Hexagonal OsB₂: Sintering, microstructure and mechanical properties

Zhilin Xie^a, Mykola Lugovy^{a,b}, Nina Orlovskaya^{a*}, Thomas Graule^c, Jakob Kuebler^c, Martin Mueller^d,
Huili Gao^e, Miladin Radovic^f and David A. Cullen^g

^aDepartment of Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA

^bInstitute for Problems of Materials Science, 3 Krzhizhanivskii Str., Kyiv 03142, Ukraine

^cEmpa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, CH-8600 Dübendorf, Switzerland

^dLaboratory of Mechanical Metallurgy, EPFL, CH-1015 Lausanne, Switzerland

^eDepartment of Mechanical Engineering, Texas A&M University, College station, TX 77843, USA

^fDepartment of Materials Science and Engineering, Texas A&M University, College station, TX 77843, USA

^gMaterials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

*** Corresponding author:** Nina Orlovskaya

E-mail: Nina.Orlovskaya@ucf.edu

Telephone: +1 407-913-4438. Fax: 407-823-0208.

Address: 4000 Central Florida Blvd., Orlando, FL 32816, USA

Abstract:

The metastable high pressure ReB₂-type hexagonal OsB₂ bulk ceramics was produced by spark plasma sintering. The phase composition, microstructure, and mechanical behavior of the sintered OsB₂ were studied by X-ray diffraction, optical microscopy, TEM, SEM, EDS, and nanoindentation. The produced ceramics was rather porous and contained a mixture of hexagonal (~80 wt%) and orthorhombic (~20 wt%) phases as identified by X-ray diffraction and EBSD analysis. Two boron-rich phases, which do not contain Os, were also identified by TEM and SEM/EDS analysis.

Nanoindentation measurements yields hardness of 31 ± 9 GPa and Young's modulus of 574 ± 112 GPa of the bulk OsB₂ indicate that the material is rather hard and very stiff; however, it is very prone to crack formation and propagation, which is indicative of a very brittle nature of this material. Improvements in the sintering regime are required in order to produce dense, homogeneous and single phase hexagonal OsB₂ bulk ceramics.

Keywords: Osmium diboride; Mechanical properties; Nanoindentation; Ceramic

1. Introduction

Modern materials science and engineering places a significant emphasis on the rational design and processing of new materials possessing superior mechanical and functional properties, and novel hard materials are one of the focal points of this development [1-9]. The synthesis and discovery of novel metastable ceramic compounds is of major importance both from a fundamental science point of view and in advancing industrial applications. Borides are an important class of the ceramic materials exhibiting many unique properties [10-22] and, therefore, much research has been performed to design and develop new boride compositions by different routes [13, 14, 23-32]. Recently, the mechanochemical synthesis of hexagonal ReB₂-type OsB₂ ceramics has been reported [33-35]. The synthesis was done utilizing high energy ball milling of elemental Os and B powder by WC balls, where the presence of severe shear stress facilitated the solid state formation of previously unknown metastable hexagonal *P63/mmc* phase of OsB₂ during mechanochemical synthesis. The obtained hexagonal OsB₂ powder with $a=2.916$ Å and $c=7.376$ Å lattice parameters was studied for high temperature stability in different environments and it was concluded that its structure is stable upon heating at 1050 °C for a significant period of time *in vacuo*. It was reported that the crystallite size of hexagonal OsB₂ increased from 5.1 nm to 19.8 nm after annealing at 1050 °C for 6 days in *vacuo* as measured by FWHM of (101) peak from X-ray diffraction pattern [33], and the crystalline grain size

increased from 4.8 nm at RT to 8.2 nm at 900°C after heating the powder in a TEM microscope column for about 1 hour. [36] It was also possible to retain the ReB₂-type hexagonal structure after densification of OsB₂ powder using spark plasma sintering (SPS). The SPS was performed at 1500 °C for 5 minutes, where a porous bulk OsB₂ ceramic was produced containing a mixture of ~80 wt% hexagonal OsB₂ (*h*-OsB₂) and ~20 wt% orthorhombic OsB₂ (*o*-OsB₂) phases. [33]

The mechanical behavior of orthorhombic OsB₂ was studied to some extent in the past. [13, 14, 37-43] In one of the first publications, the remarkably high resistance to bond shrinkage in orthorhombic OsB₂ at applied compressive stresses was reported [13]. The bulk modulus of orthorhombic OsB₂ measured using high-pressure X-ray diffraction was calculated to be in the range of 365-395 GPa depending on fitting parameters. It was also shown that the *b*-direction of the lattice is the most compressible, while the *c*-direction is the least compressible in *o*-OsB₂. It was noticed that compressibility along the *c*-axis (001) is even less than the analogous linear compressibility of diamond. Furthermore, it was suggested that *o*-OsB₂ has hardness higher than that of sapphire, as it was possible to scratch sapphire windows with the *o*-OsB₂ powder [13]. The hardness in the (001) plane of *o*-OsB₂, produced by arc-melting, was reported to be equal to 36 GPa in the 0.6-0.8 N loading range, decreasing to 30 GPa when the load increased to 1 N [37]. In another paper, the Vickers hardness of *o*-OsB₂ was also reported to be about 37 GPa with an applied load at 0.245 N [14], but decreased to less than 20 GPa when the applied load was increased to 2 N. The anisotropy in hardness value was also reported with an average hardness along <001> crystallographic direction measured to be equal to 12.5 GPa and along <100> direction measured to be equal to 23.2 GPa at 1.96 N maximum applied load. Such anisotropy in hardness was explained by highly covalent bonding with a very short bond length of 1.80 Å in the <100> direction and, in contrast, the absence of meaningful B-B bonds in the <001> direction with the closest B-B distance equal to 4.10 Å. In the same paper the average nanoindentation hardness using a Berkovich indenter was reported to be 21.6 ± 3.0 GPa at the maximum load of 490 mN. The

Young's modulus of *o*-OsB₂ was measured to be 410 ± 35 GPa by nanoindentation [14]. The ideal shear strength of OsB₂ was estimated in [38] and it was reported to be rather low (9.1 GPa). In addition to the experimental work on measuring of hardness and Young's modulus, a few papers have been published on the mechanical properties of *o*-OsB₂ estimated by first-principles calculations [39, 40, 44-47]. The hardness along the *c* axis was reported to be estimated as 45.5 GPa, along the *a* axis was reported as 25.6 GPa, and along the *b* axis was equal to 37 GPa for *o*-OsB₂ [40]. The model used in [40] was based on the bond strengths of the nearest neighboring atoms and on the projections of the direction of these bonds into the plane of indentation. The highest value of hardness along the *c*-axis was explained by high concentration of B-B bonds, which form hexagonal B rings perpendicular to the *c* axis with the large electron densities in short and highly directional strong B-B bonds. Such availability of B-B bonds results in the highest value of hardness along the *c*-axis in *o*-OsB₂ [40]. It was shown that transversely oriented bonds are the key factor determining hardness and it was also shown that no clear relationship exists between hardness and bulk modulus of a material. The estimated hardness of *o*-OsB₂ equal to 27.9 GPa was reported in [39]. In the same paper the calculations of Young's, shear and bulk moduli were reported along with hardness. For the calculations, the experimentally determined structural data were used as input parameters in the model [41, 42]. One of the structures reported in [42] was wrongfully identified as *h*-OsB₂, while most likely the phase under investigation was OsB_{1.1}; that is why no report on experimentally produced ReB₂-type OsB₂ material can be found. Thus, mechanical properties of *o*-OsB₂ have been reported in a number of publications [13, 14, 37, 39, 40, 43, 48], however the mechanical behavior of the newly synthesized *h*-OsB₂ phase is unknown. It is fair to expect that the mechanical properties, namely H and E, could be higher for *h*-OsB₂ than those of *o*-OsB₂ structure, as the density of hexagonal OsB₂ is higher, the unit cell is smaller, and, therefore, the bonds are stronger in this ceramic compound, thus giving advantage in improvement of mechanical properties of hexagonal over orthorhombic OsB₂ phase. In this paper we report the

details of the processing of bulk OsB₂, its microstructure and some of its mechanical properties, namely hardness, Young's modulus and indentation stress – indentation strain deformation behavior as measured by nanoindentation.

2. Experimental

The synthesis of hexagonal OsB₂ powder was described in a previously published paper [33]. The synthesized OsB₂ powder was sintered using fast current assisted sintering technique, commonly referred to as Spark Plasma Sintering (SPS25–10, Thermal Technologies, CA). The sintering of the powder packed in the graphite die was performed at 1500 °C, 50 MPa for 5 minutes with the heating and loading rates of 47 °C/min and 10 MPa/min, respectively. A PANalytical X'Pert Pro MPD system was used to collect XRD pattern of the bulk OsB₂ sample after Spark Plasma Sintering (SPS). The polished sample surface was examined in a Zeiss Merlin scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) detector. Electron backscatter diffraction (EBSD) analysis was performed in a JEOL JSM 6500F equipped with an EDAX EBSD system. The specimens were prepared for EBSD by mounting in epoxy and mechanically polishing the surface, with a final polish using colloidal silica. Electron transparent cross sections were prepared for transmission electron microscopy (TEM) analysis by focused ion beam (FIB) milling. Additional thinning was performed using a Fishione Nanomill. Electron diffraction patterns were acquired in an FEI Tecnai operated at 200 kV and bright-field scanning transmission electron microscopy (STEM) images were recorded in a JEOL 2200FS. Nanoindentation tests were performed using Hysitron TI950 nanoindenter equipped with a spheroconical diamond tip featuring a radius of 0.222 µm at EPFL (École Polytechnique Fédérale de Lausanne), Lausanne, Switzerland. Micrographs of the impressions were taken with the Zeiss Merlin SEM.

3. Results and discussion

3.1. SPS of OsB₂

The temperature and pressure applied during SPS of hexagonal OsB₂ powder along with the powder shrinkage measured during sintering are presented in Fig. 1. As one can see from Fig. 1, at the beginning of the heating, only a small expansion of the material was observed; this is explained by the thermal expansion of the lattice as temperature rises. The temperature was not high enough at the beginning of heating to initiate diffusion and start the densification of the powder, therefore it is not expected that a sintering process accompanied by shrinkage would occur at such low temperatures upon heating. Only expansion of the sample due to thermal expansion of the material's lattice can be detected upon heating from room temperature to around 685 °C before the pressure was applied. After a further increase of the temperature from 685 °C to 1000 °C the sintering process slowly started as a small shrinkage of the material can be seen in this temperature range. At 1000 °C pressure was applied, reaching 50 MPa maximum pressure at 1220 °C resulting in a significant densification of the whole powder (Fig. 1). Upon further temperature increase, a small shrinkage was observed in 1425-1500 °C temperature range and then slow densification continued upon isothermal dwell at 1500 °C for 5 minutes. While a non-significant amount of shrinkage occurred during the isothermal dwell, the process did not cease and therefore the material did not become fully dense. After 5 minutes dwell time, cooling of the material was initiated and, as the temperature started decreasing, further shrinkage of the bulk sample occurred mainly because of the shrinkage of the lattice upon temperature decrease. Thus, as a result of incomplete densification of *h*-OsB₂, a rather porous bulk material was produced. X-ray analysis of the bulk OsB₂ revealed that while before sintering only *h*-OsB₂ with small (5 wt%) amount of Os₂B₃ was present [33, 35, 49], after sintering no Os₂B₃ phase was identified in the material. However, a part of the hexagonal OsB₂ lattice transformed into orthorhombic structure (Fig. 2A). The bulk material after sintering consisted of 80 wt% of hexagonal (*P63/mmc*) OsB₂ and 20 wt% of orthorhombic (*Pmmn*) OsB₂ phase, as identified by Rietveld refinement of XRD pattern, and no other phase was found as all peaks were assigned to *h*-OsB₂ or *o*-OsB₂ structures. Lattice parameters of the

two phases are shown in Table 1, and Rietveld refinement files are in supplementary material. A similar phase composition in spark plasma sintered OsB₂ was identified by electron backscatter diffraction (EBSD), where 77.3 wt% of the grains were identified as belonging to the hexagonal OsB₂ structure and the remaining 22.7 wt% were identified as an orthorhombic OsB₂ (Fig. 2B). Some areas presented as a black phase on EBSD map might belong to rhombohedral B (*r*-B), however, the possible *r*-B regions did not generate enough signal to be positively indexed as elemental B. Thus, the locations are identified as either pores or *r*-B in the EBSD phase map. The EBSD map showing grains misorientation after sintering is presented in Fig. 2C. The measured density of the sintered material was equal to 9.46 g/cm³, thus the simple calculations revealed that material contained 26.9% of porosity. In the density calculations the 12.97 g/cm³ theoretical density of *h*-OsB₂ [33] and 12.83 g/cm³ theoretical density of *o*-OsB₂ [41] were used.

3.2. Microstructure of sintered OsB₂

An optical micrograph of a polished surface of OsB₂ ceramic after SPS is shown in Fig. 3A. As one can see from Fig. 3A, the OsB₂ sample has macroscopically inhomogeneous regions after sintering where areas with high level of porosity are adjusted to the areas with lower porosity. The more dense regions, with an average size of 105 μm, are typically surrounded by large pores and other highly defective areas. A STEM micrograph of OsB₂ after FIB followed by ion milling is shown in Fig. 3B, where porous regions along with ceramic grains can be seen. SEM images of the polished surface were taken both with secondary (Fig. 3C) and backscattered (Fig. 3D) electron detectors showing some non-homogeneous distribution of elements as well as presence of the porosity. The different contrast between grains in Fig. 3D taken by the back-scattered electron detector could be explained both by difference in the content of elements and also difference in crystallographic orientation of the grains. Both the STEM (Fig. 3B) and EBSD (Fig. 2B) along with SEM (Fig. 3C and D) images were used to calculate an average grain size of OsB₂ after sintering. The obtained results with a distribution of grain

sizes are presented in Fig. 4, where the average grain size of OsB₂ was calculated to be equal to $0.56 \pm 0.26 \mu\text{m}$. TEM micrographs with corresponding electron diffraction patterns as well as lattice images of typical hexagonal and orthorhombic OsB₂ grains are shown in Fig. 5. Both hexagonal and orthorhombic grains have rather sharp and well defined facets, and show clear grain boundaries. Electron diffraction shows that the grain presented in Fig. 5A has a hexagonal structure and is oriented along [110] direction as shown in Fig. 5B, and the grain presented in Fig. 5D has an orthorhombic structure with orientation of along [100] direction as presented in Fig. 5E. The corresponding lattice fringes of the two grains are presented in Fig. 5C and F along with FFT patterns of the corresponding structures. As one can see in Fig. 5A, the hexagonal grain exhibits the presence of well-defined linear defects, which could be either dislocations or even tiny micro-cracks present along the length of the grain. One of the possible reasons that such defects exist inside grains of OsB₂ is the damage caused by focused ion beam milling during sample preparation for TEM study. Regardless of the reason, the presence of such defects is indication of the brittle nature of OsB₂ since such defects might easily facilitate the brittle failure of the grain and be responsible for high overall brittleness of the OsB₂.

The distribution of elements in the OsB₂ ceramics after sintering was studied by EDS. Fig. 6 shows the overlapping EDS spectra collected from Areas 1 (within a pore) and 2 (at the surface of material surrounding a pore) where it is shown that a high B concentration within the pore with some amount of O and no Os are present in Area 1, while Os and some quantity of B along with O and W peaks can be detected from Area 2 of the polished surface. Thus, it was detected that certain B and O rich phase(s) exist inside pores. The Os, B and O maps of OsB₂ ceramic are also presented in Fig. 7. The maps show that the separation of Os and B was observed in OsB₂ ceramics, as it was found that the high concentration of B has always been detected in the grains where Os was deficient (Fig. 7 a, b and c), similar to the results presented in Fig. 6. The boron concentration within the identified locations was

much higher in comparison with the rest of the area mapped by EDS. Some oxygen was also detected within pores (Fig. 7d), but locations did not overlap regularly with Os or B signals.

STEM images of the phases located within pores of sintered OsB₂ (Fig. 8) suggested the presence of two types of phases. One phase (Fig. 8A) was identified as rhombohedral elemental B, as shown in the corresponding electron diffraction (Fig. 8B). The presence of small grains (Fig. 8D) with an average grain size of 188 nm in another examined pore (Fig. 8C) was also discovered, which based on EDS analysis, was assigned to the B₂O₃ phase. As the quantity of both *r*-B and B₂O₃ was not sufficient to be detected by X-ray analysis, XRD pattern did not show their presence, and only *h*- and *o*-OsB₂ phases were detected (Fig. 2A).

3.3 Mechanical behavior of OsB₂

3.3.1 Calculation of hardness, Young's modulus, indentation stress – indentation strain deformation behavior, elasticity and ductility indices

The nanoindentation load-displacement plots obtained by using sphericoconical indenter were used for the calculation of both hardness and Young's modulus of OsB₂ and for conversion of load-displacement into indentation stress – indentation strain plots. The Oliver and Pharr method [50] was used for the extraction of hardness and Young's modulus values. This method assumes the indenter to be an elastic isotropic solid, as well as the specimen to be isotropic. The system's reduced modulus, E_r, is defined as

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \quad (1),$$

where ν is the Poisson's ratio, E is the Young's modulus, and the subscripts s and i refer to the specimen and the indenter, respectively. The reduced modulus E_r can be estimated from the unloading part of the load-displacement curve as

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (2),$$

where S is the unloading stiffness taken as the slope of the curve at the beginning of unloading and A is the projected contact area. A is determined from the nanoindenter tip area function $A(h_c)$, where h_c is the distance from the contour of contact to the maximum penetration depth and is computed as

$$h_c = h - \frac{3}{4} \frac{P}{S} \quad (3),$$

where h and P are the maximum displacement and the maximum load measured upon a nanoindentation test [50]. In this work the area function $A(h_c)$ is represented by the following expression

$$A(h_c) = -3.14h_c^2 + 1397h_c \text{ [nm}^2\text{]} \quad (4),$$

which corresponds to the spheroconical indenter of radius 0.222 μm if penetration depth is less than 100 nm.

The hardness of the material was determined using the following standard equation:

$$H = \frac{P}{A} \quad (5)$$

where A was determined either using Eq. (4) or, in some cases, from the SEM image of the corresponding impression. From the contact area A the radius of contact for certain h and P can be calculated as

$$a = \sqrt{\frac{A}{\pi}} \quad (6).$$

Once the radius is calculated, then the following equations were used for conversion of load-displacement into indentation stress-indentation strain plots [51]

$$\sigma_{ind} = \frac{P}{\pi a^2} \quad (7)$$

and

$$\varepsilon_{ind} = \frac{4}{3\pi} \frac{h}{a} \quad (8).$$

By converting load-displacement data into indentation stress-indentation strain plots the elastic part

$$\sigma_{ind} = E_r \varepsilon_{ind} \quad (9)$$

of the loading segment of nanoindentation diagram can be revealed as well as a yield point, where the deviation from the linear behavior and the onset of plastic deformation can be visualized.

The material can be also characterized by elasticity and ductility indices. The elasticity index is defined as [52-54]

$$I_E = H/E_r \quad (10).$$

The elasticity index of the most brittle ceramics ranges from 0.3 to 0.05 and of ductile metals from 0.005 to 0.001 [52, 53]. The indentation ductility index was defined as follows [52]:

$$D = \frac{U_r}{U_t} = \frac{h_r}{h} \quad (11),$$

where U_r is the consumed energy for creating the residual impression, U_t is the total work at maximum load, h_r is the residual depth of indentation as measured from the load-displacement diagram after complete unloading. The ductility index must be 1 for a purely plastic (purely ductile) body without elastic recovery during unloading and 0 for a purely elastic body exhibiting a complete unloading recovery in an elastic manner. With the increase in the elasticity index, the ductility index decreases from 1 to 0. [52]

3.3.2 Hardness, Young's modulus, indentation stress – indentation strain behavior, elasticity and ductility indices of OsB₂

A total of 25 direct hardness measurements of the OsB₂ after SPS were obtained using equation (5). The 25 nanoindentations were performed using the spheroconical diamond indenter to peak load of 8 mN in load control mode, and then the projected area of the residual impressions was measured from SEM micrographs. The average hardness value obtained by these direct measurements was 34 ± 3 GPa. A typical representative impression is shown in Fig. 9A. It is visible from the image that, while the hardness of the material is rather high in this location, radial cracks were produced even at such low load as 8mN. The formation and propagation of the radial cracks during the indentation is an indication of the brittleness of the OsB₂ ceramics. While most of the impressions produced during the indentation

using the spheroconical indenter at 8 mN maximum load looked like the one presented in Fig. 9A, one of the 25 impressions had a very different pattern with a number of layers squeezed out of the material during indentation (Fig. 9B). The diameter of the impression was much bigger in comparison to the average value of other impressions, giving a hardness value of only 22.8 GPa. It is possible that, since material is not homogenous and some phases are not OsB₂ and are non-detectable by XRD, this particular indentation was made into a grain consisting of B or B₂O₃ phases, thus showing lower value of hardness.

In another set of experiments, 50 nanoindentations of OsB₂ was performed using spheroconical diamond tip in displacement control mode with a maximum depth of penetration of 70 nm. The load displacement data were used for the calculation of hardness and Young's modulus, as well as for the conversion of load – displacement plots into indentation stress - indentation strain plots. For the calculation of Young's modulus by Oliver and Pharr's technique [50], the value of Poisson's ratio of the material is required. The value of 0.18 was taken for the calculations, as no measured values of Poisson's ratio have been reported in the literature for hexagonal OsB₂. In one of the publications 0.27 was provided as a calculated Poisson's ratio value for the orthorhombic OsB₂ phase; [39] however, such relatively high value is more characteristic of softer ceramics [55], while stiff ceramics, such as B₄C, TiB₂ and ZrB₂ are all reported to be in the range 0.14 - 0.18 [56-58]. The difference in estimated Young's modulus values is not significant, as when Poisson's ratio is 0.18 ± 0.018 , relative error for Young modulus is only 0.7 %.

By analyzing the load-displacement plots, it was found that the majority of the indents (36 out of 50) featured “pop-in” events at the loading portion of the plots. An example of such a diagram and its conversion to the indentation stress – indentation strain plot is shown in Fig. 10. All of these indents exhibited high hardness and Young's modulus, and the average hardness calculated from such diagrams is 31 ± 9 GPa and average Young's modulus was calculated to equal 574 ± 112 GPa. Upon

conversion of the load – displacement diagram (Fig. 10A) into indentation stress – strain diagram (Fig. 10B), one can see that a very high stress level exists below the spheroconical diamond indenter during indentation. In addition to the possibility of estimation of level of stress and strain during nanoindentation, another advantage of the conversion of load – displacement into stress – strain data is a possibility to estimate a “yield” stress of the material, as it is typical that at the beginning of loading the indentation stress is directly proportional to the indentation strain and it is only after achieving a certain “yield” stress that the deviation from linear deformation starts taking place. An example of the “yield” stress σ_y estimation is presented in Fig. 10B. The σ_y calculated using all 36 indentation plots provided the 23 ± 7 GPa average value. Thus, the nanoindentation experiments indicated that both hexagonal and orthorhombic OsB₂ phases are relatively hard and rather stiff with a high yield stress values, as determined by hardness, Young’s modulus, “yield” stress and indentation stress – indentation strain deformation behavior. As it was measured that the average grain size of OsB₂ ceramics after SPS was equal to 0.56 ± 0.26 μm , it is most likely that the measured values of hardness and Young’s modulus were obtained from indentations in single grains with their unique crystallographic orientations. However, since as many as 36 grains were indented, the average values of E and H can provide reliable data on the average properties of hard phase in OsB₂ ceramics. While the measured E and H values could be obtained from grains belonging both to hexagonal and to orthorhombic OsB₂ phases, as it was not possible to discriminate the phases in the measurements, the objective lenses of the microscope allowed avoiding of performing nanoindentation in the pores and other defective areas visible optically.

In addition to the 36 load – displacement diagrams where pop-in events were present, a different type of indentation behavior was found, in which no pop-in events occurred upon loading. An example of this is shown in Fig. 11. The hardness and Young’s modulus calculated from these 14 indents were significantly lower in comparison with the 36 indents for which pop-in events took place. The average

hardness and Young's modulus values were equal to 16 ± 3 GPa and 368 ± 91 GPa, respectively. The estimated average “yield” stress of such indents was 17 ± 7 GPa and the maximum indentation stress was calculated to be ~ 30 GPa, which is considerably lower than the ~ 50 GPa that were reached when indenting the more hard OsB₂ phases present in the material. The scanning probe micrograph (SPM) images of the OsB₂ surfaces before and after indentation where the spherical impression was visible are presented in Fig. 12. Both types of the impressions are presented indicating the existence of hard and softer phases, but in both cases the cracks formed during loading are visible, indicating a brittle nature of the ceramic. These findings indicate that a mixture of hard and relatively soft phases exist in the OsB₂ sample indicating an inhomogeneous nature of the material after densification by SPS. The soft phases with lower values of hardness and Young's modulus may be obtained from the areas where B, B₂O₃ and BO are coexisted.

The elasticity and ductility indices of OsB₂ ceramics were also calculated using the nanoindentation results of 36 indents with high hardness and Young's modulus values according to the Equations (10) and (11). The computed elasticity index was equal to 0.05 and the ductility index was equal to 0.45. For comparison, the elasticity and ductility indices of copper (Cu) are equal to 0.02 and 0.95, respectively [52], while the elasticity indices of Al₂O₃, SiC and Si₃N₄ ceramics are equal to 0.08, 0.13 and 0.175, respectively and their ductility indices are equal to 0.68, 0.57 and 0.59, respectively [52]. The elasticity and ductility indices of glass are equal to 0.19 and 0.54, respectively [52]. Thus, the elasticity index of OsB₂ ceramics is in the lower range of traditional Al₂O₃, SiC, Si₃N₄, and glass materials, while the ductility index is much lower in comparison even with a glass, such low values of both indices give an indication of the highly brittle nature of OsB₂ ceramics.

4. Conclusion

ReB₂-type OsB₂ powder synthesized by mechanochemistry was densified by spark plasma sintering for the first time. The obtained bulk material contained a significant amount of porosity. It was also

discovered that during direct current sintering, a transformation from hexagonal ($P63/mmc$) to orthorhombic ($Pmmn$) structure partially occurred. Indeed, the ceramics after sintering contained 26.9% of porosity and a mixture of ~80 wt% hexagonal and ~20 wt% of orthorhombic phases according both to XRD and EBSD analysis.

The average grain size of the OsB_2 ceramics after sintering was $0.56 \pm 0.26 \mu\text{m}$. Both EBSD phase map and TEM analysis were used to identify both hexagonal and orthorhombic grains. It was discovered that at certain grains or pores a much higher concentration of B exists. The EDS maps showed separate areas on the maps that were enriched in B content, while Os was practically absent in those locations. Moreover, there were other areas which showed Os deficiency, but were enriched in oxygen. We believe that such boron-enriched areas might contain rhombohedral B, while those areas enriched in O might be residues of B_2O_3 , BO or B_6O phases. [59]

An attempt was made to probe the mechanical behavior of the SPSed OsB_2 ceramics using nanoindentation. As the sintered ceramic was not homogeneous two types of the indentation behavior was discovered. In the first type of the material's response the hardness as measured by sphericoconical nanoindentation and post-test measurement of the impression with SEM led to values of $34 \pm 3 \text{ GPa}$. Moreover, from nanoindentation diagrams it was found that the average hardness and Young's modulus of the hard OsB_2 phases are $31 \pm 9 \text{ GPa}$ and $574 \pm 112 \text{ GPa}$, respectively, while the highest value of hardness and Young's modulus measured reached 45 GPa and 773 GPa, respectively. The significant deviation (20%) from the average measured values can be explained by the fact that indentations were mostly made in individual grains, each having its own crystallographic orientation. However, because a significant number of indentations have been made in different grains, the average measured value might lie rather close to the real values of hardness and Young's modulus of the OsB_2 ceramic. As the material was inherently nonhomogeneous, the lower values of hardness and Young's modulus were obtained from the areas where different phases such as B, B_2O_3 or BO were located. The

reported values of hardness and Young's modulus of this second type indentation response was equal to 16 ± 3 GPa and 368 ± 91 GPa, respectively.

The produced bulk OsB₂ ceramics was not dense and homogeneous and its mechanical properties varied significantly depending on the location of the indentation. On the other hand, we have shown that it is possible to retain metastable high pressure ReB₂-type hexagonal OsB₂ during sintering and the potential for the structure to exhibit superior hardness and stiffness is rather high. More studies are needed to find and optimize the sintering regime to produce dense and homogeneous hexagonal OsB₂, which would exhibit superior hardness and stiffness.

Acknowledgment

This work was supported by NSF project DMR – 0748364. The bulk of electron microscopy work was performed as part of a user project supported by ORNL's Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility. M.M.'s and N.O.'s work at EPFL, which included nanoindentation experiments, was supported by the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Advanced Grant Agreement No. 291085 and N.O.'s work at Empa was supported by the Swiss National Science Foundation, International Short Visit, IZK0Z2_154379. The authors would also like to thank Prof. A. Mortensen, EPFL for his valuable suggestions and revisions of the manuscript.

References

- [1] J. Haines, J.M. Leger, G. Bocquillon, Synthesis and design of superhard materials, *Ann. Rev. Mater. Res.*, 31 (2001) 1-23.
- [2] S. Veprek, M.J.G. Veprek-Heijman, Industrial applications of superhard nanocomposite coatings, *Surface and Coatings Technology*, 202 (2008) 5063-5073.
- [3] V.L. Solozhenko, E. Gregoryanz, Synthesis of superhard materials, *Materials Today*, 8 (2005) 44-51.
- [4] R. Riedel, Novel Ultrahard Materials, *Advanced Materials*, 6 (1994) 549-560.
- [5] S. Veprek, A.S. Argon, Towards the understanding of mechanical properties of super- and ultrahard nanocomposites, *Journal of Vacuum Science & Technology B*, 20 (2002) 650-664.
- [6] V.V. Brazhkin, High-pressure synthesized materials: treasures and hints, *High Pressure Research*, 27 (2007) 333-351.
- [7] J. Haines, J.M. Léger, A. Atouf, Crystal Structure and Equation of State of Cotunnite-Type Zirconia, *Journal of the American Ceramic Society*, 78 (1995) 445-448.
- [8] N. Orlovskaya, R. Stadelmann, M. Lugovy, V. Subbotin, G. Subhash, M. Neubert, C.G. Aneziris, T. Graule, J. Kuebler, Mechanical properties of ZrB_2 -SiC ceramic composites: room temperature instantaneous behaviour, *Advances in Applied Ceramics*, 112 (2013) 9-16.
- [9] J.K. Sonber, A.K. Suri, Synthesis and consolidation of zirconium diboride: review, *Advances in Applied Ceramics*, 110 (2011) 321-334.
- [10] F. Thévenot, Boron carbide—A comprehensive review, *Journal of the European Ceramic Society*, 6 (1990) 205-225.
- [11] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykoski, Refractory Diborides of Zirconium and Hafnium, *Journal of the American Ceramic Society*, 90 (2007) 1347-1364.
- [12] H.-Y. Chung, M.B. Weinberger, J.B. Levine, A. Kavner, J.-M. Yang, S.H. Tolbert, R.B. Kaner, Synthesis of Ultra-Incompressible Superhard Rhenium Diboride at Ambient Pressure, *Science*, 316 (2007) 436-439.
- [13] R.W. Cumberland, M.B. Weinberger, J.J. Gilman, S.M. Clark, S.H. Tolbert, R.B. Kaner, Osmium Diboride, An Ultra-Incompressible, Hard Material, *Journal of the American Chemical Society*, 127 (2005) 7264-7265.
- [14] H.-Y. Chung, J.M. Yang, S.H. Tolbert, R.B. Kaner, Anisotropic mechanical properties of ultra-incompressible, hard osmium diboride, *Journal of Materials Research*, 23 (2008) 1797-1801.
- [15] D.D. Jayaseelan, Y. Wang, G.E. Hilmas, W. Fahrenholtz, P. Brown, W.E. Lee, TEM investigation of hot pressed -10 vol.% SiC- ZrB_2 composite, *Advances in Applied Ceramics*, 110 (2011) 1-7.

- [16] A.K. Khanra, M.M. Godkhindi, Effect of Ni additives on pressureless sintering of SHS ZrB_2 , *Advances in Applied Ceramics*, 104 (2005) 273-276.
- [17] E. Padovano, C. Badini, S. Biamino, M. Pavese, W.S. Yang, P. Fino, Pressureless sintering of ZrB_2 -SiC composite laminates using boron and carbon as sintering aids, *Advances in Applied Ceramics*, 112 (2013) 478-486.
- [18] H. Wu, C. Xie, W. Zhang, J. Zhang, Fabrication and properties of 2D C/C- ZrB_2 - ZrC -SiC composites by hybrid precursor infiltration and pyrolysis, *Advances in Applied Ceramics*, 112 (2013) 366-373.
- [19] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Superconductivity at 39 K in magnesium diboride, *Nature*, 410 (2001) 63-64.
- [20] T. Mori, T. Nishimura, Thermoelectric properties of homologous p- and n-type boron-rich borides, *Journal of Solid State Chemistry*, 179 (2006) 2908-2915.
- [21] S. Maruyama, Y. Miyazaki, K. Hayashi, T. Kajitani, T. Mori, Excellent p-n control in a high temperature thermoelectric boride, *Applied Physics Letters*, 101 (2012) -.
- [22] D. Gignoux, D. Schmitt, Chapter 2 Magnetism of compounds of rare earths with non-magnetic metals, in: K.H.J. Buschow (Ed.) *Handbook of Magnetic Materials*, Elsevier, 1997, pp. 239-413.
- [23] A.M. Locci, R. Licheri, R. Orrù, G. Cao, Reactive Spark Plasma Sintering of rhenium diboride, *Ceramics International*, 35 (2009) 397-400.
- [24] A. Latini, J.V. Rau, D. Ferro, R. Teghil, V.R. Albertini, S.M. Barinov, Superhard Rhenium Diboride Films: Preparation and Characterization, *Chemistry of Materials*, 20 (2008) 4507-4511.
- [25] A.B. Lyashchenko, V.N. Paderno, V.B. Filippov, D.F. Borshchevskii, Growth and some properties of rhenium diboride single crystals, *Sverkhtverd. Mater.*, 79 (2006).
- [26] S. Otani, T. Aizawa, Y. Ishizawa, Preparation of ReB_2 single crystals by the floating zone method, *Journal of Alloys and Compounds*, 252 (1997) L19-L21.
- [27] A. Latini, J.V. Rau, R. Teghil, A. Generosi, V.R. Albertini, Superhard Properties of Rhodium and Iridium Boride Films, *ACS applied materials & interfaces*, 2 (2010) 581-587.
- [28] J.V. Rau, A. Latini, New Hard and Superhard Materials: $\text{RhB}_{1.1}$ and $\text{IrB}_{1.35}$, *Chemistry of Materials*, 21 (2009) 1407-1409.
- [29] R.S. Dobedoe, G.D. West, M.H. Lewis, Spark plasma sintering of ceramics: understanding temperature distribution enables more realistic comparison with conventional processing, *Advances in Applied Ceramics*, 104 (2005) 110-116.
- [30] M. Jalaly, M. Sh. Bafghi, M. Tamizifar, F.J. Gotor, Mechano-synthesis of nanocrystalline ZrB_2 -based powders by mechanically induced self-sustaining reaction method, *Advances in Applied Ceramics*, 112 (2013) 383-388.

- [31] A.K. Khanra, L.C. Pathak, M.M. Godkhindi, Carbothermal synthesis of zirconium diboride (ZrB_2) whiskers, *Advances in Applied Ceramics*, 106 (2007) 155-160.
- [32] A.K. Khanra, L.C. Pathak, S.K. Mishra, M.M. Godkhindi, Sintering of ultrafine zirconium diboride powder prepared by modified SHS technique, *Advances in Applied Ceramics*, 104 (2005) 282-284.
- [33] Z. Xie, M. Graule, N. Orlovskaya, E. Andrew Payzant, D.A. Cullen, R.G. Blair, Novel high pressure hexagonal OsB_2 by mechanochemistry, *Journal of Solid State Chemistry*, 215 (2014) 16-21.
- [34] N. Orlovskaya, Z. Xie, R. Blair, Mechanochemical Synthesis of Hexagonal OsB_2 , U.S. Patent, 14/157,216 (2014).
- [35] Z. Xie, R.G. Blair, N. Orlovskaya, D.A. Cullen, E. Andrew Payzant, Thermal stability of hexagonal OsB_2 , *Journal of Solid State Chemistry*, 219 (2014) 210-219.
- [36] Z. Xie, R. Blair, N. Orlovskaya, D.A. Cullen, Characterization of hexagonal OsB_2 , in preparation for submission.
- [37] M. Hebbache, L. Stuparević, D. Živković, A new superhard material: Osmium diboride OsB_2 , *Solid State Communications*, 139 (2006) 227-231.
- [38] J. Yang, H. Sun, C. Chen, Is Osmium Diboride An Ultra-Hard Material?, *Journal of the American Chemical Society*, 130 (2008) 7200-7201.
- [39] H. Gou, L. Hou, J. Zhang, H. Li, G. Sun, F. Gao, First-principles study of low compressibility osmium borides, *Applied Physics Letters*, 88 (2006) -.
- [40] A. Šimůnek, Anisotropy of hardness from first principles: The cases of ReB_2 and OsB_2 , *Physical Review B*, 80 (2009) 060103.
- [41] R.B. Roof, C.P. Kempter, New Orthorhombic Phase in the Ru–B and Os–B Systems, *The Journal of Chemical Physics*, 37 (1962) 1473-1476.
- [42] C.P. Kempter, R.J. Fries, Crystallography of the Ru–B and Os–B Systems, *The Journal of Chemical Physics*, 34 (1961) 1994-1995.
- [43] Q. Gu, G. Krauss, W. Steurer, Transition Metal Borides: Superhard versus Ultra-incompressible, *Advanced Materials*, 20 (2008) 3620-3626.
- [44] X.-Q. Chen, C.L. Fu, M. Krčmar, G.S. Painter, Electronic and Structural Origin of Ultraincompressibility of 5d Transition-Metal Diborides MB_2 ($\text{M}=\text{W}$, Re , Os), *Physical Review Letters*, 100 (2008) 196403.
- [45] S. Chiodo, H.J. Gotsis, N. Russo, E. Sicilia, OsB_2 and RuB_2 , ultra-incompressible, hard materials: First-principles electronic structure calculations, *Chemical Physics Letters*, 425 (2006) 311-314.
- [46] Z.-W. Ji, C.-H. Hu, D.-H. Wang, Y. Zhong, J. Yang, W.-Q. Zhang, H.-Y. Zhou, Mechanical properties and chemical bonding of the Os–B system: A first-principles study, *Acta Materialia*, 60 (2012) 4208-4217.

- [47] M. Zhang, M. Wang, T. Cui, Y. Ma, Y. Niu, G. Zou, Electronic structure, phase stability, and hardness of the osmium borides, carbides, nitrides, and oxides: First-principles calculations, *Journal of Physics and Chemistry of Solids*, 69 (2008) 2096-2102.
- [48] F.M. Gao, L.H. Gao, Microscopic models of hardness, *Journal of Superhard Materials*, 32 (2010) 148-166.
- [49] M. Frotscher, A. Senyshyn, B. Albert, Neutron Diffraction at Metal Borides, Ru_2B_3 and Os_2B_3 , *Zeitschrift für anorganische und allgemeine Chemie*, 638 (2012) 2078-2080.
- [50] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *Journal of Materials Research*, 7 (1992) 1564-1583.
- [51] S. Pathak, S.R. Kalidindi, C. Klemen, N. Orlovskaya, Analyzing indentation stress-strain response of LaGaO_3 single crystals using spherical indenters, *Journal of the European Ceramic Society*, 28 (2008) 2213-2220.
- [52] M. Sakai, The Meyer hardness: A measure for plasticity?, *Journal of Materials Research*, 14 (1999) 3630-3639.
- [53] J. Malzbender, Comment on hardness definitions, *Journal of the European Ceramic Society*, 23 (2003) 1355-1359.
- [54] J. Chen, S.J. Bull, A critical examination of the relationship between plastic deformation zone size and Young's modulus to hardness ratio in indentation testing, *J. Mater. Res.*, 21 (2006) 2617-2627.
- [55] M. Lugovy, A. Aman, Y. Chen, N. Orlovskaya, J. Kuebler, T. Graule, M.J. Reece, D. Ma, A.D. Stoica, K. An, In-situ neutron diffraction of LaCoO_3 perovskite under uniaxial compression. II. Elastic properties, *Journal of Applied Physics*, 116 (2014) -.
- [56] N. Orlovskaya, M. Lugovy, V. Subbotin, O. Radchenko, J. Adams, M. Chheda, J. Shih, J. Sankar, S. Yarmolenko, Robust design and manufacturing of ceramic laminates with controlled thermal residual stresses for enhanced toughness, *J Mater Sci*, 40 (2005) 5483-5490.
- [57] M. Lugovy, V. Slyunyayev, V. Subbotin, F. Liang, J. Gou, N. Orlovskaya, T. Graule, J. Kuebler, Mechanical behavior and failure mechanisms of boron carbide based three-layered laminates with weak interfaces, *Ceramics International*, 37 (2011) 2255-2261.
- [58] H. Wang, F. Xue, N.H. Zhao, D.J. Li, First-Principles Calculation of Elastic Properties of TiB_2 and ZrB_2 , *Advanced Materials Research*, 150 (2011) 40-43.
- [59] X. Jiao, H. Jin, F. Liu, Z. Ding, B. Yang, F. Lu, X. Zhao, X. Liu, Synthesis of boron suboxide (B_6O) with ball milled boron oxide (B_2O_3) under lower pressure and temperature, *Journal of Solid State Chemistry*, 183 (2010) 1697-1703.

Table 1. Lattice parameters of the h -OsB₂ and o -OsB₂ in the sample after spark plasma sintering.

Composition	Structure	Space Group	Lattice Parameters, Å			Weight Fraction
			a	b	c	
h -OsB ₂	Hexagonal	$P63/mmc$ (#194)	2.916	2.916	7.376	~80%
o -OsB ₂	Orthorhombic	$Pmmn$ (#59)	2.883	4.679	4.076	~20%

Fig. 1: A sintering regime used for densification of hexagonal OsB_2 powder. Both temperature, pressure, and shrinkage data were collected during spark plasma sintering as a function of time.

Fig. 2: X-ray diffraction pattern of sintered OsB_2 ceramics (A), along with a phase composition map (B) and corresponding EBSD map (C) where the phase (A and B) as well as crystallographic orientation of each individual OsB_2 grain could be identified (C).

Fig. 3: Microstructure of OsB₂ after SPS (A). The optical micrograph shows a nonhomogeneous densification where large more dense areas are surrounded by less dense areas with a number of surrounding pores. (B) TEM micrograph of OsB₂ where the grains are clearly visible but also a high numbers of pores are present. (C) SEM micrograph of OsB₂ polished surface taken using an InLens detector and (D) the SEM micrograph of the same OsB₂ surface as in (C) but produced using backscattered ESB detector.

Fig. 4: Grain size distribution of OsB₂ ceramics after SPS calculated from the results presented in Fig. 2C, Fig. 3B and D. The average grain size is equal to $0.56 \pm 0.26 \mu\text{m}$; thus the produced OsB₂ is a submicron ceramics.

Fig. 5: TEM micrographs of hexagonal (A) and orthorhombic (D) OsB_2 grains with the corresponding electron diffraction patterns (B and E, respectively), along with their high resolution images and the corresponding FFT patterns (C and F).

Fig. 6: SEM micrograph of the polished OsB₂ ceramics with corresponding EDS spectra collected at two different areas on the surface. Area 1 is a pore, which is enriched in B and deficient of Os, while Area 2 at the surface of OsB₂ ceramics surrounding the pore shows both Os and B.

Fig. 7: SEM micrograph of the polished surface of OsB₂ ceramics after sintering with corresponding distribution of Os (B), B (C), and O (D).

Fig. 8: TEM image of the material present within a pore in OsB_2 sample after sintering (A); the corresponding electron diffraction pattern of the area highlighted with a dashed circle (B); TEM micrograph of the material located in a different pore (C); along with higher resolution image of the selected location with a pore highlighted with a dashed rectangle (D).

Fig. 9: SEM micrograph of the two impressions produced by nanoindentation of a polished OsB_2 surface with a spheroconical indenter with a load of 8 mN.

Fig. 10: Load–displacement (A) and recalculated indentation stress – indentation strain (B) diagrams produced by nanoindentation of polished OsB_2 surface where “pop-in” events were present during the loading portion of the load-displacement curve.

Fig. 11: Load – displacement (A) and recalculated indentation stress – indentation strain (B) diagrams produced by nanoindentation of polished OsB_2 surface where no pop-in event was present during loading or unloading portions of the load-displacement curve.

Fig. 12: The scanning probe micrographs of the OsB_2 surfaces before (A, D) and after (B, C, E and F) indentation.

Figure Captions

Fig. 1: A sintering regime used for densification of hexagonal OsB₂ powder. Both temperature, pressure, and shrinkage data were collected during spark plasma sintering as a function of time.

Fig. 2: X-ray diffraction pattern of sintered OsB₂ ceramics (A), along with a phase composition map (B) and corresponding EBSD map (C) where the phase (A and B) as well as crystallographic orientation of each individual OsB₂ grain could be identified (C).

Fig. 3: Microstructure of OsB₂ after SPS (A). The optical micrograph shows a nonhomogeneous densification where large more dense areas are surrounded by less dense areas with a number of surrounding pores. (B) TEM micrograph of OsB₂ where the grains are clearly visible but also a high numbers of pores are present. (C) SEM micrograph of OsB₂ polished surface taken using an InLens detector and (D) the SEM micrograph of the same OsB₂ surface as in (C) but produced using backscattered ESB detector.

Fig. 4: Grain size distribution of OsB₂ ceramics after SPS calculated from the results presented in Fig. 2C, Fig. 3B and D. The average grain size is equal to $0.56 \pm 0.26 \mu\text{m}$; thus the produced OsB₂ is a submicron ceramics.

Fig. 5: TEM micrographs of hexagonal (A) and orthorhombic (D) OsB₂ grains with the corresponding electron diffraction patterns (B and E, respectively), along with their high resolution images and the corresponding FFT patterns (C and F).

Fig. 6: SEM micrograph of the polished OsB₂ ceramics with corresponding EDS spectra collected at two different areas on the surface. Area 1 is a pore, which is enriched in B and deficient of Os, while Area 2 at the surface of OsB₂ ceramics surrounding the pore shows both Os and B.

Fig. 7: SEM micrograph of the polished surface of OsB₂ ceramics after sintering with corresponding distribution of Os (B), B (C), and O (D).

Fig. 8: TEM image of the material present within a pore in OsB₂ sample after sintering (A); the corresponding electron diffraction pattern of the area highlighted with a dashed circle (B); TEM micrograph of the material located in a different pore (C); along with higher resolution image of the selected location with a pore highlighted with a dashed rectangle (D).

Fig. 9: SEM micrograph of the two impressions produced by nanoindentation of a polished OsB₂ surface with a spheroconical indenter with a load of 8 mN.

Fig. 10: Load–displacement (A) and recalculated indentation stress – indentation strain (B) diagrams produced by nanoindentation of polished OsB₂ surface where “pop-in” events were present during the loading portion of the load-displacement curve.

Fig. 11: Load – displacement (A) and recalculated indentation stress – indentation strain (B) diagrams produced by nanoindentation of polished OsB₂ surface where no pop-in event was present during loading or unloading portions of the load-displacement curve.

Fig. 12: The scanning probe micrographs of the OsB₂ surfaces before (A, D) and after (B, C, E and F) indentation.