Multifunctional ZrB$_2$-rich Zr$_{1-x}$Cr$_x$B$_y$ thin films with enhanced mechanical, oxidation, and corrosion properties

Babak Bakhit$^a$,$^*$, Samira Dorri$^a$, Agnieszka Kooijman$^b$, Zhengtao Wu$^c$, Jun Lu$^a$, Johanna Rosen$^a$, Johannes M.C. Mol$^b$, Lars Hultman$^a$, Ivan Petrov$^{a,d,e}$, J.E. Greene$^{a,d,e}$, Grzegorz Greczynski$^a$

$^a$ Thin Film Physics Division, Department of Physics (IFM), Linköping University, Linköping SE, 58183, Sweden
$^b$ Department of Materials Science and Engineering, Delft University of Technology, Delft, 2628CD, the Netherlands
$^c$ School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou, 510006, China
$^d$ Materials Research Laboratory and Department of Materials Science, University of Illinois, Urbana, IL, 61801, USA
$^e$ Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan

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A B S T R A C T

Refractory transition-metal (TM) diborides have high melting points, excellent hardness, and good chemical stability. However, these properties are not sufficient for applications involving extreme environments that require high mechanical strength as well as oxidation and corrosion resistance. Here, we study the effect of Cr addition on the properties of ZrB$_2$-rich Zr$_{1-x}$Cr$_x$B$_y$ thin films grown by hybrid high-power impulse and direct current magnetron co-sputtering (Cr-HiPIMS/ZrB$_2$-DCMS) with a 100-V Cr-metal-ion synchronized bias. Cr metal fraction, $x = Cr/(Zr + Cr)$, is increased from 0.23 to 0.44 by decreasing the power $P_{ZrB_2}$ applied to the DCMS ZrB$_2$ target from 4000 to 2000 W, while the average power, pulse width, and frequency applied to the HiPIMS Cr target are maintained constant. In addition, $y$ decreases from 2.18 to 1.11 as a function of $P_{ZrB_2}$, as a result of supplying Cr to the growing film and preferential B resputtering caused by the pulsed Cr-ion flux. Zr$_{2.18}$B$_{6.64}$Cr$_{0.36}$B$_{1.11}$, Zr$_{0.71}$Cr$_{0.29}$B$_{1.52}$, Zr$_{0.71}$Cr$_{0.29}$B$_{1.42}$, and Zr$_{0.68}$Cr$_{0.32}$B$_{1.38}$ films have hexagonal AlB$_2$ crystal structure with a columnar nanostructure, while Zr$_{0.86}$Cr$_{0.14}$B$_{1.36}$ and Zr$_{0.86}$Cr$_{0.44}$B$_{1.11}$ are amorphous. All films show hardness above 30 GPa. Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys exhibit much better toughness, wear, oxidation, and corrosion resistance than ZrB$_2$. This combination of properties makes Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ ideal candidates for numerous strategic applications.

1. Introduction

Transition-metal (TM) nitride coatings have many industrial applications from mechanical components in aerospace industry to cutting tools [1–4]. Metastable NaCl-structure Ti$_{1.5}$Al$_{0.5}$N layers grown by magnetron sputtering are the most attractive group of TiN-based thin films, suitable as protective coatings for cutting tools, which show good hardness (typically ~30 GPa), high wear and oxidation resistance (depending on Al concentration), and self-hardening effects at elevated temperatures up to ~900 °C (resulting from spinodal decomposition) [3–5]. However, the ever-increasing demand from industry for enhanced coating properties motivates the search for alternatives.

One particularly promising group of materials are TM diborides, extensively studied in the recent years. TM diborides, which typically crystallize in a hexagonal AlB$_2$ structure (P6/mmm, SG-191) – where B atoms form graphite-like honeycomb sheets between hexagonal-close-packed TM layers [6,7], exhibit high melting points, excellent hardness, high thermal and chemical stability, and good conductivity [8]. This unique combination of properties originates from their dual ceramic/metallic nature where strong combined covalent/ionic bonding between TM and B atoms together with the covalent bonding within the honeycomb B sheets provide high melting point, hardness, and stiffness [9,10], while metallic bonding between TM atoms results in good thermal and electrical conductivities [6]. Hence, TM diborides are good candidates for a broad range of applications, particularly in extreme environments, such as hypersonic aerospace vehicles [11,12], rockets [12], nuclear reactors [8], optoelectronic and microelectronic components [13,14], solar power [15], and cutting tools [16–20].

* Corresponding author.
E-mail address: babak.bakhit@liu.se (B. Bakhit).

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However, compared to TiAlN, the industrial applications of sputter-deposited TM diboride thin films are very limited, primarily due to poor oxidation resistance [16] and high brittleness [17]. Bulk diborides, which are mostly synthesized by powder metallurgy processes [11,21], start to oxidize at temperatures below ~450 °C with oxidation products that are typically TMO2 and glassy B2O3 phases [22]. The B2O3 phase tends to rapidly evaporate at temperatures above ~1000 °C which results in the formation of a porous oxide scale that does not passivate the surface against oxidation [22]. This issue is even worse for the TM diboride thin films that are overstoichiometric (B/TM ratios > 2), in which oxide scales formed at temperatures above ~400 °C are highly B deficient with no oxidation protection; causing a poor oxidation resistance [16]. Similar to TiN-based thin films, alloying TM diborides with Al enhances their oxidation properties [16].

Moreover, the applications of sputter-deposited TM diborides are restricted due to their inherent brittleness [17]. Although these films have high hardness ranging from 30 to 50 GPa [20,22,24], this alone is not sufficient for preventing failure in applications which involve high mechanical stresses. Hardness is usually accompanied by brittleness that causes crack formation and propagation at the presence of high stresses [25]. Hence, TM diboride films require to have a combination of high hardness and ductility (referred to as toughness [26]) in order to avoid brittle cracking. To accommodate this requirement, we recently showed that alloying ZrB2 thin films with Ta can result in a simultaneous increase in both nanoindentation hardness and toughness [17]. Zr1-xTaB_x alloys with x ≥ 0.2 exhibit a self-organized columnar core/shell nanostructure in which Cr-rich stoichiometric Zr1-xTaB_x cores are surrounded by narrow dense, disordered Ta-rich (B-deficient) shells that have the structural characteristics of metallic-glass thin films; both high strength and toughness [18]. These layers also show a high thermal stability in which their hardness increases as a function of annealing temperature up to 800 °C. The age hardening observed in the Zr1-xTaB_x films with 0 ≤ x ≤ 0.3, which occurs without any phase separation or decomposition, can be explained by point-defect recovery that enhances the chemical bond density [20]. For temperatures above 800 °C, hardness decreases due to recrystallization, column coarsening, and stacking fault annihilation. All Zr1-xTaB_x films generally have hardness values H > 34 GPa up to 1200 °C [20].

Here, we study the effect of Cr addition on the properties of ZrB2-rich Zr1-xCrB_x thin films grown by hybrid high-power impulse and dc magnetron co-sputtering (Cr-HiPIMS/ZrB2-DCMS) as alloying with Cr previously showed enhanced oxidation [27,28], wear [29,30], and corrosion [30,31] properties for TM nitrides. The B/(Zr + Cr) ratio y decreases, while the Cr/(Zr + Cr) ratio x increases, gradually from ZrB2 to Zr0.77Cr0.23B2.3, Zr0.7Cr0.29B1.42, Zr0.68Cr0.32B1.38, Zr0.64Cr0.36B1.30, and Zr0.56Cr0.44B1.11 by decreasing the power Pzrb applied to the DCMS ZrB2 target from 4000 to 2000 W in 500-W increments, while other deposition parameters are maintained constant. All films have nanoindentation hardnesses H > 30 GPa. The toughness, wear, oxidation, and corrosion resistance of the films increase as a function of Cr concentration. Films with the highest Cr content, Zr0.56Cr0.44B1.11, exhibit a combination of enhanced properties.

2. Experimental

Zr1-xCrB_x thin films are grown in a CC800/9 CemeCon AG sputtering system equipped with rectangular 8.8 × 50 cm² stoichiometric ZrB2 and elemental Cr targets. Al2O3(0001), Si(001), and WC-Co substrates, 1.5 × 1.5 cm², are cleaned sequentially in acetone and isopropyl alcohol, and then mounted symmetrically with respect to the targets, which are tilted toward the substrates resulting in a 21° angle between the substrate normal and the normal to each target. The target-to-substrate distance is 20 cm. The chamber is degassed before deposition by applying 8.8 kW to each of two resistive heaters for 2 h, which results in a temperature of ~475 °C at the substrate position. The system base pressure is 3.8 × 10⁻⁶ Torr (0.5 mPa). The film growth is carried out at ~475 °C and a total Ar pressure of 3 mTorr (0.4 Pa). Prior to deposition, the targets are sequentially DCMS sputter-cleaned in Ar at 2 kW for 60 s with shutters protecting the substrate table and the opposite target. A thin continuous Cr buffer layer, with a thickness of 4 ± 1 nm, is initially deposited on all substrates to improve adhesion and minimize their influence on the film morphological evolution.

ZrB2 films are grown by DCMS with a target power of 4 kW and a negative dc substrate bias of 100 V. For growing the Zr1-xCrB_x films, a hybrid target-power scheme [32] (Cr-HiPIMS/ZrB2-DCMS) is employed in which the CrB2 target is continuously sputtered by DCMS, while the Cr magnetron is operated in HiPIMS mode to provide pulsed Cr ion fluxes. The Cr metal fraction, Cr/(Zr + Cr), is increased from 0.23 to 0.44 by decreasing the power P_{zrb} applied to the DCMS ZrB2 target from 4000 W to 2000 W in 500-W increments, while the average power, pulse width, and frequency applied to the HiPIMS Cr target are maintained constant at 700 W, 50 μs, and 100 Hz, respectively. This results in a constant peak Cr-target current density of ~0.73 A/cm². A negative substrate bias of 100 V is applied in synchronous with the 100-μs metal-ion-rich portion of each HiPIMS pulse, starting 30 μs after the cathode HiPIMS pulse. The substrates are at a negative floating potential of 10 V at all other times. The film deposition rate is ~0.85 nm/s for ZrB2, while it increases from ~0.45 nm/s for P_{zrb} = 2000 W to ~0.78 nm/s for P_{zrb} = 4000 W for the Zr1-xCrB_x films.

Cross-sectional scanning electron microscopy (XSEM) analyses are conducted in a Zeiss LEO 1550 electron microscope to obtain the thicknesses and cross-sectional morphologies of the films. 0-20 X-ray diffraction (XRD) scans are carried out using a Philips XPert X-ray diffractometer with a Cu Kα source (λ = 0.15406 nm) to determine crystal structure and orientations of the layers. Film compositions are obtained from time-of-flight elastic recoil detection analyses (ToF-ERDA) in a tandem accelerator with a 36 MeV 127I⁺ probe beam incident at 67.5° with respect to the sample surface normal. Recoils are detected at 45°. Chemical bonding in the films is evaluated by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra DLD instrument employing monochromatic Al Kα radiation (hv = 1486.6 eV). All surfaces are sputter-etched for 120 s with a 4-keV Ar⁺ ion beam incident at 70° with respect to the sample normal. Then, the Ar⁺ ion energy is reduced to 0.5 keV for 600 s to minimize surface damage. The analyzed area, which is located in the center of a 3 × 3 mm² ion-etched region, is 0.3 × 0.7 mm². The core level spectra are referenced to the Fermi edge cut-off to avoid problems caused by the referencing method based on the C 1s peak from adventitious carbon [33].

Cross-sectional transmission electron microscopy (XTEM) analyses are carried out in a monochromated and double-corrected FEI Titan 300–300 electron microscope operated at 300 kV. Images are acquired using bright-field (BF) and dark-field (DF) TEM imaging modes. TEM specimens are prepared by mechanical polishing, followed by Ar⁺ ion milling at 5 keV, with a 3° incidence angle, on both sides of each sample during rotation, in a Gatan precision ion miller. The specimens are finally sputter-cleaned using an ion energy of 0.5 keV without changing the angle of incident Ar⁺ ions.

The in-plane residual stresses of Zr1-xCrB_x thin films are obtained using the modified Stoney equation by determining the substrate wafer curvature from XRD rocking-curve measurements. More details are provided in reference 17. The nanoindentation analyses of the layers are performed in an Ultra-Micro Indentation System with a sharp Berkovich diamond tip calibrated using a fused-silica standard. For hardness H and elastic modulus E measurements, the layers are indented using a fixed load of 12 mN, while indentation depths are maintained below 10% of the film thickness. Reported values are the average of 35 indentations. The results are analyzed using the Oliver and Pharr method [34]. The films are also indented by a diamond cube-corner tip with a load of 200 mN to measure the average lengths of induced radial cracks. The average crack length, which is an indication of nanoindentation toughness [35], is obtained from four cube-corner indents for each film.

To evaluate the films’ adhesion and toughness, the Revescratch tests
are performed using an Anton-Paar-TriTec UNHT\textsuperscript{3} system equipped with a Rockwell-C diamond indenter with a tip radius of 100 μm. A progressive loading regime is used in which the load is linearly increased from 1 to 80 N with a rate of 158 N/min. The scratch length is 3 mm with a speed of 6 mm/min. The same equipment with a ball-on-disc tribometer with a 3-mm-diameter GCR15 steel ball is also used to investigate the friction and wear properties of the layers at room temperature. A load of 2 N with 0.1 m/s sliding speed (2000 laps) is applied during the wear tests. The wear track profiles are measured by a confocal laser-scanning microscope. The wear rates are obtained using the following equation [36]:

\[ \text{Wear rate} = \frac{W}{V/F \times s} \]

where \( V \) is the volume loss by wear (mm\(^3\)), \( F \) is the applied load (N), and \( s \) is the sliding distance (m).

\[ \text{ZrB}_{2.18} \text{ and Zr}_{0.56}\text{Cr}_{0.44}\text{B}_{1.11} \text{ thin films are annealed at 700 °C in air for } t_s \text{ ranging from 1.0 to 5.0 h using a high-temperature furnace from MTI Corporation (GSL-1100 × -S). The heating rate is constant at 10 °C/min, and the specimens are cooled down to room temperature, while the furnace is turned off.} \]

Open circuit potential (\( E_{ocp} \)) with superimposed linear polarization resistance (\( R_p \)) followed by potentiodynamic polarization measurements are employed to study the corrosion resistance of \( \text{ZrB}_{2.18} \) and \( \text{Zr}_{0.56}\text{Cr}_{0.44}\text{B}_{1.11} \) thin films. All measurements are carried out in an aqueous 0.1 M NaCl corrosive medium, at room temperature and without agitation, using a Bio-logic VSP-300 potentiostat/galvanostat system. A standard three-electrode system is used with a silver/silver chloride electrode (Ag/AgCl) as the reference electrode, a platinum mesh as the counter electrode, and the films as the working electrode. The \( E_{ocp} \) values of the films immersed in the corrosive medium are monitored for 25 h and reported versus the Ag/AgCl reference electrode potential, unless mentioned differently. The \( R_p \) measurement is performed after 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, 16.0, and 24.0 h of immersion by a sweeping potential of ±10 mV versus \( E_{ocp} \) with a scanning rate of 0.167 mV/s. The \( R_p \) values are obtained from the inverse of the slopes of current-potential plots at the corrosion potential (\( E_{corr} \)). Immediately afterward, the potentiodynamic polarization is performed with a sweeping rate of 0.167 mV/s from −160 to +1260 mV with respect to \( E_{ocp} \). The corrosion potentials (\( E_{corr} \)) and current densities (\( i_{corr} \)) are calculated according to the Tafel extrapolation [37,38].

3. Results and discussion

3.1. Elemental compositions and structure

Table 1 gives the elemental compositions of as-deposited \( \text{Zr}_1_x\text{Cr}_y\text{B}_y \) thin films obtained from ToF-ERDA measurements. The as-deposited ZrB\textsubscript{2} films grown using DCMS at \( P_{ZrB_2} = 4000 \) W are over-stoichiometric with the \( B/(Zr + Cr) \) ratio \( y \) of 2.18. The \( Cr/(Zr + Cr) \) ratio, \( x \), in the alloys deposited by hybrid Cr-HiPIMS/ZrB\textsubscript{2}-DCMS co-sputtering increases from 0.23 for \( P_{ZrB_2} = 4000 \) W to 0.29 for \( P_{ZrB_2} = 3500 \) W, 0.32 for \( P_{ZrB_2} = 3000 \) W, 0.36 for \( P_{ZrB_2} = 2500 \) W, and 0.44 for \( P_{ZrB_2} = 2000 \) W, while the \( B/(Zr + Cr) \) ratio, \( y \), gradually decreases from 1.52 to 1.42, 1.38, 1.30, and 1.11 with decreasing \( P_{ZrB_2} \). The total concentration of carbon, nitrogen, and oxygen is ≤ 1.6 at. %, and the Ar concentration is ≤ 0.5 at. % in all films. Alloying ZrB\textsubscript{2} with Cr using a flux of energetic Cr ions bombarding the growing film not only adds Cr atoms, but it also affects the B content via preferential sputtering. XRD \( 0-20 \) scans of as-deposited \( \text{Zr}_1_x\text{Cr}_y\text{B}_y \) thin films grown on Si (001) substrates are shown in Fig. 1. Vertical solid and dashed lines correspond to reference powder-diffraction peak positions for \( \text{ZrB}_2 \) [39] and \( \text{CrB}_2 \) [40], respectively. All reflections in the XRD patterns of \( \text{ZrB}_{2.18}, \text{Zr}_{0.7} \text{Cr}_{0.25} \text{B}_{1.25}, \text{Zr}_{0.7} \text{Cr}_{0.25} \text{B}_{1.42}, \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.38} \), and \( \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.11} \) films originate from the crystalline hexagonal AB\textsubscript{2}-type structure (solid-solution), while the patterns of \( \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.30} \) and \( \text{Zr}_{0.56} \text{Cr}_{0.44} \text{B}_{1.11} \) films show very low intensity (notice the logarithmic scale), broad 0001 and 10T0 X-ray reflections; indicating that they are X-ray amorphous. The (10T0) reflection disappears for \( \text{Zr}_{0.7} \text{Cr}_{0.25} \text{B}_{1.42} \) and \( \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.38} \) alloys. The formation of X-ray amorphous \( \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.30} \) and \( \text{Zr}_{0.56} \text{Cr}_{0.44} \text{B}_{1.11} \) films can be attributed to the collapse of the hexagonal AB\textsubscript{2}-structure that results from the lack of B between the hexagonal-close-packed Zr\textsubscript{1}Cr\textsubscript{1} layers (\( y \leq 1.30 \)) as well as the difference between the crystal structures of Zr and Cr (Zr has a hexagonal close-packed structure, while Cr has a body-centered-cubic structure [41]).

While the position of (1011) reflections does not change with increasing the Cr concentration, the positions of (0001) and (0002) reflections shift toward higher 20 values, corresponding to a decrease in the out-of-plane c lattice parameter from 0.352 nm for \( \text{ZrB}_{2.18} \) to 0.349 nm for \( \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.38} \). This is mainly due to the smaller covalent radius of Cr atoms incorporated in the diboride structure, the corresponding lower B concentrations, and a change in the film’s residual stress level. The incorporation of Cr atoms also results in a significant increase in the

Table 1

| Films       | \( P_{ZrB_2} \) [W] | B [at. %]  | Cr [at. %]  | Zr [at. %]  | Cr/(Zr + Cr) | B/(Zr + Cr) |
|-------------|---------------------|------------|-------------|-------------|--------------|--------------|
| \text{ZrB}_{2.18} | 4000                | 67.3 ± 1.0 | 0           | 30.9 ± 0.4  | 0            | 2.18         |
| \text{Zr}_{0.7} \text{Cr}_{0.25} \text{B}_{1.25} | 4000                | 59.6 ± 1.1 | 9.1 ± 0.3   | 30.0 ± 0.5  | 0.23         | 1.52         |
| \text{Zr}_{0.7} \text{Cr}_{0.25} \text{B}_{1.42} | 3500                | 57.6 ± 0.7 | 11.8 ± 0.2  | 28.9 ± 0.3  | 0.29         | 1.42         |
| \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.38} | 3000                | 57.2 ± 1.0 | 13.3 ± 0.1  | 28.1 ± 0.1  | 0.32         | 1.38         |
| \text{Zr}_{0.66} \text{Cr}_{0.34} \text{B}_{1.30} | 2500                | 55.4 ± 1.0 | 15.5 ± 0.4  | 27.2 ± 0.4  | 0.36         | 1.30         |
| \text{Zr}_{0.56} \text{Cr}_{0.44} \text{B}_{1.11} | 2000                | 51.6 ± 0.8 | 20.4 ± 0.4  | 25.9 ± 0.4  | 0.44         | 1.11         |
full-width at half-maximum values of the XRD reflections; e.g. from 0.18° for ZrB_{2.18} to 0.4° for Zr_{0.68}Cr_{0.32}B_{1.38} for the (0001) reflection.

B 1s, Zr 3d, and Cr 2p XPS core-level spectra acquired from the as-deposited Zr_{1-x}Cr_{x}B_{y} thin films grown on Si(001) substrates are plotted in Fig. 2. The B 1s and Zr 3d spectra shown in Fig. 2(a) are normalized to the intensity of the Zr 3d_{5/2} peak. The Zr 3d_{3/2} and 3d_{5/2} peaks appear at 181.3 and 178.9 eV, respectively, with no detectable change in their positions or shapes as a function of Cr concentration. The position of the B 1s peaks does not change noticeably for ZrB_{2.18}, Zr_{0.77}Cr_{0.23}B_{1.52}, Zr_{0.77}Cr_{0.29}B_{1.42}, and Zr_{0.68}Cr_{0.32}B_{1.36}. The peaks appear at ~188.0 eV. This indicates that the incorporation of Cr, which has a slightly higher electronegativity than Zr (1.66 for Cr and 1.33 for Zr, based on the Pauling scale [43]), does not change the effective valence-charge density residing on the B atoms. However, there is a slight shift in the position of the B 1s peaks toward lower binding energies for the Zr_{0.66}Cr_{0.34}B_{1.30} and Zr_{0.56}Cr_{0.44}B_{1.11} alloys (~187.7 eV). In addition, the width of B 1s peaks for these alloys is larger than the other films. These slight changes correlate to the apparent loss of crystalline structure (see Fig. 1) and, hence, cannot be directly related to the change in the bonding configuration, as likely the layer electrical properties are modified, which may have a direct effect on the screening ability [44]. Fig. 2(b) shows that increasing Cr concentration does not have an obvious effect on the positions and shapes of the Cr 2p peaks (the Cr 2p spectra in Fig. 2(b) are normalized to the intensity of the Cr 2p_{3/2} peak).

Fig. 3 compares the XSEM, BF-XTEM, and DF-XTEM images of as-deposited ZrB_{2.18}, Zr_{0.77}Cr_{0.23}B_{1.52}, Zr_{0.66}Cr_{0.32}B_{1.38}, and Zr_{0.56}Cr_{0.44}B_{1.11} thin films grown on Si(001) substrates. The corresponding selected-area electron diffraction (SAED) patterns are also shown as insets. The XTEM images and SAED patterns are acquired from regions close to the surface of the layers. The XSEM images, Figs. 3 (a)-(d), show that all as-deposited films have dense microstructures with smooth surfaces. The ZrB_{2.18} and Zr_{0.77}Cr_{0.23}B_{1.52} films exhibit a columnar microstructure with columns extending through the films, while the XSEM images of Zr_{0.66}Cr_{0.32}B_{1.38} and Zr_{0.56}Cr_{0.44}B_{1.11} alloys are featureless. The BF- and DF-XTEM images of as-deposited ZrB_{2.18} films, shown in Figs. 3(e) and 3(f), indicate that ZrB_{2.18} consists of discernable porosities, marked by black arrows in the micrograph. The ZrB_{2.18} columns with a width of 10.1 ± 2 nm near the film’s surface are continual from close to the surface to the substrate normal. The columns are inclined at an angle of 7° with respect to the substrate normal, due to the 21° angle between the substrate and the ZrB_{2.18} target. The corresponding SAED pattern, the inset in Fig. 3(e), is composed of diffraction arcs with (0001), (10T0), and (10T1) components in which the (0001) signal in the growth direction is the weakest one, in agreement with the XRD result in Fig. 1(a).

The BF- and DF-XTEM images of Zr_{0.77}Cr_{0.23}B_{1.52} and Zr_{0.66}Cr_{0.32}B_{1.38} Figs. 3(f), (j), (3), and (k), show that alloying with Cr interrupts the continuous columnar growth and produces dense nanostructure. The column length of Zr_{1-x}Cr_{x}B_{y} alloys decreases as a function of Cr concentration up to x = 0.32. Moreover, adding Cr leads to a decrease in the column width; the nanostructure of Zr_{0.66}Cr_{0.32}B_{1.38} consists of very fine columns that do not extend throughout the whole film, see Figs. 3(g) and 3(k). The corresponding SAED patterns of Zr_{0.77}Cr_{0.23}B_{1.52} and Zr_{0.66}Cr_{0.32}B_{1.38} alloys, the insets in Figs. 3(f) and 3(g), indicate the presence of (0001), (10T0), and (10T1) diffraction arcs with a decrease in the crystallinity by increasing the Cr concentration. The BF- and DF-XTEM micrographs of Zr_{0.56}Cr_{0.44}B_{1.11} in Figs. 3(b) and 3(l), together with its corresponding high-resolution BF-XTEM image and SAED pattern shown as insets in Fig. 3(h), confirm that this alloy has an amorphous nanostructure, which is consistent with its XRD 0-2θ result in Fig. 1(f).

3.2. Mechanical properties

The residual stress of as-deposited Zr_{1-x}Cr_{x}B_{y} thin films grown on Al_{2}O_{3}(0001) substrates changes from +0.91 ± 0.4 GPa for ZrB_{2.18}, to −0.83 ± 0.23 GPa for Zr_{0.77}Cr_{0.23}B_{1.52}, −1.27 ± 0.15 GPa for Zr_{0.71}Cr_{0.29}B_{1.42}, +0.15 ± 0.02 GPa for Zr_{0.68}Cr_{0.32}B_{1.38}, +0.04 ± 0.04 GPa for Zr_{0.64}Cr_{0.36}B_{1.30}, and −0.53 ± 0.02 GPa for Zr_{0.56}Cr_{0.44}B_{1.11}. Fig. 4 shows the nanoindentation hardnesses H and elastic moduli E of as-deposited layers grown on Al_{2}O_{3}(0001) substrates as a function of x. The hardness of ZrB_{2.18} is 31.8 ± 1.0 GPa, and increases to 41.7 ± 1.2 GPa for Zr_{0.77}Cr_{0.23}B_{1.52} and 41.6 ± 0.9 GPa for Zr_{0.71}Cr_{0.29}B_{1.42}, which is primarily due to their high compressive stress, solid-solution hardening [45], and narrow column widths (Hall-Petch effect [46,47]). Further increase in Cr concentration results in a decrease in H to ~31.0 GPa for Zr_{0.68}Cr_{0.32}B_{1.38}, Zr_{0.64}Cr_{0.36}B_{1.30}, and Zr_{0.56}Cr_{0.44}B_{1.11}. The decrease in H can be attributed to their (i) low B concentration, which results in a decrease in the strong bond density, (ii) tensile residual stress, (iii) high Cr concentration, which shows similar effect on the hardness of TMCrN films [48,49], and (iv) structural change from crystalline to nanocrystalline to amorphous. The elastic modulus of ZrB_{2.18} is 494 ± 19 GPa. E decreases from 507 ± 15 GPa for Zr_{0.77}Cr_{0.23}B_{1.52}, to 497 ± 11 GPa for Zr_{0.71}Cr_{0.29}B_{1.42}, 422 ± 19 GPa for Zr_{0.68}Cr_{0.32}B_{1.38}, and 404 ± 10 GPa for Zr_{0.64}Cr_{0.36}B_{1.30}. Then, it shows a slight increase to 408 ± 14 GPa for Zr_{0.56}Cr_{0.44}B_{1.11}.

The relative ductility of as-deposited ZrB_{2.18}, Zr_{0.77}Cr_{0.23}B_{1.52}, Zr_{0.66}Cr_{0.32}B_{1.38}, and Zr_{0.56}Cr_{0.44}B_{1.11} thin films grown on Al_{2}O_{3}(0001) substrates is assessed by nanoindentation using a sharp cube-corner indenter. The minimum indentation force required to create radial cracks at nanoindentation corners is below 50 mN for ZrB_{2.18}, Zr_{0.77}Cr_{0.23}B_{1.52}, and Zr_{0.68}Cr_{0.32}B_{1.38}, while this force is 150 mN for the
Fig. 3. XSEM, BF-XTEM, and DF-XTEM images of as-deposited (a, e, i) ZrB$_{2.18}$, (b, f, j) Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, (c, g, k) Zr$_{0.68}$Cr$_{0.32}$B$_{1.38}$, and (d, h, l) Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films grown on Si(001) substrates. The corresponding SAED patterns are given in insets. The high-resolution BF-XTEM image of Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ is shown as inset in (h). The brightness appearing at the substrate/film interfaces in XSEM images of Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$ and Zr$_{0.68}$Cr$_{0.32}$B$_{1.38}$ films originates from charging.
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Fig. 4. Nanoindentation hardness $H$ and elastic modulus $E$ of as-deposited Zr$_{1-x}$Cr$_x$B thin films grown on Al$_2$O$_3$(0001) substrates as a function of $x$ ranging from 0 to 0.44.

Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys. Fig. 5 compares the SEM images of the cube-corner nanoindentations made by a load of 200 mN. The average length of radial cracks induced by 200 mN significantly decreases from $C_m = 4260 \pm 200$ nm for ZrB$_{2.18}$, to 2050 $\pm$ 190 nm for Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, 1370 $\pm$ 110 nm for Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$, and 720 $\pm$ 64 nm for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ films. Spalling, which is a common characteristic of indented brittle materials, can be observed around the nanoindentations of ZrB$_{2.18}$ and Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, while there is a significant pileup around the nanoindentations of Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$, proving a higher ductility for these alloys.

The adhesion strengths of as-deposited ZrB$_{2.18}$, Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$, and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films grown on WC-Co substrates are evaluated by Revescratch tests. Optical microscope images from the scratch tracks, together with corresponding SEM micrographs acquired from the regions indicated by dashed and solid boxes in the optical microscope images, are exhibited in Fig. 6. The optical microscope images show that all films follow a similar scratch-failure mode; starting with chips spallation on the side of tracks, then wedge spallation, and eventually substrates exposure, which are the common failure modes observed for hard thin films [50, 51]. The minimum load at which peeling and spallation occurs, referred to as the critical load ($L_{c2}$) [52], is considered as the representative of adhesive failure, i.e. film delamination and spallation. The ZrB$_{2.18}$ film exhibits a poor adhesion together with severe chipping and buckling along its scratch track, with $L_{c2} = \sim 29$ N, due to its high brittleness. Although the $L_{c2}$ value of the Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$ alloys ($\sim 28$ N) is almost similar to that of ZrB$_{2.18}$, it increases significantly to $\sim 42$ and $\sim 49$ N for Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$, respectively. The SEM images from the regions indicated with dashed boxes, at distances between $\sim 1.0$ mm and $\sim 1.1$ mm ($\sim 30$ N), in the optical microscope images of ZrB$_{2.18}$ and Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$, reveal angular cracks (indicated with black arrows) appeared close to the scratch tracks, which form due to their tensile stresses [51, 53]. However, the SEM images of the Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films, from the same distances ($\sim 1.0$ to $\sim 1.1$ mm), do not show such angular cracks as they have compressive stresses.

The reduction in chipping debris observed for Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$, compared to ZrB$_{2.18}$ and Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, confirms the increase in the film toughness. While the most striking surface feature in the SEM images from the regions at distances between $\sim 1.0$ mm and $\sim 1.1$ mm is peeling and spallation for ZrB$_{2.18}$ and Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$, the SEM images of Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ from similar distances, dashed boxes, do not indicate any obvious change in the microstructure of scratched surfaces. Compared to the SEM images of ZrB$_{2.18}$ and Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$ acquired from the $L_{c2}$ regions primarily showing chipping debris, the SEM micrographs of Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$ and

Fig. 5. SEM images from the cube-corner nanoindentations of as-deposited (a) ZrB$_{2.18}$, (b) Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$, (c) Zr$_{0.66}$Cr$_{0.32}$B$_{1.38}$, and (d) Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films grown on Al$_2$O$_3$(0001) substrates made with a load of 200 mN.

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Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\) alloys obtained from their Lc2 regions, indicated by blue solid boxes in their optical microscope images, consist of chipping debris and transverse semicircular cracks appeared in the scratch tracks, an indication of plastic deformation [51].

The friction coefficients (\(\mu\)) and wear rates of as-deposited ZrB\(_{2.18}\), Zr\(_{0.77}\)Cr\(_{0.23}\)B\(_{1.52}\), Zr\(_{0.68}\)Cr\(_{0.32}\)B\(_{1.38}\), and Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\) thin films grown on WC-Co substrates are given in Table 2. Optical microscope images from the wear tracks of these layers are also compared in Fig. 7. The friction coefficient is 0.518 \(\pm\) 0.004 for ZrB\(_{2.18}\), 0.538 \(\pm\) 0.007 for Zr\(_{0.77}\)Cr\(_{0.23}\)B\(_{1.52}\), 0.565 \(\pm\) 0.007 for Zr\(_{0.68}\)Cr\(_{0.32}\)B\(_{1.38}\), and 0.522 \(\pm\) 0.007 for Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\). The results show that adding Cr does not have a significant influence on the friction coefficients of the Zr\(_{1-x}\)Cr\(_x\)B\(_y\) alloys. However, the wear resistance of ZrB\(_{2.18}\) thin films is considerably improved by alloying with Cr. The wear rate decreases from \((7.9 \pm 0.4) \times 10^{-16} \text{ m}^3/(\text{Nm})\) for ZrB\(_{2.18}\), to \((2.5 \pm 0.3) \times 10^{-16} \text{ m}^3/(\text{Nm})\) for Zr\(_{0.77}\)Cr\(_{0.23}\)B\(_{1.52}\), \((2.1 \pm 0.2) \times 10^{-16} \text{ m}^3/(\text{Nm})\) for Zr\(_{0.68}\)Cr\(_{0.32}\)B\(_{1.38}\), and \((0.6 \pm 0.1) \times 10^{-16} \text{ m}^3/(\text{Nm})\) for Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\).

The broad wear track of ZrB\(_{2.18}\), Fig. 7(a), shows a higher material loss (i.e. higher wear rate) occurring during the wear test with a typical wear caused by plastic deformation. There is a decrease in the width of wear tracks as a function of Cr concentration in the alloys. Compared to ZrB\(_{2.18}\), the adhesive wear is the primary wear mechanism of as-deposited Zr\(_{1-x}\)Cr\(_x\)B\(_y\) thin films, Figs. 7(b), (c), and 7(d). The adhesion of the alloys to the GCr15 steel produces a high material loss of the friction ball, instead of the alloys, which reduces the wear rate.

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**Table 2**

Friction coefficients (\(\mu\)) and wear rates of as-deposited ZrB\(_{2.18}\), Zr\(_{0.77}\)Cr\(_{0.23}\)B\(_{1.52}\), Zr\(_{0.68}\)Cr\(_{0.32}\)B\(_{1.38}\), and Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\) thin films grown on WC-Co substrates.

| Films          | \(\mu\)  | Wear rate \([\times 10^{-16} \text{ m}^3/(\text{Nm})]\) |
|----------------|---------|-----------------------------------|
| ZrB\(_{2.18}\) | 0.518 \(\pm\) 0.004 | 7.9 \(\pm\) 0.4               |
| Zr\(_{0.77}\)Cr\(_{0.23}\)B\(_{1.52}\) | 0.538 \(\pm\) 0.007 | 2.5 \(\pm\) 0.3               |
| Zr\(_{0.68}\)Cr\(_{0.32}\)B\(_{1.38}\) | 0.565 \(\pm\) 0.007 | 2.1 \(\pm\) 0.2               |
| Zr\(_{0.56}\)Cr\(_{0.44}\)B\(_{1.11}\) | 0.522 \(\pm\) 0.007 | 0.6 \(\pm\) 0.1               |
enhanced wear resistance can be attributed to the combination of high hardness (>30 GPa) and increased toughness. Out of all compositions investigated, Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys are chosen for further oxidation and corrosion studies as they have metallic-glass structure, relatively low residual stress, good hardness and toughness, and the highest wear resistance.

3.3. Oxidation properties

Fig. 8 compares the XSEM images of ~2800-nm ZrB$_{2.18}$ and ~2100-nm Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films annealed in air at 700 °C for the time $t_a$ of 1, 3, and 5 h. The thickness of the oxide scale on ZrB$_{2.18}$ increases from $830 \pm 50$ nm for $t_a = 1$ h, to $2620 \pm 80$ nm for $t_a = 3$ h, and $3460 \pm 90$ nm for $t_a = 5$ h. The oxide-scale thickness changes linearly as a function of oxidation time ($d_{ox} = 708 \cdot t_a + 135$). However, the oxide scales formed on the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys are significantly thinner than those on ZrB$_{2.18}$ over the entire $t_a$ range. The thickness of the oxide scale on Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ increases from $350 \pm 30$ nm for $t_a = 1$ h, to $550 \pm 50$ nm for $t_a = 3$ h, and $665 \pm 55$ nm for $t_a = 5$ h, following a $d_{ox} = 352.4 \cdot t_a^{0.4}$ relationship.
The enhanced oxidation resistance observed for the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys is attributed to their elemental composition and nanostructure. The TMB$_2$ oxidation, which is mainly influenced by the evaporation rate of B$_2$O$_3$ (g) phase, largely depends on the oxygen partial pressure, annealing temperature, and B concentration [11,54]. At constant oxygen partial pressure and annealing temperature, the vapor pressure of B$_2$O$_3$ (g) phase increases as a function of B concentration that results in decreasing the oxidation resistance [54]. We recently showed that sputter-deposited columnar TiB$_{2.4}$ thin films, in which the excess B segregates to the column boundaries, are highly prone to continuous vigorous oxidation in air [16]. The B$_2$O$_3$ (g) phase preferentially forms at the column boundaries, which are B-rich, during annealing at temperatures above 400 °C. The evaporation of this phase, together with the coarsening of TiO$_2$ (s), lead to the formation of large gaps between the TiO$_2$ (s) columns that act as wide channels for oxygen to readily access the unoxidized regions; consequently, causing a continuous oxidation of B$_2$O$_3$ (g). The B$_2$O$_3$ (g) phase as a function of B concentration; hence, the higher oxidation resistance of Zr$_{2.18}$Ti$_{0.1}$Cr$_{0.28}$N films. Similar effect can be expected for the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys.

3.4. Corrosion properties

The corrosion properties of as-deposited ZrB$_{2.18}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films grown on WC-Co substrates are obtained by electrochemical measurements during the immersion of the layers in the 0.1 M NaCl corrosive medium for 25 h, at room temperature and without agitation. The open circuit potential (E$_{ocp}$), linear polarization resistance (R$_p$), and potentiodynamic polarization curves of ZrB$_{2.18}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films are shown in Fig. 9. The electrochemical data determined from the polarization curves are summarized in Tables 3 and 4. Fig. 9(a) compares the E$_{ocp}$ values of ZrB$_{2.18}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ as a function of immersion time (t$_{ocp}$). The low-intensity peaks in these curves result from the R$_p$ measurements at t$_{ocp}$ = 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, 16.0, and 24.0 h. Both films have negative E$_{ocp}$ values over the entire t$_{ocp}$ range. The open circuit potential of ZrB$_{2.18}$ continuously decreases from ~180 ± 28 mV for t$_{ocp}$ = 0.25 h to ~230 ± 18 mV for t$_{ocp}$ = 16.0 h and then reaches an almost stable potential (~230 mV) after 2.0 h immersing in the corrosive medium. In general, the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloy has lower negative E$_{ocp}$ values, i.e., more noble, than the ZrB$_{2.18}$ films over the entire t$_{ocp}$ range. This reveals that the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ films have a better electrochemical stability in the 0.1 M NaCl medium compared to ZrB$_{2.18}$ [56].

Fig. 9(b) exhibits the R$_p$ values of as-deposited ZrB$_{2.18}$ and Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ thin films determined at times ranging from 0.25 to
and Zr

Table 3

| Time [h] | E_{ocp} [mV] | R_p [MΩ cm$^2$] |
|----------|--------------|-----------------|
| 0.25     | -180 ± 28    | 2.0 ± 0.3       |
| 0.5      | -180 ± 22    | 2.1 ± 0.3       |
| 1.0      | -190 ± 19    | 2.1 ± 0.3       |
| 2.0      | -200 ± 16    | 2.2 ± 0.3       |
| 4.0      | -210 ± 14    | 2.2 ± 0.3       |
| 8.0      | -220 ± 17    | 2.1 ± 0.2       |
| 16.0     | -230 ± 18    | 2.2 ± 0.3       |
| 24.0     | -230 ± 17    | 2.2 ± 0.3       |

24.0 h. The alloys have significantly higher R_p values than the ZrB$_{2.18}$ films (see Table 3); the R_p value of Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ obtained after a 24.0-h immersion in the corrosive medium is about twelve times higher than that of ZrB$_{2.18}$ (2.2 ± 0.3 MΩ cm$^2$ for ZrB$_{2.18}$ and 27.3 ± 2.9 MΩ cm$^2$ for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$). Comparing the potentiodynamic polarization curves acquired after 25.0 h, Fig. 9(c), indicates that the Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys have lower corrosion current densities ($i_{corr}$) than the reference ZrB$_{2.18}$ films. The $i_{corr}$ value decreases from (4.6 ± 2.0) × 10$^{-6}$ mA/cm$^2$ for ZrB$_{2.18}$ to (0.54 ± 0.1) × 10$^{-6}$ mA/cm$^2$ for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ at the E$_{corr}$ values of ~250 ± 49 mV and ~180 ± 59 mV, respectively. This indicates that the corrosion rate of Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ is almost nine times lower than that of ZrB$_{2.18}$. The anodic polarization curves of both films consist of passive regions (from ~450 to ~1050 mV), where the one for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ is to some extent metastable, but at lower anodic current densities compared to that for ZrB$_{2.18}$. The passive current density $i_{pass}$ is (1.3 ± 0.3) × 10$^{-7}$ mA/cm$^2$ for ZrB$_{2.18}$ and (0.6 ± 0.1) × 10$^{-7}$ mA/cm$^2$ for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$.

Allowing directly influences on the corrosion properties of materials by changing their nobility [56–58]. The lower E$_{ocp}$ value obtained for Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ demonstrates that the electrochemical stability of these alloys is higher than that of ZrB$_{2.18}$ as Cr is a more noble element. The other factors that effectively change the corrosion resistance are the column boundaries and their density [59,60]. The column boundaries of ZrB$_{2.18}$ are more prone to corrosion attack than inside the columns, due to heterogeneity in their structure and chemistry (e.g. the B-rich phase). Thus, the absence of column boundaries for amorphous Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ may contribute to a better corrosion resistance compared to that of polycrystalline ZrB$_{2.18}$ [61].

4. Conclusions

We demonstrate control of the composition, nanostructure, and properties of ZrB$_2$-rich Zr$_{1-x}$Cr$_x$B$_y$ films grown by hybrid Cr-HiPIMS/ZrB$_2$-DCMS co-sputtering. The reference ZrB$_{2.18}$ layers are deposited by DCMS with a negative dc substrate bias of 100 V. For the Zr$_1$Cr$_{29}$B$_{77}$ alloy growth, the ZrB$_2$ target is continuously sputtered by DCMS, while the Cr magnetron is operated in HiPIMS mode providing pulsed Cr-ion fluxes. The Cr metal fraction, Cr/(Zr + Cr), is increased from $x = 0.23$ to $x = 0.44$ by decreasing the power $P_{200}$ applied to the DCMS ZrB$_2$ target from 4000 to 2000 W in 500-W increments, while the average power, pulse width, and frequency applied to the HiPIMS Cr target are maintained constant at 700 W, 50 μs, and 100 Hz, respectively. Concurrently, $y$ decreases from 2.18 to 1.11 as a function of $P_{200}$, due both to the addition of Cr (primarily) and preferential B resputtering. The energetic Cr-ion bombardment increases the density of the alloys and causes re-nucleation of the column growth. As a result, there is a refinement of the columnar structure with increasing the Cr concentration accompanied by increasing hardness to ~42 GPa for Zr$_{0.77}$Cr$_{0.23}$B$_{1.52}$ and Zr$_{0.71}$Cr$_{0.29}$B$_{1.42}$. However, the further increase of Cr concentration leads to a significant B deficiency that results in the collapse of the hexagonal AlB$_2$-structure into amorphous dense alloys, as revealed by XRD, TEM, and SAED patterns, with hardness values above 30 GPa.

The changes in the composition and nanostructure result in enhanced toughness and wear properties. The Zr$_{0.56}$Cr$_{0.44}$B$_{1.11}$ alloys, with the highest Cr concentration, exhibit considerably better toughness and wear resistance compared to ZrB$_{2.18}$. The wear rate decreases from
~7.9 × 10^{-16} \text{m}^3/(\text{Nm}) for \text{ZrB}_2\text{B}_1 to ~0.6 × 10^{-16} \text{m}^3/(\text{Nm}) for \text{Zr}_0.56\text{Cr}_0.44\text{B}_1.1. In addition, these alloy films exhibit significantly higher oxidation and corrosion resistance. The thickness of oxide scale formed after air-annealing at 700 °C for 5.0 h markedly decreases from ~3460 nm for \text{ZrB}_2\text{B}_1 to ~665 nm for \text{Zr}_0.56\text{Cr}_0.44\text{B}_1.1. The corrosion rate of \text{Zr}_0.56\text{Cr}_0.44\text{B}_1.1 is about nine times lower than \text{ZrB}_2\text{B}_1. The \text{Zr}_0.56\text{Cr}_0.44\text{B}_1.1 alloys with the structural characteristics of metallic-glass thin films show simultaneously several enhanced properties, which are essential for many strategic applications.

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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References

[1] T. Leyendecker, O. Lemmer, S. Eser, J. Ebberink, The development of the PVD coating TiAlN as a commercial coating for cutting tools, Surf. Coating. Technol. 48 (2) (1991) 175–178.
[2] B. Subrahmanian, C.V. Muraleedharan, R. Ananthakumar, M. Jayachandran, A comparative study of titanium nitride (TiN), titanium oxide nitride (TiON) and titanium aluminum nitride (TiAlN), as surface coatings for bio implants, Surf. Coating. Technol. 205 (21) (2011) 5014–5020.
[3] L.E. Toth, Transition Metal Carbides and Nitrides, Academic Press, NY, 1971.
[4] R. Rachbauer, S. Massl, E. Stergar, D. Holec, D. Kiener, J. Keckes, J. Patscheider, M. Stiefel, H. Leitner, P.H. Mayrhofer, Decomposition pathways in age hardening of TiAl-based hard compound films, J Vac. Sci. Technol. A 4 (6) (1986) 2695–2700.
[5] N.P. Bansal, Handbook of Ceramic Composites, Kluwer Academic Publishers, Boston MA, 2005.
[6] N.L. Okamoto, M. Kusakari, K. Tanaka, H. Inui, S. Otani, Anisotropic elastic constants and thermal expansivities in monocrystal CrB_2 TiB_2 and ZrB_2. Acta Mater. 38 (1) (2000) 76–84.
[7] I.V. Matvovich, G.V. Samsonov, P. Hagenmuller, Prog. Mater. Sci. 107 (2020), 100591.
[8] B. Bakhit, D.L.J. Engberg, J. Lu, J. Rosen, P.O. Persson, L. Hultman, J. Petrov, J.E. Greene, G. Grezczynski, Controlling the B/ Ti ratio of TiB_2 thin films grown by high-power impulse magnetron sputtering, J Vac. Sci. Technol. A 36 (3) (2018), 030604.
[9] B. Bakhit, J. Palisaitis, Z. Wu, M.A. Sorticai, D. Primetzhofer, P.O. Persson, J. Rosen, L. Hultman, J. Petrov, J.E. Greene, G. Grezczynski, Self-organized columnar ZrTiO_2 B_2 core-shell nanostructure thin films, Surf. Coating. Technol. 401 (2020), 125277.
[10] B. Bakhit, I. Petrov, J.E. Greene, L. Hultman, J. Petrov, G. Grezczynski, Strategy for simultaneously increasing both hardness and toughness in ZrB_2-rich Zr-Ta-B thin films, J Vac. Sci. Technol. A 37 (3) (2019), 030606.
[11] B. Bakhit, J. Palisaitis, P.O. Persson, B. Alling, J. Rosen, L. Hultman, J. Petrov, J.E. Greene, G. Grezczynski, Self-organized columnar ZrTiO_2 B_2 core-shell nanostructure thin films, Surf. Coating. Technol. 204 (2010) 5999–6010.
[12] A. Kimbauer, A. Wagner, V. Moraes, D. Primetzhofer, M. Hans, J.M. Schneider, P. Polcik, P.H. Mayrhofer, Thermal stability and mechanical properties of sputtered (H,Ta,V,W,Zr)-diborides, Acta Mater. 200 (2020) 559–569.
[13] G. Sade, J. Pelleg, Co-sputtered TiB_2, P.H. Mayrhofer, Thermal stability and mechanical properties of sputtered (H,Ta,V,W,Zr)-diborides, Acta Mater. 200 (2020) 559–569.
[14] J. Sung, D.M. Goedde, G.S. Girolami, J.R. Abelson, Remote-plasma chemical vapor deposition of conformal ZrB_2 films at low temperature: a promising diffusion barrier for ultralarge scale integrated electronics, J. Appl. Phys. 91 (6) (2002) 3139–3143.
[15] E. Sani, M. Mexuci, L. Mercatelli, A. Balbo, C. Musa, R. Licheri, R. Orrà, G. Cao, Titanium diboride ceramics for solar thermal absorbers, Sol. Energy Mater. Sol. Cells 169 (2017) 313–319.
[16] B. Bakhit, J. Palisaitis, J. Thornberg, J. Rosen, P.O.A. Persson, L. Hultman, I. Petrov, J.E. Greene, G. Grezczynski, Improving the high-temperature oxidation resistance of TiB_2 thin films by alloying with Al, Acta Mater. 196 (2020) 679–689.
[17] B. Bakhit, D.L.J. Engberg, J. Lu, J. Rosen, H. Hogberg, L. Hultman, J. Petrov, J.E. Greene, G. Grezczynski, Strategy for simultaneously increasing both hardness and toughness in ZrB_2-rich Zr-Ta-B thin films, J Vac. Sci. Technol. A 37 (3) (2019), 030606.
[52] S. Zhang, X. Zhang, Toughness evaluation of hard coatings and thin films, Thin Solid Films 520 (7) (2012) 2375–2389.

[53] K. Holmberg, A. Laukkanen, H. Ronkainen, K. Wallin, S. Varjus, J. Koskinen, Tribological contact analysis of a rigid ball sliding on a hard coated surface: Part I: modelling stresses and strains, Surf. Coating. Technol. 200 (12-13) (2006) 3793–3809.

[54] L. Kaufman, E.V. Clougherty, Investigation of Boride Compounds for Very High Temperature Applications, RTD-TRD-N63-4096, Part II, ManLabs Inc., Cambridge, MA, 1965.

[55] I.C.I. Okafor, R.G. Reddy, The oxidation behavior of high-temperature aluminides, JOM 51 (6) (1999) 35–40.

[56] B. Bakhit, A. Akbari, F. Nasirpouri, M.G. Hosseini, Corrosion resistance of Ni-Co alloy and Ni-Co/SiC nanocomposite coatings electrodeposited by sediment codeposition technique, Appl. Surf. Sci. 307 (2014) 351–359.

[57] ASM Handbook, Corrosion: Fundamentals, Testing, and Protection, ASM International, Materials Park Ohio, 2003.

[58] B. Bakhit, A. Akbari, Nanocrystalline Ni-Co alloy coatings: electrodeposition using horizontal electrodes and corrosion resistance, J. Coating Technol. Res. 10 (2) (2013) 285–295.

[59] J.W. Dini, The Materials Science of Coatings and Substrates, William Andrew publishing, Noyes, 1993.

[60] B. Bakhit, A. Akbari, Effect of particle size and co-deposition technique on hardness and corrosion properties of Ni-Co/SiC composite coatings, Surf. Coating. Technol. 206 (23) (2012) 4964–4975.

[61] T. Rabizadeh, S.R. Allahkaram, Corrosion resistance enhancement of Ni-P electroless coatings by incorporation of nano-SiO₂ particles, Mater. Des. 32 (1) (2011) 133–138.