Electron redistribution during deformation
Blue regions represent weakened bonds

Normalized Shear properties of TMB_2
 G -shear modulus, γ -critical shear strain
 τ -ideal shear strength, Q -activation energy

Effects of Transition Metal (TM = Zr, Hf, Nb, Ta, Mo, W) Elements on the Shear Properties of TMB₂s: a First-principles Investigation

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Abstract: Transition metal diborides (TMB₂s) exhibit unique combination of excellent properties makes them promising candidates for extreme environmental applications. It is believed that activation of dislocation plasticity is beneficial to retain fracture strength of TMB₂s based materials at high temperature, since plastic deformation can release elastic energy accumulated in the material and then fracture is suppressed. In this paper, shear properties of TMB₂s (TM = Zr, Hf, Nb, Ta, Mo, W) for both (0001)[2110]/3 and (0110)[2110]/3 shear modes are evaluated by first-principles and the dependence of shear properties on TM elements is discussed by electron redistribution during the deformation. The results show that properties of the (0001)[2110]/3 shear are solely determined by TM-B bond and exhibit substantial dependence on TM elements, while the (0110)[2110]/3 shear are controlled by both TM-B bond and B-B σ bond, which makes the dependence of shear properties on TM elements not that obvious. The simulated ideal shear strengths demonstrate that dislocation nucleation become easier in an order of ZrB₂ ($\approx$ HfB₂), NbB₂, TaB₂, MoB₂, WB₂, which reasonably explains some experimental observations and provides useful information for the design of TMB₂ based materials by alloying.

Keywords: transition metal diborides; ideal shear strength; first-principles; dislocation nucleation; electron redistribution

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Introduction

Recent interest in transition metal diborides (TMB₂s, i.e. ZrB₂ and HfB₂) is motivated by searching for materials that can withstand extreme environments encountered by leading-edge and nose-tip of hypersonic vehicles, where the materials will work at ultra-high temperature (>2000 °C) for a long time [1, 2]. To realize their service in ultra-high temperatures, strength of TMB₂ based materials at evaluated temperature has received increasing attention [3-8]. However, experimental measurements reveal that flexural strengths of ZrB₂ based materials usually drop down rapidly at temperature higher than 1200 °C [3], which impedes their applications. In a recent study, Wu *et al.* [4] suggested that retention of strength at high temperature can be achieved by activation of dislocation plasticity, since the large energy absorbing process during the plastic deformation will increase the required fractural strength for rupture. Interestingly, ZrB₂ or HfB₂ based materials with addition of TaSi₂, MoSi₂, WSi₂ or WC generally show promise retention of strength at high temperature [3, 5-8], where evident dissolution of Ta, Mo or W into ZrB₂ or HfB₂ grains has been reported [5-7]. Dissolution of these elements into ZrB₂ or HfB₂ grains might reduce the barrier for dislocation nucleation and ultimately improve the retention of strength at high temperature. Therefore, it is desirable to evaluate the effect of transition metal (TM) elements on dislocation nucleation.

The ideal strength of a material represents the minimum stress required to yield or break a perfect crystal, an accurate evaluation of which provides a fundamental understanding of mechanical properties of materials. Since it is difficult to acquire the ideal strength from experiments, first-principles methods based on density functional theory provide a good choice to evaluate the ideal strength of materials and to demonstrate the dependence of the ideal strength on the interatomic bonding nature⁹. Previously, first-principles calculations have been adopted to investigate the electronic structure and elastic properties of TMB₂s [10-13]. However, there is no report on the ideal strength of TMB₂s. The present work deals with a first-principles investigation on the ideal shear strength of TMB₂s (TM = Zr, Hf, Nb, Ta, Mo, W) to illustrate the

effect of TM elements on dislocation nucleation.

Computational Details

The first-principles calculations were performed using the CASTEP code [14] with the Vanderbilt-type ultrasoft pseudopotential [15] and generalized gradient approximation of Perdew-Burke-Ernzerh (PBE) scheme [16]. The plane wave cutoff energy was set to be 400 eV and $15 \times 15 \times 15$ k -points mesh constructed according to the Monkhorst-Pack method [17] was adopted in the Brillouin zone. Lattice parameters of the investigated diborides were optimized by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [18] minimization scheme. To simulate the stress-strain relation, the unit cell was incrementally deformed in the imposed strain direction. At each step, the crystal structure was fully relaxed by employing BFGS minimization scheme until all other stress components vanished. Then, the relaxed cell was taken as the starting structure for the next step to ensure the stress-strain curves being continuous. During the optimization, the convergence criteria were set as follows: the difference in total energy within 1×10^{-6} eV/atom, the maximum ionic Hellmann-Feynman force within 0.002 eV/Å, the maximum ionic displacement within 1×10^{-4} Å, and maximum stress difference within 0.02 GPa.

Results and Discussions

TMB₂ crystals are AlB₂-like structure with the space group of P6/mmm, stacking alternatively by close-packed TM layers and graphite-like hexagonal B layers, as illustrated in Fig. 1a. TM atoms and boron atoms are respectively located at 1a (0, 0, 0) and 2d (1/3, 2/3, 1/2) Wyckoff positions. As reported, plastic deformation in ZrB₂ is dominated by $\langle 2110 \rangle/3$ dislocations [4, 19, 20], where $\langle 2110 \rangle/3$ is the Burgers vector. Thus, two types of $\langle 2110 \rangle/3$ shear modes are simulated in the current work. One is shear in (0001) plane along $[2110]/3$ direction (basal plane shear, Fig. 1b), while the other is shear in (0110) plane along $[2110]/3$ direction (prismatic plane shear, Fig. 1c). Fig. 2 shows the simulated stress-strain curves for ZrB₂. In the figure, the stress is the true stress, while the strain is the engineering strain calculated from $(\mathbf{FF}^T - \mathbf{I})/2$,

where $\mathbf{F}$ is the deformation matrix and $\mathbf{I}$ is the unit matrix. The superscript T means transpose of the matrix. From a stress-strain curve, shear modulus G can be determined as the slope of the linear part in the curve. The maximum shear stress that the material can bear is the ideal shear strength τ . When the stress reaches the maximum value, the crystal will loss stability, accompanying with nucleation of dislocations. The strain corresponding to the maximum stress is the critical shear strain γ . The area under the stress-strain curve approximately represents the work that external force should do to activate instability of the crystal (Q , activation energy of instability). As can be seen from Fig. 2, though with almost identical shear modulus, the ideal shear strength of the basal plane shear is higher than that of the prismatic plane shear. In addition, the area under the stress-strain curve of the basal plane shear is significantly larger than that of the prismatic plane shear. Therefore, both the ideal shear strength and the activation energy indicate that dislocation nucleation in the prismatic plane might be easier for ZrB_2 . It provides a reasonable explanation why slip occurs in the prismatic plane at room temperature [19, 20], though the simulation is carried out at 0 K.

The determined values of shear modulus G , critical shear strain γ , ideal shear strength τ and activation energy Q of TMB_2s for both shear modes are listed in Table 1, where Q values are energy differences between the instable cell and the un-deformed cell. To illustrate the dependence of shear properties on TM elements, G , γ , τ and Q of TMB_2s are plotted in Fig. 3, where all values are normalized by the corresponding value of ZrB_2 in the basal plane shear mode, i.e., G_b and G_p are normalized by G_b of ZrB_2 . The subscript b and p respectively means the value corresponding to the basal plane shear and the prismatic plane shear. For the basal plane shear, shear properties exhibit evident and simple dependence on the TM elements. The values of shear modulus G_b , critical shear strain γ_b , ideal shear strength τ_b and activation energy Q_b all follow the order $\text{ZrB}_2 \approx \text{HfB}_2 > \text{NbB}_2 > \text{TaB}_2 > \text{MoB}_2 > \text{WB}_2$, and their dependences on TM elements are substantial with the decrease of G_b , γ_b , τ_b and Q_b from ZrB_2 to WB_2 being about 50%, 60%, 70% and 90%. Therefore, nucleation of $\langle 2110 \rangle / 3$ dislocation on the basal plane becomes easier in an order of

ZrB₂ ($\approx$ HfB₂), NbB₂, TaB₂, MoB₂, WB₂. For the prismatic plane shear, the effect of TM elements on shear properties is not that obvious. TM elements only modulate the shear modulus G_p at a ratio around 10%. Comparing with ZrB₂ and HfB₂, the critical shear strains γ_p of NbB₂ and TaB₂ are higher, while those of MoB₂ and WB₂ are lower. Fortunately, the ideal strength for the prismatic plane shear exhibits similar tendency as that for the basal plane shear, except that τ_p of NbB₂ is approximately equals to, instead of lower than, those of ZrB₂ and HfB₂. Owing to the higher critical strain γ_p and lower ideal strength τ_p , activation energies Q_p of NbB₂ and TaB₂ are almost identical to those of ZrB₂ and HfB₂, while those of MoB₂ and WB₂ are much lower. Both τ_p and Q_p suggested that nucleation of $\langle 2110 \rangle/3$ dislocation on the prismatic plane becomes easier in an order of ZrB₂ ($\approx$ HfB₂ $\approx$ NbB₂), TaB₂, MoB₂, WB₂.

Electron redistribution during deformation may shed some light to understand the dependence of shear properties on TM elements. Fig. 4 shows the relative electron density difference on $\{2110\}$ planes between the instable state and the un-deformed state*. In the figure, blue regions indicate reduction of electron density during the deformation, which means weakening of the bonding. Thus, the primary weakened bonds are TM-B bonds in (1120) and (1210) plane for the basal plane shear (Fig. 4b), where the weakened bonds are significantly elongated during the deformation. It is reasonable why the basal plane shear exhibits simple dependence on TM elements, since its properties dominate solely by TM-B bond. According to the simulation results, the stiffness and strength of TM-B bond may decrease in an order of Zr-B ($\approx$ Hf-B), Nb-B, Ta-B, Mo-B, W-B. In contrast, the primary weakened bonds are TM-B bond and B-B σ bond in (1210) plane for the prismatic plane shear (Fig. 4c). It means that the B-B σ bond also plays key role in controlling the prismatic plane shear except for the TM-B bond. Therefore, TM elements do not show simple effect on determining shear properties of the prismatic plane shear.

* For a point with inner coordinate (u, v, w), the relative electron density difference is calculated as $(d_i - d_u)/d_u$. d_i is the electron density at the point in the instable state, while d_u represents the electron density at the point in the un-deformed state.

The above results provide reasonable interpretations to the phenomena observed by Silvestroni *et al.* [5-7]. As they reported, ZrB₂ or HfB₂ grains exhibit a core-shell structure with the shell dissolution of Ta, Mo or W, and dislocations are found only concentrated in shells. Our simulations indicate that the strength of Ta-B, Mo-B and W-B bonds are lower than that of Zr-B and Hf-B bonds. Thus, dissolution of Ta, Mo or W into ZrB₂ or HfB₂ matrix may reduce the stress and activation energy for dislocation nucleation, which explains why dislocations concentrate in shells. Reducing the barrier for dislocation nucleation might play some role in retention of high temperature strength, since elastic energy will mainly be dissipated by plastic deformation and fracture is suppressed. Accordingly, (Zr, X)B₂ or (Hf, X)B₂ based composites are possible candidate materials which can retain high fractural strength at evaluated temperature. The selection of alloy element X can be guided by the bonding nature between X and B, where weak X-B bond is preferred. Previously, Shein *et al.* [12] have systematically investigated elastic properties of metal diborides with the metal elements including I-VI groups s, p and d metals. Their results possibly provide some guidelines for the selection of X element, where they showed that BeB₂, AgB₂, AuB₂ and NaB₂ are instable against shear deformation ($G_b = C_{44} < 0$ or $G_p = (C_{11} - C_{12})/2 < 0$). Then, introducing these elements into ZrB₂ or HfB₂ based materials might be beneficial to the retention of strength at high temperature.

Conclusions

In the current work, we systematically studied the ideal shear strength of a series of TMB₂s (TM = Zr, Hf, Nb, Ta, Mo, W) for both (0001)[2110]/3 and (0110)[2110]/3 shear modes by first-principles calculation. The results show that properties corresponding to the (0001)[2110]/3 shear mode exhibit substantial dependence on TM elements, since these properties are solely determined by TM-B bond. In contrast, properties of the (0110)[2110]/3 shear mode are controlled by both TM-B bond and B-B σ bond, which makes the dependence of shear properties on TM elements not that obvious. The ideal shear strength demonstrates that dislocation nucleation become easier in an order of ZrB₂ ($\approx$ HfB₂), NbB₂, TaB₂, MoB₂, WB₂, which reasonably

explains some experimental observations. Our simulation provides useful information for the design of ZrB₂ or HfB₂ based materials by alloying, which indicates that dissolution of X elements with weak X-B bond will reduce the barrier for dislocation nucleation and is possibly beneficial to the retention of strength at high temperature.

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References

- [1]. W. G. Fahrenholtz, G. E. Hilmas, I. G. Talmy, and J. A. Zaykoski, *J. Am. Ceram. Soc.* **90**, 1347 (2007).
- [2]. D. M. Van Wie, D. G. Jr. Drewry, D. E. King, and C. M. Hudson, *J. Mater. Sci.* **39**, 5915 (2004).
- [3]. E. W. Neuman, and G. E. Hilmas, in *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*, edited by W. G. Fahrenholtz, E. J. Wuchina, W. E. Lee, and Y. Zhou (Wiley, New York, 2014), pp. 167–196.
- [4]. W. W. Wu, Y. Sakka, M. Estili, T. S. Suzuki, T. Nishimura, and G. J. Zhang, *Sci. Technol. Adv. Mater.* **15**, 014202 (2014).
- [5]. L. Silvestroni, H. J. Kleebe, S. Lauterbach, M. Müller, and D. Sciti, *J. Mater. Res.* **25**, 828 (2010).
- [6]. L. Silvestroni, and D. Sciti, *J. Am. Ceram. Soc.* **94**, 1920 (2011).
- [7]. L. Silvestroni, and D. Sciti, *J. Alloys Comp.* **602**, 346 (2014).
- [8]. J. Zou, G. J. Zhang, C. F. Hu, T. Nishimura, Y. Sakka, J. Vleugels, and O. Biest, *J. Am. Ceram. Soc.* **95**, 874 (2012).
- [9]. S. Ogata, J. Li, N. Hirosaki, Y. Shibutani, and S. Yip, *Phys. Rev. B* **70**, 104104 (2004).
- [10]. P. Vajeeston, P. Ravindran, C. Ravi, and R. Asokamani, *Phys. Rev. B* **63**, 045115 (2004).
- [11]. J. W. Jr Lawson, C. W. Bauschlicher, and M. S. Daw, *J. Am. Ceram. Soc.* **94**, 3494 (2011).

- [12]. I. R. Shein, and A. L. Ivanovskii, J. Phys.: Condens. Matter **20**, 415218 (2008).
- [13]. Y. Zhou, J. Wang, Z. Li, X. Zhan, and J. Wang, in *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*, edited by W. G. Fahrenholtz, E. J. Wuchina, W. E. Lee, and Y. Zhou (Wiley, New York, 2014), pp. 60–82.
- [14]. M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clarck, and M. C. Payne, J. Phys.: Condens. Mater **14**, 2717 (2002).
- [15]. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- [16]. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [17]. J. D. Pack, and H. J. Monkhorst, Phys. Rev. B **16**, 1748 (1977).
- [18]. B. G. Pfrommer, M. Côté, S. G. Louie, and M. L. Cohen, J. Comput. Phys. **131**, 233 (1977).
- [19]. J. S. Haggerty, and D. W. Lee, J. Am. Ceram. Soc. **54**, 572 (1971).
- [20]. D. Ghosh, G. Subhash, and G. R. Bourne, Scr. Mater. **61**, 1075 (2009).

Table 1. Simulated shear modulus G , critical shear strain γ , ideal shear strength τ and activation energy Q of TMB₂s for the basal plane shear and the prismatic plane shear

	G_b (GPa)	γ_b	τ_b (GPa)	Q_b (eV)	G_p (GPa)	γ_p	τ_p (GPa)	Q_p (eV)
ZrB ₂	251.3	0.253	40.7	1.28	254.8	0.193	36.9	0.76
HfB ₂	253.9	0.253	40.2	1.25	254.3	0.192	37.4	0.76
NbB ₂	216.6	0.222	33.1	0.75	243.3	0.208	37.5	0.75
TaB ₂	189.6	0.189	25.8	0.50	221.2	0.220	31.5	0.72
MoB ₂	144.1	0.183	19.3	0.33	231.5	0.115	23.5	0.23
WB ₂	129.0	0.131	12.4	0.16	240.5	0.114	22.5	0.23

Subscript b and p respectively means the basal plane shear and the prismatic plane shear.

Figure 1. (Color online) (a) Schematic illustration on the crystal structure of TMB₂. (b) shear in (0001) plane along [2110] direction (basal plane shear), (c) shear in (0110) plane along [2110] direction (prismatic plane shear).

Figure 2. (Color online) Simulated shear stress-strain curves for ZrB₂. The area under the stress-strain curve approximately represents the work that external force should do to activate instability.

Figure 3. (Color online) Normalized shear properties of TMB_2 s with respect to TM elements. From top to bottom is respectively shear modulus G , critical shear strain γ , ideal shear strength τ and activation energy Q . All values are normalized by the corresponding value of ZrB_2 in the basal plane shear mode, i.e., G_b and G_p are normalized by G_b of ZrB_2 .

Figure 4. (Color online) (a) Schematic illustration of $\{2110\}$ planes in ZrB_2 . F_1 , F_2 and F_3 is respectively (1120), (2110) and (1210) plane. Arrows on $\{2110\}$ planes represent the left to right direction in (b) and (c). Relative electron density difference on $\{2110\}$ planes between the instable state and the un-deformed state: (b) the basal plane shear, (c) the prismatic plane shear.