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Exploring the effects of interlamellar binding modes on the hardness of ReB₂ and MoB₂ with Laminar structure

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ABSTRACT

The properties of structure, elasticity and electron for ReB₂ and MoB₂ are investigated, using first-principles calculations, as well as the role of chemical bonds between metal layer and boron layer in determining the hardness. The weakest shear crystalline plane of two diborides is determined by the bonding force of adhesive layers. The interlamellar bonding force in ReB₂ is stronger than that in MoB₂, resulting in a higher hardness for ReB₂. The hardness of ReB₂ (about 31 GPa) is still far below the threshold value for superhard materials due to the weak interlamellar covalent hybridization.

Keywords: Molybdenum diboride, Rhenium diboride, Vickers hardness, Superhard material, First principle

1. Introduction

Ultra-incompressible and superhard materials ($H_v \geq 40$ GPa) have attracted widespread research interest, because of applying as cutting tools and wear-resistant coatings.[1-3] Recently, transition-metal borides (TMBs) have drawn considerable attention due to their strong B–B covalent bond and TM-B covalent bond which play an important role in forming superhard materials.[4-6] Such bonding characteristics are structurally favorable to resist severe shear strain or shape change. The hardness of TMB₂ and TMB₄ (TM=Os, Ir, Re, Ru, or W), beyond 40 GPa, are obtained by theoretical calculations and could be analogous to the hardness of c-BN that is generally accepted as a superhard material.[7-9] Up to now, several TMBs have been synthesized and declared as superhard materials, such as ReB₂ and WB₄. [2,7] However, neither of them demonstrates an asymptotic hardness larger than 40 GPa which is

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generally accepted as the threshold of superhard materials.[10,11] On the other hand, Chen reported that the low hardness of TMBs is due to the covalent bonds between the transition metal and light element are weaker than those between light covalent elements.[12] Much of TMBs have layered structure with TM layers and B layers stacked alternately. The B layers would form strong covalent bonds. So, the complex chemical bonds of TM-B are very important to resist the layer slip caused by shear stress. The reason for TMBs as hard material but not superhard material may be explained by no strong covalent bonds at the interlayer between TM layer and B layer which would cause slip deformation easily along the XY plane. The predicted covalent bond forming between TM atom and B atom is the key factor in determining the high hardness of the TMBs. Therefore, exploring the bond type of these TMBs is of great significance to uncover the mystery of why TMBs don't display so high hardness as predicted in theory.

ReB₂ (P6₃/mmc) and MoB₂ (R-3m), having layered structure with TM layers and B layers stacked alternately as shown in Fig. 1, are two promising superhard materials and ReB₂ (P6₃/mmc) was predicted as superhard material due to covalent bonds formed between the TM atoms and the B atoms by the first-principle calculation.[5,6] However, neither of them demonstrated a high hardness beyond 40 GPa under high loading force. The value of hardness of ReB₂ (31 GPa) is higher than that of MoB₂ (22 GPa) under the same applied load with 4.9 N.[2,13] This difference may be caused by the difference in strength of interlayer bonding. Exploring the strength of TM-B bonds is meaningful to uncover the hardness mechanism and to design much harder TMBs with layer structure.

In this paper, we systematically investigated the electron localization function (ELF), density of states (DOS), elastic, bulk modulus and shear modulus of ReB₂ and MoB₂. It was found that the chemical bonds formed between TM and B atoms possess the character of covalent in ReB₂, and the character of ionic in MoB₂. The covalent hybridization of Re-B bond in ReB₂ (P6₃/mmc) makes it harder than MoB₂. This study explained that the hardness of TMBs with layered structure are bound up with TM-B bonds at the interlayer.

2. Experimental procedure

In the first stage of the calculations, the equilibrium geometries of the MoB₂ and ReB₂ were obtained, and then the mechanical and electronic properties of them were calculated by using density functional theory method within the CASTEP code.[14] The exchange correlation energy was treated with the generalized gradient approximation (GGA-PBE),[15] the Vanderbilt ultrasoft pseudopotential was used with the cutoff energy of 500 eV, the *k* points of 10×10×4 for ReB₂ in the P6₃/mmc phase and

$9 \times 9 \times 2$ for MoB_2 in the R-3m phase are generated using the Monkhorst-Pack scheme.[6,16,17] ELF, DOS and Mulliken population were carried out to estimate the type of TM-B and B-B bonds in TMB_2 . Furthermore, the elastic constants of TMB_2 were calculated.

Fig. 1 Crystal structures of ReB_2 ($P6_3/mmc$) and MoB_2 (R-3m). Blue spheres, Green spheres and Orange spheres represent Mo atoms, Re atoms and B atoms, respectively. ReB_2 has structure with...ABAB... stacking sequence. Here A are puckered B layers and B are closepacked Re layers. MoB_2 has structure with...AHA K BHB K... stacking sequence. Here A, B and C are closepacked Mo layers. H is a graphite-type layer and the K type layer is a puckered.

3. Results and discussion

After full geometry optimization, two structures keep the same symmetry as the initial symmetries as shown in Fig. 1. Table I list the calculated equilibrium lattice parameters, elastic constants, shear modulus and bulk modulus of the two diborides. The previous theoretical and experimental results are also listed for comparison. The calculated lattice parameters and the elastic constants agree well with the available theoretical and experimental values. The calculated lattice parameters are very close to the previous theoretical values with deviations less than 1%.[4, 6] Generally, the elastic constants, shear modulus and bulk modulus are important parameters for understanding physical properties of solids materials including the stiffness and compression properties. The calculated elastic constants of ReB_2 and MoB_2 satisfy the Born–Huang’s stability criterion,[18] indicating that both of ReB_2 and MoB_2 are mechanically stable. Bulk modulus (B) and shear modulus (G) are two significant elastic properties correlated with the hardness, which were calculated, shown in Table 1. The bulk modulus of ReB_2 is larger than that of MoB_2 . This result demonstrates that the ReB_2 possessed better ability of resistance to compression than MoB_2 . Shear modulus value, which relates to lattice resistance against an applied shear deformation, of MoB_2 is lower than that of ReB_2 . The low shear modulus may also caused

by different strength of interlayer bonding to resists plastic deformation and limit the creation and propagation of defects. Poisson ratio values are usually used to determine the ionic, covalent or the metallic nature of materials. The typical Poisson ratio values for covalent, ionic and metallic are 0.1, 0.25 and 0.33, respectively.[19] The value of the Poisson's ratio (ν) of MoB_2 is $\nu = 0.201$ which is corresponding to that of ionic materials. The value of the Poisson's ratio (ν) of ReB_2 is 0.182 which is lower than that of MoB_2 , indicating ReB_2 has more covalent character than MoB_2 . The Poisson ratio value of MoB_2 is smaller than 0.25 which may attribute to the synergistic action of the strong B-B covalent bond and Mo-B ionic bond. Besides, for covalent and ionic materials, the typical relations between bulk and shear modulus are: $G \approx 1.1B$ and $G \approx 0.6B$, respectively.[19] The calculated value of G/B for MoB_2 is 0.746, indicating that the ionic contribution to interatomic bonding between Mo atom and B atom is more suitable. So, it is conjectured that Mo-B ionic bond may exist in MoB_2 . So, exploring the bond strength of TM-B in ReB_2 and MoB_2 are the key factor to explain that the value of the hardness of ReB_2 is higher than that of MoB_2 and uncover the hardness mechanism in TMBs with layered structure.

Table 2. Lattice parameter, elastic constants, bulk modulus, shear modulus and Vickers hardness of different materials

Compound	a	c	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B(GPa)	G(GPa)	Reference
ReB_2	2.9095	7.48415	657.7	145.0	142.3	1025.6	265.7	349.1	280.9	This work
ReB_2	2.8809	7.4096	667.9	136.7	147.4	1062.7	273.2	301.1	224.7	6
MoB_2	3.017	20.87	571.0	123.7	168.1	661.4	228.2	301.1	224.7	This work
MoB_2	3.019	20.961	609	123	152	718	239	310	238	4

In order to confirm and understand the chemical bonds between TM and B in ReB_2 and MoB_2 , the ELF were calculated with the geometry optimization parameters. The results of ELF for ReB_2 and MoB_2 are shown in Fig. 2. The electron density is clearly located at the center of B-B bonds in two diborides (Fig. 2 (a)-(c) and (f)-(g)), indicating the strong covalent bonding that creates a 2D network. TM layers in the both structures are similar (Fig. 2 (b) and (e)), no electron density is located among TM atoms. However, we can find some free electrons around TM atoms, indicating metallic behavior between the TM atom and the TM atom. To gain a more detailed insight into the bonding between TM atoms and the boron atoms, the ELF distribution in $(11\bar{2}0)$ plane are plotted in Fig. 2(c) and (g). There are no proofs of direct Mo-B covalent bonds even at low ELF values. It can be found the spherical-like density for Mo atoms which is typical for ionic character bonding.[6] But we can see some electrons located at interlayer between two B atoms and one Re atom, indicating a directional covalent Re-B bonding exists

in these ReB_2 compound. But hybridization between Re and B atoms is very weak compared with the hybridization between B atoms, indicating that the weakest shear crystalline plane which should be along the XY plane is caused by weak binding energy between interlayers. So, ReB_2 having higher hardness than that of MoB_2 is due to the strength of the chemical bonds between layers in ReB_2 is stronger than that of MoB_2 .

Fig. 2. (a) , (b) and (d), the ELF plane in the puckered B layer, graphite-like B layer and Mo layer of MoB_2 , respectively. (c), the ELF in $(11\bar{2}0)$ plane in MoB_2 . (e) and (f), the ELF plane in the Re layer and B layer of ReB_2 , respectively. (g), the ELF in $(11\bar{2}0)$ plane in ReB_2 .

The DOS is calculated at zero pressure within the GGA method. The site projected and total DOS for ReB_2 and MoB_2 are shown in Fig. 3, where the vertical line indicates Fermi level E_F . It is found that the electrons from TM-5*d* or 4*d* and B-2*p* states both contribute to the density of states at the Fermi level; hence these two compounds exhibit metallic behavior. The typical feature of the total DOS of these compounds is the presence of what is called as a “pseudogap” which is considered as the borderline between the bonding states and antibonding states.[5,6] There are two mechanisms proposed to explain the formation of a pseudogap in the binary alloy. One is ascribed to ionic bond, and the other

is from the hybridization effects.[20] The chemical bond between Re and B atom shows covalent hybridization as demonstrated in ELF. So the presence of pseudogap in ReB_2 is ascribed to the covalent hybridization between Re and B atom. In the analysis of ELF, there is no electron density located at the center of Mo–B bond. The presence of pseudogap in MoB_2 may be caused by ionic bond. Moreover, the results of Mulliken populations calculation in this work indicate a large electronegativity difference between Mo (0.85 eV) and B (-0.49 eV, -0.36 eV). The quantity of electric charge transfer from Mo atoms to B atoms indicates that ionic character bonding is the major chemical bonding between Mo atoms and B atoms.[19] This result is consistent with the ELF analysis. The electronegativity difference between Re (0.67 eV) and B (-0.33 eV) in ReB_2 is smaller than that in MoB_2 . The less electric charge transfer from Re atoms to B atoms indicates that ionic bond and covalent bond are co-existent in chemical bonding between Re atoms and B atoms. The electronegativity difference between Re and B atoms is small, hence, the character of ionic does not play a major role on the bonding behavior of these compounds which is consistent with the analysis of ELF. The character of boron layer having six-membered ring structure is that B atoms have saturated electron structure. If B atoms of six-membered ring structure B layers in TMBs gain more electrons, the redundant electrons in B layers should be used to form ionic bonds at the interlayer. In MoB_2 , large electrons drift toward the boron atoms (-0.49 eV) in graphite-like boron layers giving rise to an ionic contribution to the bonding between Mo layers and graphite-like boron layers. Covalent chemical bonds having character of strong direction formed in Re-B makes B layers puckered. And the character of the chemical bonds between B atoms in puckered B layers and Mo atoms in MoB_2 should have some character of covalency, too. The charge transfer toward the boron atoms in puckered boron layers in MoB_2 is 0.36 eV which is slightly larger than that in ReB_2 and much smaller than that in graphite-like boron layer in MoB_2 . It is likely that less electrons charge transfer and puckered B layers could form covalent chemical bond between TM atoms and B atoms. The combination energy between graphite-like boron layer and TM layers should always have the major character of ionicity. So the materials with graphite-like boron layer shows low hardness far below 40 GPa which is the threshold of superhard materials even in boron-rich materials such as WB_4 . [7] It was reported that the charge transfer effect can be influenced by the total valence electrons and the crystal structure. [4] The transferred charge of transition metal decreases with the increase of total valence electrons. When the transition metal borides have the same crystal structure. In this work, the number of total valence electron of Re is larger than that of Mo and ReB_2 has similar crystal structure to MoB_2 . So, large charge transfer appeared in Mo. Furthermore, based on the analysis above, we can conclude that less charge transfer and covalent hybridization is more likely obtained

in TMBs with puckered B layers. This can well clarify that the hardness of TMBs with puckered quasi-3D B layers are always harder than that of TMBs with 2D graphitic boron layers.

Fig. 3. Total and partial density of states for MoB₂ and ReB₂. The dotted line at zero is the Fermi energy level.

Recently, computational physics have made it possible to bring more insight into deformation behavior and hardness of single crystalline materials by calculating the stress-strain relations of a crystal in various shear deformation directions under normal compressive pressure beneath an indenter.[12,21] This method can describe more accurately material's strength under indentation hardness tests than pure ideal shear strength which is calculated neglecting the normal pressure beneath the indenter. The lowest peak stress defines the corresponding ideal strength, which is the minimum stress needed to plastically deform a perfect crystal under strain. These results establish key benchmarks for the intrinsic hardness property of a material. Zang performed calculations of the ideal strength of ReB₂ in various shear deformation directions beneath the Vickers indenter, respectively.[12] And got a result that the weakest shear crystalline plane is the (001) $[1\bar{1}0]$ plane with the lowest Vickers shear peak stress of 27.6 GPa which is consistent with the experiment value 27 GPa with an orientation along XY plane.[2] The weakest shear crystalline plane in the [001] indicating that ReB₂ would cause slip deformation easily along the XY plane beneath the Vickers indenter. This result is consistent with our conclusion that ReB₂ (P6₃/mmc) as a hard material was explained by no strong covalent bonds at the interlayer between A layer and B layer which would cause slip deformation easily along the XY plane.

4. Conclusion

In summary, the roles of chemical bonds between interlayers in determining the hardness are investigated by means of the pseudopotential plane-waves method. Chemical bonds formed between Re and B atoms in ReB_2 shows character of weak covalency and chemical bonds formed between Mo and B atoms in MoB_2 are more likely with the character of ionicity. The relative higher bonding energy between interlayers in ReB_2 makes ReB_2 having higher hardness than MoB_2 . The bonding force between adhesive layers is the key factor in determining the hardness of materials. So, enhancing the strength of the chemical bonds between layers is significant to design new harder TMBs with layer structure.

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