Correlation between hardness and elastic moduli of the ultraincompressible transition metal diborides RuB_2, OsB_2, and ReB_2

Hsiu-Ying Chung,[1] Michelle B. Weinberger,[2] Jenn-Ming Yang,[1] Sarah H. Tolbert,[2] and Richard B. Kaner[1,2,a)]
[1]*Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095, USA*
[2]*Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California 90095, USA*

(Received 6 April 2008; accepted 17 May 2008; published online 1 July 2008)

The ultraincompressible transition metal diborides RuB_2, OsB_2, and ReB_2 were synthesized by arc melting the elemental metals and boron under an argon atmosphere at ambient pressure. The hardness and Young's modulus were measured using nanoindentation with a Berkovich diamond indenter. The bulk modulus and shear modulus were derived based on an isotropic model and then plotted as a function of hardness. A strong correlation is observed between the hardness and shear modulus for these transition metal diborides. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2946665]

Hard and superhard materials are of great interest because of their widespread industrial applications as abrasives, cutting tools, and in wear prevention. Superhard materials are often defined as having a microhardness exceeding 40 GPa.[1] However, hardness is a complex parameter involving elasticity and plasticity and is governed by both intrinsic properties, i.e., bond strength, cohesive energy and crystal structure, and extrinsic properties, i.e., defects, stress fields, and morphology. In general, a superhard material possesses a high bulk modulus, a high shear modulus, and a high shear strength.[2] A material with a high bulk modulus tends to elastically resist volume compression, while a material possessing a high Young's modulus tends to elastically resist linear compression. A material having a high shear modulus tends to resist elastic deformation in a direction different from that of the applied load thus resisting shape change rather than volume change. A material is considered to be hard if it resists plastic deformation involving irreversible motion of atoms with respect to each other via the creation and movement of dislocations. The activation and mobility of dislocations are governed by the resolved shear stress. However, the shear strength of a material is difficult to measure. Therefore, considerable effort has been devoted to correlate hardness with other physical properties such as bulk modulus[1,3,4] and shear modulus.[2,5,6]

A promising approach to design superhard materials is to combine transition metals possessing a high bulk modulus with small, covalent bond-forming atoms such as boron, carbon, nitrogen or oxygen.[7] Recently, both OsB_2 and ReB_2 have been experimentally demonstrated to have high bulk moduli of 365–395 (Ref. 8) and 360 GPa,[9] respectively, which are not that far from diamond (443 GPa).[10,11] The theoretical bulk moduli for OsB_2 and ReB_2 based on first-principles calculations have also been recently determined.[12–16] In order to elucidate possible relationships between hardness and elastic moduli, we report here on the hardness values and Young's moduli of three ultraincompressible transition metal diborides—RuB_2, OsB_2, and ReB_2—measured using nanoindentation techniques. The bulk and shear moduli are then calculated using an isotropic model and the correlation between hardness and stiffness is further examined.

RuB_2, OsB_2, and ReB_2 were synthesized by arc melting elemental boron with the metals Ru, Os or Re with an applied current of 80 A under an argon atmosphere at room temperature. The arc-melted crystals were crushed into powder and then characterized using a PANalytical XPert Pro x-ray powder diffractometer with Cu $K\alpha$ radiation. The experimental details are described in Ref. 9. The nanoindentation testing was performed using a MTS Nano Indenter XP instrument with a diamond Berkovich indenter. The hardness (H) and Young's modulus (E) were calculated using the method developed by Oliver and Pharr.[17]

The load-displacement curves with a 0.05 s^{-1} strain rate and 720 mN maximum load were performed on single grains for each of the three different transition metal diborides (Fig. 1). Under the same load, the diamond indenter penetrated deeper in OsB_2, and RuB_2 than into ReB_2, implying that ReB_2 is the hardest substance among these three transition

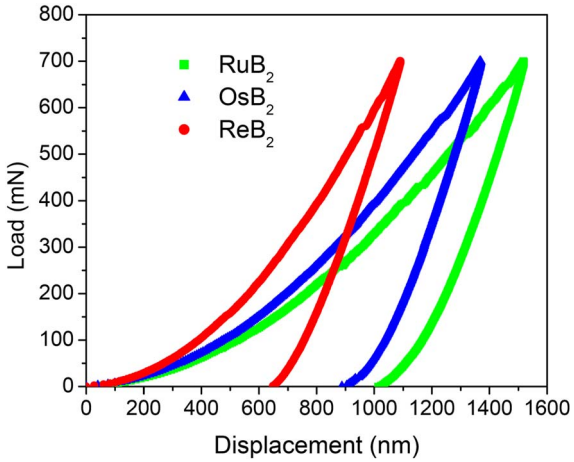

FIG. 1. (Color online) Load-displacement curves for RuB_2, OsB_2, and ReB_2 with the maximum load of 720 mN.

a)Author to whom correspondence should be addressed. Electronic mail: kaner@chem.ucla.edu.

TABLE I. The hardness H, Young's modulus E, and Poisson's ratio ν, for RuB_2, OsB_2, and ReB_2.

Material	H (GPa)	E (GPa)	$E_{\text{first-principles calculation}}$ (GPa)	ν
RuB_2	19.2 ± 2.1	366 ± 45	⋯	0.27[a]
OsB_2	21.6 ± 3.0	410 ± 35	426–444[a]	0.27[a]
ReB_2	37.0 ± 1.2	712 ± 43	683–699[b]	0.18[b]

[a]Reference 12.
[b]Reference 16.

metal diborides. The average measured hardness values are 19.2 ± 2.1, 21.6 ± 3.0, and 37.0 ± 1.2 GPa for RuB_2, OsB_2, and ReB_2, respectively. Clearly, ReB_2 is significantly harder than RuB_2 and OsB_2 and we believe it is the hardest of the known transition metal diborides. Note that the nanoindentation data for ReB_2 differ from our previously reported microindentation values,[9] since the Vicker's technique measures the residual indent without taking into account the material's elastic response.

Since the Poisson's ratios (ν) of these three transition metal diborides have not been experimentally measured yet, the theoretical values recently reported, 0.27 for RuB_2 and OsB_2 (Ref. 12) and 0.18 for ReB_2,[16] were used to calculate the Young's moduli. The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. The smaller Poisson's ratio for ReB_2 compared to OsB_2 and RuB_2 indicates a stronger degree of covalent bonding resulting in the higher hardness. The measured Young's moduli are compared with those predicted from first-principles calculations, as given in Table I. Both of the experimental Young's moduli for OsB_2 and ReB_2 are in good agreement with the theoretical values. In addition, ReB_2 possesses the highest measured Young's modulus, 712 ± 43 GPa, of any known transition metal diboride. This can be compared to, for example, the Young's modulus of TiB_2, 446–540 GPa.[18]

As seen in Fig. 1, the loading curves for RuB_2, OsB_2, and ReB_2 contain multiple pop-in events. The mechanisms of pop-in events observed in other materials are associated with a burst of dislocations, cracking, and elastic-plastic deformation transitions.[19–22] However, the discontinuities reported here result from crack initiation and propagation around the indentations, since there are no cracks observed near the indentation when the applied load is lower than that for the first pop-in event. In OsB_2, cracks form in grains oriented with the {010} planes at the lower critical force.[23] In contrast, a higher critical force is needed to produce cracks for grains less oriented with the {010} planes. In ReB_2, the critical force for the first pop-in event is about 600 mN and the deviation is not significant due to less asymmetry in hexagonal ReB_2 when compared to orthorhombic OsB_2. Additionally, the length of the crack surrounding the indentation impression is much shorter for ReB_2 than that observed within OsB_2. In RuB_2, there are few visible cracks found around the residual indentation impression. These results indicate that the critical forces needed to cause pop-in events depend on the materials, crystallographic orientation, and quality (i.e., impurities, defects, etc.) of the grains.

Gou *et al.*[12] and Wang[24] have demonstrated that OsB_2 and ReB_2 have little elastic anisotropy; therefore, an isotropic model is used to estimate the bulk modulus (B) and shear modulus (G) based on the Young's modulus (E) derived from nanoindentation experiments carried out on these three transition metal diborides. The calculated bulk and shear moduli are compared with first-principles calculations and x-ray experimental data in Table II. Both the bulk modulus and shear modulus of ReB_2 calculated from an isotropic model are in excellent agreement with those based on x-ray measurements and first-principles calculations. The measured bulk modulus for OsB_2 ranges from 365–395 GPa depending on the value of B_0' used in the Birch–Murgnaham equation of state.[8] Theoretical calculations of the bulk modulus for OsB_2 based on first-principles calculations are reported to be 307–365 GPa.[12–15] However, the bulk modulus derived from an isotropic model is 297 ± 25 GPa which is 18%–25% smaller than the x-ray measurement and lies within the lower bound of the first-principles calculation. Additionally, the shear modulus reported here is also within the lower bound of the first-principles calculation. For RuB_2, the isotropically calculated (265 ± 33 GPa) and experimentally measured bulk modulus (281 GPa when B_0' is set to 4) are consistent with each other. However, the bulk modulus (335 GPa) based on first-principles calculation is 16%–21% higher since the exchange-correlation energy function is treated with the local density approximation, resulting in an underestimation for the equilibrium volume, and thus an overestimation for the bulk modulus.[13]

As mentioned earlier, many attempts have been made to correlate hardness with other physical properties for a wide range of hard materials.[1–6] The hardness as a function of bulk modulus and shear modulus for the transition metal diborides RuB_2, OsB_2, and ReB_2 are plotted in Figs. 2(a) and 2(b), respectively. The data of hardness versus shear modulus lie along the same straight line, while the data of hardness versus bulk modulus scatter away from a linear relationship. This is likely due to the bulk modulus' dependency on the spatially averaged electron density within the three-dimensional densely packed networks without respect to the

TABLE II. The bulk modulus B and shear modulus G for RuB_2, OsB_2, and ReB_2.

	B (GPa)	$B_{\text{x-ray}}$ measurement (GPa)	$B_{\text{first-principles}}$ calculation (GPa)	G (GPa)	$G_{\text{first-principles}}$ calculation (GPa)
RuB_2	265 ± 33	281	335[c]	144 ± 18	⋯
OsB_2	297 ± 25	365–395[d]	307–365[a,c,e,f]	161 ± 14	168–254[a,c]
ReB_2	371 ± 22	360[g]	347–377[b]	302 ± 18	285–299[b]

[a]Reference 12.
[b]Reference 16.
[c]Reference 13.
[d]Reference 8.
[e]Reference 14.
[f]Reference 15.
[g]Reference 9.

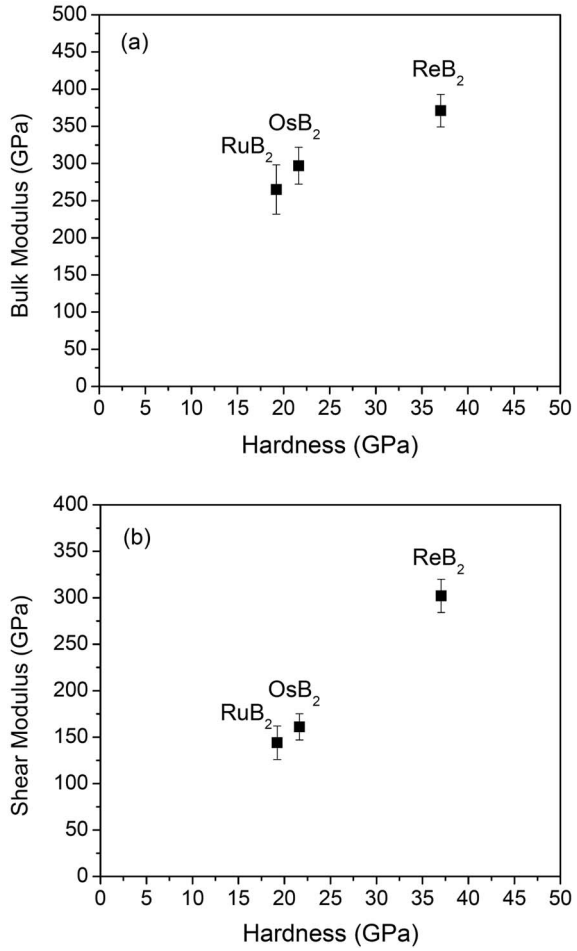

FIG. 2. Hardness as a function of the (a) bulk modulus and (b) shear modulus for selected transition metal diborides.

type of bonds formed, i.e., metallic, ionic or covalent. On the other hand, the shear modulus is sensitive to the nonuniform distribution of valence electron density corresponding to the kind of directional bonds that in turn act as barriers for dislocation movement. Therefore, the shear modulus is a significantly better qualitative predictor of hardness than the bulk modulus. This result therefore may provide a guiding principle for seeking superhard transition metal borides since incompressibility (the reciprocal of bulk modulus) is a necessary but insufficient attribute of a hard material.

In summary, three ultraincompressible transition metal diborides—RuB_2, OsB_2, and ReB_2—were synthesized by arc melting at ambient pressure. The hardness and Young's modulus of ReB_2 measured using nanoindentation are 37 and 712 GPa, respectively. Thus, ReB_2 is currently the hardest known transition metal diboride. Bulk and shear moduli were derived using an isotropic model and then plotted versus hardness. A strong correlation is observed between the hardness and shear modulus for the transition metal diborides resulting from the sensitivity of shear modulus on the directionally nonuniform distribution of valence electron density.

This work was funded by the National Science Foundation under Grant No. DMR-0453121 (R.B.K.) and CMS-0307322 (SHT). The authors thank Dr. J. Gilman, Dr. R. Cumberland, and Jonathan B. Levine for their assistance with this research.

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