Effect of Bias Induced Microstructure on the Mechanical Properties of Nanocrystalline Zirconium Tungsten Nitride Coatings

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ABSTRACT

The utilization of substrate bias voltage to accelerate the sputtered ions in sputtering plasmas is an effective way to alter the properties of coating. In this work, hard nanocrystalline ZrWN coatings were sputter-deposited at relatively low deposition temperature (200 °C) by varying the substrate bias voltage from -20 V to -120 V. The effect of negative substrate bias on the microstructure and mechanical properties of nanocrystalline ZrWN coatings has been studied in detail employing X-ray diffraction, field emission scanning electron microscopy, energy dispersive x-ray spectroscopy, atomic force microscopy, transmission electron microscopy, nano-indentation and micro-indentation. The results indicate that the microstructure and morphology were significantly altered as a function of the increasing bias voltage. The bias voltage of -20 V to -60 V lead to enhanced ion current density and deposition rate while the resputtering effect was induced as the bias voltage increased beyond -60 V. A dense glassy structure along with a maximum compressive stress (8 GPa) and hence optimum mechanical properties (hardness~ 34 GPa, reduced elastic modulus E_r ~ 145 GPa, wear resistance~ 0.23 and fracture toughness~ 2.25 MPa $\sqrt{m}$) were obtained in the ZrWN nanocrystalline coatings at a bias voltage of -100 V. The results demonstrate that the enhancement of mechanical properties in ZrWN coatings can be achieved by carefully controlling the processing conditions, which in turn facilitate controlling the microstructure evolution, stress and mechanical properties.

Keywords: ZrWN Coatings; Negative Bias Voltage; Microstructure; Mechanical Properties

1. Introduction

To meet the challenges of emerging applications in tribology systems, recent attention has been mainly focused towards the development of more exotic nitride coatings with various design architectures that can further enhance performance and stability [1-6]. At the same time, coatings with self-adaptability to the increasingly harsh and rapidly changing application conditions of future tribological systems are of enormous recent interest. Many transition metal nitride coatings, such as TiN, ZrSiN, TiAlN, TiSiN, TiAlVN, CrTiAlN, CrAlN, CrNiN, ZrNiN, ZrWN, have been successfully explored in the past few decades as wear protective coatings to prolong the service life of components used in aggressive environments [1-18, 19]. It has been observed in many of these earlier efforts that the microstructure of these hard coatings is the key parameter that must be tailored in order to achieve high thermal stability, hardness and wear resistance [9 and references there in]. Recently, tuning a dense voids-free microstructure (non-columnar microstructure) with tailored lattice constants of transition metal nitrides coatings have gained special attention because such nitride coatings can achieve high hardness (H), low effective elastic modulus (E_r), high elastic recovery ($W_e > 60\%$) and high fracture toughness, which are critical to the modern tribological applications [11-16]. For instance, Ehiasarian et al. [20] have reported that the dense microstructure of Cr based nitride coatings exhibit superlattice multilayer comparable sliding wear resistance. Sandu et al. [6] have reported that the Zr-Si-N film of featureless dense microstructure with (002) preferred orientation of grains possesses high hardness (39 GPa) as compared to that (25 GPa) of films with (111) orientation. However, the literature survey and associated brief analysis indicates that such microstructure and growth behavior of metal nitride coatings is highly sensitive to ad-atom and ad-ions energy, which are further strongly influenced by negative bias applied [3-7,15-18]. Thus, a proper tuning of

negative bias voltage may result in dense voids-free microstructure [6, 15]. Moreover, negative bias induced compressive stress further aid in realizing higher fracture toughness [16]. Petrov et al. [21] have reported that only a high flux of energy ions ~ 20 eV benefits thin film structure modification, including increased density, reduced surface roughness and refined grain size, while excessive ion energy ~ 100 eV may roughen the surface and reduce the tribological properties of nanostructured coatings. Wang et al. [4] have observed that the negative bias induced dense microstructure and compressive stress increased the hardness from 10 to 26 GPa, improved toughness from 1.67 to 2.02 MPa $\cdot\sqrt{m}$ in addition to increase the adhesion strength of CrAlN coatings. Therefore, deposition of wear protective coatings using negative bias voltage is attractive for commercial aspects. Moreover, Dubey et al. [17, 18] reported the microstructure induced mechanical properties of polycrystalline (*fcc*) and amorphous (*a*) ZrWN thin films deposited at ground potential. The crystallization-induced enhancement in stability and resistance to the plastic deformation and wear resistance of ZrWN thin films has been reported [17, 18]. In this context, the present work, attempts to produce ZrWN nanocrystalline coatings with controlled microstructure and mechanical properties. While preliminary results were reported in a communication elsewhere [22], a thorough understanding of the effect of substrate bias voltage induced microstructure evolution and linkage to the associated mechanical properties of ZrWN coatings is derived based on structural, chemical and mechanical properties measurements. It is demonstrated that the substrate bias combined with nano-morphology allows to produce mechanically high-quality ZrWN coatings at relatively low temperature (200 °C). Furthermore, as presented and discussed in this paper, a functional, direct relationship is formulated between bias voltage, ions energy, microstructure, fracture toughness and hardness.

Such functional structure-property relationship suggests that tailoring mechanical properties of ZrWN coatings can be achieved by tuning the processing conditions and microstructure.

2. Experimental details

2.1. Fabrication

ZrWN coatings were produced onto mirror polished and well cleaned Si-(100) (~0.067 cm thick , ~1cm x 2 cm) substrates by DC/RF unbalanced magnetron co-sputtering of Zr-target (5 cm diameter, 0.5 cm thick, 99.98% purity) and W-target (5 cm diameter, 0.5 cm thick, 99.95% purity) in Ar (8 sccm) and N₂ (32 sccm) discharge. The Zr-target and W-target were operated in DC-mode (Aplab H1010, 3kW) and RF mode (Advance energy, CESAR 136, 13.56 MHz, 600 W), respectively. Based on our previous experimental observations, the conductive W-target operating in DC mode becomes a poor conductor in reactive N₂ environment with time. Hence, in order to maintain a constant deposition rate, W target was operated in RF mode. In negative half cycle (3/4 in amplitude), Ar and N₂ ions are accelerated towards the target surface to sputter material. While, in the positive half cycle (1/4 in amplitude), charge neutrality is achieved through the free electron. The RF power is operated at very high frequency (13.56 MHz), hence only the electrons near to target surface are synchronized with positive half cycle. Hence, RF positive half cycle not affected the negative biasing of the sample. Moreover, substrate holder was isolated from the sputtering system and operated at negative bias with respect to ground potential. The deposition parameters employed are listed in Table 1. The substrate temperature was kept constant at 200 °C. Targets were fixed at an angle of 45° to the substrate normal. Si substrates were mounted on the substrate holder held at negative potential with the help of silver paste. The substrate holder was rotated at 5 rpm using a DC motor to ensure uniformity in coatings. The N₂ partial pressure and working pressure were 0.13 Pa and 0.67 Pa, respectively.

For a constant deposition time (1.5 h), the typical thickness (h) was varied nonmonotonically (1.6 to 2 μm) with increasing bias voltage. The maximum thickness (2 μm) was obtained at $V_s = -60$ V.

2.2. Characterization

The crystallographic structure of the ZrWN coatings was characterized using x-ray diffraction (XRD) (Bruker, D8 advance, Cu-K α radiation, Bragg-Brentano (2θ - 2θ) geometry, $\lambda = 1.54$ Å, step=0.02°, scan speed=2 sec/step) and transmission electron microscopy (TEM) (200kV, FEI, TECNAI G²). The ion milling technique (Gatan Model 691 PIPS, 4 keV and milling angle < 4°) was used to prepare plan view TEM samples for Zr-W-N thin films. The surface and cross-section of the coatings were observed by field emission scanning electron microscopy (FE-SEM) (FEI, QUANTA 200F). Atomic force microscopy (AFM) (NT-MDT, NTEGRA) was used in semi-contact mode to evaluate the coating topography and root-mean-square (RMS) roughness. The elemental composition analysis of ZrWN films carried out using energy dispersive x-ray analysis (OXFORD, X-Max) with variation of ± 0.3 at.% for heavy elements (Zr, W) and ± 2 at.% for light elements (N₂).

The residual stress was calculated using Stoney's equation (Eq. (1)) [23].

$$\sigma = (E_s t_s^2 / (6 t_f (1 - \nu_s))) (1/R - 1/R_0) \quad (1)$$

where E_s , ν_s , and t_s are the elastic modulus (130 GPa), Poisson's ratio (0.3) and the thickness (0.067 cm) of the substrate, t_f is the thickness of the deposited film, R_0 and R are the curvature radii of the substrate before and after deposition, respectively. The radius of curvature was measured by stylus profilometer (Mitutoyo, SurfTest SJ-400, Japan). The stylus was scanned about 25 mm diagonally around the centre of sample. The radii of curvatures which were almost equal

in orthogonal directions on same sample indicate spherical deformation of the sample. All the silicon pieces used for deposition have been cut from same Si wafer (15 cm diameter). The measured radius of curvature of all the Si samples before deposition was almost similar; however, the mean values of R_0 (1.7×10^3 m) and R (4.8m: -20 V, 2.6 m: -40V, 1.6m: -60V, 1.3 m: -80V, 1: -100V m and 2.4 m: -120V) have been used for the calculation of residual stress.

The lattice parameter is determined using Nelson-Riley function [24].The lattice parameter (a) for *fcc* system is obtained using Eq. 2 (Bragg's equation) and Eq. 3 for (111), (200) and (220) lattice planes.

$$d = \lambda / 2 \sin \theta \quad (2)$$

$$a = d / (h^2 + k^2 + l^2)^{1/2} \quad (3)$$

where d is interplanar spacing, λ is wavelength ($1.54 \text{ \AA}$), θ is the Bragg angle and h, k, l are the Miller indices of the lattice planes. The absorption, divergence and refraction of the X-ray beam by the samples involve a number of systematic errors in the measurement of θ and hence in the calculation of the lattice spacing d and lattice constants. Therefore, it is required to obtain the correct value of lattice constants free from all these systematic errors. This can be obtained from the intercept of the Nelson–Riley function ($F(\theta)$) (Eq. 4)[24] at the Y-axis.

$$F(\theta) = [(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta)] / 2 \quad (4)$$

where θ is the Bragg angle. The plots of $F(\theta)$ (at X-axis) versus calculated values of lattice constant (at Y-axis) for different lattice planes, which is a straight line, intersected the Y-axis by extrapolating Nelson–Riley function i.e. $F(\theta) \rightarrow 0$. The intersection of the plot at the Y-axis provides the lattice parameter value which is more or less free from systematic errors.

The hardness (H), effective elastic modulus (E_r) and elastic recovery (W_e) of these coatings were measured by nano-indentation (NT-MDT, Nanoslerometry) using a Berkovich diamond indenter with normal angle of 65.3° between tip axis and faces of triangular pyramid. The radius of curvature of nanoindenter tip employed was ~ 70 nm. The H, E_r and W_e of coatings have been measured at 10 mN load to assure the penetration depth should not more than the 10% of total thickness of coatings to minimize the substrate effect. The films were scratched with 2 to 10mN loads at constant loading velocity (20 nm/s) and scratch velocity (500 nm/s) for adhesion test purpose. Plastic deformation energy (U_p) [25] of the films is calculated by the area of loading-unloading curve in the load-displacement profile. The toughness was evaluated using micro indentation with a Vickers micro hardness tester (UHL VMHT). The micro indentations were done at varying loads (100 mN to 2000 mN). For each load, at least three readings were taken. The toughness K_{IC} is calculate by equation (5) [26].

$$K_{IC} = \delta (E_r/H)^{1/2} (P/C^{3/2}) \quad (5)$$

where P is the applied indentation load; E_r and H are the effective elastic modulus and hardness of the coating as obtained from nanoindentation, respectively. δ is an empirical constant which depends on the geometry of the indenter, for Vickers indenter $\delta = 0.016$. c is the crack length which was measured from optical microscopy (Olympus DME3) images. In order to reduce the substrate effect on film toughness, K_{IC} calculated from Eq. (5) was plotted versus indentation depth and then the curve was extrapolated to one-tenth of the film thickness to obtain the film toughness [4,25,27].

3. Results and Discussion

3.1. Deposition rate and elemental composition analysis

The variation in thickness and deposition rate (a_D) of ZrWN coatings, substrate ions current density (i_s) and kinetic energy (E_{bi}) of ions bombarding on the films as a function of substrate bias voltages (V_s) are presented in Table 2. **The plasma is considered fully ionized and collisionless for the deposition pressure (0.67 Pa).** The kinetic energy (E_{bi}) of bombarding ions in collisionless plasma sputtering is calculated by the following equation (6) [28, 29].

$$E_{bi} \text{ (J/cm}^3\text{)} \approx (i_s V_s)/a_D \quad (6)$$

The deposition rate and substrate ions current density varied non-monotonically with increasing V_s . For $-20 \text{ V} \leq V_s \leq -60 \text{ V}$, the a_D and i_s values increased from $\sim 19 \text{ nm/min}$ to $\sim 22 \text{ nm/min}$ and $5.1 \times 10^{-5} \text{ A/cm}^2$ to $8.5 \times 10^{-5} \text{ A/cm}^2$ respectively. With further increase in V_s , a_D decreased up to $\sim 17 \text{ nm/min}$ and i_s became constant at $8.5 \times 10^{-5} \text{ A/cm}^2$ value for $V_s > -60 \text{ V}$. The increase in i_s for $V_s \leq -60 \text{ V}$ indicates that the ionization of the coating flux was increased at selected deposition parameters (sputtering pressure $\sim 0.67 \text{ Pa}$ and target substrate distance $\sim 6 \text{ cm}$) which results in an increase of a_D values [15]. The drop observed in a_D values **is attributed to the** resputtering of the coating [3].

The atomic concentration of the various elements in ZrWN coatings as a function of V_s is shown in Fig. 1. The variation of atomic percentages i.e. 22.3–19.6%, 21.2–17.8% and 60.8–58.9% of Zr, W and N respectively, indicates that V_s **has** no significant effect on the elemental composition of ZrWN coatings. The nominal elemental composition is found to be $\text{Zr}_{21}\text{W}_{19}\text{N}_{60}$.

3.2. Microstructure analysis

Figure 2 shows the XRD patterns of ZrWN coatings as a function of substrate bias voltage. The diffraction peaks of polycrystalline ZrWN coatings as shown in Fig. 2a demonstrate a strong dependence of **coatings'** texture on V_s . The most important **feature is that the** XRD

patterns exhibit only one group of peaks of *fcc* structure indicating a single phase solid-solution nitride formation rather than the co-existence of respective nitrides, like ZrN and W₂N, or a composite [14]. For comparison, data reported for bulk ZrN and W₂N are also shown in Fig. 2. It has been observed that coatings' texture is very sensitive to V_s . The intensity variation and preferred growth direction changes with increasing V_s are evident in XRD. Therefore, normalized peak intensities N_{hkl} ($I_{hkl} / (I_{111} + I_{200} + I_{220})$) for (111), (200) and (220) peaks are plotted (Fig. 2b) as a function of V_s to further analyze the texturing behavior of these coatings. The preferred crystallographic orientation of grains was drastically changed from (111) to (200) and again (111) at $V_s \geq -60$ V. The competition in atomic peening, adatoms mobility and resputtering with increasing V_s controls the microstructure of coatings [30-32]. The atomic peening leads to re-arrangement of the lattice atoms thus rendering considerable stress into the coating. The intensive ion bombardment induced finite number of collisions in adatoms increases the local substrate temperature (thermalized adatoms) which in turn leads to a higher mobility of adatoms. Such thermally-induced increase in the ad-atom mobility induces growth in those crystallographic directions, where the strain energy density is minimum, leading to a strong texturing and/or changes in texturing orientation [33-36]. We believe that this mechanism is primarily causing the observed change in (111) to (200) texturing in ZrWN coatings. Finally, the resputtering as a result of high energy ion bombardment induces defects and low deposition rate [29-37]. It can be observed that the intensity of (111) XRD peak decreases with increasing V_s , except at $V_s = -120$ V. The kinetic energy of most of the bombarding ions ≤ -100 V was transferred to adatoms in-place to penetrate into the atomic layers, thereby increasing the surface mobility and decreasing the intensity of (111) XRD peak. The change of preferred growth orientation from (200) to (111) at $V_s = -120$ V is, therefore, attributed to the incorporation of

point defects. The change in preferred growth orientation with increasing bias voltage and induced point defect growth has also been observed for ZrN and TiN coatings [2, 38].

To further confirm the XRD findings and the absence of other secondary nanocrystalline phases, TEM analysis has been carried out on the ZrWN samples. Figure 3 shows the TEM bright field images and corresponding selected area electron diffraction patterns (SAED) of ZrWN coatings deposited at -80 V, -100 V and -120 V. Indexing of the observed SAED patterns is as noted in the images (Fig. 3). It is remarkable to note that the SAED patterns fully agree with the XRD data indicating that only the *fcc* ZrWN phase appears in all these coatings. No formation of a secondary phase is noted for any of the V_s values employed. Moreover, higher intensity of the (111) diffraction ring at $V_s = -120$ V in comparison to $V_s = -80$ V and -100 V confirms the strong preferential grain growth in (111) orientation as already evidenced in XRD measurements [39].

3.3 Morphology analysis

3.3.1. Crystallite size and microstrain

The average crystallite size and microstrain in the ZrWN coatings are evaluated based on further analysis of XRD data, specifically the observed peak shift (Fig. 2a) as a function of V_s . The shifting of XRD peaks toward lower angle is a result of energized ion bombardment induced atomic peening that might expand the interplaner spacing [15]. The broader nature of the diffraction peaks of indicate the formation of small crystallites and the occurrence of microstrain in the coatings [3,4]. The approximate average crystallite size and microstrain of ZrWN coatings (Table 2) are calculated by Williamson-Hall method (Eq. (7)) using Gaussian profile fitting [40]:

$$\beta_s \cos\theta = \lambda/D + 2\varepsilon \sin\theta \quad (7)$$

where D is the coherent scattering length (crystalline size), λ is Cu-K α radiation (1.54 Å), ε is the inhomogeneous internal strain (in %), θ is the Bragg reflection angle and β_s is the measured integral width of the peak. The integral width has been calculated by multiplication of **shape factor (dimensionless)** whose value is approximately **1.06** for **Gaussian profile** to full width at half maximum (FWHM) of the peak (i.e. 1.06 x FWHM). The (111), (200) and (220) reflection peaks of the coatings were used in the peak broadening analysis. **The FWHM has been measured in radian.** The analysis has been done in two steps. In first step, the **experimental** width (β_e) of every peak was measured as the integral breadth. The instrumental integral broadening (β_i) was determined from polycrystalline silicon standard and found to be 0.0106 in our case. The peak integral width due to sample (strain + size), β_s was calculated according to Eq. (8):

$$\beta_s^2 = \beta_e^2 - \beta_i^2 \quad (8)$$

In the second step, the **crystallite** size (D) and internal strain (ε) were obtained by fitting the Williamson-Hall equation (Eq. 7) in a liner regression function (Eq. (9))

$$Y = mX + C \quad (9)$$

where $\beta_s \cos\theta$ and $\sin\theta$ values of different peaks ((111), (200) and (220)) of same phase are **treated** as Y and X coordinates of the line. **Hence the slope (m) of straight line and intercept of straight line at y-axis provide the values of microstrain and crystallite size, respectively.**

The crystallite size determined is seen decrease from ~13 to 3 nm with increasing bias voltage increased (Table 2). The increased generation of defects with increasing V_s **leads** to an **increase in the** number of preferential nucleation sites, resulting in smaller crystallites [4]. The

microstrain also increased with increasing V_s . Maximum microstrain (0.023) has been obtained at $V_s = -100$ V. The average columnar size values were calculated using the AFM Image analysis 2.1.2 software. The $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ scanned topographical images have been used for the purpose. The columnar size calculation of the coating deposited at $V_s = -20, -60, -100$ and -120 volts is presented in Fig. 4 a-d. The average columnar size determined for ZrWN coatings deposited at $V_s = -20, -40, -60, -80$, and -120 volts are 51 nm, 44 nm, 40 nm, 37 nm, and 28 nm respectively. However, the columnar size calculation for -100 V could not be done, because the columnar boundaries are not prominent (Fig. 4c) to make the calculation appropriately. It is noted that the average columnar size as well as average crystallite size values follow the same trend i.e., decreases with increasing bias voltage.

FESEM micrographs of the cross-sections of the ZrWN coatings deposited at various V_s are shown in Fig. 5. For $V_s > -80$ V, morphology evolves from columnar structure to a dense glassy (-100 V) (crystallite size < 4 nm) structure. A kind of diffused morphology at $V_s = -100$ V (Fig. 4c) also supports the dense glassy structure of the films deposited at this bias voltage. The change in microstructure and morphology of the coatings are the consequences of a competition in atomic peening, adatoms mobility and resputtering with increasing V_s [29-32]. The most dense morphology at $V_s = -100$ V might be the result of large dissipation of the energy of bombarding ions to re-arrange the lattice atoms of growing surface with enhanced mobility which prevalent grain boundary migration and restructuration and lead to a dense structure [29,38,41]. The change in preferred crystallography orientation (Fig. 2), crystallite size values and compressive stress values (section 3.4) support FESEM micrograph findings.

Figure 6 shows the surface roughness graph and selected topological view of ZrWN coatings at various V_s . For $-20\text{ V} \leq V_s \leq -100\text{ V}$, RMS roughness value increases from ~ 4 nm to 6

nm and then shows a two-fold raise (~ 10 nm) at $V_s = -120$ V. The bombardment of the growing film surface with ions having kinetic energy ≤ 70 J/cm³ results in non-penetration of ions beyond the first atomic layer and thus their energy is essentially transferred to adatoms which results in a smooth surface with RMS roughness remaining nearly constant during growth. Maximum kinetic energy ($E_{bi} \sim 99$ J/cm³) at -120 V induced bulk displacements of adatoms and resputtering of the near-surface atoms. Consequently, films grown at $V_s = -120$ V have a rough surface whose RMS roughness increases substantially due to the contribution of a shadowing effect [31]. This effect can be seen from the insets of Fig. 6.

3.4. Mechanical Properties

The residual stress and lattice parameter variation as a function of V_s is presented in Fig. 7. The residual stress as calculated by Stoney's equation (Eq. (1)) using substrate curvature was found to be compressive in nature (negative sign of radius of curvature). The stress values determined were found to be increasing from -1.7 to -8 GPa with increasing bias voltage from -20 to -100 V [42,43]. The lattice parameter as evaluated from Nelson-Riley function [24,44] exhibit a strong dependence on V_s . The lattice parameter values of the deposited coatings increase with increasing V_s and are different from the lattice parameters of fcc phase pure ZrN (4.58 Å) and W₂N (4.12 Å) compounds. The increase in lattice parameter from 4.367 Å (at ground potential) to 4.511 Å (-100 V) is most likely a result of increased compressive stress with V_s . The bombarding ions of sufficient kinetic energy (> 34 J/cm³) knock out the loosely bond atoms from their lattice position as a result of atomic collision cascade. As a result of rearrangement of lattice atoms, internal stress is induced into the coatings. However, above -100 V, compressive stress is reduced to -3.7 GPa. This might be due to the sufficient energy (99 J/cm³) of impinging ions that made resputtering more prominent than atomic rearrangement.

The mechanical response of ZrWN coatings deposited at various V_s is shown in Table 3. Hardness (H) and effective elastic modulus (E_r) values increased with V_s . Maximum H of ~33 GPa and E_r of ~145 GPa are obtained at $V_s = -100$ V. Moreover, a continuous increase in % elastic recovery (W_e) has been observed for ZrWN coatings with increasing V_s . A high value of W_e (84%) at $V_s = -100$ V indicates that the deposited film exhibit high elasticity to stand with high shear forces. The increase in H, E_r and W_e values is attributed to the **combined** effect of V_s induced microstructure (preferred orientation, crystallite size, non-columnar growth) and residual stress. The obtained range of H (22 to 33 GPa) values of ZrWN coatings suits the recommended hardness (25 to 35 GPa) values for tribological coatings. However, the obtained range of E_r (104 to 145 GPa) values is substantially **lower** than the quoted E_r (250 to 400 GPa) values for tribological coatings [11,45]. It has been demonstrated [11-13] that a high hardness is not necessarily **a** prime requirement of tribological coatings. Indeed high ($> 75\%$) W_e , nominal ductility ($E_r < 200$ GPa), high toughness with high H (30 to 40 GPa) **plays** an important role for tailoring the mechanical properties of coatings for tribological applications. Oberle [46] has introduced a parameter called plasticity index (H/E_r) which is quoted as a valuable measure **for** determining the elastic strain to failure in surface contact. The higher value (>0.1) of H/E_r ratio is a strong indication of the coating resistance to wear damages [46]. All the studied ZrWN coatings exhibit $H/E_r \sim 0.2$ and maximum value (0.23) of H/E_r is obtained for ZrWN coating deposited at $V_s = -80$ V and -100 V.

Figure 8a-c show the AFM topographical view of scratch scars and indentation marks on the surface of films deposited at $V_s = -80$ V, -100 V and -120 V. The scratch scars at 10 mN load and indents at 3 to 50 mN loads have been made on the surface of films for adhesion and fracture toughness measurements, respectively. The scratch scars at 10 mN load using Berkovich

diamond nano indenter have been made on the surface of films for adhesion measurements. The films neither peeled off nor developed any crack during the scratch test at 10 mN load. Although, the film with high (8 GPa at $V_s = -100$ V) compressive stress endured with the substrate. Chhowalla et al. [43] reported the **withstanding** of high stressed (-9 GPa) Zr-N film with the substrate. Moreover, enlarged views of nanoindent at 50 mN load reveal that no crack **propagation** on the surface of the ZrWN coatings. Despite the fact, no buffer layer has been used to enhance the adhesion of the films with the substrate. The results indicate that the films have high adhesion with the substrate. However, absence of **crack** generation up to 50 mN load restricts to calculate fracture toughness of the film quantitatively. Hence, micro indentations by vicker hardness tester have been done at varying loads (200 mN to 2000 mN) to calculate the fracture toughness of coatings. Figure 9 displays diamond indenter impressions created at 1000 mN load into the ZrWN films deposited at $-20\text{V} \leq V_s \leq -120\text{V}$. It is evident from Fig. 9 that no radial cracks were generated at $V_s = -100\text{V}$ under 1000 mN load, however, radial cracks were generated at 2000 mN load. It is also observed that crack threshold load (L_t) value has been increased for $-20\text{V} \leq V_s \leq -100\text{V}$. The ZrWN coatings deposited at $-40\text{ V} \leq V_s$ were easily fractured at $200\text{ mN} \leq L_t \leq 500\text{ mN}$ While deposited at $V_s = -60\text{ V}, -80\text{ V}, -120\text{ V}$ were fractured at $500\text{ mN} \leq L_t \leq 1000\text{ mN}$. Only the **sample** deposited at $V_s = -100\text{ V}$ was fractured at $L_t \sim 2000\text{ mN}$. Moreover, the **crack length** decreases as V_s **increases** to -100 V . Hence maximum fracture toughness value ($2.25\text{ MPa}\sqrt{m}$) is obtained for **the sample** deposited at $V_s = -100\text{ V}$. A non-columnar dense structure (Fig. 5) and maximum compressive stress (8 GPa) (Fig. 7) **supports** the realization of higher fracture toughness in ZrWN coatings deposited at $V_s = -100\text{ V}$ [11, 45]. A dense non-columnar structure prevents the formation of voids and large columnar boundaries, **which results in the** retardation of microcrack initiation and propagation under higher load. Since

cracking is generally initiated by tensile stress, compressive residual stress has to be overcome first [29]. Musil [45] has introduced another important parameter H^3/E_r^2 labeled as resistance to plastic deformation. This parameter provides an assessment of film resistance to plastic deformation. To estimate the film resistance to plastic deformation, H^3/E_r^2 has been calculated as shown in Table 3. A comparison of H^3/E_r^2 parameter for the deposited ZrWN coatings indicate that the samples deposited at $V_s = -100$ V exhibit the highest values (1.8 GPa) of H^3/E_r^2 ratio. It has been reported that the higher value of H^3/E_r^2 indicates higher fracture toughness [45]. The trend of calculated fracture toughness and H^3/E_r^2 values as shown in Table 3 simulates the same assessment.

4. Conclusions

High quality ZrWN nanocrystalline coatings were produced at 200 °C, which is a relatively low deposition temperature. Bias voltage induced microstructure has remarkable effect on the mechanical properties of magnetron sputtered nanocrystalline fcc phase ZrWN coatings. The ZrWN coatings studied exhibit: (i) high wear resistance $H/E_r > 0.1$ (ii) high elastic recovery $W_e > 70\%$ (iii) compressive macrostress ($\sigma < 0$) and (iv) dense, voids-free microstructure. With increasing V_s from -20 to -100 V, ZrWN coatings' morphology evolved from columnar structure to dense glassy type structure coupled with a reduction in crystallite size while changing from (111) to (200) texturing. Correspondingly, the compressive stress increases from -1.7 to -8 GPa. Owing to synergetic contributions of dense structure, preferred orientation, crystallite size and compressive stress, wear resistance of the coatings ZrWN increased from 0.21 to 0.23 and fracture toughness improved from 1.4 to 2.25 MPa $\sqrt{m}$. The results, thus, demonstrate a significant, simultaneous enhancement in fracture toughness and wear resistance can be achieved by carefully controlling the processing conditions and microstructure. Under controlled growth

and structure, ZrWN coatings exhibit pronounced mechanical properties: $H \sim 34$ GPa, $H/E_r = 0.23$, $H^3/E_r^2 = 1.8$ GPa and $K_{IC} \sim 2.25 \text{ MPa}\sqrt{m}$.

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Figure Captions

Fig. 1. EDS analysis of ZrWN coatings deposited at different V_s .

Fig. 2. (a) XRD patterns of ZrWN coatings deposited at different V_s and (b) The dependence of the normalized hkl XRD peak intensities, N_{hkl} ($I_{hkl} / [I_{111} + I_{200} + I_{220}]$), of the ZrWN coatings as a function of V_s .

Fig. 3. TEM bright field images and corresponding SAED patterns of ZrWN coatings deposited at $V_s = -80$ V, -100 V and -120 V.

Fig. 4. The AFM topographical images of the films deposited at V_s : (a) -20 V, (b) -60 V, (c) -100 V and (d) -120 V.

Fig. 5. Cross-sectional FESEM images of ZrWN coatings deposited at varying V_s .

Fig. 6. The surface roughness and topological view of ZrWN coatings deposited at varying V_s .

Fig. 7. The residual stress and lattice parameter values of ZrWN coatings deposited at varying V_s .

Fig. 8. The AFM topographical view of scratch scars and indentation marks on ZrWN coatings deposited at V_s (a) -80 V, (b) -100 V and (c) -120 V.

Fig. 9. The optical micrographs of diamond indenter impressions created at 1000 mN load into the ZrWN films deposited at varying V_s .

<i>Sputtering Parameters</i>	
Target	Tungsten (W, 99. 95% purity) and Zirconium (Zr, 99. 98% purity)
Gas used	Ar (8 sccm) and N ₂ (32 sccm)
Residual pressure	< 0.5E-3 Pa
Sputtering pressure	0.67 Pa
Deposition time	1.5 h
Power density for W target	~ 4 Watt/cm ² (85 W-RF)
Power density for Zr target	~ 6 Watt/cm ² (120 W-DC)
Substrate target distance	6 cm at 45° to the substrate ⊥
Substrate temperature	200°C
Negative Bias Voltages	-20,-40,-60, -80, -100, -120 V

Table 1 Sputtering parameters for Zr-W-N films

<i>Negative Bias (V_s)</i>	<i>Substrate ion current density (i_s)</i>	<i>Kinetic energy (E_{bi})</i>	<i>Deposition rate (a_D)</i>	<i>crystallite size</i>	<i>Micro strain</i>	<i>Macro strain</i>
<i>(Volt)</i>	<i>(A/cm²)</i>	<i>(J/cm³)</i>	<i>(nm/min)</i>	<i>(nm)</i>	<i>(*10⁻³)</i>	<i>(*10⁻³)</i>
-20	5.1E-5	9.04	18.8	13 ± 3	14 ± 7	10
-40	6.8E-5	22.11	20.5	11 ± 2	18 ± 4	15
-60	8.5E-5	37.94	22.4	11 ± 3	21 ± 6	21
-80	8.5E-5	55.82	20.3	10 ± 3	17 ± 7	28
-100	8.5E-5	72.64	19.5	4 ± 2	23 ± 3	33
-120	8.5E-5	98.80	17.2	3 ± 2	10 ± 6	19

Table 2 Summary of experimental results of ZrWN coatings deposited at varying V_s.

<i>Negative Bias (V_s)</i>	<i>Hardness</i>	<i>Elastic modulus</i>	<i>% Elastic recovery</i>	<i>Plasticity index parameter</i>	<i>Resistance to Plastic deformation</i>	<i>Toughness</i>
<i>(Volt)</i>	<i>H(GPa)</i>	<i>E_r(GPa)</i>	<i>W_e</i>	<i>H/E_r</i>	<i>H³/E_r²(GPa)</i>	<i>K_{IC} (MPa√m)</i>
-20	22.3	104	75.2	0.21	1.0	1.4
-40	24.2	112	76.3	0.21	1.1	1.65
-60	26.5	120	78.5	0.22	1.3	1.77
-80	28.3	122	79.7	0.23	1.5	2.06
-100	33.6	145	84.3	0.23	1.8	2.25
-120	27.8	136	81.6	0.20	1.2	1.93

Table 3 Mechanical response of the ZrWN coatings deposited at varying V_s.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical Abstract