Strength of tungsten triboride under pressure up to 86 GPa from radial X-ray diffraction

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1. Introduction

Many experimental and theoretical studies on boron-tungsten system (WB 4) have suggested that tungsten tetraboride (WB 4) is potentially a superhard material [1,2]. Gu et al. [1] synthesized the compounds formed by transition metals (TMs) and B, and measured their Vickers hardness (HV) by microindentation tests. The obtained hardness values of WB 4 are 46.2(1.2) GPa and 31.8(1.2) GPa under applied loads of 0.49 N and 4.9 N, respectively. Subsequently, Wang et al. [2] calculated the hardness values of WB 4 to be 41.1–42.2 GPa, consistent with Gu et al. [1], and they [2] pointed out that WB 4 has an ultra-low compressibility with the bulk modulus between 292.7–324.3 GPa. The early works suggested that WB 4 is a potential superhard material and has an ultra-low compressibility. Successively, Mohammadi et al. [3] also measured the hardness by microindentation method as 43.3(2.9) GPa and 28.1(1.4) GPa under an applied load of 0.49 N and 4.9 N, respectively, and reported a bulk modulus K 0 = 339(3) GPa at ambient conditions, for WB 4 from high-pressure X-ray diffraction (XRD) up to 30 GPa in a DAC with neon as the pressure medium. Liu et al. [4] performed the high-pressure XRD of WB 4 up to 51 GPa with silicone oil as the pressure medium and obtained K 0 = 325(9) GPa with K' 0 = 5.1(0.6). Both K 0 and K' 0 are defined in the Birch-Monaghan equation of state (EoS). Xie et al. [5] measured the compression behavior of WB 4 with neon as the pressure medium up to 59 GPa and obtained K 0 = 369(9) GPa with K' 0 = 1.2(0.5) by fitting the data at pressures lower than 42 GPa. Xiong et al. [6] reported a bulk modulus K 0 = 319(5) GPa with K' 0 = 4.1(0.2) at ψ = 54.7° by fitting the radial X-ray diffraction (RXD) nonhydrostatic compression data up to 86 GPa.

However, subsequent theoretical studies indicated that the structure of WB 4 is unstable and the previously believed WB 4 is in fact WB 3 [7,8]. Liang et al. [7] evaluated the structure stability of WB 3 from first principles, and questioned the stability of WB 4 for the first time. They reported that long-believed WB 4 is actually WB 3 because their Gibbs energy shows that the WB 3 is thermodynamically stable and WB 4 is not. Subsequently, Liang et al. [9] reported that WB 3 is superhard due to its three-dimensional covalent network consisting of boron honeycomb planes interconnected with strong zigzag W-B bonds. Liang et al. [9] calculated the Vickers hardness of WB 3 (16.8 GPa) and WB 3 (43.1 GPa) using the linear correlation existing between the Vickers hardness and shear modulus for many of the known hard materials and superhard materials. They obtained the Vickers hardness of WB 3 (16.8 GPa, 6.8 GPa) is ~39% of WB 3 (43.1 GPa, 39.4 GPa). Zhang et al. [8]...
compared experimental and theoretically calculated XRD patterns between \( \text{WB}_4 \) and \( \text{WB}_3 \), along with the thermodynamic, mechanical, and phonon instabilities of \( \text{WB}_4 \) using density functional theory. They found that \( \text{WB}_4 \) with a three-dimensional boron network is identified as \( \text{WB}_3 \) with two-dimensional boron nets. In addition, they suggested that \( \text{WB}_3 \) may not be an intrinsically superhard material due to its much lower ideal shear strengths compared with the superhard material of c-BN. Zang et al. [10] calculated the stress–strain relation and the ideal strength of \( \text{WB}_3 \) using the first-principles, leading the authors to conclude that the Vickers hardness of \( \text{WB}_3 \) is a superhard material. Previous studies have shown that \( \text{WB}_3 \) cannot be a superhard material under debate. Despite several theoretical calculations for \( \text{WB}_3 \), there are no direct experimental measurements. There are different opinions regarding whether \( \text{WB}_3 \) is a superhard material. Previous studies have shown that the hardness of materials has some relationship with strength which reflects the contributions of both plastic and elastic deformation. In this study, we have investigated the strength of \( \text{WB}_3 \) to 86 GPa under nonhydrostatic compression using radial X-ray diffraction (RXD) in diamond-anvil cell.

2. Experimental details

The \( \text{WB}_3 \) powder was synthesized in a DS6 * 8MN cubic press [14] at high-pressure and temperature conditions. The synthesized \( \text{WB}_3 \) sample possesses an average grain size of 0.5–1 \( \mu \text{m} \) determined via scanning electron microscopy (SEM). Fig. 1 displays the XRD pattern of the synthesized \( \text{WB}_3 \) and simulated patterns for \( \text{WB}_4 \) and \( \text{WB}_5 \) reported by Zhang et al. [8]. It can be seen that the XRD pattern of synthesized sample matches much better with that of the simulated \( \text{WB}_4 \) from Zhang et al. [8]. The measured XRD pattern shows the highly crystalline and pure phase. At ambient conditions, the synthesized \( \text{WB}_3 \) has a hexagonal structure (space group \( P6_3/mmc \), see Fig. 2) with lattice parameters \( a = 5.199(0.001) \text{Å} \) and \( c = 6.347(0.001) \text{Å} \).

A twofold panoramic DAC with a pair of beveled diamond anvils (150 \( \mu \text{m} \) culet diameter) was used to exert uniaxial compression on both the \( \text{WB}_3 \) sample and Mo standard in the RXD measurements. A beryllium gasket was pre-indented to \( \approx 25-\mu \text{m} \) thickness at \( \approx 20-\text{GPa} \) and a hole of 50-\( \mu \text{m} \)-diameter was drilled in the center of the preindented area for use as a sample chamber. Special attention was paid to make sure that the sample hole was well centered with respect to the anvil culet. The \( \text{WB}_3 \) sample was loaded into the gasket hole and a piece of Mo flake with a diameter of \( \approx 20-\mu \text{m} \) was placed on top within 5 \( \mu \text{m} \) of the sample center serving as a pressure standard [15] as well as the positioning reference for X-ray diffraction. No pressure-transmitting medium was used to ensure maximum nonhydrostatic stresses. By design, the DAC was tilted at an angle of 28° to minimize the contributions of \( \text{Be} \) diffraction to the sample patterns [16]. Angle-dispersive radial X-ray diffraction experiments were performed at the 4W2 beam line of Beijing Synchrotron Radiation Facility (BSRF), Chinese Academy of Sciences. A Si(1 1 1) monochromator was used to tune the synchrotron source to a wavelength of 0.6199 Å, and the incident monochromatic X-ray beam was focused by a pair of Kirkpatrick-Baez mirrors to an approximately 20-\( \mu \text{m} \)-spot of full width at half maximum (FWHM) and directed through the Be gasket and the sample. Two-dimensional diffraction patterns were collected by a Mar345 image plate detector and analyzed with the program Fit2D [17]. The sample-to-detector distance and orientation of the detector were calibrated by a CeO2 standard. At each pressure, the RXD pattern was collected typically for 15–20 min after about 30 min of stress relaxation.

3. Theory

The radial X-ray diffraction data was analyzed using the lattice strain theory developed by Singh and co-workers [18,19]. According to the lattice strain theory, the measured d-spacing \( d_m(hkl) \) is a function of the azimuthal angle \( \psi \) between the DAC loading axis and the diffraction plane normal \( (hkl) \), and can be calculated using the relation as

\[
d_m(hkl) = d_0(hkl)[1 + (1 - 3 \cos^2 \psi)Q(hkl)]
\]

where \( d_0(hkl) \) is the measured d-spacing, \( d_0(hkl) \) is the d-spacing under the equivalent hydrostatic pressure, and \( Q(hkl) \) is the orientation dependent lattice strain.

Under isostress conditions (the Reuss limit), the differential stress, \( t \), can be expressed as

\[
t = 6GQ(hkl)
\]

where \( Q(hkl) \) represents the Q value averaged over all observed reflections of \( Q(hkl) \), and \( G \) is the aggregate shear modulus of the polycrystalline sample. The pressure dependence of \( G \) can be obtained from extrapolation of ultrasonic or theoretically calculated single-crystal elastic constants. If the differential stress \( t \) has reached the limiting value of yield strength at high pressures when
materials start to deform plastically, $6(Q/hkl) = \tau/G$ will reflect the ratio of yield strength to shear modulus. In addition, this ratio might be a good qualitative indicator of hardness as it reflects the contributions of both plastic and elastic deformation [20].

Eq. (1) indicates that the $d_{\psi}(hkl)$ vs $(1-3\cos^2 \psi)$ plot is a straight line for given $d_{\psi}(hkl)Q(hkl)$, and its slope, $d_{\psi}(hkl)$, is directly related to $6(Q/hkl) = \tau/G$ [20], $d_{\psi}(hkl)$ is normally at $\psi = 54.7^\circ$. With additional, independent constraints on the high-pressure shear modulus, the differential stress or yield strength at high pressure can be determined.

For the conventional RXD experiments, the incident X-ray beam is perpendicular to the compression axis and passes through a Be gasket which contributes intense diffraction lines to the sample patterns. Thus, we can tilt the DAC to an angle of $\alpha$ between the compression axis and the incident X-ray to minimize the Be contribution to the sample patterns ($\alpha = 28^\circ$) [16]. In this geometry, $\psi$ in Eq. (1) can be rewritten as [21]

$$\cos \psi_{hkl} = \sin \alpha \cos \delta \cos \theta_{hkl} + \cos \alpha \sin \theta_{hkl}$$

where $\theta$ is the diffraction angle and $\delta$ is the azimuthal angle in the plane of the detector.

4. Results and discussion

The RXD diffraction patterns are integrated over each azimuthal sector with a $5^\circ$ interval using Fit2D [17] for data analyzes. The program Multifit 4.2 is used to perform macro decomposition of the 2D diffraction images into azimuthal slices within Fit2D [17], yielding one-dimensional plots of X-ray intensity as a function of $2\theta$, as well as peak positions, intensities, and FWHM of the diffraction peaks. To determine the variation of the diffraction peak positions with $\delta$, we integrated the diffraction patterns with segments of $5^\circ$ in the azimuth angle, in the range of 180–270°, and fit peak positions. RXD spectra of WB$_3$ were collected up to an equivalent pressure of 86 GPa, where pressures were derived from the EoS of Mo [15] with the unit cell volume obtained from RXD in the DAC. It can be seen that, the differential stress, $\tau$, increases slowly above 30 GPa, indicating that WB$_3$ begins to experience macro yield with plastic deformation as $\tau$ reaches its limited value (yield strength) of 25.5 GPa at this pressure. In addition, after ~77 GPa, the differential stress begins to level off, and similar behaviors were observed for c-BC$_2$N$_2$ [22].

At ~77 GPa, differential stress as high as ~30 GPa is supported by WB$_3$. For comparison, a differential stress of ~38 GPa is supported by c-BC$_2$N$_2$ at ~66 GPa, B$_6$O [23] supports a maximum differential stress of ~30 GPa at a confining pressure of 65 GPa, and $\gamma$-Si$_3$N$_4$ [24] reaches a maximum differential stress of 23 GPa at a pressure of 68 GPa. The differential stress of WB$_3$ is very large at each pressure step as $\tau = 6G(Q/hkl)$.
due to its large $t/G$ and large shear moduli. It can be seen that, the maximum differential stress in the pressure range studied of WB$_3$ is close to that of B$_6$O [23], which is much larger than that of $\gamma$-Si$_3$N$_4$ [24], but lower than that of c-B$_2$C$_7$N$_2$ [22].

The differential stress of WB$_3$ is even “harder” than that of c-B$_2$C$_7$N$_2$, B$_6$O, and $\gamma$-Si$_3$N$_4$ below 40 GPa, and it seems that WB$_3$ is “harder” than these materials. However, the Vickers hardness should consider the maximum differential stress before yield [20], as well as grain size [25]. WB$_3$ experiences macro yield with plastic deformation at $\sim$40 GPa and sustains a differential stress of $\sim$25.5 GPa. For comparison, c-B$_2$C$_7$N$_2$ begins to yield at a pressure of $\sim$66 GPa with a maximum differential stress of $\sim$38 GPa, and B$_6$O started to yield at nonhydrostatic compression of $\sim$65 GPa and differential stress reaches its limiting yield strength value of 29.5 GPa. For $\gamma$-Si$_3$N$_4$, the yield point is $\sim$67 GPa with a yield strength of $\sim$23 GPa. In addition, the strength of polycrystalline materials is also known to increase with decreasing grain size, and grain-size effects on high-pressure strength have been documented in previous RXD experiments [25]. Hence, grain-size effects on high-pressure strength should also be taken into account when comparing WB$_3$ (microcrystalline), c-B$_2$C$_7$N$_2$ [22] (nanocrystalline), B$_6$O (microcrystalline) [23] and $\gamma$-Si$_3$N$_4$ (nanocrystalline) [24].

The results probably indicate that the Vickers hardness of WB$_3$ is lower than that of c-B$_2$C$_7$N$_2$ ($\sim$70 GPa [29]), B$_6$O, (45 GPa [25]), and $\gamma$-Si$_3$N$_4$ (35 GPa [26] and 43 GPa [27,28]).

Liang et al. [9] obtained a Vickers hardness of 39.4 GPa for WB$_3$ from theory calculation using Chen’s model of hardness [15] and 43.1 GPa using the correlation [31] existing between the Vickers hardness and shear modulus. However, Zhang et al. [8] demonstrate that WB$_3$ cannot be intrinsically superhard because of its much lower ideal strengths compared to c-BN. And Zang et al. [10] argue that the Vickers hardness of WB$_3$ should be well below that of ReB$_2$ (30.1 GPa [11], 26.6 GPa [1], and 18.4 GPa [12]) as calculating the stress–strain relation and the ideal indentation strength from first-principles shows that the calculated ideal indentation strength of WB$_3$ is considerably lower than that of ReB$_2$ via calculating the stress–strain relation and the ideal strength.

5. Conclusion

We have examined the strength of WB$_3$ in a diamond anvil cell under nonhydrostatic compression up to 86 GPa at room temperature using radial X-ray diffraction together with the lattice strain theory. The differential stress of WB$_3$ increases with pressure from 0.4% of the shear modulus at 1 GPa to 7.8% at 77 GPa. Given the theoretically calculated values for the shear modulus at high pressures, the supported differential stress ranges from 1 GPa at 1 GPa to 30 GPa at 77 GPa. The change of $t$ with pressure indicates that WB$_3$ starts to yield with plastic deformation and $t$ reaches 26 GPa at a nonhydrostatic compression of $\sim$40 GPa. The increase in $t$ with pressure reaches a maximum value of 30 GPa at $\sim$77 GPa. The differential stresses of WB$_3$ are comparable to those of several reported superhard materials (c-B$_2$C$_7$N$_2$, B$_6$O, $\gamma$-Si$_3$N$_4$).

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References


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