A pathway of hardness enhancement in transition-metal borides

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Abstract The mechanical behaviours of OsB, Os_2B_3 and OsB_2 are systematically investigated by the first-principles calculations. It is found that the changing trends of bulk modulus and hardness are completely different for OsB, Os_2B_3 and OsB_2, which indicates that the underlying sources of incompressibility and hardness are fundamentally different. The incompressibility is related to elastic deformation that is closely associated with valence electron density, whereas the hardness depends strongly on plastic deformation that is determined by bonding nature. It is shown that incorporating small boron atoms into osmium should be a valid pathway of hardness enhancement. This strategy is in principle also applicable to other transition metal borides, carbides, nitrides.

The importance of superhard materials is well known. However, hardness is a macroscopic concept, which is characterized by making an indent in material and measures its size, and thus depends strongly on "plastic" deformation. The difficulty in calculating hardness directly has led people to correlate hardness with other physical quantity. A frequently used candidate is bulk modulus. In fact, bulk modulus measures resistance to volume change and is related to "elastic" deformation. Although the underlying deformations (plastic and elastic) are fundamentally different, hardness is often confused with incompressibility since in many compounds hardness increases with bulk modulus. Therefore, it is highly desirable to study a sort of materials with different trends of hardness and incompressibility to reveal their differences.

Recently it was reported that Os has very high bulk modulus [1], very close to that of diamond. However, its hardness is much lower than that of diamond. Kaner *et al* [2-4] suggested that incorporating boron atoms into transition metals is a possible pathway to obtain high hardness. It is therefore expected that osmium borides to be promising candidates as very hard materials, which attracts much attention. So far, two hexagonal phases (OsB and Os_2B_3) and an orthorhombic phase (OsB_2) have been experimentally synthesized [4, 5]. In this work, we systematically investigate the incompressibility, shear properties and hardness of OsB, Os_2B_3 and OsB_2 by the first-principles calculations.

Table 1. Calculated elastic constants C_{ij} (GPa), bulk modulus B_0 (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio υ and Vicker's hardness H_v (GPa) for diamond, Os, OsB, Os_2B_3 and OsB_2. All hardness values come from the experiment in reference [5].

Material	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	B	G	E	υ	H_v
Diamond	1049	1049	1049	127	127	127	573	573	573	433	525	1123	0.069	94
Os	747	747	832	227	231	231	254	254	260	411	262	649	0.237	4
OsB	635	635	809	201	200	200	193	193	217	362	217	543	0.250	14.4
Os_2B_3	556	556	910	202	193	193	215	215	177	348	212	530	0.247	21.8
OsB_2	588	578	846	184	222	121	163	286	215	336	225	552	0.226	23.5

Table 1 presents elastic constants, bulk modulus, shear modulus, Young's modulus, Poisson's ratio and Vicker's hardness for OsB, Os_2B_3 and OsB_2, respectively. For comparison, diamond and Os are also calculated. The details of calculated methods were described in our previous works [6, 7]. From this table, it can be seen that diamond possesses the highest bulk modulus (433GPa), shear modulus (525 GPa), Young's modulus (1123 GPa) and hardness (94 GPa), and the lowest Poisson's ratio (0.069), and thus it is an ultra-incompressible and superhard material. For Os, it shows a high bulk modulus (411 GPa) but only a very small hardness (4 GPa), implying that it is an ultra-incompressible but not hard material. Hence, a high incompressibility does not guarantee a high hardness. However, can an ultra-compressible material transform into a hard or superhard one? In diamond, the four sp^3 hybrids of carbon form a three-dimensional network composed of strong covalent bonds, which is responsible for its hardness. At the same time, its high valence electron density results in its exceptionally high bulk modulus [4]. The high bulk modulus and low hardness of Os can be explained from the high electron density being responsible for the compressibility and the weak metallic bonds that allows plastic deformation. Hence, in order to enhance the hardness of a material, the non-directional metallic bonds must be changed to directional covalent bonds by inserting small boron atoms into transition metals.

For OsB, Os_2B_3 and OsB_2, we notice that the changing trend of bulk modulus is completely different from that of hardness. The values of bulk modulus decrease from 362 GPa for OsB to 348 GPa for Os_2B_3, and then to 336 GPa for OsB_2. The values of hardness descend from 14.4 GPa for OsB to 21.8 GPa for Os_2B_3, and then to 23.5 GPa for OsB_2. The opposite trends not only demonstrate that the underlying sources of incompressibility and hardness are fundamentally different but also provide us an illustrative case that can be studied explicitly to differentiate their natures.

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Upon incorporating boron into the interstitial sites of the Os lattice to form OsB, the crystal volume largely expands. This volume expansion results in the drop in valence electron density and thus gives rise to a negative contribution to its bulk modulus. On the other hand, the structure of OsB can be described as stacking of Os- and B-layers along the *c*-direction and the covalent bonds of Os-B are formed, which achieves the sharp hardness enhancement from Os to OsB. With the increasing of boron content, the valence electron density continues to fall slowly, and thus the bulk modulus slightly decreases from OsB to Os_2B_3, then to OsB_2. However, for Os_2B_3, the boron atoms of puckered layers are tetrahedrally surrounded by four Os atoms and three additional boron neighbors. The boron atoms of planar layers have a trigonal prismatic environment of six Os atoms and no adjacent boron atoms. The higher degree of covalent bonding makes the hardness of Os_2B_3 increase. In OsB_2, there exist well-defined zigzag covalent chains along the *c* direction, interconnected by shared B and Os atoms. This feature of covalent bond network plays a key role in enhancing its hardness. However, the presence of soft metallic Os-Os layers [8] limits its enhanced hardness at a large load. Ideally, a compound richer in boron would be a preferred ultrahard material, as a higher concentration of boron may easily lead to a three-dimensional B-B bonding and thus a harder material. In order to split a crystal, electron-pair covalent bonds must first be broken and remade. Accordingly, hardness depends strongly on plastic deformation that that is determined by bonding nature. However, bulk modulus measures resistance to elastic compression of volume, which has little direct connection with hardness from dislocation theory. In elastic deformation, the basic relations between atoms do not change. Therefore, valence electron density mostly determines the bulk modulus of materials, but the bonding nature, optimal filling of bonding states, and crystal structure also contribute to incompressibility.

The accurate calculation of elasticity is essential for understanding the macroscopic mechanical properties of solids, for establishing the constitutive equations and for the design of hard materials. For the cubic, hexagonal and orthorhombic lattices, there are three (C_{11}, C_{12}, C_{44}), five (C_{11}, C_{12}, C_{13}, C_{33}, C_{44}) and nine independent elastic constants (C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}, C_{66}), respectively. Others are related to them. All calculated elastic constants C_{ij} are checked, which shows that each of the five materials is mechanically stable at zero pressure. We find that there is substantial anisotropy in the mechanical behavior of OsB, Os_2B_3 and OsB_2. The elastic constants C_{11} or C_{33} measure the *a*- or *c*-direction resistance to linear compression, respectively. It is observed that C_{11} for OsB (635 GPa), Os_2B_3 (556 GPa) and OsB_2 (588 GPa) are smaller by 39%, 47% and 44%, respectively, compared with that of diamond (1049 GPa). However, C_{33} for OsB (809 GPa), Os_2B_3 (910 GPa) and OsB_2 (846 GPa) are comparable to that of diamond. Moreover, Young's moduli for OsB (543 GPa), Os_2B_3 (530 GPa) and OsB_2 (552 GPa) are only half of that of diamond (1123 GPa). It is obvious that the off-diagonal elastic constants and Possion's ratios for OsB, Os_2B_3 and OsB_2 are much larger than the corresponding value of diamond. Therefore, the mechanical properties of OsB, Os_2B_3 and OsB_2 are inferior to that of diamond, although they also are ultrastiff materials.

Shear modulus measures the resistance to shape change at a constant volume. Covalent materials generally show high bond-bending force constants, contain highly directional bonds, and generally possess high shear modulus. The shear modulus is therefore a significantly better qualitative predictor of hardness than the bulk modulus. The shear moduli of OsB, Os_2B_3 and OsB_2 are calculated to be 217 GPa, 212 GPa and 225 GPa, respectively, which only approach 50% of that of diamond (525 GPa). The elastic constants C_{44} and C_{55} are also an important parameter to describe the deformation property of a material. It is found that C_{44} (193 GPa) is smaller than C_{55} (217 GPa) for OsB whereas C_{44} (215 GPa) is larger than C_{55} (177 GPa) for Os_2B_3, but they much lower than C_{44} of diamond (573 GPa). For orthorhombic OsB_2, the elastic constants C_{44}, C_{55} and C_{66} are calculated to be 163 GPa, 286 GPa and 215 GPa, respectively. Therefore, our results indicate that OsB, Os_2B_3 and OsB_2 should be ultra-incompressible and hard materials, but not candidates of superhard materials.

In summary, the mechanical behaviors of OsB, Os_2B_3 and OsB_2 have been systematically studied by performing the first-principles calculations. We have found that the changing trends of bulk modulus and hardness are completely different for OsB, Os_2B_3 and OsB_2, which indicates that the underlying sources of incompressibility and hardness are fundamentally different. The present study provides not only important insights into the nature of hardness but also a useful strategy in the quest for intrinsically superhard transition-metal borides, carbides and nitrides.

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