Sputter deposited NbC_xNy films: Effect of nitrogen content on structure and mechanical and tribological properties

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ABSTRACT

NbC_xNy thin films were deposited on Si(100) substrates by direct current magnetron sputtering from a Nb–C compound target in a mixture of N_2 and Ar. The mechanical and tribological properties show a significant dependency on composition, chemical bonding and structure, as characterized by X-ray diffraction, and photoelectron and Raman spectroscopies. Increasing the nitrogen flow rate from 0 to 5 to 30 sccm causes a continuous increase of the nitrogen content y from 0 to 0.44 to 1.01. The films exhibit a Nb(C,N) solid solution at low N content, while an additional hexagonal NbN phase develops for y ≥ 0.69. A maximum hardness H = 42.1 GPa and elastic modulus E = 362 GPa is reached for the NbC_{1.44} N_{0.44} film, which also exhibits the highest compressive stress of 6.1 GPa and the highest H/E^2 value, yielding the best wear resistance. Increasing the N content leads to an increasing amorphous phase, which ultimately causes a reduction of stress, hardness, H/E^2, and wear resistance. The nitrogen also reduces the root mean square surface roughness from 1.27 to 0.46 nm, and causes a reduction of the friction due to an increase in the sp^3-graphitelike carbon phase, with the lowest friction coefficient of 0.18 for the NbC_{1.99} N_{0.69} film.

1. Introduction

Transition metal carbides and nitrides possess excellent properties, such as high hardness, high melting points, low friction coefficient, exceptional wear resistance, and good catalytic activity, and have been widely used in applications such as protective and decorative coatings [1–4]. Among the transition metal nitrides and carbides, Nb-based coating materials have been extensively studied and evaluated with respect to industrial applications [5,6]. NbN has gained some interest due to its relatively high superconducting transition temperature of T_c = 17.3 K [7]. It is also promising as a protective coating material due to its high chemical stability, high hardness of 38 GPa, and high melting point of 2204 K [5.8–11]. NbN layers have been proposed as wear protective coatings at high temperature [12], but the friction coefficient of 0.7 is rather large [13]. In contrast, we recently reported that the friction coefficient of NbC films can reach a minimum of 0.10 at 69 at.% C with a hardness of 18 GPa [14]. It is envisioned that the ternary NbC_xNy will combine the good wear resistance and lubricious properties of NbN and NbC, respectively, and hence outperform both components as a lubricious wear protective coating. Similar advantages in ternary alloys have been reported, for example, for the solid solution TiC_N_y compound deposited by cathodic arc ion plating, which outperforms TiN in tribological applications due to its higher hardness and decreased friction and wear associated with carbon incorporation [15]. It addition, CrC_xNy coatings produced by evaporation in a thermionic-arc-ion-plating apparatus at 450 °C show a higher corrosion resistance than CrN coatings [16], and MoC_xNy films deposited by reactive direct-current magnetron sputtering have a higher hardness than both MoC and MoN films [17].

While both binaries NbN and NbC are well-studied, relatively little is known regarding deposition and properties of ternary NbC_xNy coatings. L.J. Lin et al. [18] deposited NbN_xC_y thin films on Si substrates using low-energy dual ion-beam sputtering and reported a maximum T_c of 132 K, and a resistivity of 80–150 μΩcm at 20 K, for layers exhibiting predominantly a B1 crystal structure. NbC_xNy films have also been prepared by reactive magnetron sputter deposition, their microstructure was characterized by XRD by E. F. Skelton et al. [19], and a maximum T_c = 17.8 K was reported for NbC_{0.15} N_{0.85} by T. L. Francavilla et al. [20]. However, mechanical and tribological properties of NbC_xNy films are still unknown but are essential to evaluate the potential as protective coating for the machining industry.

In this article, we present results of an investigation focusing on the deposition of NbC_xNy coatings by reactive sputter deposition from a niobium-graphite compound target in a mixed N_2 and Ar atmosphere. The nitrogen flow rate is used to control the N content y = 0–1.01, which in turn affects the microstructure consisting of a cubic Nb(C,N) solid solution at low y, but a mixture of cubic, hexagonal, and amorphous phases for large y. A maximum hardness H = 42.1 GPa is reached...
for the NbC_{1.44} N_{0.44} film. The increasing amorphous phase with increasing y causes a reduction of stress, hardness, H^2/E^2, and wear resistance. The N also reduces the surface roughness and causes a reduction of the friction coefficient, which reaches its lowest value of 0.18 for the NbC_{1.99} N_{0.69} film.

2. Experimental details

2.1. Sample deposition

NbC_{x}N_{y} films were deposited in a DC magnetron sputtering system using a 60-mm-diameter single graphite/niobium 99.95%-pure compound target containing 75 at.% C and 25 at.% Nb. The distance between the target and the substrate holder was fixed at 80 mm, and the diameter of the target erosion ring was 24–48 mm. The chamber was evacuated by a turbomolecular pump to a 4 × 10^{-4} Pa base pressure prior to sputtering. The substrates, 25 × 25 × 0.5 mm² Si(100) wafers were ultrasonically cleaned in acetone, alcohol and deionized water, and then mounted on the substrate holder. The target was pre-sputtered with Ar⁺ for ten minutes to remove the surface oxide layer. A thin Nb layer was deposited onto the substrate prior to deposition of the NbC_{x}N_{y} film, in order to improve the film-substrate adhesion. Deposition was conducted at a target current of 0.3 A, a substrate bias voltage of −80 V, and a substrate temperature of 200 °C. In order to study the effect of nitrogen on the structure and properties of the NbC_{x}N_{y} thin films, the nitrogen flow rate F_{N2} was varied from 0 to 5, 10, 15, and 30 sccm, while the flow rate of Ar was kept constant at 60 sccm, yielding N\_s partial pressures of 0%, 8%, 14%, 20% and 33%, respectively. The total pressure was kept constant at 0.8 Pa during all depositions by controlling the pumping speed with a throttling valve, and the deposition time was adjusted to achieve a nominal thickness for all films of 1.5 μm.

2.2. Sample characterization

After deposition, the samples were cut and the center piece was used for characterization. The crystal structure was determined by X-ray diffraction (XRD) using a Bragg–Brentano (Bruker D8) diffractometer in a 0–20 configuration with a Cu Kα line at 0.15418 nm as a source. The chemical composition of deposited films was determined by X-ray photoelectron spectroscopy (XPS) (ESCALAB MKII) with monochromatic Al Kα radiation. In order to remove the surface oxides and contamination from adsorbed hydrocarbons, the samples were sputter cleaned using 800 eV Ar⁺ ions for 20 min prior to XPS analysis [21]. Raman spectroscopy (Renishaw 1000, 514.5 nm laser) was also employed to obtain more information about the carbon bonding. The surface morphology was determined by atomic force microscopy (AFM, Dimension Icon, Veeco Instruments/Bruker, Germany) using ScanAsyst mode in air, from which the root mean square (RMS) surface roughness was determined.

The hardness H and Young’s modulus E of the films were evaluated in continuous stiffness measurement mode using a MTS Nanoindenter XP. The films were indented by a Berkovich type pyramidal diamond tip to a maximum depth of 800 nm, the hardness values were taken at approximately 100–200 nm depth to avoid both surface and substrate effects, following the procedure described in Ref. [22]. The tribological properties of the films were determined using a CSM Instruments ball-on-disk tribometer in ambient air at 297 K with a relative humidity of 60%. A tungsten carbide ball (Ø = 6 mm) was used as a sliding counterpart under a N load at a velocity v = 50 mm/s, and a radius of the contact track of 2.5 mm. Testing was done for up to 10,000 cycles, and micrographs of the wear track were acquired by scanning electron microscopy (SEM) (XL30ESEM-FEG). The wear rates of the films were determined by measuring the traces of surface profiles taken across the wear track using a surface profiler (Veeco Dektak 150). Moreover, the curvatures of the samples before and after deposition were also measured by the surface profiler, taking a minimum of eight measurements along two orthogonal surface directions and rejected outlier data points, and the total residual stress was obtained using the Stoney equation [23].

3. Results and discussion

3.1. Composition and chemical bonding

The measured composition of NbC_{x}N_{y} films deposited using different nitrogen fluxes F_{N2} is summarized in Table 1. The data is obtained from the relative intensities of the Nb3d, C1s, and N1s XPS peaks. Deposition in pure Ar (F_{N2} = 0 sccm) yields a NbC_{1.53} layer. That is, the C:Nb ratio of 1.53 in the layer is considerably smaller than the ratio of 3.00 in the compound target, suggesting that a larger fraction of the sputtered C is scattered in the processing gas in comparison to the heavier Nb. In addition, the XPS results may also be affected by some preferential sputtering during sputter cleaning. For depositions with F_{N2} = 5 to 30 sccm, the measured nitrogen content y in the layers increases monotonically from 0.44 to 1.01. At the same time, x decreases slightly from 1.53 at F_{N2} = 0 sccm to 1.44 at F_{N2} = 5 sccm, but then increases and remains approximately constant at 1.99 to 2.03 for F_{N2} = 10–30 sccm.

XPS measurements are also employed to investigate the chemical bonding state of the as-deposited films. Figs. 1, 2(a), and 3(a) show XPS core-level spectra in the energy regions of Nb3d, C1s, and N1s, respectively, for films with different nitrogen concentrations. The Nb3d spectrum from the nitrogen-free (y = 0) film in Fig. 1 exhibits two distinct peaks at binding energies of 203.4 and 206.2 eV, attributed to Nb3d_{5/2} and Nb3d_{3/2} states, respectively. The Nb3d_{5/2} peak is at the reported position for Nb-C bonding [14], indicated by the dashed vertical line in Fig. 1. The film with y = 1.01 exhibits the same peaks. However, they are shifted by 0.19 eV to higher binding energies, which are attributed to an increasing fraction of Nb–N bonds, with a reported Nb3d_{5/2} binding energy of 203.8 eV [24] as indicated with a dash-dotted blue line in Fig. 1. This shift is relatively small, such that it is not possible to determine the relative Nb3d subpeak intensities corresponding to Nb–C and Nb–N bonding. Therefore, quantitative bonding analyses are done by examining XPS C1s and N1s spectra, as discussed in the following.

Fig. 2(a) shows typical XPS core-level spectra near the C1s binding energy for NbC_{x}N_{y} films prepared with y = 0 and 1.01. The spectrum from the binary NbC_{x} exhibits two deconvoluted peaks at 282.7 and

Table 1

The deposition rate at different F_{N2}, overall film composition, C:Nb and N:Nb ratios within the crystalline phase, C and N content in the amorphous phase expressed as at.% of all atoms in the film, and cubic and hexagonal grain sizes D₁ and D₂ for NbC_{x}N_{y} films deposited with different N₂ flow rates F_{N2}. Compositions are obtained from XPS analyses. Grain sizes are determined with Scherrer’s equation using the cubic 111 and hexagonal 100 XRD peaks.

<table>
<thead>
<tr>
<th>F_{N2} (sccm)</th>
<th>Deposition rate (nm/min)</th>
<th>NbC_{x}N_{y}</th>
<th>Crystal phase</th>
<th>Amorphous phase</th>
<th>D₁ (nm)</th>
<th>D₂ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.3</td>
<td>NbC_{1.53}</td>
<td>0.72</td>
<td>0.32</td>
<td>13.8</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>21.4</td>
<td>NbC_{1.44} N_{0.64}</td>
<td>0.49</td>
<td>0.38</td>
<td>33.2</td>
<td>4.1</td>
</tr>
<tr>
<td>10</td>
<td>22.6</td>
<td>NbC_{1.41} N_{0.60}</td>
<td>0.40</td>
<td>0.53</td>
<td>43.6</td>
<td>4.0</td>
</tr>
<tr>
<td>15</td>
<td>24.8</td>
<td>NbC_{1.10} N_{0.62}</td>
<td>0.43</td>
<td>0.58</td>
<td>42.4</td>
<td>6.0</td>
</tr>
<tr>
<td>30</td>
<td>23.0</td>
<td>NbC_{0.91} N_{0.61}</td>
<td>0.40</td>
<td>0.71</td>
<td>40.7</td>
<td>3.5</td>
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284.5 eV. They are attributed to C bonded to Nb in niobium carbide [25, 26] and C which shows sp²–hybridized bonding in an amorphous carbon phase (a-C) [27]. Introduction of nitrogen leads to the development of an additional shoulder peak at 287.2 eV, which is apparent for all ternary samples, and can be attributed to C–N bonds [28]. Fitting of the C1s spectra using these three peaks associated with C–Nb, sp² C–C, and C–N bonds yields values for the relative C content in the corresponding NbC, a-C, and CN carbon-containing phases. The result is summarized as a function of y in Fig. 2(b). Increasing y from 0 to 0.69, causes a decrease in C bonded to Nb from 47 to 21%, while C–C and C–N bonds increase from 53 to 73% and from 0 to 7%, respectively. For y ≥ 0.69, the relative bond fractions remain approximately constant. These results suggest that introduction of N in NbC films causes some C to form an amorphous carbon phase and to bond as carbon nitride, while some Nb–C bonding is preserved. This is similar to what has been reported for the CrCxNy nanocomposite system, for which the Cr–C bond decreases from 77.0 to 38.4% as the nitrogen content increases from 0 to 13.5% [29], but is different from the TiCxNy nanocomposite system [28], where introduction of nitrogen, causes replacement of all Ti–C bonds with Ti–(C,N) bonds.

A typical N1s XPS spectrum from a NbC1.44 N0.44 film is presented in Fig. 3(a). The primary peak at 397.1 eV is attributed to N bonded to Nb [30], while the additional broad shoulder peak at 398.9 eV suggests the formation of some amorphous CN [31]. The area under the primary peak of this spectrum is seven times stronger than for the shoulder peak, as obtained by fitting the spectrum using these two peaks. This indicates that 87% of the N is bonded to Nb, while 13% is bonded to C. The corresponding data from fitting the XPS N1s spectra from all films provides a quantitative measure of the relative importance of nitrogen bonding to Nb and C, which can be interpreted as the relative phase content in the coatings, as plotted in Fig. 3(b) as a function of y. The fraction of N that is bonded to C increases from 13 to 29% as y increases from 0.44 to 0.82, but remains approximately constant with a
further increase to \( y = 1.01 \). Correspondingly, the fraction of N that forms N-Nb bonds decreases with increasing \( y \).

Table 1 summarizes the information obtained from the above XPS analyses. In addition to obtain the overall composition, XPS is also used to determine (a) the composition of the crystalline phase as specified by the atomic ratios C/Nb and N/Nb within the niobium carbonitride, and (b) the fraction of atoms that are contained within the amorphous phase, as described by the atomic percentage of C and N atoms that are contained within the amorphous phase, where 100% corresponds to the sum of all Nb, C, and N atoms within the film. In particular, the nitrogen-free film has an overall composition corresponding to NbC_{1.53}. However, the bonding analysis shown in Fig. 2(b) indicates that only 47% of the carbon is contained in the crystalline phase such that the crystalline phase is understoichiometric with a C/Nb ratio of 0.72. The remaining C forms C-C bonds within an amorphous matrix which contains 32% of all atoms, as also indicated in Table 1. Similar microstructures with sub-stoichiometric NbC grains embedded in a-C have been reported by Nils Nedfers et al. for non-reactively sputtered layers with C/Nb = 0.66–0.84 [26]. The film deposited with a N flux \( F_{\text{N2}} = 5 \) sccm has an overall composition corresponding to NbC_{1.44}N_{0.44}. As shown in Fig. 3(b), the majority (87%) of this nitrogen incorporates into Nb-carbonitride grains, yielding a N/Nb ratio within the grains of 0.38, while C/Nb = 0.49, as determined from the data in Fig. 2(b). The sum is 0.87, indicating that these grains are also substochiometric but have a considerably higher non-metal to metal ratio than the Nb-C grains with C/Nb = 0.72 for the nitrogen-free film. We also note that introduction of nitrogen leads to a decrease of C/Nb from 0.72 to 0.49, indicating that nitrogen replaces C within the carbonitride phase, which in turn results in a larger fraction of C (63% instead of 53%) being incorporated into the amorphous phase. Nevertheless, the total fraction of 35 at.% of atoms in the amorphous phase for this NbC_{1.44}N_{0.44} film is only slightly higher than that for the NbC_{1.53} film, which has 32 at.% in the amorphous matrix. Increasing \( F_{\text{N2}} \) further to 10, 15, and 30 sccm results in a monotonous increase of the overall content \( y = 0.69, 0.82, \) and 1.01, respectively, and a corresponding nitrogen increase in the niobium carbonitride phase of N/Nb ratio = 0.53, 0.58, and 0.71, while the C within the carbonitride phase remains approximately constant at C/Nb = 0.40–0.43. This indicates a transition to a stoichiometric and then over-stoichiometric composition, which is associated with the emergence of a hexagonal NbN phase in addition to the Nb(C,N) solid solution rock-salt phase, as discussed in more detail below. In parallel, the nitrogen content in the amorphous phase also continuously increases with \( F_{\text{N2}} \) to reach 7 at.% for \( F_{\text{N2}} = 30 \) sccm, while the amorphous C content remains approximately constant at 40–43 at.% for \( F_{\text{N2}} \geq 10 \) sccm, similar to the constant C within the crystalline phase. For the layer with the highest N content of \( y = 1.01 \), nearly half of the atoms (47%) are contained within the amorphous phase, which consist of both C and N with a N/C ratio of 0.17.

In summary, our coatings consist of a nanocrystalline NbC_{x}N_{y} (and NbN) phase in an amorphous matrix phase (a-C and C–N), which is similar to many reported metal–C materials systems [28,32,33].

3.2. Structure and morphology

Fig. 4 shows XRD 0–20 spectra over the measured 20 = 10–65° range for NbC_{x}N_{y} films with varying nitrogen concentrations ranging from \( y = 0–1.01 \). The nitrogen-free (\( y = 0 \)) film shows diffraction peaks at 34.5°, 40.1°, and 57.9° which are assigned to 111, 200, and 220 reflections of the cubic NaCl-structure NbC (JCPDF 65–0281), respectively. The peaks are at 0.2–0.4° lower 20 than the literature values indicated by vertical dash-dotted lines in Fig. 4, indicating an out-of-plane tensile strain of 0.5%–0.7%, consistent with a measured biaxial compressive stress of 5.0 GPa presented below. The peak width of the 111 reflection is 0.7°, which yields, using the Scherrer formula [34], an estimated grain size of 14 nm, as also listed in Table 1. The \( y = 0.44 \) film shows the same three diffraction peaks, indicating a cubic NaCl structure where C and N form a solid solution on the non-metal lattice sites. The peaks are 7 times weaker and 3 times broader than for the NbC film, which is attributed to a lower crystalline quality associated with the randomness of the solid solution and to a lower crystallite size of 4.1 nm, associated with the larger fraction of this layer exhibiting an amorphous phase. The spectra from the films with higher nitrogen concentration corresponding to \( y = 0.69, 0.82, \) and 1.01 exhibit the same peaks from the cubic phase. However, they show an additional peak at 37.6° that increases in intensity with increasing \( y \) and can be attributed to a hexagonal NbN phase (JCPDF 20–0801) with a reported NbN 102 peak position at 38.5°. The measured peak position indicates a 2.3% larger interplanar spacing than for the reported pure hexagonal NbN. This deviation cannot be solely accounted for by the compressive stress but must be related to the incorporation of carbon atoms in the hexagonal phase which is expected to expand the lattice [35,36], and to the increasing non-metal to metal ratio within the crystalline phase, as determined by XPS, which leads to overstoichiometric compositions and therefore nitrogen and/or carbon interstitials in the hexagonal phase. The estimated grain size of the hexagonal phase increases slightly from 8.7 nm for \( y = 0.69 \) to 10.6 nm for \( y = 1.01 \). The formation of the hexagonal phase at high nitrogen content is attributed to the larger electronegativity of N in comparison to C, leading to a lower Gibbs free energy for formation of NbN versus NbC, and therefore leading to a nitrogen-rich secondary phase [37]. A similar effect has been reported for Ti(C,N) solid solutions [28,37,38].

Raman spectroscopy is employed to analyze the atomic bonding in the amorphous matrix phase of the NbC_{x}N_{y} films. Fig. 5(a) shows a typical Raman spectrum from a film with \( y = 0.44 \), over a Raman shift range from 1050 to 1950 cm\(^{-1}\). The spectrum exhibits an asymmetric peak which can be fit using two Gaussian peaks centered around 1350 and 1550 cm\(^{-1}\), which are associated with D and G bands, respectively. The D peak is typically attributed to breathing modes of sp\(^2\) bonded atoms in benzene rings or microcrystalline disordered graphite, and the G peak to sp\(^2\) stretch vibrations in graphite, rings or conjugated chains [39,40]. It is known empirically that the sp\(^2\)/sp\(^3\) ratio can be quantified by the G peak position and the Raman intensity ratio I_D/I_G [41]. Fig. 5(b) is a plot of the measured peak positions and the ratio I_D/I_G as a function of \( y \) for all samples. Both D and G positions remain approximately constant within the experimental and fitting uncertainty [42], at 1542–1549 and 1347–1353 cm\(^{-1}\). In contrast, the I_D/I_G ratio shows a clear continuous trend, increasing from 1.4 for \( y = 0 \) to 2.8 for \( y = 1.01 \). The increase of I_D/I_G ratio indicates an increase in the sp\(^2\) carbon domain phase, which is preferentially formed at high nitrogen concentrations and reveals the graphitic characteristics of NbC_{x}N_{y} films at high non-metal to metal ratios [43–45]. A similar graphitization trend has been reported for the TiCN system, in which an increase in the
nitrogen content leads to a larger fraction of the nanocomposite consisting of a graphitic matrix [28].

Fig. 6(a) and (b) show representative AFM micrographs, from 2 × 2 μm² areas from NbCxNy films with y = 0 and 0.69, respectively. The nitrogen free layer in Fig. 6(a) exhibits a surface with mounds that are 40–150 nm wide and 4.0 nm (peak-to-valley) high, corresponding to a root mean square (RMS) surface roughness $R_q = 1.27$ nm. The surface in Fig. 6(b) from the layer with y = 0.69 shows mounds that are 150–400 nm wide and 1.5 nm high. Thus, these mounds are 3 times wider and their peak-to-valley height is 3 times smaller than for the nitrogen free film, indicating a considerably smoother surface with a $R_q = 0.46$ nm. The surface shown in Fig. 6(c) which is a plot of $R_q$ vs y. The surface roughness decreases from 1.27 nm for y = 0 to 0.68 for y = 0.44, and then remains relatively constant within 0.46–0.63 nm as y is increased further to 1.01. We note that the coating with the highest measured content of C–C bonds, as presented in Fig. 2(b), has the lowest surface roughness, suggesting that the amorphous or graphitic carbon phase within these coatings promotes a smooth surface and may, in turn, facilitate low friction, as presented below.

3.3. Residual stress and hardness

The residual stress in the NbC$_x$N$_y$ coatings is determined from the measured substrate curvature and is plotted in Fig. 7 as a function of y. All films show an in-plane biaxial compressive stress. Its magnitude increases from 5.0 GPa for y = 0 to 6.1 GPa for y = 0.44, and then continuously decreases to reach 3.7 GPa for y = 1.01. We attribute the compressive stress to bombardment of the film surfaces by energetic particles during the sputter deposition process, a mechanism which is referred to as atomic peening [46–48]. The energetic particles include sputtered atoms, working gas ions that are accelerated by the substrate bias and neutralized ions that are back scattered from the target. We attribute the increased compressive stress upon introduction of N$_2$ in the processing gas to N$_2^+$-ions that are implanted in the growing film, occupy interstitial sites, and cause compressive stress; while the majority of implanted Ar$^+$ ions will diffuse to the surface, causing less pronounced stress. In addition, backscattered N-atoms have a higher energy than backscattered Ar and, in turn, can cause larger layer densification and compressive stress [49,50]. The reduction in the compressive stress for y $\geq$ 0.44 is attributed to the increasing fraction of the amorphous matrix phase, as evidenced by the larger C–C and C–N bond fraction measured by XPS, which may provide pathways for stress relaxation through diffusion of interstitial C and N from the Nb–carbonitride phase to the amorphous matrix phase as well as plastic shear deformation within the amorphous matrix. In addition, the emergence of the hexagonal
NbN phase may also reduce the overall compressive stress. We note here that the deposition rate is an important factor affecting stress [51]. However, it varies only slightly in this study, ranging from 21.3 to 24.8 nm/min as listed in Table 1, and therefore is expected to have negligible effect on the stress.

Fig. 8(a) is a plot of the measured hardness $H$ and elastic modulus $E$ as a function of $y$. The hardness for the nitrogen free film is 35.1 GPa, it increases with introduction of nitrogen to a maximum of 42.1 GPa for $y = 0.44$ and then continuously decreases to 28.0 GPa for $y = 1.01$. The maximum hardness of 42.1 GPa is significantly higher than what has been reported for related transition metal carbonitride coatings including TiCxNy (22.2 GPa), ZrCxNy (25.4 GPa), and CrCxNy (29.2 GPa) [28,29,35]. The elastic modulus exhibits a similar composition dependence, increasing from $E = 352$ GPa for $y = 0$ to a maximum of $E = 362$ GPa for $y = 0.44$ and a subsequent decrease to 313 GPa for $y = 1.01$. The composition dependence of $H$ and $E$ is attributed to a combination of phase structure, residual stress, and grain size [52]. The increase in hardness from $y = 0$ to 0.44 is attributed to (i) a decrease in the carbide grains from 14 to 4.1 nm, as determined by XRD, leading to an increase in $H$ as predicted by the classical Hall–Petch law [53]; (ii) the development of an amorphous phase between the small crystalline grains which induce grain incoherence strains [54] and therefore suppress dislocation movement and enhance hardness similar to what we have recently reported for the binary NbC/a-C system which exhibits a maximum hardness for a composition with 53.9 at.% C [14]; (iii) the ternary Nb(C,N) phase which, in contrast to the binary NbC for $y = 0$, exhibits solid solution strengthening [55] which contributes to the high hardness of the composite film similar to reported solid solution hardening in ZrCxNy films [35]; and (iv) the measured residual stress within our NbCxNy coatings, which shows a similar composition dependence as the measured $H$, indicating that the stress could be responsible for the increase in hardness, similar to what has been reported for N doped WC coatings [56]. At higher nitrogen concentrations, $y > 0.44$, the measured hardness and elastic modulus decrease steeply with increasing $y$. This is attributed to a combination of multiple microstructural trends including the decreasing residual stress, the emergence of a hexagonal NbN phase, the slight increase in grain size, and/or the increasing fraction of the amorphous matrix phase within the composite.

### 3.4. Tribological properties and wettability

Fig. 9(a) shows the measured friction coefficient $\mu$ vs number of cycles, during sliding of a WC ball against NbCxNy films with different $y$. The friction of the nitrogen-free film gradually increases from 0.14 to 0.27 during the first 2000 cycles, and then remains relatively constant at $\mu = 0.27 \pm 0.02$. In contrast, all layers containing nitrogen exhibit a higher initial friction of $\mu = 0.25 \pm 0.03$, but reach quickly a steady state friction that is considerably lower than for the nitrogen-free coating. We note that the peak around 8000 cycles for the NbC$_{2.01}$N$_{0.01}$ film is attributed to partial layer delamination and failure, consistent with the highest wear rate of this film, as discussed below. The friction results are summarized in Fig. 9(b), which is a plot of the average stable $\mu$ as a function of $y$, obtained by averaging over the measured $\mu$ for cycles 2000 to 10,000. The friction coefficient of the NbC$_{1.53}$ film is $0.27 \pm 0.02$. Increasing $y$ to 0.44 causes a drop in $\mu$ to 0.19 $\pm$ 0.02, while further increases in the nitrogen content have little effect on $\mu$, which reaches its lowest value of 0.18 $\pm$ 0.02 at $y = 0.69$. We attribute the observed decrease in friction primarily to a combination of chemical composition and structure [57,58]. More specifically, introduction of nitrogen leads to an increase of the amorphous carbon and CN phase and an increase in sp$^2$ bonding, as determined by the XPS and Raman analyses, respectively. This facilitates the formation of a graphitic surface layer which acts as a solid lubricant and decreases the friction coefficient [59–61]. In addition, the decrease in roughness with increasing nitrogen content also contributes to the reduction in $\mu$. For $y \geq 0.69$, the friction coefficient remains approximately constant or even increases slightly, consistent with the amorphous carbon content that decreases slightly from 43 to 40 at.% as shown in Table 1.

Fig. 10(a) and (b) are representative SEM micrographs showing wear tracks after 10,000 cycles of tribological testing against a WC ball, for the NbC$_{1.53}$ and NbC$_{1.44}$N$_{0.44}$ films, respectively. The wear track from the N-free sample in Fig. 10(a) shows deep cracks as well as wear debris particles and deep pits that expose the silicon substrate. In contrast, the wear track of the NbC$_{1.44}$N$_{0.44}$ film in Fig. 10(b), which is typical for all N-containing films ($y = 0.44–1.01$), consists of regular elongated scratches with a relatively low density of deep cracks. The wear rate, as determined from the cross-sectional profile after 10,000 cycles, is plotted in
Fig. 10(c) as a function of $y$. It decreases from $1.48 \times 10^{-6}$ mm$^3$/Nm for $y = 0$ to $0.80 \times 10^{-6}$ mm$^3$/Nm for $y = 0.44$, and then continuously increases to reach $3.97 \times 10^{-6}$ mm$^3$/Nm for $y = 1.01$. This composition dependence is primarily attributed to the change in hardness, or more specifically, to the ratio $H^3/E^2$ which has previously been proposed as one of the key parameters that determines wear behavior [62,63]. Fig. 10(d) is a plot of $H^3/E^2$ vs $y$ for the same NbC$_x$N$_y$ coatings, showing a similar composition dependence as the individual $H$ and $E$ curves in Fig. 8. The maximum of $H^3/E^2 = 0.57$ GPa at $y = 0.44$ is at the same composition as the minimum in wear rate in Fig. 10(c). This is consistent with the expected correlation of the $H^3/E^2$ ratio and the wear rate, as high $H^3/E^2$ values indicate a high resistance to plastic deformation and correspondingly a high wear resistance [64], similar to what has been reported for other carbide-based nanocomposite coatings [62,65]. In addition, the hexagonal secondary phase that forms at high nitrogen concentrations ($y \geq 0.69$) may lead to abrasive particles that increase the wear rate and therefore deteriorate the wear resistance of the NbC$_x$N$_y$ films with high $y$.

4. Conclusions

NbC$_x$N$_y$ films were deposited by sputtering from a Nb–C compound target in a mixture of N$_2$ and Ar. XRD together with the analyses of chemical bonding by XPS and Raman suggest that increasing $F_{N_2}$ from 0 to 30 sccm leads to a continuous increase in the nitrogen content $y$ from 0 to 1.01. The nitrogen is incorporated in solid solution Nb(C,N) grains but also facilitates an increasing amorphous C(N) matrix phase as well as a separate hexagonal NbN phase. The compressive stress, hardness, and elastic modulus are highest for the film with $y = 0.44$, which also exhibits the lowest wear rate. The smallest surface roughness and lowest friction coefficient is measured for the film with the largest amorphous C concentration and $y = 0.69$. The changes in the tribological properties with increasing $y$ are primarily attributed to the increasing sp$^2$-graphitelike carbon phase, which acts as a source for a lubricious surface layer and can support a high hardness of the nanocomposite at moderate concentrations, but ultimately causes a reduction in the mechanical strength and a degradation of the wear protective properties.
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