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New Hard and Superhard Materials: $RhB_{1.1}$ and $IrB_{1.35}$

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Hard and superhard materials possess a combination of outstanding properties, such as high elastic modulus and hardness, scratch resistance, chemical stability, and the ability to sustain extreme differential stresses, which makes them promising materials for various technological applications. Nowadays, the experimental and theoretical efforts are focused on the design and discovery of new superhard materials. Hardness is a measure of structural stability, which is in turn determined by elastic stiffness and plastic resistance, which depend on bonding type (electronic structure). Two design parameters are of utmost importance for the selection of superhard compounds, i.e., a high valence electron density and the presence of covalent bonding.[1,2] High value of bulk modulus is not a direct predictor of high hardness, but provides some guidance toward finding high hardness, a starting point. Some authors[2−4] believe that shear modulus—a measure of resistance to shape change—is more pertinent to hardness and, therefore, a key to providing high hardness. A correlation between hardness and Young and shear moduli has been reported in the literature. [1−3,5] To the group satisfying all the mentioned above parameters belong the compounds of transition metals with light elements, such as boron, carbon, nitrogen, and oxygen, which can be synthesized in a comparably simple way at ambient pressure, avoiding extreme conditions. [1,2,6,7]

Very recently, the superhardness of one of the transition metal borides, ReB_2 (55.5 GPa), was discovered,[7] whereas OsB_2 and RuB_2 were found to be hard.[5,6,8,9] Despite all the research activity into the synthesizing of superhard materials, many opportunities still remain unexplored. In the present work, the choice of elements to be coupled with boron was determined by high values of their shear moduli. The element with the highest shear modulus is C (diamond). The runner-up to diamond is Ir among the known values, whereas that of Rh is lower but still among the highest.[2] Therefore, it is expected that rhodium and iridium borides have high hardness. This study focused on the synthesis of $RhB_{1.1}$ and $IrB_{1.35}$ bulk materials, which were characterized by X-ray diffraction and microindentation techniques.

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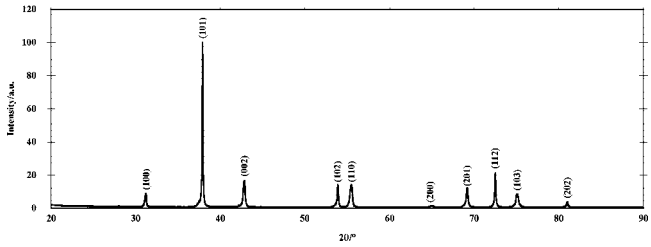

Figure 1. X-ray powder diffraction pattern of $RhB_{1.1}$.

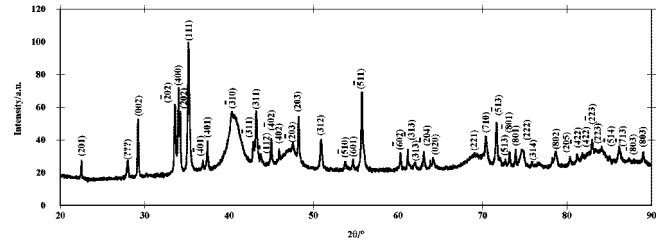

Figure 2. X-ray powder diffraction pattern of $IrB_{1.35}$.

For rhodium and iridium boride ($RhB_{1.1}$ and $IrB_{1.35}$) synthesis, an electron beam apparatus[10] was used. Rhodium powder (Engelhard, ~325 mesh, purity >99%) and crystalline boron powder (Alfa Aesar, ~325 mesh, purity 98%), used in stoichiometric amounts, were carefully mixed in an agate mortar with the addition of acetone to facilitate intimate mixing. After the mixing and drying procedure, the obtained powder was cold pressed into a pellet (diameter 18 mm). The pellet, contained in a TiB_2/BN composite crucible (GE Advanced Ceramics, U.K.), was positioned into the pocket of an electron beam gun (model EV1-8, Ferrotec, Germany) inside a high vacuum chamber, evacuated by a turbo pump. The pellet was melted twice (the second melting was performed after the repositioning of the pellet upside-down), so to ensure the completeness of the reaction. The pressure inside the chamber during the synthesis was about 1×10^{-4} Pa. For the melting process, an accelerating voltage of the electron beam of −3.5 kV and an emission current in the range of 30−100 mA were used. Iridium boride, $IrB_{1.35}$, was synthesized according to the same procedure adopted for the synthesis of rhodium boride. In this case, iridium powder (Chempur, <60 μm, purity 99.9%) and boron powder were taken in molar ratio of 1:1.5, respectively, in order to compensate the evaporative loss of boron during the synthesis, because its vapor pressure is sensibly higher than that of iridium in all the functional temperature range.[11] All the other operating conditions were the same as above.

$RhB_{1.1}$ and $IrB_{1.35}$ were analyzed using a Panalytical X'Pert Pro powder diffractometer (Bragg-Brentano geometry, Cu $K_{\alpha 1}$ radiation, $\lambda = 1.54056$ Å) equipped with a gas filled proportional detector. For both samples $\theta-\theta$ scans were performed, using an incident beam slit of 1° coupled with a 10 mm mask, a collimator of 0.04 rad and a Ni filter for the K_β component of the Cu radiation. For the analyses, pieces of the electron beam synthesized materials were crushed in an agate mortar in order to obtain fine powders suitable for diffraction analysis. The diffraction patterns were collected in the angular range of 20−90°. Once collected, the diffractograms were analyzed using the MAUD Rietveld software package. By means of the Rietveld method, refined unit-cell parameters were obtained, and the crystallite size and the r.m.s. microstrain analyses were performed.

The diffractograms reported in Figures 1 and 2 refer, respectively, to $RhB_{1.1}$ and $IrB_{1.35}$ powder samples.

The diffractograms clearly show that in both cases the samples are phase pure. $RhB_{1.1}$ possesses hexagonal crystal structure (space group $P6_3/mmc$, No.194, $a = 3.309$ Å, $c = 4.224$ Å[12]), whereas $IrB_{1.35}$ is monoclinic (space group $C2/m$, No.12, $a = 10.525$ Å, $b = 2.910$ Å, $c = 6.099$ Å, $\beta = 91.0°$[12]). In the case of the $IrB_{1.35}$ pattern, a peak at 28° could not be assigned.

The refined structural parameters obtained for $RhB_{1.1}$ powder are: $a = 3.3100$ Å and $c = 4.2242$ Å, whereas those for $IrB_{1.35}$ powder are: $a = 10.523$ Å, $b = 2.8979$ Å, $c = 6.1003$ Å, $\beta = 91.143°$, in excellent agreement with the reference data. In both cases, the crystallite size is in the hundred of nanometers range and the r.m.s. microstrain is not significant.

Vickers microhardness measurements were carried out by means of a Leica VMHT microhardness apparatus (Leica GmbH, Germany) equipped with a standard Vickers pyramidal indenter (square-based diamond pyramid of face angle 136°). During the hardness measurements, the indenter is pressed into the material under a defined load, and after unloading, the average value of the two diagonals of the plastic deformation remaining is measured by means of a microscope. The Vickers hardness is proportional to the ratio of the applied load and the area of the plastic deformation and is given in giga pascal units

$$H_v = \sin 68° P/D^2 = 1.8544 P/D^2$$

where P is the indentation load and D is the arithmetic mean of the two measured diagonals of the indent. The loading and unloading speed was 5×10^{-6} m/s and the time under the peak load was 15 s. Indentations were made with 6 loads ranging from 0.49 to 9.81 N. Standard deviation of the diagonal measurements was about 5−9% of the diagonal length. The number of indentations made at each load varied from 10 to 15.

In Figures 3 and 4, the experimental plots of Vickers hardness (H_v) versus the inverse imprint diagonal ($1/D$) for $RhB_{1.1}$ and $IrB_{1.35}$, respectively, are shown. The plots were fitted with a linear regression.

The experimental results obtained in this work for the boron-richest phases of the Rh−B and Ir−B systems and, for comparison, our previously published data[13,14] for ruthe-

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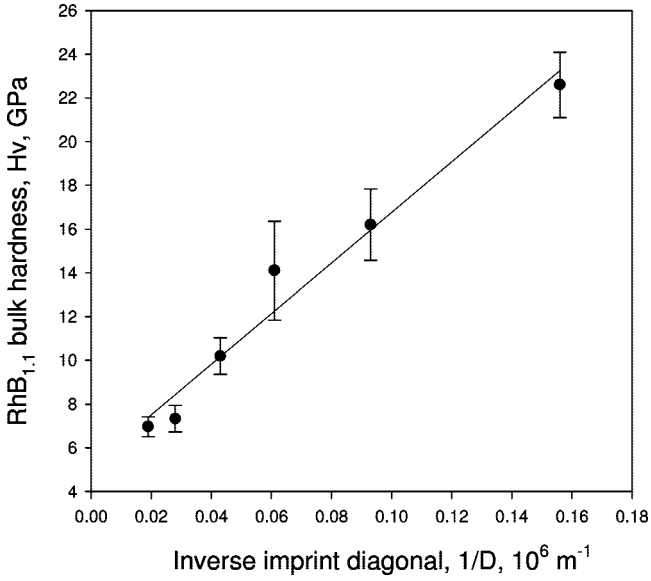

Figure 3. Hardness of $RhB_{1.1}$ versus inverse imprint diagonal.

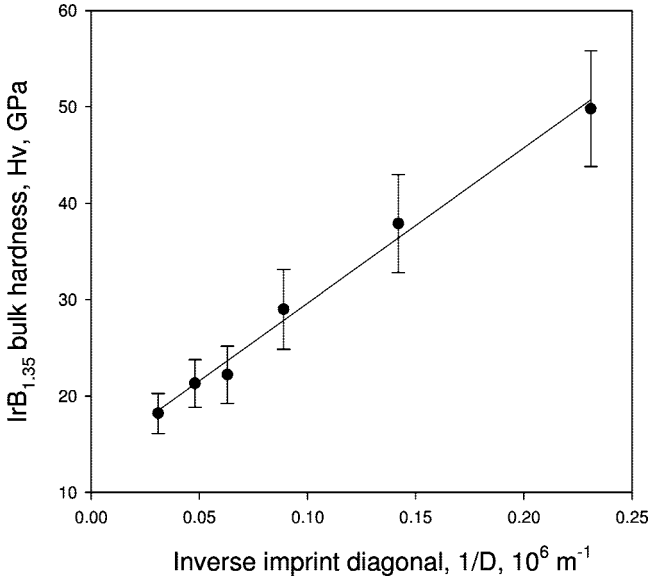

Figure 4. Hardness of $IrB_{1.35}$ versus inverse imprint diagonal.

nium and rhenium diborides are summarized in Table 1, where the load-dependent hardness data are presented. The data obtained in this work evidence much higher hardness of $IrB_{1.35}$ than that of $RhB_{1.1}$. Under 0.49 N of applied load, $IrB_{1.35}$ exhibits the maximum hardness of 49.8 ± 6.0 GPa; this value is very close to the hardness of ReB_2 reported in literature.[7,13] As the load was increased from 0.49 to 9.81 N, the average hardness decreased from 49.8 to 18.2 GPa. $RhB_{1.1}$ is much less hard: under 0.49 N of applied load, it exhibits a hardness of 22.6 ± 1.5 GPa. As the load was increased from 0.49 to 9.81 N, the average hardness decreased from 22.6 to 7.0 GPa. Therefore, the experimental

Table 1. Vickers Hardness of 5th and 6th period transition metal borides

	Vickers hardness (GPa)			
applied load (N)	RuB_2[14]	$RhB_{1.1}$ (this work)	ReB_2[13]	$IrB_{1.35}$ (this work)
0.49	17.0	22.6	49.9	49.8
0.98	14.8	16.2	35.5	37.9
1.96	14.3	14.1	34.3	29.0
2.94	11.8	10.2		22.2
4.90	11.2	7.3	25.6	21.3
9.81	10.9	7.0	20.8	18.2

results clearly show that for ReB_2 and $IrB_{1.35}$, in all the load region, the Vickers hardness is much higher than that for RuB_2 and $RhB_{1.1}$. Another simple evidence is that these two boride groups of transition metals belong to the 6th and 5th periods of the Mendeleev's periodic table, respectively.

In the introduction, we underlined the crucial role of shear modulus for material's hardness. The obtained results, however, could not be justified by the slightly higher value of Ir shear modulus rather than that of Rh.[2] Comparison of bulk moduli shows that for Re and Ir, these values are very close; the results are also close for Ru and Rh. It should be noted, however, that for the 6th period transition metals (Re and Ir), bulk modulus values are higher than those for the 5th period ones (Ru and Rh),[2] and hardness has the same trend (see Table 1).

Therefore, from the obtained results, it follows that the relationships between hardness and shear and bulk moduli should be further investigated, because neither shear nor bulk moduli values of the aforementioned borides could justify the experimentally obtained hardness trend. It is likely that other factors should be taken into account while predicting potentially superhard materials. On the basis of our experimental results, one can hypothesize that the electronic structure might be the reason, and some relativistic effects favoring the bond strength and likely stronger overlap between d orbitals of transition metals and 2p orbitals of boron.

In conclusion, phase-pure $RhB_{1.1}$ and $IrB_{1.35}$ bulk materials were synthesized. Powder X-ray diffraction patterns for both borides are presented, together with the Rietveld analysis results. Obtained Vickers microhardness data reveal the superhard nature of $IrB_{1.35}$: under 0.49 N of applied load, it exhibits a maximum hardness of 49.8 ± 6.0 GPa. $RhB_{1.1}$ bulk was found to be hard: under 0.49 N of applied load, it exhibits a hardness of 22.6 ± 1.5 GPa. The trend in hardness of borides of the transition metals belonging to the 5th and 6th periods of the periodic table of the elements likely could be explained taking into account the electronic structure and, namely, the factors influencing the bond strength. To understand this, further studies are needed, which, however, are out of the scope of this short communication.

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