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nc-MeB₂/a-MPEA structured (HfMoNbZr)_xTi_{1-x}B_y films for enhanced hardness, toughness and tribological performance

Jigang Xie^a, Yiming Ruan^a, Hao Du^{a,b,*}, Lin He^a, Jie Shi^c, Hengning Hu^c, Yun Chen^c, Liuquan Yang^d, Rui Shu^{e,**}

^a School of Mechanical Engineering, Guizhou University, Guiyang 550025, PR China

^b State Key Laboratory of Public Big Data, Guizhou University, Guiyang 550025, PR China

^c Chengdu Tool Research Institute CO., Ltd., Chengdu 610500, PR China

^d School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK

^e Department of Science and Technology, Linköping University, SE-60174 Norrköping, Sweden

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ABSTRACT

This study demonstrated the composite concept to precisely control the grain boundary composition to address TiB₂ films inherent brittleness. Such concept was realized by combining high-power impulse magnetron sputtering (HiPIMS) with direct current magnetron sputtering (dcMS). By employing an HfMoNbZr-HiPIMS/TiB₂-dcMS co-sputtering configuration, we successfully replaced the B in the grain boundaries with a B-containing amorphous multi-principal element alloy (MPEA). The results showed that TiB₂ film deposited by dcMS alone typically had an overstoichiometric composition, with a B/Ti ratio of 2.96, and a relatively low hardness (*H*) of 26.6 \pm 1.2 GPa. In contrast, the formation of a nanocomposite structure (nc-MeB₂/a-MPEA, i.e., nanocrystalline MeB₂ (Me = HfMoNbZrTi) embedded in an amorphous MPEA matrix), with MeB₂ in-plane grain sizes ranging from 2 to 5 nm, increased the hardness to 41.8 \pm 3.7 GPa, while also enhancing indentation fracture toughness and reducing wear rate. This strengthening mechanism was attributed to lattice distortion within the MeB₂ grains and the suppression of grain boundary sliding by the MPEA. In addition, density functional theory (DFT) calculations indicated that the higher bulk modulus (*B*) /shear modulus (*G*) ratio of the TM_{0.44}Ti_{0.56}B₂ (TM = HfMoNbZr) solid solution compared to TiB₂ suggested that the brittleness of the TM_{0.44}Ti_{0.56}B₂ solid solution was lower. This study paves a way for the structure design of diborides for various applications.

1. Introduction

Refractory transition metal based ceramics including carbides, nitrides, and borides, are well known for their high hardness, with some even classified as superhard materials [1–4]. The mechanical properties, such as toughness, and effective fracture resistance, can be effectively tailored by adjusting the valence electron concentration (VEC) [5–10]. This adjustment influences the population of shear-sensitive metallic states [11–13], thereby affecting the ability to deform plastically under loading. In nitrides and carbides, high hardness arises predominantly from robust non-metal-metal bonds, as demonstrated by chemical bonding analyses [5,11,12]. In contrast, the hardness of diborides is additionally attributed to strong B—B interactions. For many years, research in the film industry has focused on improving the properties of these materials for use as protective and functional films [14–18]. Among these, the transition metal diborides, which generally exhibit higher hardness than their nitride and carbide counterparts, have attracted considerable research interest [19,20].

Transition metal diborides typically possess a hexagonal AlB₂-type structure, where hexagonal metal atomic layers alternate with boron atom layers along the c-axis. The boron layers are graphite-like while the metal atomic layers are nearly densely packed [1]. There are three types of bonding in transition metal diborides, strong covalent bonding within the B atomic layer, metallic bonding within the metal atomic layer, and ionic-covalent bonding between the metal and the B atoms [21,22]. This unique structure imparts the material with both metal and ceramic properties, such as high hardness, high thermal and chemical stability, and good electrical conductivity [1]. These excellent properties make

** Corresponding author.

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^{*} Correspondence to: H. Du, School of Mechanical Engineering, Guizhou University, Guiyang 550025, PR China.

E-mail addresses: hdu3@gzu.edu.cn (H. Du), rui.shu@liu.se (R. Shu).

transition metal diborides ideal for a wide range of applications, including protective films for microelectronic components [23,24], thermal solar absorber [25], cutting tools [26,27], and components in the aerospace and nuclear industries [28,29].

Among the transition metal diboride family, TiB₂, is the most widely studied and used, where overstoichiometric TiB₂ films with a hardness exceeding 40 GPa have been reported under optimized conditions [30–33]. However, the application of TiB₂ films is greatly limited by their low oxidation resistance and intrinsic fracture toughness (~3.6 MPa $m^{1/2}$ [34]). In comparison, the fracture toughness of Ti-Al-N film could achieve \sim 8.0 MPa m^{1/2} [35]. In particular, TiB₂ films grown by conventional magnetron sputtering usually suffer from excessive boron at the grain boundary, depending on the deposition parameters such as working pressure and the target-to-substrate angle and distance [36–39]. This boron excess leads to oxidation at elevated temperatures, resulting in the formation of B₂O₃ gas, which easily evaporates and leaves behind a porous structure. This porosity creates pathways for oxygen ingress, accelerating the oxidation process [40-42]. Another critical issue with TiB₂ films, is their low intrinsic fracture toughness, primarily caused by the high stiffness of Ti—B and B—B chemical bonds and the inability of the material to yield before cleavage under tensile loading [43]. These challenges can be addressed by replacing amorphous boron at the grain boundaries with other elements (e.g., C, N, Si, Al, Ni, Cu) through HiPIMS and dcMS co-sputtering. For example, Ti-Al-B alloy films deposited by HiPIMS (Al) and dcMS (TiB₂) co-sputtering were observed that the column boundaries changed from B-rich to Alrich, significantly enhancing the oxidation resistance of the films [41]. Additionally, introducing metallic elements such as Ni [44] or Cu [45] into TiB₂ films to form nanocomposite structure, improves toughness while maintaining high hardness. An alternative approach to simultaneously increase film hardness and toughness is also suggested by precisely control the B/Ti ratio, promoting the formation of metallicelement-rich planar defects in substoichiometric diborides [46,47].

Refractory multi-principal element alloys (MPEAs), composed mainly of high melting point metal elements (Hf, Mo, Nb, Zr, Ti, V, Ta, W, etc.), have attracted particular attention due to their excellent mechanical properties and outstanding thermal properties at high temperatures. For instance, Mo-Ta-W MPEA films with a nanocrystalline structure show excellent mechanical properties with a hardness of about 20 GPa [48]. Georg et al. [49] deposited three bcc-structured (MoNbTaTiW, MoNbTaVW and CrMoNbTaW) films using HiPIMS, which demonstrated stability at a 1200 °C annealing temperature. Inspired by the remarkable mechanical performance of MPEAs, the properties of TiB₂ film could be further enhanced through alloying with MPEAs, in particular by controlling the composition of the amorphous matrix at the grain boundary. To successfully implement this amorphous matrix, a MPEA with low crystallinity should be adopted. Our recent studies have demonstrated that HfMoNbZr-based alloy films exhibit an amorphous structure when deposited at either room temperature or 500 °C, with hardness (~13 GPa) exceeding their metal counterparts [18,50]. This makes them a suitable replacement material for the amorphous boron in TiB₂ film.

In this work, we introduced an amorphous multicomponent HfMoNbZr into TiB₂ films by using HiPIMS-powered Hf₂₅Mo₂₅Nb₂₅Zr₂₅ (TM) target. By varying the average discharge power of the TM target, the amount of TM and the total amount of metallic element (Me, where Me = HfMoNbZrTi) could be altered, allowing for control over the B/Me ratio and the grain boundary structure of the TM_xTi_{1-x}B_y films. A detailed investigation into the microstructure and mechanical performance was conducted. First-principles calculation was also employed to investigate the electronic structure and to further understand its interplay with the mechanical property.

2. Experimental details

2.1. Film deposition

TM_xTi_{1-x}B_y films were grown in a high vacuum chamber with a base pressure of 2×10^{-3} Pa utilizing two 3-in. circular targets: TiB₂ (99.80 %) and Hf₂₅Mo₂₅Nb₂₅Zr₂₅ (TM, 99.95 %), both with a thickness of 6 mm for the discharge. Single-side polished Si (001) wafers, AISI 316 L stainless steel (used for tribology tests, with Ra = 14.97 \pm 2.02 nm, see Fig. S1) and WC-8Co (used for indentation fracture toughness test) were used as substrates. The substrates were cleaned with petroleum ether and ethanol in an ultrasonic bath for 15 min each, prior to being mounted on the substrate holder positioned 11 cm from the target. Films were grown at a working pressure of 0.45 Pa, with a flow of 40 sccm 99.997 % Ar and a substrate temperature at 500 °C. The TiB2 and TM targets were powered by direct current magnetron sputtering (dcMS) and high-power impulse magnetron sputtering (HiPIMS), respectively. For the dcMS process, the discharge power ($P_{dcMS,TiB2}$) was set at 250 W by regulating the discharge current. Simultaneously, HiPIMS discharge powers (P_{HiPIMS,TM}) of 0, 100, 200, and 300 W were applied to the TM target (see Table 1) by altering the target voltage, while keeping the pulse length of 20 µs and the frequency of 1000 Hz constant. This resulted in peak target currents of 10.9 A (0.24 A/cm²), 20.5 A (0.45 A/ cm²), and 27.7 A (0.61 A/cm²) for P_{HiPIMS.TM} of 100 W, 200 W, and 300 W each. The substrate holder was kept floating during the deposition process. All the films were deposited for 180 min and were cooled to 80 °C before breaking vacuum.

2.2. Film characterization

The elemental compositions of the TMxTi1-xBy films were determined by Electron Probe Micro Analysis (EPMA, JXA-8530F PLUS) with ZAF correction and an accelerating voltage of 15 kV. The cross-sectional morphology and thickness were examined under a scanning electron microscope (SEM, Sigma 300, Zeiss) operated at an accelerating voltage of 3.0 kV. The crystal structures of the films were characterized by θ -2 θ X-ray diffraction (XRD) using a Philips X'Pert high-resolution X-ray diffractometer with Cu K α radiation ($\lambda = 1.540597$ Å), with a step size of 0.01° and a scan speed of 2° /min. The average crystallite size of the films was calculated from the full-width at half-maximum by Scherrer's equation [51]. A detailed microstructural investigation of the TM_{0.41}Ti_{0.59}B_{1.74} sample (TM discharge power of 200 W case) was conducted using scanning/transmission electron microscopy (S/TEM, Talos F200X G2, ThermoFisher) with a field emission gun operated at 200 kV. The plan-view and cross-sectional specimens were prepared via the focused ion beam (FIB, Scios 2 HiVac, ThermoFisher) using a 30 kV Ga ion beam for initial polishing, followed by a 5 kV Ga ion beam for the final polishing.

To evaluate the hardness (H) and elastic modulus (E) of the films, nanoindentation measurements were performed using a nanoindentation system (TTX-NHT3, Anton Paar) with a fixed load of 10 mN, ensuring the indentation depths did not exceed 10 % of the films thickness. For each sample, 12 indentations were conducted to calculate the averaged values and absolute errors. In addition, the indentation fracture toughness of the films was assessed using the same indentation system with a Berkovich diamond tip, indented to a depth of 500 nm (Fig. S2). Following indentation, the top-view indentation morphologies were examined using SEM. A ball-on-disk tribometer (MFT-5000, Rtec) was employed to investigate the tribological properties of the films against an Al₂O₃ ball with 6 mm in diameter. The test was conducted in a linear reciprocating sliding mode with a normal load of 2.5 N, sliding velocity of 8 mm/s, and a wear-track length of 4 mm, for a total sliding duration of 50 min. The wear track morphologies were evaluated by using a three-dimensional optical profiler (Contour Elite K, Bruker). The wear rates (W_r) of the films were calculated using the equation [18,52]:

Table 1

Target discharge power of TiB₂ target (P_{dcMS,TiB_2}) and Hf₂₅Mo₂₅Nb₂₅Zr₂₅ target ($P_{HiPIMS,TM}$), and the resulting elemental composition, TM/Me ratio, and B/Me ratio of the TM_xTi_{1-x}B_y films. The TM denotes the total elemental concentration of Hf, Zr, Nb, and Mo. The Me denotes total elemental concentration of the TM and Ti.

Film	$P_{\rm dcMS,\ TiB2}$ (W)	$P_{\rm HiPIMS,TM}$	<i>P</i> _{HiPIMS,TM} Elemental composition (at. %)							B/Me ratio
		(W)	В	Ti	Hf	Zr	Nb	Мо		
TiB _{2.96}	250	0	74.77	25.23						2.96
TM _{0.29} Ti _{0.71} B _{2.1}	250	100	67.72	22.86	2.22	2.24	2.41	2.55	0.29	2.10
TM _{0.41} Ti _{0.59} B _{1.74}	250	200	63.54	21.44	3.48	3.60	3.91	4.02	0.41	1.74
$TM_{0.52}Ti_{0.48}B_{1.39} \\$	250	300	58.27	19.67	5.14	5.31	5.76	5.86	0.53	1.40

$$W_{\rm r} = \frac{V}{F \times S} \tag{1}$$

Where *V* represents the wear volume (m^3) , *F* is the normal load (N), and *S* is the total sliding distance (m).

2.3. DFT calculation

The Vienna Ab-initio Simulation Package (VASP) [53] was applied to conduct first-principles calculations, primarily to calculate the electronic structure and mechanical properties of the material. The projector augmented-wave (PAW) [54] method was employed to describe the interaction between electrons and ions. The general gradient approximation (GGA) by Perdew-Burke-Ernzerhof (PBE) was used to approximate the exchange-correlation functional [55]. The plane-wave cut-off energy of 600 eV was applied, and the Brillouin zone was meshed using the Γ -centered method with a 4 \times 4 \times 3 k-grid. For structures optimization, the convergence criterion of energy and force were set to 10^{-8} eV per supercell and 0.01 eV/Å, respectively. The models of TiB₂ and $TM_{0.44}Ti_{0.56}B_2$ were constructed using a 3 \times 3 \times 3 supercell containing 81 atoms (see Fig. S3). To create the chemical disorder in the TM_{0.44}Ti_{0.56}B₂ solid solution, a special quasi-random structure (SQS) [56] method was employed, using the mcsqs module of Alloy-Theoretic Automated Toolkit (ATAT) code [57]. The post-processing was performed using VASPKIT [58]. The electron localization function (ELF) was visualized by using VESTA software [59]. The mechanical properties were calculated from the elastic constants obtained by the stressstrain method using the VASP code. Theoretical hardness values (H_v) were estimated using Chen's [60] empirical model as follows:

$$H_{\rm v} = 2\left(G^3/B^2\right)^{0.585} - 3\tag{2}$$

where *G* and *B* is shear modulus and bulk modulus, respectively. The average atomic displacement (Δd) is calculated as follows:

$$\Delta d = \frac{1}{N} \sum_{i=1}^{N} \sqrt{\left(x_{i} - x_{i}^{\prime}\right)^{2} + \left(y_{i} - y_{i}^{\prime}\right)^{2} + \left(z_{i} - z_{i}^{\prime}\right)^{2}}$$
(3)

Where *N* is the total number of atoms in a given element, (x_i, y_i, z_i) and (x'_i, y'_i, z'_i) are the reduced coordinates of the unrelaxed and relaxed positions of atom *i*, respectively.

3. Results

3.1. Elemental composition and crystal structure

The elemental composition, TM/Me ratio, and B/Me ratio for the $TM_xTi_{1-x}B_y$ films are presented in Table 1. The film deposited only with the TiB₂ target with power of 250 W exhibits an overstoichiometric composition, which is in line with previous studies that typically reported B/Ti ratios ranging from 2.4 to 3.5 [33,61,62]. As Hf, Mo, Nb, and Zr are sputtered from the equimolar TM target, their contents are nearly identical. The total TM elemental concentration increases with higher $P_{\text{HiPIMS,TM}}$, reaching a peak TM/Me ratio of 0.52 at $P_{\text{HiPIMS,TM}}$ = 300 W. Simultaneously, the B content decreases with the increase of $P_{\text{HiPIMS,TM}}$, leading to the composition change from overstoichiometry to

substoichiometry ($P_{\text{HiPIMS,TM}} = 200 \text{ W}$ and 300 W).

The X-ray diffractograms of TM_xTi_{1-x}B_v films grown at varied P_{HiPIMS}. TM values are presented in Fig. 1. As shown in Fig. 1(a), the TiB_{2.96} film $(P_{\text{HiPIMS,TM}} = 0 \text{ W})$ predominately exhibits reflections from the out-ofplane (1010) and (1011) planes of AlB₂-type TiB₂ (JCPDS 35–0741). Compared to the TiB2.96 films, the TM0.29Ti0.71B2.1 film shows a significant increase in the intensity of X-ray diffraction peaks (Fig. 1(a)), indicating an enhancement in the out-of-plane crystallinity of the film. With the increase of the TM content (decrease of B atomic percentage), the positions of $10\overline{1}0$ and $10\overline{1}1$ peak slightly shift to lower diffraction angles, consistent with the theoretical calculations, showing expansion of the out-of-plane lattice constant (Fig. 1(b)). Additionally, broadening of $10\overline{1}0$ and $10\overline{1}1$ diffraction peaks is observed at higher $P_{\text{HiPIMS,TM}}$ cases, indicating a reduction in the out-of-plane crystallite size (Fig. 1 (c)). Notably, the broadest reflection, corresponding to the smallest crystallite size along the (0001) plane, is achieved for the $TM_{0.41}Ti_{0.59}B_{1.74}$ film ($P_{HiPIMS,TM} = 200$ W). Further increase in TM content $(TM_{0.52}Ti_{0.48}B_{1.39})$ results in a vanishing of diffraction peaks, indicating that the crystalline films transitioned to an amorphous structure in the out-of-plane direction. The similar phenomenon was also observed in multicomponent nitride [63].

Fig. 2 shows the cross-sectional and plan-view SEM morphologies of TM_xTi_{1-x}B_y films. For the single target discharge case, the TiB_{2.96} film has a thickness of about 2.632 µm, while the TM_{0.29}Ti_{0.71}B_{2.1} film (*P*_{HiPIMS,TM} = 100 W) exhibits a significantly reduced thickness of approximately 1.774 µm when deposited using the co-sputtering configuration. As the *P*_{HiPIMS,TM} increases from 100 W to 300 W, the film thickness increases. These variations in growth rate are accompanied by changes in both cross-sectional and plan-view morphologies. As *P*_{HiPIMS,TM} increases from 100 W to 300 W, the film surface become smoother.

3.2. Mechanical property and tribological performance

Fig. 3 illustrates the hardness (*H*) and elastic modulus (*E*) as a function of B/Me ratio of $TM_xTi_{1-x}B_y$ films. The measured *H* of $TiB_{2.96}$ is approximately 26.6 ± 1.2 GPa, which is within the lower range of the hardness typically reported for overstoichiometric TiB_2 films grown by dcMS [64,65]. With the decrease of B/Me ratio, *H* initially increases and reaches a maximum value for $TM_{0.41}Ti_{0.59}B_{1.74}$ film before declining. The changes in *E* follow a similar trend, with the $TM_{0.41}Ti_{0.59}B_{1.74}$ film exhibiting the highest *E* value.

The indentation fracture toughness of films was qualitatively evaluated by examining the surface and sub-surface after performing an indentation test on the WC-8Co substrate. At an indentation depth of 500 nm, the applied loads on the TiB_{2.96}, TM_{0.29}Ti_{0.71}B_{2.1}, TM_{0.41}Ti_{0.59}B_{1.74} and TM_{0.52}Ti_{0.48}B_{1.39} films were 108.8 mN, 133.2 mN, 141.1 mN, and 115.4 mN, respectively (Fig. S2), with the highest load applied on the TM_{0.41}Ti_{0.59}B_{1.74} film, indicating that it has the strongest resistance to deformation. As shown in Fig. 4, the TiB_{2.96} film not only exhibits radial cracks but also shows ring-like cracks, indicating that the TiB_{2.96} film has high brittleness. As the *P*_{HiPIMS,TM} increases from 100 W to 300 W, the length of the radial cracks significantly decreases and disappears when the *P*_{HiPIMS-TM} reaches 300 W, indicating that the ability of the films to resist crack initiation and propagation increases



Fig. 1. (a) X-ray diffractograms of TiB_{2.96} ($P_{\text{HiPIMS,TM}} = 0$ W), TM_{0.29}Ti_{0.71}B_{2.1} ($P_{\text{HiPIMS,TM}} = 100$ W), TM_{0.41}Ti_{0.59}B_{1.74} ($P_{\text{HiPIMS,TM}} = 200$ W), and TM_{0.52}Ti_{0.48}B_{1.39} ($P_{\text{HiPIMS,TM}} = 300$ W) films. (b) out-of-plane *d*-spacing and (c) full width at the half maximum (FWHM) as a function of B/Me ratio. The intensity of X-ray diffractograms in (a) are in linear scale.



Fig. 2. Cross-sectional and plan-view SEM micrographs of $TM_xTi_{1-x}B_y$ films: (a) $TiB_{2.96}$ ($P_{HiPIMS,TM} = 0$ W), (b) $TM_{0.29}Ti_{0.71}B_{2.1}$ ($P_{HiPIMS,TM} = 100$ W), (c) $TM_{0.41}Ti_{0.59}B_{1.74}$ ($P_{HiPIMS,TM} = 200$ W), and (d) $TM_{0.52}Ti_{0.48}B_{1.39}$ ($P_{HiPIMS,TM} = 300$ W).

with the $P_{\rm HiPIMS,TM}$. This qualitative evaluation of changes in indentation morphologies conclude that the hardness-toughness trade-off is successfully mitigated by the nanocomposite structure (nc-MeB₂/a-MPEA), as demonstrated in the case of TM_{0.41}Ti_{0.59}B_{1.74}.

Fig. 5 shows the coefficient of friction (COF) as a function of sliding time, profiles of wear tracks, wear rate and the three-dimensional morphologies of wear tracks for $TM_xTi_{1-x}B_y$ films deposited on 316 L stainless steel. It is observed in Fig. 5 (a) that the COF value fluctuates in the running-in period, and gradually increases during the steady-state wear stage with an increment of <0.1. Changes in COF during the steady-state wear stage are highly correlated with the alloyed-TM content. The TiB_{2.96} film exhibits a COF value of approximately 0.65, which increased significantly with the introduction of TM (e.g.,

TM_{0.29}Ti_{0.71}B_{2.1}). However, when the film turns to substoichiometric, the COF decreases to below that of TiB_{2.96} film before increasing again as the TM content rises. At the same time, the wear track of TiB_{2.96} film exhibits the greatest depth (1.94 μ m) and width (0.207 mm) in Fig. 5(b). As TM is introduced into the films, the depths of wear tracks are significantly reduced. Although this trend reverses with higher TM content, as seen in the TM_{0.52}Ti_{0.48}B_{1.39} film. According to the calculated wear rate (Fig. 5(c)), the lowest wear rate, in the order of 10^{-16} m³N⁻¹ m⁻¹, is achieved by the TM_{0.41}Ti_{0.59}B_{1.74} film, while the other films exhibit wear rates in the order of 10^{-15} m³N⁻¹ m⁻¹. Comparing the three-dimensional morphologies of the wear tracks are notably reduced in the TM_{0.29}Ti_{0.71}B_{2.1} and TM_{0.41}Ti_{0.59}B_{1.74} films compared to the



Fig. 3. Hardness H and elastic modulus E of $TM_xTi_{1-x}B_y$ films.

 $TiB_{2.96}$ (a localized magnified image of the wear track seen in Fig. S4) and $TM_{0.52}Ti_{0.48}B_{1.39}$ films, suggesting lower fatigue and abrasive wear in the former. Additionally, the wear tracks of $TM_{0.29}Ti_{0.71}B_{2.1}$ and

 $TM_{0.41}Ti_{0.59}B_{1.74}$ are shallower and exhibit smoother surfaces, resembling a polishing effect.

3.3. Nanocomposite structure

As shown in Fig. 6, given the enhanced mechanical properties of the TM_{0.41}Ti_{0.59}B_{1.74} film, plan-view and cross-sectional TEM micrographs were acquired to provide further insights into its microstructure. Fig. 6 (a) is a low-magnification bright field image, revealing the presence of dark dot-like areas embedded within the matrix. The higher magnification images (Fig. 6(b) and (c)) indicate the dark dot-like areas are nanocrystalline. In Fig. 6(b), the interplanar spacing between $(10\overline{1}0)$ planes $(d_{10\overline{10}})$ of MeB₂ solid solution is measured to be 0.262 nm, which exactly matches the value of standard TiB_2 (0.262 nm). In contrast, the $d_{10\overline{1}1}$ spacing of MeB₂ is 0.208 nm, slightly larger than the TiB₂ value of 0.204 nm (JCPDS 35–0741). Moreover, comparing $d_{10\overline{1}1}$ of MeB₂ to those of HfB₂ and ZrB₂ shows a lower $d_{10\overline{1}1}$ value for MeB₂, implying the formation of solid solution of MeB₂ within the TiB₂ crystallites due to the incorporation of TM. In general, the *d*-spacing values measured from HRTEM image are consistent with those calculated from the peak positions in the X-ray diffractograms (seen in Fig. 1(b)), so it indicates the TM incorporation results in the lattice expansion of the TiB₂ crystallites.

The SAED pattern inserts in Fig. 6(a) and 6(h) confirms that the film exhibits hexagonal AlB₂-type structure. The diffraction rings in the SAED are almost continuous, also illustrating nanocrystalline feature of the $TM_{0.41}Ti_{0.59}B_{1.74}$ film, which is in line with the HRTEM images



Fig. 4. The indentation site morphologies of (a) $TiB_{2.96}$ ($P_{HiPIMS,TM} = 0$ W), (b) $TM_{0.29}Ti_{0.71}B_{2.1}$ ($P_{HiPIMS,TM} = 100$ W), (c) $TM_{0.41}Ti_{0.59}B_{1.74}$ ($P_{HiPIMS,TM} = 200$ W), and (d) $TM_{0.52}Ti_{0.48}B_{1.39}$ ($P_{HiPIMS,TM} = 300$ W) on WC-8Co substrate.



Fig. 5. (a) The coefficient of friction (COF) as a function of sliding time, with semi-transparent lines representing the raw (unsmoothed) data for comparison. (b) 2D profiles of wear tracks, (c) wear rate and average COF, and (d) the three-dimensional morphologies of wear tracks of $TM_xTi_{1,x}B_y$ films.

shown in Fig. 6(b) and (c). No obvious diffraction ring is detected from the body-centered cubic (BCC) TM alloy, which again indicates that there is no agglomeration or crystallite formation by the TM alloy [18,50]. In Fig. 6(c), diffusely distributed nano-scale grains with a inplane size of 2-5 nm, surrounded by amorphous matrix, are observed. The detailed nanocrystalline/amorphous structure is confirmed in the high-resolution TEM image and the FFT pattern shown in Figs. 6(c)-(e), where AlB₂-type MeB₂ nanocrystallites are in variable shape and size, and surrounded by large volume of amorphous matrix. Therefore, the nanocrystalline component consists of MeB₂, while the amorphous matrix located between individual grains is primarily composed of MPEA (where MPEA is composed of Me and lower concentration of boron). EDX map (see in Fig. S5) and Atom Probe Tomography (APT, see in Fig. S6) analysis further confirms that no significant segregation is observed between the grains and the amorphous matrix. Additionally, the HRTEM image in Fig. 6(h) shows that no significant lattice fringing was observed, which indicates that the $TM_{0.41}Ti_{0.59}B_{1.74}$ film is low crystallinity in the cross-sectional direction.

3.4. DFT calculation

The total density of states (TDOS) and partial density of states (PDOS) of TiB₂ and TM_{0.44}Ti_{0.56}B₂ are shown in Fig. 7. In Fig. 7(a), the DOS of TiB₂ shows a pseudo-gap on the Fermi level [66]. The presence of a non-zero electronic density of states on the Fermi level suggests that the metallic property of TiB₂. In the DOS of B atom, the overlap of *s* and *p* orbitals is correlated with the formation of B—B covalent bonds. The states from -5 eV to the Fermi level are mainly contributed by the overlap of Ti *3d* and B *2p* orbitals. The strong hybridization of the Ti *3d* and B *2p* orbitals suggests that Ti—B bond has covalent characteristics

[66,67]. In Fig. 7(b) and (c), the DOS for $TM_{0.44}Ti_{0.56}B_2$ has similar characteristics as that of TiB₂, owing to the similarity in crystallographic structure and chemical bonding of these diborides [68]. However, the DOS of $TM_{0.44}Ti_{0.56}B_2$ shifts to a low-energy range, and higher values compared to TiB₂ at the Fermi energy level. This indicates a higher metallicity [21] and lower chemical stability for $TM_{0.44}Ti_{0.56}B_2$ [69,70]. This shift is mainly attributed to the increase of VEC for $TM_{0.44}Ti_{0.56}B_2$, where the valence electron number is 4 for Ti, Zr, and Hf, and 5 and 6 for Nb and Mo, respectively. This results in increasing concentration of *d* electrons per formula unit (provided by Mo and Nb substitutions) at the Fermi level. Furthermore, as the number of valence electrons increases, the Me-B interactions are enhanced, suggesting a greater contribution of covalent bonds to Me-B bonding.

The electronic localization function (ELF) for TiB2 and $TM_{0.44}Ti_{0.56}B_2$ on the (0001) and (1120) planes is shown in Fig. 8. On the (0001) plane, non-localized electrons accumulate between neighboring metallic atoms indicating typical metallic bonding characteristic for both diborides. On the $(11\overline{2}0)$ plane, the yellow region between neighboring B atoms shows highly localized electrons, suggesting the presence of strong covalent bonds between the B atoms. Charge transfers occur mainly from the metal atoms to the B atoms due to the differences in electronegativity, reflecting the ion-covalent feature of Me-B bond. Comparing the ELF in Fig. 8(a) and Fig. 8(b), the ELF values between neighboring metal atoms and between Me and B atoms increase after the introduction of TM. The Me-B and Me-Me (dd) bonding are strengthened by the addition of TM atoms. However, the strengthened Me-Me and Me-B bonding results in a weaker B-B bonding strength, which could reduce material theoretical hardness (see charge distribution between B atoms in Fig. S7). Overall, the addition of TM leads to a non-uniform bonding distribution by regulating Me-B and Me-Me bonding, which



Fig. 6. (a), (b) and (c) are the plan-view TEM images of $TM_{0.41}Ti_{0.59}B_{1.74}$ film, (d) and (e) are the FFT images in the blue and yellow boxes of the TEM image in (c), respectively. (f), (g) and (h) are the cross-sectional (S)TEM images of $TM_{0.41}Ti_{0.59}B_{1.74}$ film. The inserts in (a) and (h) are selected area electron diffraction (SAED) patterns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. The calculated total and partial electronic density of state (DOS) of (a) TiB_2 , (b) and (c) $TM_{0.44}Ti_{0.56}B_2$. The Fermi level is represented by a vertical dashed line.

in turn influences the bonding-related properties, such as mechanical properties, electrical conductivity, and thermal conductivity.

The bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), Poisson's ratio (ν), *B/G* and Vickers Hardness (*H*_v) of TiB₂ and TM_{0.44}Ti_{0.56}B₂ are listed in Table 2. The bulk modulus of TM_{0.44}Ti_{0.56}B₂ are is higher than that of TiB₂, while the *G*, ν and *H*_v of TM_{0.44}Ti_{0.56}B₂ are lower due to the change in bonding characteristics regulated by the VEC. As the theoretical *B* is a monotonic function of VEC, the introduction of TM increases the VEC from 10 for TiB₂ to 10.33 for TM_{0.44}Ti_{0.56}B₂, leading to an increase in *B* [71]. Additionally, the increase of VEC strengths Me *dd* bonding, in turn, leads to a reduction in resistance to shear deformation and a decline in the *G* [72]. Both TiB₂ and



Fig. 8. The electron localization function (ELF) of (a) TiB_2 , (b) $TM_{0.44}Ti_{0.56}B_2$ is shown on planes parallel to (0001), which pass through boron layers, and on ($11\overline{2}0$) that are across both metal and boron atoms. The interval of the contour lines is 0.1. ELF values of 0 and 1 correspond to the delocalized state and the localized state, respectively, while an ELF of 0.5 represents a uniform electron gas.

Table 2

Bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio (v), B/G and Vickers Hardness Hv values of TiB2 and TM0.44Ti0.56B2.

Material	VEC	В	G	Ε	ν	B/G	$H_{\rm v}$
TiB_2	10	252.84	257.84	577.28	0.119	0.981	49.09
TM _{0 44} Ti _{0 56} B ₂	10.33	259.39	235.08	541.62	0.152	1.103	40.02

 $TM_{0.44}Ti_{0.56}B_2$ materials have a Pugh's ratio [73] *B/G* of <1.75, indicating their intrinsic brittleness. However, $TM_{0.44}Ti_{0.56}B_2$ is expected to exhibit higher ductility because of its higher *B/G* value.

4. Discussion

The B/Me ratio and the content of TM are crucial in determining the film structure during growth. The out-of-plane crystallite size of the $TiB_{2.96}$ film ($P_{HiPIMS,TM} = 0$ W) is estimated to be approximately 5–6 nm, based on the $(10\overline{1}1)$ and $(10\overline{1}0)$ diffraction peaks (Fig. 1(c)). This crystallite size of TiB₂ could be limited by the excess segregated amorphous B at the grain boundaries, as the growth of crystallites was inhibited [38,46,61,74,75]. The $TM_{0.29}Ti_{0.71}B_{2.1}$ film has smaller out-ofplane crystallite sizes (3-4 nm) but improved crystallinity compared to the TiB_{2.96} film. This improvement is due to the addition of TM atoms, which act as nucleation sites, promoting crystallite refinement of the MeB₂ phase. As the TM content increases, the X-ray diffraction peaks broaden and eventually vanish for the film deposited with $P_{\text{HiPIMS.TM}} =$ 300 W, indicating a structural transition from nanocrystalline to amorphous. This transformation can be explained by the deficiency of B in the film. In the diboride solid solution, a severe lack of B (B-B covalent bond) causes significant lattice distortion, which subsequently leads to lattice collapse and thus results in the complete loss of crystallinity [76]. A similar phenomenon is often observed in high-entropy alloys where high lattice distortion induces the formation of amorphous structure

[77,78]. Moreover, the excess TM formed the disordered amorphous matrix, rather than metal-rich planer defects observed in the $TiB_{1.43}$ case [40]. Additionally, the amorphization brings a more uniform and smoother film surface in line with the cases where Ni [44] and Cu [45] were added.

As shown in Fig. 4, the hardness of the TiB_{2.96} film is only 26.6 ± 1.2 GPa, while the TM_{0.41}Ti_{0.59}B_{1.74} film achieves a significantly higher hardness at 41.8 \pm 3.7 GPa. However, theoretical calculations indicate that TiB₂ has an intrinsic hardness of 49.1 GPa, which is higher than the intrinsic hardness of TM_{0.44}Ti_{0.56}B₂ solid solution (40.0 GPa). This discrepancy arises because the theoretical hardness H, as estimated by Chen empirical model, only based on elastic moduli alone, and does not consider factors such as lattice distortion and microstructure [60,79]. The hardness of TiB_x films (1.2 \leq x \leq 2.8) prepared by co-sputtering of TiB₂ and Ti targets decreases from \sim 29 GPa to \sim 26 GPa with decreasing B content. In contrast, our films exhibited a trend of hardness initially increasing and then decreasing (ranging from approximately 27 GPa to 42 GPa and subsequently dropping to 30 GPa). This difference suggests that the enhanced hardness in our best samples may be attributed to the solid-solution strengthening and the formation of a nc-MeB₂/a-MPEA structure resulting from the introduction of TM. In the $TM_{0.44}Ti_{0.56}B_2$ solid solution, local lattice distortions occur due to the coexistence of multiple metal elements. The average atomic displacements (Δd) from their unrelaxed positions for Hf, Mo, Nb, Zr, Ti, and B are estimated to be 0.667, 0.334, 1.137, 1.138, 0.827, 0.004 respectively. This lattice

distortion is supported by the X-ray diffractograms (see Fig. 1(a)) and HRTEM images (Fig. 6(c)), where the diffraction peaks shift to lower angles and the interplanar spacing $d_{10\overline{1}1}$ increases in the TM_{0.41}Ti_{0.59}B_{1.74} film compared to standard TiB₂.

While the solid solution strengthening effect increases the film hardness with probability of compromising toughness. The primary mechanism of plastic deformation during nanoindentation is the proliferation and movement of dislocations. As the crystallite size decreases, the number of grain boundaries increases, which prevents dislocation formation, thereby enhancing the material's strength [80]. This phenomenon is known as the Hall-Petch effect, which fails when the crystallite size is reduced to tens or even a few nanometers [81]. According to the previous reports by Veprek et al. [82,83] and Christiansen et al. [84], dislocations barely form in nanocrystals smaller than 3–6 nm, the plastic deformation is dominated by grain boundary sliding and grain boundary softening [85]. This explains why the Hall-Petch effect fails in nanocrystalline structure. In our case, the TM_{0.41}Ti_{0.59}B_{1.74} film exhibits a nc-MeB₂/a-MPEA structure (see in Fig. 6(b) and 6(c)), where a few nanometer crystallites are embedded in the amorphous matrix. Effective dislocation formation is initially suppressed in such small crystallites, and the huge amorphous matrix inhibits grain sliding [86], increasing the hardness of the $TM_{0.41}Ti_{0.59}B_{1.74}$ film. Our results demonstrate that the nc-MeB₂/a-MPEA structure has a significant strengthening effect, resisting the Hall - Petch breakdown. The amorphous MPEA, however, is significantly softer than the crystalline MeB₂, with previous experimental results indicating hardness varied between 9.0 GPa [50] and 13.2 GPa [18] for amorphous HfMoNbZr films. This softness partially accounts for the improved plasticity, toughness, and fracture resistance observed in the TM_xTi_{1-x}B_y films. Another contributing factor is the increased concentration of d electrons per formula unit (provided by Mo and Nb substitutions) at the Fermi level, analogous to nitrides and carbides [5,12,87]. Although the incorporating of a large amount of softer amorphous TM in the film will further improve the film indentation fracture toughness, it will inevitably reduce its hardness, as seen in the $TM_{0.52}Ti_{0.48}B_{1.39}$ case (Fig. 3).

Hardness is a crucial parameter for evaluating the tribological properties of films, as the wear rate is mainly determined by the hardness at low loads [88]. In Fig. 5(b), the wear rate decreases when the film gets harder. Due to the poor indentation fracture toughness of TiB2.96 film (Fig. 4(a)), cyclic stress promotes crack initiation and propagation during the wearing, resulting in substantial plastic deformation and the highest wear rate among the films. For the $TM_{0.29}Ti_{0.71}B_{2.1}$ and $TM_{0.41}Ti_{0.59}B_{1.74}$ films, the surfaces of the wear track appear relatively smooth, similar to a polishing effect. Meanwhile, the addition of TM inhibits the growth and expansion of cracks as the indentation fracture toughness is enhanced. In contrast, the TM_{0.52}Ti_{0.48}B_{1.39} film exhibits furrows in the wear track, a typical feature of abrasive wear. This is due to a further increase in amorphous component (TM content), reducing hardness. The abrasive particles generated during wearing become involved in the process, leading to the creation of furrows and increases in wear rate.

5. Conclusion

 $TM_xTi_{1-x}B_y$ films, with varying compositions ranging from x=0 to 0.52, were synthesized by co-sputtering using a TM-HiPIMS/TiB₂-dcMS configuration. Combining the experiments and theoretical calculations, we investigated the effect of TM content on the microstructure and mechanical properties of $TM_xTi_{1-x}B_y$ films. The results showed that the main phase of the films is hexagonal TiB₂ with no crystalline TM phase detected. With the increase of TM content, the film structure transitioned from nanocrystalline to amorphous structure, and surface smoothness improved. The hardness initially increased from 26.6 \pm 1.2 GPa to 41.8 \pm 3.7 GPa, and then dropped to 30.9 \pm 1.0 GPa in the TM_{0.52}Ti_{0.48}B_{1.39} film with a fully amorphous structure. Meanwhile, the

indentation fracture toughness of the films increased significantly with the increase of TM content. Theoretical calculations indicated that the VEC of $TM_{0.44}Ti_{0.56}B_2$ solid solution increased with introduction of TM, i.e., which enhancing the metallicity and consequently improving toughness compared to TiB₂. The TEM characterization for the $TM_{0.41}Ti_{0.59}B_{1.74}$ film, which exhibited the highest hardness confirmed that the film had a nc-MeB₂/a-MPEA structure. This unique structure not only improved the indentation fracture toughness but also maintained its high hardness. Additionally, the $TM_{0.41}Ti_{0.59}B_{1.74}$ film showed excellent wear resistance, which is in relation with its higher hardness.

CRediT authorship contribution statement

Jigang Xie: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Yiming Ruan: Writing – original draft, Data curation. Hao Du: Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. Lin He: Writing – review & editing, Project administration, Conceptualization. Jie Shi: Writing – review & editing, Investigation, Formal analysis, Data curation. Hengning Hu: Writing – review & editing, Investigation. Yun Chen: Writing – review & editing, Investigation. Liuquan Yang: Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization. Rui Shu: Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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