

# Superhard Rhenium Diboride Films: Preparation and Characterization

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Recently, the superhardness of rhenium diboride was discovered. This study presents a first successful preparation and characterization of thin ReB<sub>2</sub> films. The films were deposited by the pulsed laser deposition (PLD) technique. The morphology, microstructure, and hardness of the films were investigated. The films are compact and continuous, with a preferred (002) orientation. The composite Vickers hardness of the film–substrate systems was measured, and the intrinsic hardness of the films was separated using an area law-of-mixtures approach taking into account the indentation size effect. The obtained films are found to be superhard: the intrinsic film hardness value (52 GPa) is close to that of the ReB<sub>2</sub> bulk.

## Introduction

Today, many technological processes require the use of hard coatings for cutting and forming tools in order to enable new machining processes and improve the lifetime of the tools. Carbides, borides, and nitrides of transition metals are widely used as hard coatings. However, the performance of hard coatings cannot fulfill the demands of some applications, and superhard coatings (“superhard” means materials whose Vickers hardness exceeds 40 GPa) are necessary in these cases. Diamond (first hardest material 70–100 GPa) and cubic boron nitride (c-BN) (second hardest material 45–50 GPa) are the most used materials in superhard coatings. But these two widely used substances suffer of severe limitations. In the case of diamond, it cannot be used for ferrous alloys (the most widely used ones) because of the tendency of carbon to dissolve in iron; also, diamond cannot be used at moderately high temperatures (>800 °C) because it transforms into graphite. Also c-BN suffers from reactivity issues toward Fe<sup>1</sup> (though much less than diamond), and the extremely high pressures needed for its synthesis (>5 GPa) make it expensive. To overcome these problems, research on other superhard materials continues animatedly. CrB<sub>2</sub><sup>2,3</sup> and TiB<sub>2</sub><sup>4,5</sup> superhard coatings have been studied widely; ultrahard fullerite<sup>6</sup> and aggregated diamond nanorods<sup>7</sup> have

been discovered, and the superhardness of boron suboxide<sup>8</sup> and boron carbonitride<sup>9</sup> has been established; finally, the evanescent compound  $\beta$ -carbon nitride ( $\beta$ -CN<sub>x</sub>) has been synthesized.<sup>10</sup> Also, OsB<sub>2</sub> was discovered to be very hard.<sup>11</sup> In recent years, films of two of these new superhard substances, i.e., boron suboxide B<sub>6</sub>O (though with no data on the hardness of the coatings)<sup>12</sup> and boron carbonitride BC<sub>2</sub>N,<sup>13</sup> have been realized. Very recently, a paper of Chung et al.<sup>14</sup> proposed a new superhard material that does not present chemical reactivity problems toward ferrous alloys and does not need high pressures to be synthesized, i.e., rhenium diboride ReB<sub>2</sub>. Authors<sup>14</sup> supposed this material as superhard by the optimization of two parameters: high valence electron density (Re has the second highest valence electron density of all the transition metals) and bond covalency (B, C, and N form the strongest covalent bonds). In fact, the tests (confirmed in the present work) showed that ReB<sub>2</sub> possesses a maximum Vickers hardness of 55.5 GPa<sup>14</sup> (it is harder than any other known metal diboride)

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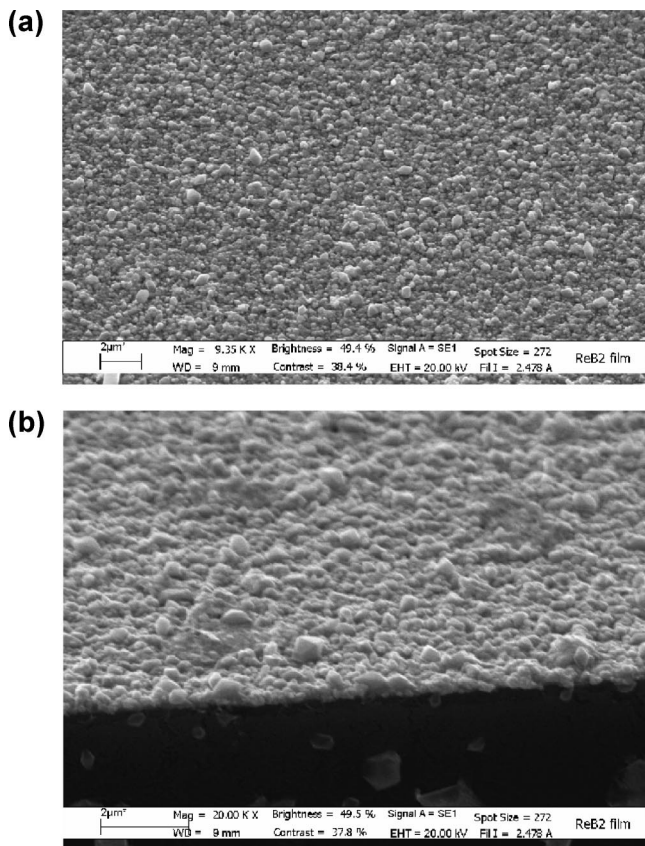
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**Figure 1.** SEM micrograph of ReB<sub>2</sub> film on SiO<sub>2</sub> substrate: (a) plane view; (b) cross-section view.

and is able to scratch diamond. The aim of this paper is to present the first successful deposition of ReB<sub>2</sub> films by the pulsed laser deposition (PLD) process and their characterization by means of morphological (scanning electron microscopy (SEM)) coupled with a system for microanalytical (energy-dispersive X-ray spectroscopy (EDXS)), structural (X-ray diffraction (XRD)), and mechanical (microindentation (Vickers hardness measurements)) techniques.

### Experimental Section

**Synthesis of the ReB<sub>2</sub> Target.** Rhenium diboride in bulk was synthesized by means of an electron beam synthesis technique, the details of which can be found elsewhere.<sup>15</sup> In brief, rhenium powder (Chempur, <10 μm, purity 99.99%) and crystalline boron powder (Alfa Aesar, ~60 mesh, purity 99.5%) in a 1:2.5 molar ratio, respectively, were carefully mixed in an agate mortar with the addition of some acetone to facilitate intimate mixing. Boron was used in excess in order to compensate the evaporation loss during the synthesis, because the vapor pressure of boron is much higher than that of rhenium. After the mixing procedure and the drying of the powder, the mixture was cold-pressed into a pellet (diameter 18 mm). The pellet, contained in a TiB<sub>2</sub>/BN composite crucible (GE Advanced Ceramics, UK), 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 two times (the second melting was performed after repositioning the pellet upside-down) so to ensure the completeness of the reaction. The pressure inside the chamber during the synthesis

was  $\sim 1 \times 10^{-4}$  Pa. For the melting process, an accelerating voltage of the electron beam of -3.5 kV and an emission current in the range 50–150 mA were used.

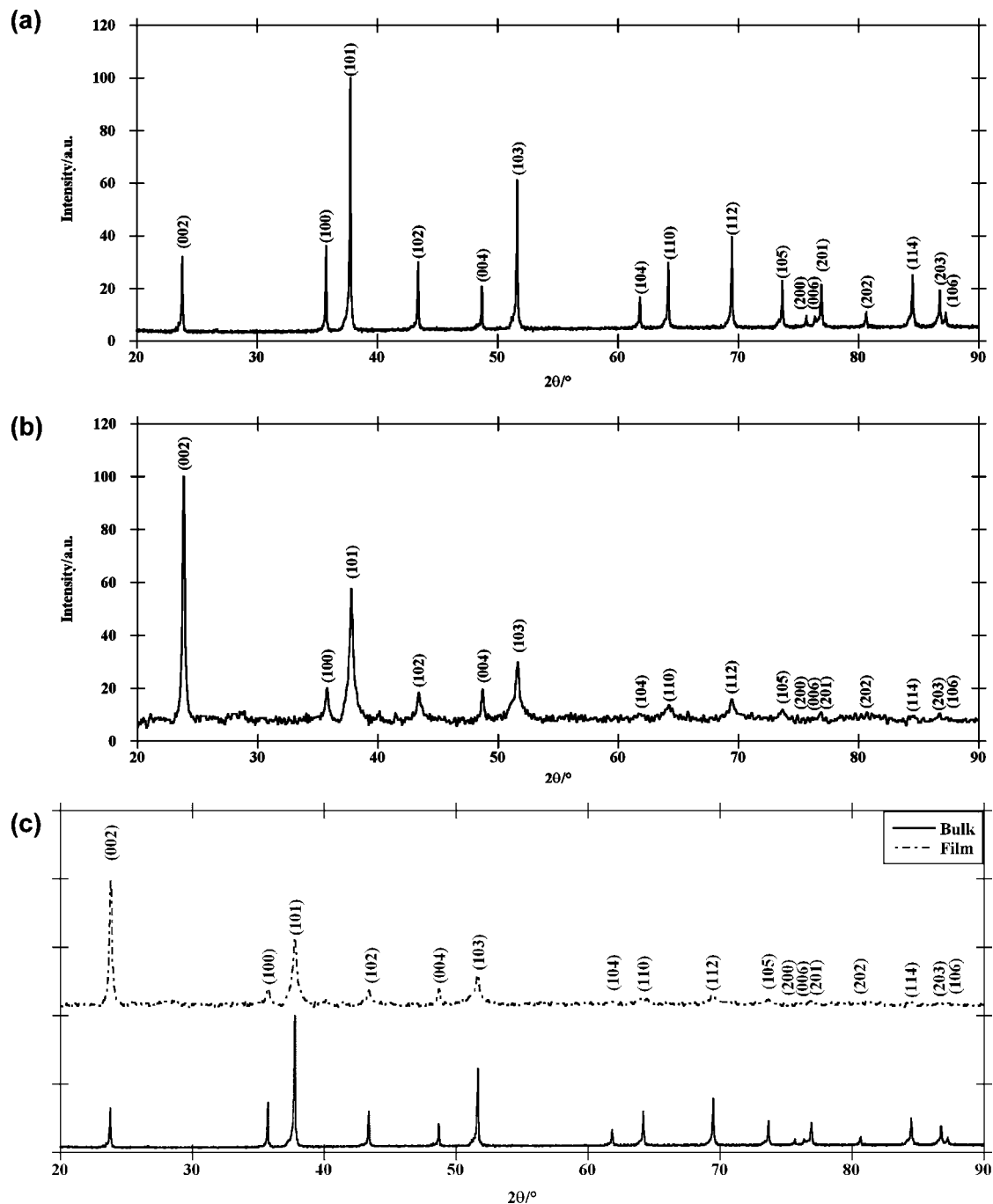
**Pulsed Laser Deposition.** ReB<sub>2</sub> films were deposited on the SiO<sub>2</sub> substrate (1 mm thick fused silica slides) by means of the PLD technique. In this technique a pulsed laser beam is focused on a target and the evaporated material is collected onto a substrate, placed in a suitable position, giving origin to a thin film. Our PLD apparatus for film deposition consisted of a multiport stainless steel vacuum chamber evacuated by a rotary-turbomolecular pumping system. The working pressure was  $4 \times 10^{-4}$  Pa. The chamber was equipped with a support for the target, rotating with a speed of 1 rpm to minimize craterisation effects, quartz windows for the inlet of the laser beam and a substrate holder, resistively heated. The ablation laser source was a frequency doubled Nd:glass laser ( $\lambda = 527$  nm,  $E = 2.8$  mJ, repetition rate = 10 Hz, pulse duration = 250 fs) from Light Conversion. The laser beam, focused by a suitable optical system, was oriented with an inclination angle of 45° with respect to the target and the spot area was 0.1 mm<sup>2</sup>. The SiO<sub>2</sub> substrate was kept in front of the ReB<sub>2</sub> target at a distance of 1.5 cm. The deposition time was 6 h and the films were deposited at 570 °C substrate heating temperature. The obtained films were dark colored.

**Scanning Electron Microscopy (SEM) Morphological Analysis.** Scanning electron microscopy technique (SEM) (a LEO 1450 variable pressure apparatus) working in secondary electron mode was used to observe the ReB<sub>2</sub> film. The SEM apparatus is coupled with a system for microanalysis (energy-dispersive X-ray spectroscopy, EDXS) INCA 300 that allows to perform qualitative/quantitative analysis of the elements. The atomic number contrast presented on the SEM images as gray color hues can be observed because of the ability of the Everhart Thornley detector to collect the part of the backscattered electrons allowed by the suitable geometry of sample and detector. This approach has been adopted for the film thickness measurements, since it permits to distinguish the precise film boundary. To confirm the results of the atomic number contrast, we have carried out the EDXS analysis of the chemical nature of the observed phase. The thickness of the ReB<sub>2</sub> film was estimated to be about  $0.30 \pm 0.05$  μm.

**X-ray Diffraction.** ReB<sub>2</sub> bulk and film were both analyzed using a Panalytical X'Pert Pro diffractometer (Bragg-Brentano geometry, Cu Kα<sub>1</sub> radiation,  $\lambda = 1.54056$  Å) equipped with a gas filled proportional detector. For both ReB<sub>2</sub> powder and film,  $\theta/2\theta$  scans were performed, using an incident beam slit of 1° coupled with a 20 mm mask. In both cases a collimator of 0.04 rad and a Ni filter for the removal of the Kβ component of the Cu radiation were used. For the bulk material, a sample for XRD analysis was obtained by crushing a piece of the electron beam synthesized target in an agate mortar (though with difficulty, because of the exceptional hardness of the material, that abrades the mortar) in order to obtain a fine powder. Once collected, the spectra were subtracted of the Kα<sub>2</sub> contribution via the diffractometer software (X'Pert graphics and identify). Rietveld analysis of the diffraction patterns was performed by using the MAUD (material analysis using diffraction) software package. From the Rietveld method, refined unit-cell parameters were obtained for both powder and film, whereas crystallite size, texture, and microstrain analyses were performed only for film.

**Vickers Hardness Measurements.** The microhardness measurements were performed by means of a Leica VMHT apparatus (Leica GmbH, Germany) equipped with a standard Vickers pyramidal indenter (square-based diamond pyramid of face angle 136°).

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**Figure 2.** (a) X-ray diffraction pattern of  $\text{ReB}_2$  powder; (b) X-ray diffraction pattern of  $\text{ReB}_2$  film on  $\text{SiO}_2$  substrate; (c) comparison of X-ray diffraction patterns of  $\text{ReB}_2$  powder and film.

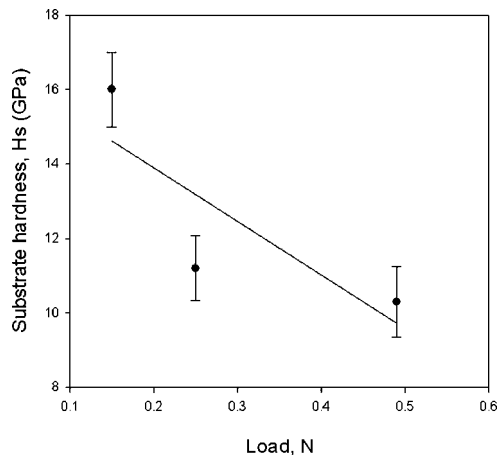
## Results and Discussion

SEM micrographs of PL deposited  $\text{ReB}_2$  films are shown in images a and b in Figure 1. In Figure 1a, the plane view of the film is presented, the film surface appears to be compact and continuous with a grain texture. In Figure 1b, the cross-section view is presented. According to the SEM-EDXS data, the Re/B atomic ratio in the films is close to its stoichiometric ratio of 1:2. As estimated by the SEM cross-sectional observation, thickness of the films is about  $0.30 \pm 0.05 \mu\text{m}$ .

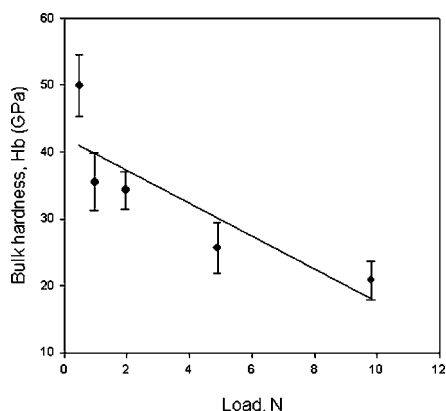
The X-ray diffraction patterns reported in panels a and b in Figure 2 refer to  $\text{ReB}_2$  powder and film, respectively,

whereas in Figure 2c, a comparison of the two is shown.  $\text{ReB}_2$  possesses hexagonal crystal structure (space group  $P6_3/mmc$ , No.194,  $a = 2.9 \text{ \AA}$ ,  $c = 7.478 \text{ \AA}$ <sup>16</sup>). The obtained refined unit-cell parameters are  $a = 2.9022 \text{ \AA}$ ,  $c = 7.4812 \text{ \AA}$  and  $a = 2.9035 \text{ \AA}$ ,  $c = 7.485 \text{ \AA}$ , for powder and film, respectively, both in excellent agreement with the reference data. No other Re–B phases were detected in the diffraction patterns. No significant microstrain was detected in the film. Considering the homogeneous grain texture of the film (as shown by SEM micrographs), the intensity of the (002) reflection in its XRD pattern suggests a preferred orientation

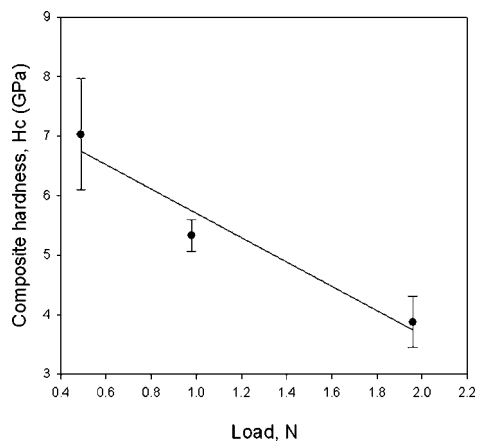
(16) Powder Diffraction File 2 Database JCPDS CARD 73-1392; International Centre for Diffraction Data: Newtown Square, PA.



**Figure 3.** Vickers hardness of SiO<sub>2</sub> substrate versus load.  $R^2$  value for the fitted line = 0.67.



**Figure 4.** Vickers hardness of ReB<sub>2</sub> bulk versus load.  $R^2$  value for the fitted line = 0.73.



**Figure 5.** Composite Vickers hardness of the film/substrate (ReB<sub>2</sub>/SiO<sub>2</sub>) system versus load.  $R^2$  value for the fitted line = 0.95.

along this direction. To take into account this effect in the Rietveld refinement procedure, a March–Dollase texture model was used; the obtained March–Dollase coefficient for the (002) reflection was 0.90. The refinement procedure gave an estimation of the average crystallite size of 100 nm, which agrees with SEM observations.

In Vickers hardness measurements, the measured hardness was that of the film–substrate composite system. The loading and unloading speed was  $5 \times 10^{-6}$  m/s, time under the peak load being 15 s. To separate the hardness of the film–substrate

system on its constituents from the film and the substrate, a model based on an area “law-of-mixtures” approach originally proposed by Jönsson and Hogmark was applied,<sup>17</sup> where the composite hardness  $H_c$  of the film–substrate system is expressed as

$$H_c = (A_f/A)H_f + (A_s/A)H_s \quad (1)$$

where  $A$  is total contact area;  $H$  is the hardness; subscripts f and s denote film and substrate, respectively;  $A = A_f + A_s$  is the total contact area. From the geometric considerations, eq 1 has been specified as follows

$$H_f = H_s + (H_c - H_s) / [2c(t/d) - c^2(t/d)^2] \quad (2)$$

where  $c = 2\sin^2 11^\circ \approx 0.07$  for hard brittle film on softer substrate;  $d = D/7$  (for Vickers pyramidal indenter) is the indentation depth, where  $D$  is the imprint diagonal;  $t$  is the film thickness. The model is applicable at large indenter penetration depth where the surface displacement is more than thickness of the film. The indentation size effect (ISE) was then taken into account.<sup>18,19</sup> The reasonable expression for the  $H_c$  based on an area law-of-mixtures approach and accounting for ISE is

$$H_c = H_{s0} + [B_s + 2c_1 t(H_{f0} - H_{s0})] / D \quad (3)$$

where  $c_1 = c(D/d) \approx 0.5$ ;  $H_{f0}$  and  $H_{s0}$  are the intrinsic hardness of film and substrate, respectively;  $B_s$  is the coefficient, which can be determined from a separate experiment on the substrate hardness. To calculate the intrinsic hardness of the film, we paid special attention to choose the indentation depths range correctly, i.e., in the interval where the model<sup>17</sup> is adequate. According to the estimations, the indentation load should be in the range from 0.49 to 1.96 N, corresponding to the relative indentation depth,  $d/t$ , from about 5 to approximately 15 providing the substrate-dominated mixed region where the film is fractured through thickness as it is bent to conform to the plastically deformed substrate.<sup>20</sup> Over this range of  $d/t$ , the estimations based on the Jönsson and Hogmark model have been demonstrated to produce the best fit to the experimental hardness data and to coincide well with the estimations resulting from more complicated models.<sup>20,21</sup> To evaluate  $H_{s0}$  and  $B_s$  values, we measured the intrinsic hardness of the SiO<sub>2</sub> substrate in a separate experiment. The experimental plot hardness of the substrate,  $H_s$ , versus load presented on Figure 3 was approximated well by a linear regression. A least-squares fit of the plots to eq 3 results in the slope  $B_c = B_s + 2c_1 t(H_{f0} - H_{s0})$ . Evaluated from this plot values of  $H_{s0}$  and  $B_s$  equal to 5.3 GPa and  $43.5 \times 10^{-6}$  GPa m, respectively.

The hardness of the melted ReB<sub>2</sub> bulk used as target for deposition was then measured. The indentations were made with 5 loads ranging from 0.49 to 9.81 N. The results are presented on Figure 4, where the experimental plot average hardness,  $H_b$ , versus load for the ReB<sub>2</sub> bulk is shown.

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The average bulk hardness increased from  $20.8 \pm 2.9$  to the maximum of  $49.9 \pm 4.6$  GPa under 0.49 N of load. The 49.9 GPa hardness value is in good agreement with the literature data<sup>14</sup> reported 55.5 GPa under the same load.

In Figure 5, the experimental plot composite hardness,  $H_c$ , versus load for the deposited ReB<sub>2</sub> film on the SiO<sub>2</sub> substrate is shown. The indentations were made with 3 loads ranging from 0.49 to 1.96 N. The plot was approximated well by a linear regression. A least-squares fit of the plots to the eq 3 results in the slope  $B_c = 57.5 \times 10^{-6}$  GPa m. Taking into account these data and the film thickness the intrinsic hardness for the deposited ReB<sub>2</sub> film is  $52 \pm 6$  GPa. The obtained value is close to that of bulk.

All the film samples present a very poor adhesion to the substrate. However, it might be easily improved, for instance, by using an interlayer of Cr between the film and the substrate and/or using a higher substrate temperature during

the deposition process. In our case, this last option was not possible due to the limited temperature range available in our instrument equipment (maximum of about 600 °C).

### Conclusion

Here, the first successful preparation of thin (0.3 μm) ReB<sub>2</sub> films is reported. The films were deposited by PLD technique on the SiO<sub>2</sub> substrates. The films were composed of ReB<sub>2</sub> phase without the evidence of other Re–B phases. From the X-ray diffraction analysis emerged the preferred (002) orientation of the films, with an estimated crystallite size in the ~100 nm range. The SEM analysis observations revealed the films to be compact and uniform. The obtained films exhibit a high hardness of  $52 \pm 6$  GPa, being close to that of the ReB<sub>2</sub> bulk and higher than any other metal diboride coating.

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