Osmium Diboride, An Ultra-Incompressible, Hard Material

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Ultra-incompressible, hard materials are of great interest due to their usefulness in a wide variety of industrial applications. These include abrasives, cutting tools, and coatings where wear prevention, scratch resistance, surface durability, and chemical stability are a priority.[1,2] Therefore, the development of a new class of hard materials is of great practical interest. In this paper, we demonstrate that valence electron density and bond covalency can be used as design parameters for creating ultra-incompressible, hard materials. As an example, we report on the synthesis, bulk modulus, and preliminary hardness testing of osmium diboride, OsB_2.

The incompressibility (bulk modulus) of a wide variety of substances can be directly correlated with their valence electron densities, electrons/$Å^3$.[3] For example, diamond, the hardest known substance, has a high valence electron density (0.705 electrons/$Å^3$) and an exceptionally high bulk modulus ($B_0 = 442$ GPa).[4] Since high bulk modulus is often correlated with hardness, maximizing the valence electron density is a potentially useful design parameter.[5,6] Osmium has one of the highest valence electron densities for a pure metal (0.572 electrons/$Å^3$), and recent measurements of its bulk modulus give values in the range of 395–462 GPa.[7–9] However, while the bulk moduli of diamond and osmium are very close, their hardnesses vary greatly. Diamond has a hardness of 8000–10 000 kg/mm^2, while osmium metal has a hardness of only 400 kg/mm^2.[10,11] This deviation can be explained simply: osmium has metallic bonds, whereas diamond possesses covalent bonds. The atomic orbitals in diamond are all sp^3 hybridized and overlap to form short, directional, highly covalent bonds in an infinite tetrahedral network. The strength and directionality of the bonds determine a material's ability to resist deformation.[5,12] In contrast, osmium's hexagonal close-packed (HCP) crystal structure has a Fermi-liquid of valence electrons which do not participate in localized or directional bonding and, consequently, offer little resistance to dislocation motion.[13]

While many transition metals are soft in their pure elemental state, they can be converted into hard materials by combining them with small, covalent main group elements, such as boron, carbon, or nitrogen. For example, consider the third row transition metal tungsten. The hardness of tungsten is increased from 900 to 1400 kg/mm^2 by the addition of boron to form tungsten diboride, WB_2. Alternatively, tungsten can be combined with carbon to form tungsten carbide, WC, which increases its hardness to 3000 kg/mm^2.[10]

Applying this idea, we incorporated boron atoms into osmium metal to create localized covalent bonding and, thus, improve its hardness. Directional covalent bonding has also been suggested in ab initio calculations carried out on a related material, RuO_2. Here Ru d- and O p-orbitals overlap, resulting in covalent bonding and a high calculated bulk modulus both for this material and for its osmium analogue, OsO_2.[6] Other potentially hard compounds include osmium carbides and nitrides. However, attempts to synthesize OsC were unsuccessful, and OsN was only recently observed spectro-

scopically and has not yet been obtained in a crystallographically pure form.[14] Because of boron's small size (0.87 Å) and electron accepting properties, it can be inserted into the interstices which comprise 26% of HCP osmium to form OsB_2 (valence electron density = 0.511 electrons/$Å^3$) while retaining nearly all of the high valence electron density of osmium metal. The incorporation of boron slightly perturbs the hexagonal structure of Os metal into the related body-centered orthorhombic structure. Both structures have a similar overall geometry, but the order in the $a–b$ plane of OsB_2 is distorted from hexagonal close-packed into an orthorhombic structure with inequivalent a and b parameters. This material should combine a high bulk modulus with high hardness. Although the crystal structure of osmium diboride is known, its mechanical properties are not well characterized.[15,16]

Two synthetic methods were employed to form OsB_2. In both methods, vacuum or inert atmosphere was used to prevent formation of osmium tetroxide, which is a hazardous compound. In the first method, MgB_2 was used as a precursor in solid-state metathesis reactions.[17] The reaction of a 2:3 mixture of $OsCl_3$:MgB_2, initiated with a resistively heated Nichrome wire, self-propagated and went to completion in less than 1 s. After washing away the $MgCl_2$ byproduct salt, X-ray diffraction indicated the formation of OsB_2 along with Os_2B_3, OsB, and Os. Heating this product with a 3 M excess of boron at 1000 °C for 3 days yielded OsB_2 as the only crystalline product. In the second method, a 1:2 molar ratio of Os:B heated at 1000 °C produced a mixture of osmium borides. However, using a 1:5 molar ratio of Os:B, as suggested from our experience with the metathesis reactions, and heating at 1000 °C for 3 days yielded phase pure crystalline OsB_2 and amorphous boron. This material was used to determine bulk modulus and hardness.

The compressibility of OsB_2 was measured using high-pressure X-ray diffraction in a Diacell diamond anvil cell with ethylcyclohexane as the pressure medium. Diffraction patterns were collected from ambient pressure to 32 GPa on beamlines 11.3.1 and 7.3.3 at the Advanced Light Source at LBNL. Application of high pressures produced remarkably small shifts in peak positions, indicating a small volume compressibility, that is, a large bulk modulus (B). The data were fit using the third-order Birch–Murnaghan equation of state to calculate both the zero pressure bulk modulus, B_0, and its derivative with respect to pressure, $B_0′$ (Figure 1).[4,18] The resulting value is $B_0 = 365$ GPa if $B_0′$ is fixed to the canonical value of 4. However, if $B_0′$ is allowed to freely vary, the resulting bulk modulus is 395 GPa and the first derivative is 1.4. Because $B_0′ = 1.4$ is lower than that obtained for most materials, we can only conclude that the actual bulk modulus is in the range of 365–395 GPa. All values in this range are exceptionally high, exceeding or matching other hard materials, including boron carbide (B_4C, $B_0 = 200$ GPa), silicon carbide (SiC, $B_0 = 248$ GPa), sapphire (Al_2O_3, $B_0 = 252$ GPa), and cubic boron nitride (c-BN, $B_0 = 367$ GPa), and approaching that of diamond ($B_0 = 442$ GPa).[20]

Like the volume of the unit cell of OsB_2, the individual axes also change linearly with increasing pressure. However, because

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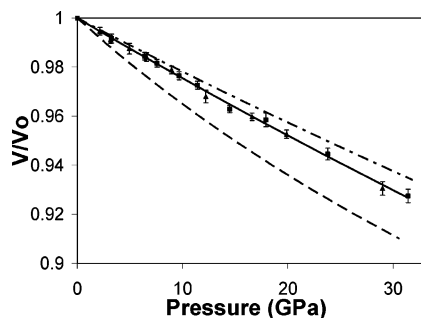
Figure 1. Pressure versus fractional unit cell volume for OsB_2 ($\blacksquare$, $\blacktriangle$, and —), corundum (- - -), and diamond (- $\cdot$ -).[19] Both the literature curves and OsB_2 fit correspond to the third-order Birch−Murnaghan equation of state: $P = (^3/_2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - (^3/_4)(4 - B_0')[(V/V_0)^{-2/3} - 1]\}$.
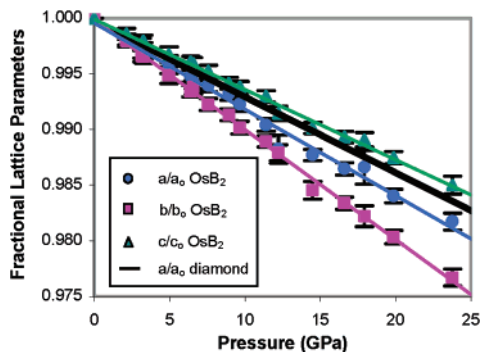

Figure 2. Comparison of the compressibility of the individual lattice parameters of OsB_2 with diamond. The a (blue), b (pink), and c (green) parameters in OsB_2 are fit with straight lines, while the diamond line (black) is taken from ref 4. Note that the c-axis in OsB_2 is less compressible than diamond.
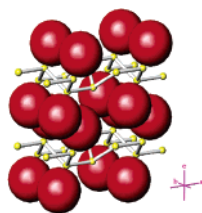
Figure 3. Crystal structure of orthorhombic osmium diboride. Osmium atoms are shown as red spheres and boron atoms as yellow spheres.

the OsB_2 unit cell is not cubic, compression of the axes shows interesting anisotropy (Figure 2). The b-direction of the crystal is most compressible, while the c-direction is the least compressible. Remarkably, the compressibility of OsB_2 along the c-axis (001) is even less than the analogous linear compressibility of diamond. This variation in compressibility among the axes can be understood by analysis of the orthorhombic crystal structure of OsB_2 (Figure 3). In the a- and b-directions, the boron and osmium atoms are arranged in planes that are offset from each other. Upon compression, the boron and osmium atoms are not pushed directly into each other and, therefore, the electrostatic repulsion, which maximizes incompressibility, is not optimized. In contrast, along the c-direction, the boron and osmium atoms are almost directly aligned, resulting in highly repulsive electronic interactions. This result implies that higher symmetry borides, where boron is more evenly distributed throughout the crystal lattice, could show more isotropic and potentially higher incompressibilities.

A preliminary hardness characterization of OsB_2 was done with a qualitative scratch test. The Mohs hardness scale (1−10) ranks the relative hardness of a material based on its ability to scratch another material. Osmium diboride was compared to sapphire, which is a 9 on the Mohs scale (diamond is a 10). A sample of OsB_2 powder readily scratches a polished sapphire window (Figure 4).
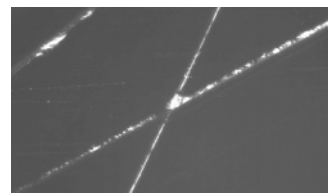
Figure 4. Sapphire window scratched by OsB_2 powder under 500X magnification. The image was taken with an optical microscope.

This measurement provides a sense of relative hardness. However, the hardness of sapphire is 2000 kg/mm², and the hardness of diamond is 8000−10 000 kg/mm².[11] While there is significant variation between these values, it establishes a lower limit for the hardness of OsB_2 at $\geq$2000 kg/mm². More quantitative measurements are now in progress using micro- and nano-indentation techniques.

The measured incompressibility and hardness of OsB_2 demonstrate that it is possible to apply design parameters for the synthesis of highly incompressible, hard materials. By combining small, light, main-group elements with large, electron-rich transition metals, it is possible to build in covalency while maintaining extremely high electron density. Like osmium, ruthenium also has a high electron density, and our preliminary experiments indicate that RuB_2 also has a high bulk modulus. Because hardness is known to increase when two dissimilar phases are intermixed, it may also be possible to exceed the bulk modulus and hardness of either OsB_2 or RuB_2 with a solid solution between Os and Ru, that is, $Os_{1-x}Ru_xB_2$. Given the possible atomic permutations that follow the concepts presented here, it is likely that other combinations might lead to materials with even more impressive mechanical properties.

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