracture mechanics, the flaw size should be approximately 300 μm (cluster of 3–4 TaB grains).

In summary, this is the first study to report the strength of the tantalum monoboride bulks prepared by reactive consolidation. 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 (SPS run 2). This ceramic showed good level of macroscopic hardness of 18.5±0.2 GPa (at 196 N load) and exceptionally high indentation fracture toughness of 9.8±0.4 MPa $m^{1/2}$. At room temperature, TaB showed a relatively lower strength than reported for TaB_2 [8] (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 [1] will have the strength of 220±18 MPa at 1800 °C.

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

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

We would like to submit the revised version (R1) of the manuscript entitled "Reactive consolidation of tough, deformation resistant tantalum monoboride" by Dmytro Demirskyi, Kyousuke Yoshimi, Tohru S. Suzuki, 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 light-yellow background in the revised copy (r1) of the manuscript.
Finally, the answers to the comments are summarized below.

Reviewer #1:

In the abstract, the phrase "fairly elongated grains" is vague. Can this be replaced with a more quantitative description such as typical length or aspect ratio?

The highest average aspect ratio (length/width of the grains) was 4.8, the lowest was 2.4*.
* Obviously, there were almost equiaxed grains present, as well as slightly elongated, the 'shape' (length to width ratio) followed a normal distribution, hence a range between 2.4 and 4.8 should cover 87% of the cases (i.e. $\mu \pm 1.5\sigma$).

The text in the abstract was altered to:
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On Page 2, line 30, eliminate the phrase "fairly large size" and simply replace with the actual dimensions.

Agreed

The paper needs to be more clear about the composition that was the focus of the mechanical testing. The procedure mentions that all of the compositions were tested. Then, the description of the results only states at one point that the mechanical tests were conducted on the "run 2" material. I suggest that the figure captions be modified to emphasize that data from the "run 2" material is included in the figure.

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Page 5, line 50 uses the term "deformation resistivity". This term is not well defined. It is suggested that the discussion simply focus on what was measured and analyzed, which is the strength. Neither elastic nor plastic deformation was not directly measured to provide quantification of deformation of the material.

Agreed, we attempted to highlight the difference, we will be sure on the resistivity to deformation after compressive/tensile creep tests.

The labels on Figure 3c need to be larger.

Agreed. Thank you.

Page 7, line 39 states "the formation of the monoboride was observed only when processing at 2150°C". This is misleading and could be mis-interpreted since TaB was also reported at other temperatures. Do you mean "nominally phase-pure" or "phase pure by XRD"?

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1) In other cases, the XRD or SEM showed the secondary phases which contribute above 5 vol. %. This is technically in the realm of the composites.
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We cannot justify if the experiments performed by, for instance, Ma et al. had the same problems, hence, for clarity we added a short explanation defining the '*criteria for success*' which are simple: single phase XRD and ~5 vol.% of the secondary phases.

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1. In this mauscript, the language should be improved, for example, '……,which is consistent with the data of Portnoi et al. [4] (3090±20 °C), which is on the same level as the melting point of tantalum diboride (3040±30 °C).'.

We corrected language again.

2. From the Table 1, why there is only the formation of monoboride in Run 2, because all Runs were used the 1:1 molar ratio between reagents, please make the corresponding explaination and also add the XRD patterns.

Ok, added the typical XRD patterns.

3. In Fig. 1, the authors stated that crack deflection will most likely occur at the TaB/TaB interfaces, which should be marked.

Difficult to visualize, see the red arrows in figure 1. To clearly visualize we need to show 3-4 different indents.

4. In Fig. 3b, why there is so many black points, how they were formed.

The explanation is already in the manuscript. But briefly:

- For the specimens made using SPS run 2 these are boron (not boron carbide).
- These boron grains are due to the reaction of the Ta foil with C/graphite forming an outer layer TaC (~50 μm thick).
- Some portion of the Ta powder will assist in forming TaC.
- This will locally shift from 1:1 ratio required for the formation of TaB, and, hence, there is a shift in the composition $Ta_{1-x}B_1$, where *x* is not greater than 0.1.
- The increase in Ta content (excess in Ta for 1:1 mixture), will result in the formation of Ta_2B and TaB_2 instead of TaB.

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

On behalf of the authors,
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4. In Fig. 3b, why there is so many black points, how they were formed.

The explanation is already in the manuscript. But briefly:

- For the specimens made using SPS run 2 these are boron (not boron carbide).
- These boron grains are due to the reaction of the Ta foil with C/graphite forming an outer layer TaC (~50 μm thick).
- Some portion of the Ta powder will assist in forming TaC.
- This will locally shift from 1:1 ratio required for the formation of TaB, and, hence, there is a shift in the composition $Ta_{1-x}B_1$, where *x* is not greater than 0.1.
- The increase in Ta content (excess in Ta for 1:1 mixture), will result in the formation of Ta_2B and TaB_2 instead of TaB.

On behalf of the authors,
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