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

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This study investigated the high-temperature strength of spark plasma sintered tantalum diboride (TaB_2) for the first time. TaB_2 exhibited a unique elastic fracture behavior below 1900°C, unlike other transition metal diborides. The consolidation process involved spark plasma sintering at 2000–2200°C yielding dense TaB_2 samples. The flexural strength was measured at elevated temperatures up to 2000°C, showing a quite high flexural strength of 400±20 MPa at 1900°C. These findings provide valuable insights into the high-temperature behavior of TaB_2, highlighting its potential for advanced applications.

1 Introduction

Tantalum diboride (TaB_2) has not been studied as extensively as other transition metal diborides that belong to the ultra-high-temperature ceramics family (UHTC), such as ZrB_2 and HfB_2. Similar to these diborides, TaB_2 has the hexagonal AlB_2 structure [1] and exhibits a relatively high elastic modulus [2,3].

Similar to other UHTC compounds, TaB_2 is a difficult material to densify. Licheri et al. [4] employed both reactive and non-reactive consolidation methods and found that the latter route resulted in a lower relative density of approximately 94%. Musa et al. reported that reactive consolidation using spark plasma sintering (SPS) at 1850°C yielded a bulk density of 96% of the theoretical density (TD). Zhang et al.

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[2] utilized reactive hot-pressing at 2000°C and 2100°C achieving densities of 97% and 98% TD, respectively. Notably, Elliot and Lavendel [3] densified TaB_2 to 94% of the TD using pressureless sintering under vacuum at 2100°C. The difficulty in densification arises from the presence of mixed ionic-covalent and ionic-metal bonds in the TaB_2 crystal, which indirectly indicates an enhanced thermal resistance in the temperature range of approximately 2000°C.

The mechanical properties of TaB_2, such as flexural strength, have been primarily reported for low temperatures. Licheri et al. [4] reported that non-reactive SPS-prepared tantalum diboride exhibited the flexural strengths of 240±94 MPa and 39±7 MPa at room temperature and 1200°C (in argon), respectively. Zhang et al. [2] reported a flexural strength of 555 MPa for TaB_2 at room temperature. Additionally, Demirskyi et al. [5] demonstrated that the room-temperature strength exhibited a quasi-linear behavior consistent with the Hall-Petch relation supporting the findings of Zhang et al. [2]. However, it should be noted that coarse-grained tantalum diboride (>20 μm) exhibited the lower strength of 300 MPa at room temperature.

Other tantalum-based UHTCs, such as TaC [6], TaN [7], or TaB [8], have exhibited diverse trends in the relationship between the flexural strength and temperature. However, a common observation is that the flexural strength up to 1600°C is expected to be comparable to that at room temperature, which contradicts the findings of Licheri et al. [4].

Based on this information, the objective of the present study was to prepare tantalum diboride specimens using non-reactive SPS with commercially-available powder. Three specimens with densities above 95% of the theoretical density (TD) and varying grain sizes were utilized. The primary focus of this investigation is to report the strength of bulk TaB_2 ceramics at elevated temperatures up to 2000°C, while employing a protective argon atmosphere.

2 Materials and Methods

The received untreated powders from Wako Pure Chemicals were used. 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 [5] and argon as the atmosphere.

The schedule for the SPS 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 2000°C, 2100°C, and 2200 °C (see **Table 1**); (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 45 MPa was maintained during the heating, consolidation and cooling stages.

After completing the SPS, the specimens were polished by diamond abrasives to 0.5 μm. For each consolidation temperature, 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 [7]. In order to comply with the requirements of ASTM C1211-02 (2008) above 1900°C, various loading rates were used.

3 Results and Discussion

Figure 1 illustrates the flexural strengths of the bulk TaB_2 and ZrB_2 as a function of the temperature and loading rate utilizing data from Neuman et al. [9]. For ZrB_2, the strength was tested in air up to 1600°C and in argon from 1500°C to 2300°C. To emphasize the impact of the loading rate on the strength, the size of the symbols in the plot corresponds proportionally to the crosshead speed employed during the flexural tests (**Table 2**).

Unlike a majority of diborides [6,9–11], the elastic curves were observed even at 1900–1950°C when using the 0.5 mm/min loading rate. Currently, there is no clear

explanation for this observation. Based on the data from this study, this feature may be associated with the consolidation temperature and/or grain size. Specimens consolidated at 2000°C (SPS ID2) displayed plastic strain-stress curves at 1900°C, whereas specimens consolidated at higher temperatures only exhibited a fairly linear strain-stress curve during testing at 2000°C (plastic end not shown). NbB_2 consolidated at 1900°C exhibited signs of plasticity at 1800°C [10], while for ZrB_2 hot-pressed at 2150°C [9], this was apparent in the 1500–1600°C range. TiB_2 also exhibited plastic fracture at 1600°C [6]. Another important factor to consider may be the melting point, as the activation of plasticity can be expected within a different temperature range between 0.5 and 0.7 of the melting temperature [12]. However, NbB_2 and TaB_2 have lower melting points compared to diborides of the IV^{th} group of transition metals [1].

Similar to the discussion on the higher brittle to plastic transition temperature in [10], it can be hypothesized that the different thermal strengths of the diborides are primarily attributable to the varying strength of the Me–B bonds. Size of the cell can be also considered TaB2 (a = 3.06 Å, c = 3.26 Å, volume 26.4 $Å^3$), ZrB_2 (a = 3.16 Å, c = 3.53 Å, volume 30.6 $Å^3$), as the Burgers vector is proportional to the cell size.

Additionally, a recent study of the flexural strength of tantalum monoboride [8] also indicated that plastic deformation only occurs above 1800°C. These findings suggest that the resistance to deformation at elevated temperatures for the tantalum borides may be superior to other diborides. Furthermore, the significant increase in flexural strength with an increase in the loading rate (**Table 2**) suggests that the fracture behavior is partially influenced by creep-like mechanisms similar to the findings of Frost and Ashby [12]. Considering that ZrB_2 in [9] showed an increasing trend at the higher loading rates, it is reasonable to conclude that this relationship should consistently be observed for other diborides.

The fracture behavior did not exhibit changes with an increase in the consolidation temperature (**Fig. 2**). At 2000°C, intergranular fracture was the dominant mechanism. The specimen consolidated at 2000°C clearly exhibited a transition period between the intermediate and final stages of sintering at which the grain growth [10] was not fully active. As the SPS temperature increased, a significant number of pores became evident at the triple points between the grains, indicating that the densification of the diboride was in the final stage of sintering. In the specimen consolidated at 2200°C (**Fig. 2 (c)**), the fracture was predominantly intergranular with only a few visible pores entrapped in the coarse grains. The grains that fractured in a transgranular manner indicated that sliding occurred through the grains. According to reports [1,13,14], the various fracture modes observed in the diborides can be attributed to the orientation of the crystal plane within the grains relative to the plane of the crack propagation, where the dominant slip system {1010} <1120> should prevail at elevated temperatures, while the secondary one is {0001} <11-20> (which is clearly seen in **Fig. 1 (a,b)**) and is consistent with previous observations for high-temperature fracture in [15].

It should be noted that a mixed fracture mode was clearly observed only in the specimen consolidated at 2200°C, which exhibited the highest strength at 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. Such a situation is not novel and has been previously observed [16]. The stability to deformation at elevated temperatures can be attributed to factors such as the presence of stresses at elevated temperature, local bonding [10], or the grain size [1]. Coarse grains may enhance the strength at elevated temperatures due to 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. Therefore, it is likely that the results reported by Licheri et al. [4] (~40 MPa at 1200°C) are primarily due to the poor density or relatively low consolidation temperature. These observations indicated that consolidation above 2000°C should be preferred along with the optimization of the grain size/density through processing.

Conclusions

Dense TaB_2 specimens with a grain size ranging from 3 to 7 μm were successfully produced by spark plasma sintering at temperatures between 2000°C and 2200°C. The three-point flexural strength was measured as a function of temperature up to 2000°C in an argon atmosphere. 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 [9] exhibited strengths of 220±18 MPa at 1800°C and 223±18 MPa at 2000°C.

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Table 1 Summary of spark plasma sintering experiments

SPS run ID	Temperature, °C	Grain size, μm av. (max.)	Porosity, %
2	2000	3±1 (7)	7.9±0.3
1	2100	5±2 (10)	5.1±0.2
3	2200	7±1 (18)	0.3±0.1

Table 2. Elevated temperature mechanical properties for TaB_2 and ZrB_2 [9] ceramics above at room temperature, and above 1800°C.

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

Figures Captions

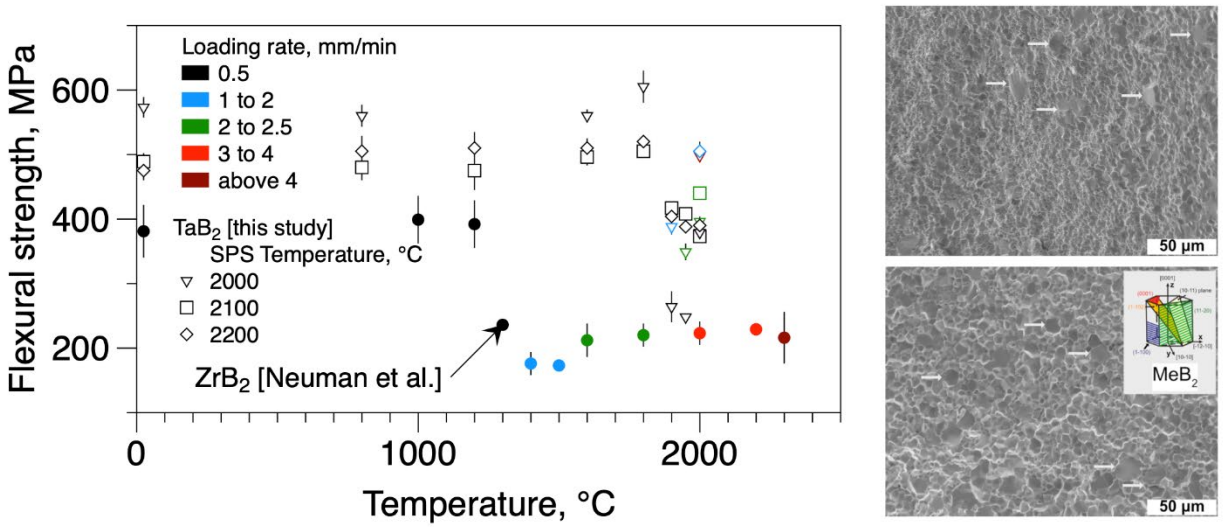

Figure 1. Temperature dependence of the flexural strength of TaB_2 and ZrB_2 [9]. The loading rate utilized during the flexural test is indicated by a specific color. (a) and (b) show fracture at 1950°C for the specimens consolidated at 2000 °C and 2200 °C, respectively. Arrows show the {0001} surface of the TaB_2 crystal.

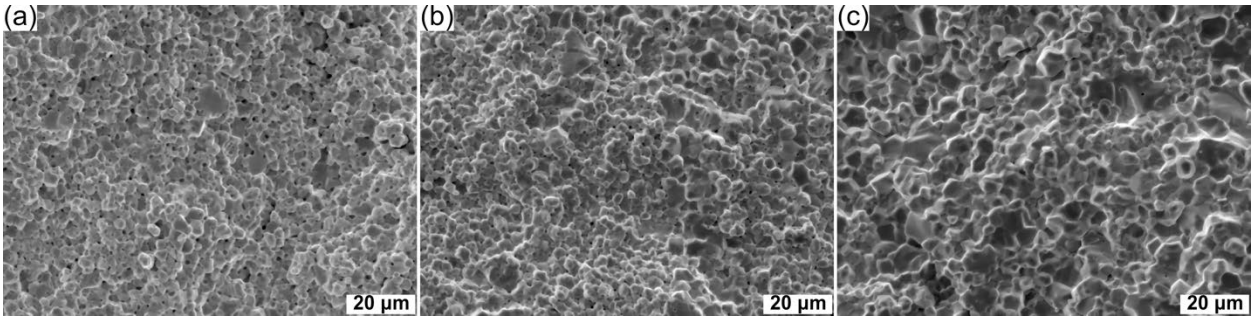

Figure 2. Effect of consolidation temperature on the fracture behavior of the tantalum diboride at 2000 °C: a) 2000 °C, b) 2100 °C, and c) 2200 °C.