Self-passivating (Re,Al)B₂ coatings synthesized by magnetron sputtering

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(Re₀.₆₇Al₀.₃₃)B₂ and (Re₀.₇₄Al₀.₂₆)B₂ solid solution as well as Re₀.₈₅B₂ thin films were deposited by hybrid RF-DC magnetron sputtering. X-ray diffraction (XRD) showed that all films exhibit the ReB₂ (P₆₃/mmc) crystal structure. X-ray photoelectron spectroscopy (XPS) analyses performed on atmosphere exposed thin film surfaces suggest that ReB₂ corrodes, consistent with literature, by forming perhrenic acid (HReO₄) already after two days, while (Re₀.₇₄Al₀.₂₆)B₂ forms a self-passivating Al-oxide layer preventing corrosion in a time period ≥ 60 days. Hence, it is evident that Al additions to ReB₂ significantly increase the chemical stability during atmosphere exposure.

The increasing number of highly specialized industrial machining applications creates a demand for suitable new hard coating material systems. Commonly known superhard (H ≥ 40 GPa) materials such as diamond (up to 150 GPa), cubic BN (up to 80 GPa)¹, B₄O (up to 45 GPa)², and cubic B₁₃N (up to 75 GPa)³, are all electrical insulators and can sometimes not be utilized, e.g. during machining of ferrous alloys with diamond-like coatings⁴ due to carbide formation. Borides are used as hard and wear-resistant coatings⁵, e.g. in Al machining due to low Al adhesion on the coated tool surface⁶. ReB₂ (P₆₃/mmc), first synthesized in 1962 by La Placa et al.⁷, is metallic⁸ and was first suggested to exhibit a hardness above 40 GPa little more than a decade ago by Chung et al.⁹. Density functional theory calculations of ReB₂⁹–¹² show that B-B and Re-B bonds are short and highly directionally covalent, therefore strong, whereas Re-Re bonds are predominantly metallic.

Chung et al.⁹ reported a hardness of 48 GPa at 0.5 N indentation load which, however, decreased with increasing load down to 30 GPa at 5 N load. Other experimental studies report largely scattered values of measured hardness (H = 38(11) GPa⁴¹³⁻¹⁴, notation: average value (standard deviation on the last significant digits)). One reason for this scattering can be the presence Re₇B₃ phase impurities which are often reported¹⁷,¹⁹–²² and which highlight the necessity of obtaining phase-pure samples for a reliable characterization. Despite several of the studies mentioned above have suggested that ReB₂ may be a promising candidate for hard coating applications, only two studies have synthesized ReB₂ thin films by pulsed laser deposition¹⁵,¹⁸. Experiments employing methods which can be used on large industrial scales, such as magnetron sputtering, are yet lacking.

Besides the need for further research on thin film synthesis, there is a necessity to evaluate the material’s chemical stability. Two studies¹⁶,²³ reported formation of a viscous liquid layer on their samples exposed to air. Orlovskaya et al.²³ hypothesized that on their mechanically milled powders, Re₂O₇ and B₂O₃ oxides react with water from air and form perhrenic acid (HReO₄) and boric acid (H₃BO₃), respectively. Due to hygroscopicity of these acids, they may adsorb further water from air and continue to degrade the bulk material. The authors’ hypothesis was based on thermodynamic data and not proven experimentally. Very recently, Granados-Fitch et al.²⁴ extended Orlovskaya et al.’s work by experimentally studying the reaction of mechanically milled powders in humid air over duration of 26 months. Theses ReB₂ powders decomposed entirely into HReO₄ (liquid), H₃BO₃, HBO₂, and ReO₃. The corrosive reaction is possibly accelerated by the catalytic activity of perhrenic acid²⁵,²⁶.

Alloying of Al may represent a method to counteract the potential corrosive reaction. The addition of Al to TiN thin films results in the formation of alumina upon oxidation and an improved oxidation resistance of the ternary TiAlN, compared to the binary TiN²⁷. Even in borides with a small Al content, such as amorhous AlYB₁₀, Al is preferentially oxidized.²⁸ Furthermore, Al is not only known for its oxygen affinity and stable Al₂O₃ oxide which is commonly used as a diffusion barrier;²⁹ it also forms a hexagonal diboride AlB₂ (P₆₃/mmm) (though not isostructural to ReB₂ as B layers in AlB₂ are flat and not puckered). It has been shown previously that alloying W, which also forms a hexagonal diboride WB₂ (P₆₃/mmc) with both flat and puckered B layers, into ReB₂ can yield...
in solid solutions with high hardness (up to 48 GPa)\(^{29}\). Hence, it is promising to investigate Al solubility in ReB\(_2\) with its inherently strong B-B and metal-B bonds and the mechanical properties of such solid solution thin films.

Herein, it will be demonstrated that Re\(_{0.85}\)B\(_2\) as well as (Re\(_{0.67}\)Al\(_{0.10}\))B\(_2\) and (Re\(_{0.74}\)Al\(_{0.11}\))B\(_2\) thin films synthesized by RF-DC magnetron sputtering exhibit the ReB\(_2\) (\(\text{P6}_3\)/mmc) structure. Additionally, an investigation of surface chemical reactions by X-ray photoelectron spectroscopy (XPS) will show that the Re\(_{0.85}\)B\(_2\) thin film corroded upon exposure to atmosphere by forming perrhenic acid, whereas the (Re\(_{0.74}\)Al\(_{0.11}\))B\(_2\) thin film formed a passivating Al-oxide layer suppressing a corrosive reaction. Furthermore, nanoindentation data will be compared to ab initio predictions of the elastic properties.

**Results and Discussion**

Diffractograms of both Re\(_{0.85}\)B\(_2\) and (Re\(_{0.67}\)Al\(_{0.10}\))B\(_2\) films (Fig. 1., bottom and top curves, respectively) utilized for further mechanical characterization only display peaks attributable to the ReB\(_2\) crystal structure (JCPDS card 00-11-5081). No other Re-B phases or Al-borides are detected by XRD; hence, it is reasonable to assume that the 3.5 at.% Al in (Re\(_{0.67}\)Al\(_{0.10}\))B\(_2\) is dissolved in the ReB\(_2\) crystal lattice and a solid solution is formed. While the Al concentration induced changes in lattices parameters measured by XRD (\(\Delta a = +0.31\%\), \(\Delta c = -0.31\%\)) are opposite in trend to the values predicted by DFT (\(\Delta a = -0.08\%\), \(\Delta c = +0.25\%\)), it has to be noted that the magnitude of the obtained deviations are according to Paier et al.\(^{30}\) in line with the exchange-correlation functionals employed here.

The films appear slightly B over-stoichiometric, potentially resulting in segregation of an amorphous B tissue phase\(^{31}\) or Re sub-lattice vacancies\(^{32}\). This is not further investigated here. Considering the measurement technology (energy dispersive X-ray spectroscopy) inherent errors which, according to Goldstein et al.\(^{33}\) can be larger than ±5% (relative) for rough samples and compounds containing light elements, the stoichiometric diboride composition lies within the error bars. For the chemical quantification, only intentionally introduced elements are considered here; however the samples contain C (ca. 4.5 at.%), O (ca. 1.0 at.%) and Fe (ca. 1.0 at.%) impurities, probably stemming from the B targets, residual gas contamination\(^{34}\), and RF sputtered chamber walls, respectively.

Surface chemical reactivity of Re\(_{0.85}\)B\(_2\) in air was analyzed employing XPS measurements. The sample investigated here was transferred to the XPS system immediately after deposition. The initial air exposure time was less than 120 seconds. Subsequent measurements are conducted after exposing the sample to atmosphere for 2 days and 13 days. High resolution XPS spectra of the B 1s and Re 4f transitions are shown in Fig. 2(a,b), respectively. The bottom panels show the scans recorded right after the deposition. The minor signals that can be observed at lower binding energies next to the main signals are satellite peaks introduced by the non-monochromatic Al K\(_\alpha\) radiation. The main B 1s signal stemming from ReB\(_2\) is located at 187.9 eV. Information on the fitting of other components in the XPS spectra can be found in the supplementary material.

After two days in air, the lower peak-to-background ratio indicates a strongly decreased intensity of the B 1s signal. A strong new component emerges at 46.3 eV in the Re 4f scan, which can be assigned to the perrenhite ion (ReO\(_4\))\(^{2-}\). The ReO\(_4\)\(^{2-}\) ion is a constituent of Re\(_2\)O\(_7\), which, when solved in water, forms perrhenic acid\(^{35}\). After 13 days in air, the Re 4f signal consists almost completely of the ReO\(_4\)\(^{2-}\) component and the B 1s signal has entirely disappeared. Over less than two weeks, the surface of Re\(_{0.85}\)B\(_2\) becomes covered by several nanometers of perrhenic acid, taking into account that XPS depth resolution is in the order of a few nanometers and the B 1s signal is undetectable. Orlovskaya et al.'s\(^{28}\) hypothesis about and Granados-Fitch et al.'s\(^{24}\) observation of formation...
of perrhenic acid during atmosphere exposure mechanically milled powders are confirmed here for thin films. There is no evidence for the formation of boric acid or ReO$_3$ in this corrosion stage.

High resolution XPS spectra of the B 1 s, Re 4 f, and Al 2 s transitions of an (Re$_{0.74}$Al$_{0.11}$)B$_2$ film after different air exposure durations are shown in Fig. 3(a–c), respectively. The Al 2 s transition is used instead of the more commonly used 2p transition because the latter is convoluted with the Re 4 f energy loss background. After approximately six hours in air, there is only one Al-oxide component in the Al 2 s signal located at 119.0 eV, which coincides excellently with literature values of Al$_2$O$_3$ [36]. It should be noted that this means that the bonding environment and the resulting electron binding energy is comparable to that of Al$_2$O$_3$; it does not necessarily mean that the composition of the Al-oxide measured here is exactly that of Al$_2$O$_3$ and one cannot infer in which phase it is present. In the B 1 s scan, only the component of (Re,Al)B$_2$ at 187.4 eV can be observed. The Re 4 f signal, similar to the unalloyed sample, shows the main (Re$_{0.74}$Al$_{0.11}$)B$_2$ component located at 40.2 eV and a smaller component at 41.0 eV, which may originate from incipient oxidation or impurity bonds as discussed previously. After three days in air (measured but not shown in Fig. 3.), Al and B signals do not exhibit any change. A minor component located at higher binding energy (46.0 eV, labeled as ReO$_3$ here), which exhibits an oxidation state between ReO$_3$ and ReO$_4$−, emerges in the Re 4 f scan. After 16 days in air (center panels in Fig. 3), this component increases only minimally from 4.2 to 5.1% of the total integrated intensity. Al and B spectra do still not exhibit any change. After 66 days in air, small oxidized components (B$_{3-x}$O, B$_2$O) appear in the B 1 s spectrum; however, these components together make up only 13.7% of the total integrated intensity of the B signal, showing that B is not significantly oxidized after 66 days. The oxidized component in the Re 4 f spectrum, $i$, is increased to only 5.6% of the total integrated intensity after 66 days atmosphere exposure, so exhibiting approximately a 3.83 × $t^{0.09}$ dependence, where $t$ is the oxidation time in days. From a practical perspective, passivation of the film is achieved since $i$ increases by only 0.05% from 4.71% after 9 days to 4.76% after 10 days of the film air exposure. Furthermore, no N is detected in this film. Initially, Re oxidizes a little while the Al-oxide layer is not fully evolved; nonetheless, the Al-oxide seems to passivate the film in the long term. Even if this passivation is mechanically destroyed (e.g. by wear), the Al-oxide layer will be restored since Al is incorporated in the ReB$_2$ structure.

Hardness and elastic modulus measured by nanoindentation are given in Table 1. The Re$_{0.85}$B$_2$ film ($H_{exp} = 32$ GPa, $E_{exp} = 522$ GPa) does, on average, exhibit a hardness which is lower than the average of previously reported values ($H_{lit} = 38(11)$ GPa [13–38]) and the elastic modulus is 21.7% lower than theoretically predicted ($E_{DFT} = 667$ GPa). The standard deviation on both quantities is with 25.7% relatively large. The (Re$_{0.87}$Al$_{0.13}$)B$_2$ film, on the contrary, shows a higher hardness of 40 GPa, higher stiffness ($E = 562$ GPa, 7.7% higher than Re$_{0.85}$B$_2$), and lower standard deviations on the measured quantities. For both films, the indentation depth does not exceed the conventional 10% of the film thickness (Table 1); hence, a substrate influence is unlikely to explain the significant difference in measured mechanical properties. Instead, the measured surface roughness (Table 1) indicates that the Re$_{0.85}$B$_2$ film is much rougher than the (Re$_{0.87}$Al$_{0.13}$)B$_2$ film. The Re$_{0.85}$B$_2$ film’s measured root mean square surface roughness of 38(1) nm is considerably large compared to the indenter tip radius of 100 nm. When
indenting into a surface asperity, there is no continuous material on the sides opposing plastic deformation. The \((Re_{0.67}Al_{0.10})B_2\) film's surface roughness of 18(2) nm lies below the microscope's assumed resolution limit of 20 nm, suggesting 18 nm to be an upper limit of the surface roughness. The 100 nm radius indenter, therefore, indents into a continuous film rather than into surface asperities. This may contribute to the lower measured average and higher scattering of \(H\) and \(E\) of the rougher \(ReB_2\) film. The presence of porosity in the films may affect these quantities as well. A stark difference in surface roughness between the two films and indications for porosity in the \(Re0.85B2\) film can be seen in SEM images in the supplementary information in Figs S1 and S2.

In summary, \((Re_{0.67}Al_{0.10})B_2\) and \((Re_{0.74}Al_{0.11})B_2\) solid solution and \(Re0.85B2\) films were synthesized by hybrid RF-DC magnetron sputtering. All films crystalize in the \(ReB_2\) \((P6_3/mmc)\) crystal structure, as probed by XRD. \(Re0.85B2\) reacts in humid air and forms perrhenic acid already after two days of atmosphere exposure, as shown by XPS. This corrosive reaction renders unalloyed \(ReB_2\) coatings unsuitable for application in humid air. Upon atmosphere exposure at room temperature (\(Re_{0.74}Al_{0.11}\))B2, however, forms a self-passivating Al-oxide layer retarding the formation of perrhenic acid and, hence, corrosion. It is evident that Al additions to \(ReB_2\) significantly increase the chemical stability during atmosphere exposure.

**Methods**

**Experimental details.** \((Re_{0.67}Al_{0.10})B_2\), \((Re_{0.74}Al_{0.11})B_2\) and \(Re0.85B2\) films were deposited by magnetron sputtering at 900 °C in a vacuum chamber accommodating four magnetrons (50 mm diameter) tilted to the substrate normal by 20° at a substrate-target distance of 12.4 cm. The average base pressure laid below 6.67 \(\times 10^{-5}\) Pa \((5 \times 10^{-3}\) Torr) in a vacuum chamber accommodating four magnetrons (50 mm diameter) tilted to the substrate normal by 20° at a substrate-target distance of 12.4 cm. The average base pressure laid below 6.67 \(\times 10^{-5}\) Pa \((5 \times 10^{-3}\) Torr). Ar was used as sputtering gas at constant working pressure of 0.67 Pa \((5 \times 10^{-3}\) Torr). The substrates’ backsides were coated with Mo for a better intake of radiative heat from the heater and, prior to deposition, the substrates were baked out for 20 minutes at deposition temperature. Re and Al targets were sputtered with direct current (DC) power supplies, while two B targets, facing each other, were sputtered by radio frequency (RF) power supplies.

Two \(Re0.85B2\) samples were synthesized under identical conditions in the same batch \((20\) W at Re target, \(2 \times 148\) W at B targets, 150 minutes) on polished MgO substrates at symmetry-equivalent positions on a rotating sample holder. The \((Re_{0.67}Al_{0.10})B_2\) sample was taken from a selected area of a combinatorial deposition \((70 \times 148\) W at B targets, 150 minutes) on polished MgO. The \((Re_{0.74}Al_{0.11})B_2\) sample was taken from a selected area of a combinatorial deposition \((20 \times 148\) W at B targets, 150 minutes) on polished MgO.

![Figure 3. XPS scans of \((Re_{0.74}Al_{0.10})B_2\) films](image)

| Sample      | at.% B | at.% Al | \(H\) (GPa) | \(E\) (GPa) | \(E_{\text{DFT}}\) (GPa) | \(h\) (nm) | \(D\) (μm) | \(R_q\) (nm) |
|-------------|--------|---------|-------------|------------|-----------------------------|-----------|---------|------------|
| Re0.85B2    | 70.1   | 0.0     | 32(9)       | 522(134)   | 667                         | 90(17)    | 1.52(6) | 38(1)      |
| (Re0.67Al0.10)B2 | 72.4   | 3.5     | 40(5)       | 562(56)    | 621                         | 72(8)     | 1.83(9) | 18(2)      |

Table 1. Chemical composition and nanoindentation data for Re0.85B2 and \((Re_{0.67}Al_{0.10})B_2\) films. The columns display B and Al concentrations, average values of measured (standard deviation on the last significant digit is given in parenthesis) hardness, \(H\), elastic modulus, \(E\), indentation depth, \(h\), film thickness, \(D\), and root mean square surface roughness, \(R_q\).
B$_2$ sample was taken from a selected area of another combinatorial deposition (no rotation, 15 W at Re target, 5 W at Al target, 2 × 150 W at B targets, 60 minutes) on polished sapphire.

The phase composition was analyzed by X-ray diffraction (XRD) employing Cu K$_\alpha$ radiation (U = 40 kV, I = 40 mA) at a constant incident angle $\omega = 10^\circ$ and a 20 range from 10$^\circ$ to 100$^\circ$ in a Bruker AXS D8 Discover General Area Detection Diffraction System (GADDS). Cross-sectional scanning electron microscope (SEM) images, taken in a FEI Helios 660 system, were employed for film thickness determination. Root mean square surface roughness was measured by confocal laser scanning microscopy in a Keyence VK-9700 system (resolution limit ca. 20 nm) on 1000 $\mu$m$^2$ areas. Hardness and elastic modulus were investigated by nanoindentation with a 100 nm radius Berkovich diamond tip at 10 mN load in a depth-sensing nanoindenter (Hysitron TribolIndenterTM). 100 indentations were performed for each sample for sufficient statistics. A fused silica standard was measured before and after the deposited films was used to calibrate the tip area function. Load-displacement curves exhibiting pop-in events (only one) were not considered for analysis. The Oliver-Pharr method$^{37}$ was applied to obtain the reduced elastic modulus. A Poisson’s ratio of 0.18$^{38}$ was assumed for the samples to calculate the samples’ elastic moduli.

The chemical composition of the films was quantified by energy dispersive X-ray spectroscopy (EDX) with an EDAX Genesis 2000 analyzer in a JEOL JSM-6480 SEM at an electron beam acceleration voltage of 5 kV. Chemical composition of the synthesized films was measured directly after the deposition and samples were stored in a high vacuum vessel (5.5 × 10$^{-3}$ Pa base pressure) between all measurements due to the expected reactivity. One Re$_{0.85}$B$_2$ sample and the (Re$_{0.74}$Al$_{0.11}$)$_2$B$_2$ sample were stored in air to evaluate their chemical stability. Chemical states at the surface of these two samples were investigated by XPS in a JEL JAMP-9500F system with an Al K$_\alpha$, x-ray source (1486.5 eV), a hemispherical electron energy analyzer in fixed analyzer transmission mode with a pass energy of 20 eV, and an electron take-off angle perpendicular to the analyzer. The energy resolution is approximately 0.15 eV. For energy calibration, the Cu 2p 3/2 and 3p 3/2 lines (Ar$^+$ cleaned) were employed. Charging of the sample was corrected against the C 1 s peak (284.8 eV) of adventitious carbon. Voigt functions and Shirley backgrounds were used for fitting the data.

**Computational details.** Electronic structure calculations were used to calculate elastic properties of the pure ReB$_2$ system and systems in which Re is randomly substituted by varying concentrations of Al. The systems considered contained 0.0, 3.1, and 8.6 at% of Al. Values of calculated lattice parameters and elastic moduli for the experimentally found compositions have been linearly interpolated. All supercells contained 162 atoms. The computational details.

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Author Contributions

P.B. conceived, designed and performed the research and wrote the paper. S.M. and S.S. helped in the design of the research, performed some experimental aspects of the research and co-wrote the paper. O.H. and J.M.S. helped in the design of the research and co-wrote the paper.

Additional Information

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