Tribological and Mechanical Properties of Multicomponent CrVTiNbZr(N) Coatings

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Abstract: Multi-element material coating systems have received much attention for improving the mechanical performance in industry. However, they are still focused on ternary systems and seldom beyond quaternary ones. High entropy alloy (HEA) bulk material and thin films are systems that are each comprised of at least five principal metal elements in equally matched proportions, and some of them are found possessing much higher strength than traditional alloys. In this study, CrVTiNbZr high entropy alloy and nitrogen contained CrVTiNbZr(N) nitride coatings were synthesized using high ionization cathodic-arc deposition. A chromium-vanadium alloy target, a titanium-niobium alloy target and a pure zirconium target were used for the deposition. By controlling the nitrogen content and cathode current, the CrNbTiVZr(N) coating with gradient or multilayered composition control possessed different microstructures and mechanical properties. The effect of the nitrogen content on the chemical composition, microstructure and mechanical properties of the CrVTiNbZr(N) coatings was investigated. Compact columnar microstructure was obtained for the synthesized CrVTiNbZr(N) coatings. The CrVTiNbZrN coating (HEAN-N165), which was deposited with nitrogen flow rate of 165 standard cubic centimeters per minute (sccm), exhibited slightly blurred columnar and multilayered structures containing CrVN, TiNbN and ZrN. The design of multilayered CrVTiNbZrN coatings showed good adhesion strength. Improvement of adhesion strength was obtained with composition-gradient interlayers. The CrVTiNbZrN coating with nitrogen content higher than 50 at.% possessed the highest hardness (25.2 GPa) and the resistance to plastic deformation H3/E* (0.2 GPa) value, and therefore the lowest wear rate was obtained because of high abrasion wear resistance.

Keywords: high entropy alloy; multilayer; tribological; hard coating

1. Introduction

Physical vapor deposition (PVD) thin films and coatings are now frequently used to improve the mechanical and tribological performance of cutting tools, such as milling and drilling tools, and machinery components. The materials of the milling and drilling tools are usually high speed steels, which have high hardness (~HRc 62). However, the high speed steel cannot resist abrasion wear during high speed cutting processes. Hard coatings have higher hardness and better wear resistance, which can solve the mechanical tooling and wear problems under contact attack. Transition metal nitride hard coatings, mainly TiN and CrN-based, have been used for tribological protection applications, and they exhibit exceptional properties in oxidation resistance, mechanical and especially tribological and wear properties [1–3]. At present, many researchers focus on the multicomponent structure design of coatings. CrAlN and TiAlN coatings in the form of cubic NaCl structure, where Al substitutes for Cr and Ti in the CrAlN and TiAlN lattice, are now well acknowledged and currently commercially available. As a result, ternary nitrides containing Al (e.g., TiAlN and CrAlN) and quaternary nitrides containing...
Si (e.g., TiAlSiN and CrAlSiN), demonstrating improved mechanical performance and better wear resistance, have been studied [4–9]. The urgent requirement of coated tools for high speed and high temperature cutting stimulate the development of coatings with more complex composition and architecture, in particular, coatings based on metal nitrides, such as Ti, Cr, Zr, Al, and Nb. The use of the multicomponent material nitrides with composition-gradient interlayer design based on these elements in various combinations and architectures makes it possible to obtain new coatings possessing excellent mechanical properties [10]. Multicomponent material systems have received much attention to improve the mechanical performance. For example, R.L. Boxman et al. [11] deposited TiZrN, TiNbN and ZrNbN using a cathodic arc deposition system. The ternary nitride coatings had higher hardness than that of the binary nitrides. These ternary nitride coatings had a single-phase microstructure, and the intermediate values of the lattice parameters showed formation of solid solution in the nitride coatings. A.D. Pogrebnjak et al. [12] used vacuum arc deposition to prepare ZrTiNbN and ZrTiNbCrN coatings. All the deposited coatings were found to have nanocrystalline structures. The multicomponent nitride coatings are also found to be a single-phase face-centered cubic (fcc) microstructure. The prepared coatings had hardness higher than 24 GPa depending on the coating composition and architecture. However, they are still focused on ternary and quaternary systems and seldom beyond quaternary ones. The latest design approach is the concept of high entropy alloy (HEA), which can be depicted as multicomponent materials with five or more elements, and has led to a growing field of research exploring multiprincipal element materials where the atomic percentage of each element should be between 5% and 35% [13,14]. Most of the previous studies using the high-entropy concept are based on metallic alloy materials, but there is also a growing interest in these alloy materials with addition of N, O, or C, leading to the formation of high-entropy nitrides (HENs), oxides (HEOs) and carbides (HECs), respectively [15–21].

Because of the potential of excellent properties, the evolvement of hard nitride coatings based on the concept of HEA is considered, and it can show various excellent properties according to the composition of the elements [22–24]. The HEA nitride coatings can also be designed in a multilayered structure to improve mechanical and corrosion properties. W. Zhang et al. [25] fabricated AlCrMoNbZr/AlCrMoNbZrN multilayer coatings with similar individual layer thicknesses. The AlCrMoNbZr/AlCrMoNbZrN coatings showed a multilayer structure composed of a crystalline AlCrMoNbZrN layer and an amorphous AlCrMoNbZr layer. Under a proper multilayer structure, the corrosion resistance was enhanced a lot. By regulating the nitrogen content, the microstructures and mechanical properties of HEA and HEA nitride coatings can be controlled. Recently, P. Cui et al. [26] studied the effect of nitrogen on the microstructures and mechanical properties of high-entropy alloy nitride AlCrTiZrHf(N) coatings, and they found that the AlCrTiZrHf(N) coatings transformed to a face-centered-cubic structure with the increase of the N$_2$ flow rate. When the N$_2$ to Ar ratio was at a specific ratio of 5:4, the hardness reached the maximum value of ~33 GPa. As a result, the design of HEA CrVTiNbZr(N) coatings was explored in this study. The HEA nitride coatings were synthesized using high ionization cathodic-arc deposition. The main objective was to synthesize an HEA nitride hard coating which could display good mechanical and tribological performance.

2. Materials and Methods

In this study, CrVTiNbZr high entropy alloy and nitrogen contained CrVTiNbZr(N) coatings were synthesized and deposited on the samples of SKH9 high speed steel (HSS) and Si (100) substrates by co-evaporating single-element metal and alloy targets with a purity of 99.99% in a multi-target cathodic-arc deposition system (Surfwell Tech. Co., Taichung, Taiwan). A chromium-vanadium alloy target (40 at.% of Cr and 60 at.% of V), a titanium-niobium alloy target (60 at.% of Cr and 40 at.% of V) and a pure zirconium target were used for the deposition. Compressed dry air was then used to dry the substrate samples prior to their loading on the deposition substrate holder. Before the deposition
process, the vacuum chamber was pumped down and the vacuum background pressure was less than $1 \times 10^{-3}$ Pa, and the sample holder was rotated at 2 rpm for the deposition. The distance between all targets and substrate was 17 cm. The samples were cleaned in a bath of acetone and ethanol. Then, the substrate samples were cleaned by an ion bombardment with Ar ions at 1000 V for 20 min. The Ar sputtering process was helpful for eliminating the surface oxides on the substrate samples. During the coating process of CrVTiNbZr and CrVTiNbZr(N), CrV was deposited as interlayers to enhance adhesion strength between the coatings and substrates. The cathode current of the targets was 60–100 A to control the composition of the CrVTiNbZr and CrVTiNbZr(N) coatings. The cathode arc current of the Zr, TiNb, and CrV targets was 60 A, 100 A and 100 A, respectively, for the deposition of CrVTiNbZr and CrVTiNbZr(N). By controlling the different nitrogen flow rates (0, 50 and 165 sccm), the CrVTiNbZr(N) coating with gradient and multilayered composition control possessed different microstructures and mechanical properties. The deposition was carried out in a flowing mixed Ar and nitrogen atmosphere under a working pressure controlled at 3.0 Pa. HEA, HEAN-N50 and HEAN-N165 were denoted as the deposited coatings with nitrogen flow rates of 0, 50 and 165 sccm, respectively. The coated samples were left inside the chamber after deposition for at least 1 h under high vacuum for cooling and to minimize post-deposition oxidation.

Phase characterization and identification of the HEA and HEA nitride coatings were obtained by X-ray diffraction (XRD, D8 Discover, Bruker Inc., Kanagawa, Japan) operated using a $2^\circ$ grazing angle. The HEA and HEA nitride coatings were analyzed in between the range of 20–90° with a step size of 0.02° and a step time of 1 s. The microstructure of the deposited coatings was characterized by field emission scanning electron microscope (FESEM, JEOL JSM-7800F, JEOL Ltd., Tokyo, Japan) and high resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL Ltd., Tokyo, Japan) equipped with Energy Dispersive Spectrometry (EDS). In FESEM, back scattering electron images (BEI) were used for the compositional contrast of the coating.

Mechanical properties, such as the hardness (H) and elastic modulus (E), were measured by means of nanoindentation. The measured hardness (H) and elastic modulus (E) of the coatings were obtained using a Hysitron TriboLab nanoindentation (Hysitron TI980 Tribolindenter, Bruker, Billerica, MA, USA) with the indentation depth of about 300 nm. Poisson’s ratio of $\nu = 0.25$ was assumed for the deposited coatings. The Rockwell-C indentation test was performed using a Rockwell-C hardness tester (HR-200, Mitutoyo Taiwan Co., Taichung, Taiwan) with an applied load of 150 kg to evaluate the adhesion strength following the ISO 26443 standard [27,28]. Similar to Verein Deutscher Ingenieure (VDI) 3198 indentation test evaluation, ISO 26443 specifies a method for the qualitative evaluation of the adhesion of ceramic coatings by indentation with a Rockwell diamond indenter. The formation of cracks after indentation reveals cohesive failure of the hard coatings. The tribological properties were evaluated by a ball-on-disk tribometer (CSM Instrument, Anton Paar Switzerland AG., Buchs, Switzerland) with a WC-Co ball of 6 mm in diameter at room temperature. The tribological test was conducted with a 30 cm/s sliding speed under 5 N load and a total sliding distance of 500 m. The wear track morphology and wear volumes were analyzed and determined using a confocal laser-scanning microscope (VK-X120, Keyence Inc., Osaka, Japan).

3. Results and Discussion

3.1. Microstructure Characterization

Figure 1 showed cross-sectional SEI and BEI images of the CrVTiNbZr(N) coatings with different nitrogen flow rates. Assisted by the SEI and BEI, the HEA coating contained CrVTiNbZr top layer (~1.15 µm) with CrV as bottom layer (~0.2 µm) and CrVTiNb as interlayer (~0.15 µm). When nitrogen was introduced to form nitride coatings (HEAN-N50 and HEAN-N165), continuous columnar growth was observed. It can be observed a compact columnar microstructure for the synthesized coatings. Similar results can be found in previous studies of VAlTiCrMo high-entropy alloy nitride coatings [29] and AlCrTiZrHf.
Coatings 2021, 11, x FOR PEER REVIEW...nitride coatings. Some of the nitrogen atoms were expected to be interstitially incorporated in the coatings [23,32].

The thicknesses of the deposited HEA and HEA nitride coatings were ~1.5 μm. The chemical composition of the top layer of the deposited coatings was measured by EDS. Table 1 shows the chemical contents of the CrVTiNbZr(N) coatings with different nitrogen flow rates. According to the measuring error of our EDS, the SD was ~10% of the measured value. When no nitrogen is introduced, the contents of five metal elements in the CrVTiNbZr HEA coating are between 14.13–26.8 at.%. It can be found that the HEA coating conforms to the high entropy alloy definition the atomic percentage of each element within the range of 5% and 35%. With increasing the nitrogen flow rate, the nitrogen content in the HEA nitride coatings increased rapidly at first and then stabilized due to the high ionization of cathodic arc evaporation [30,31]. A recent study by S. Avtaeva et al. [31] had shown that the most probable mechanism of nitrogen dissociation in the low-pressure arc conditions was the excitation transfer between Ar and nitrogen. When nitrogen flow rate of 50 sccm was introduced, the nitrogen content of HEAN-N50 increased to 41.27 at.%. The nitrogen content of the HEA nitride coatings greatly increased with increasing nitrogen flow rate. When the nitrogen content continued to increase, the N atom dissolved into the lattice of the HEA nitride coating. With increasing nitrogen flow rate to 165 sccm, the nitrogen content in the coating increased above 50 at.% and tended to be stable. An increase of the nitrogen flow rate in the deposition environment led to decrease in the average energy of deposited metal and nitrogen particles because of collision losses, and increase in the saturation of HEA nitride coatings with nitrogen content. The HEA nitride coatings were regarded as saturated nitride coatings. Some of the nitrogen atoms were expected to be interstitially incorporated in the coatings [23,32].

![Figure 1. Cont.](image-url)
Figure 1. Cross-sectional SEM micrographs including SEI and BEI images of the CrVTiNbZr(N) coatings with different nitrogen flow rates (HEA, HEAN-N50 and HEAN-N165). A schematic illustration shows the compact columnar microstructure of the HEAN-N165 coating.

Table 1. The chemical composition of the CrVTiNbZr(N) coatings with different nitrogen flow rates (HEA, HEAN-N50 and HEAN-N165).

| Element | HEA   | HEAN-N50 | HEAN-N165 |
|---------|-------|----------|-----------|
| Cr      | 14.13 | 9.71     | 8.5       |
| V       | 20.45 | 14.81    | 12.62     |
| Ti      | 22.55 | 11.55    | 7.74      |
| Nb      | 16.07 | 7.67     | 4.77      |
| Zr      | 26.80 | 14.98    | 12.08     |
| N       | -     | 41.27    | 54.29     |

Figure 2 shows the XRD patterns of HEA, HEAN-N50 and HEAN-N165 coatings deposited at different nitrogen flow rates. The observed high intensities and low peak widths indicate a highly crystalline material in the coatings. First, for the metallic CrVTiNbZr HEA coatings deposited without N\textsubscript{2} introduction, the diffraction pattern showed major peaks located between 36.1° and 82.8°, indicating the presence of a dominant body-centered cubic (bcc) phase. This phenomenon was consistent with the results of previous studies regarding some multicomponent coatings deposited using pure element and binary alloy targets [24,29,33–36]. For the HEAN-N50 coating using nitrogen flow rate of 50 sccm, in addition a small fraction of bcc structure, diffraction peaks between 33.9° and 43.7° were observed, and it was assigned to the planes of face-centered cubic (fcc) NaCl-type structure, including TiNbN, CrVN and ZrN. The TiNbN, CrVN and ZrN phases were obtained by the deposition with sample rotation and evaporating single-element metal and alloy targets of TiNb, CrV and Zr. When the nitrogen flow rate increased to 165 sccm, the HEAN-N165 coating exhibited reflections corresponding to fcc NaCl-type phases of TiNbN, CrVN and ZrN while the bcc diffraction peaks disappeared. The nitrogen atoms in the coatings formed the ionic chemical bonds and occupied octahedral interstitial sites, typical for NaCl-type lattice. Such structural changes in forming fcc nitride phases led to an increase in hardness of the HEA nitride coatings deposited with high nitrogen flow rates [37]. P. Cui et al. [26] studied the AlCrTiZrHf(N) HEA nitride coatings with different nitrogen content. The HEA nitride coatings transformed from amorphous structure to an fcc structure with the increase of nitrogen flow rate. Kumar et al. [38] also found that the microstructure of the AlCrTaTiZr(N) coatings changed from amorphous structure to nanocrystalline structure with the increase of nitrogen flow rate. In this study, the formation of intermetallic compounds is inhibited in the HEA coating. When nitrogen was introduced into the CrVTiNbZr coating, the fcc crystallinity of the film was obvious, and the (111), (200) and (220) diffraction peaks appeared in the HEAN-N165 nitride coating,
which indicated that the CrVTiNbZr nitride coating was composed of TiNbN, CrVN and ZrN. The structures of the binary and ternary nitrides of TiNb, CrV and Zr were all fcc phases. This phenomenon was considered to be the result of recrystallization when the nitrogen content was high enough to form fcc nitrides [39,40].

Figure 2. Glancing angle X-ray diffraction pattern of the deposited CrVTiNbZr(N) coatings with different nitrogen flow rates (HEA, HEAN-N50 and HEAN-N165).
Figure 3a,b shows the cross-sectional TEM images of the CrVTiNbZrN coating (HEAN-N165) deposited with 165 sccm nitrogen flow rate. It can be seen that the columnar structure grows from the specific CrV alloy and CrVN bottom layers to the top CrVTiNbZrN layer without interruption. The high magnification image of the top layer exhibited slightly blurred columnar and multilayered structures containing CrVN, TiNbN and ZrN. The results of EDS measurement showed that the dark layer (#1) was ZrN contributed by Zr target, the gray layer (#2) was TiNbN contributed by TiNb target, and the bright layer (#3) was CrVN contributed by CrV target, as shown in Table 2. The multilayer structure was obtained by periodic rotation of the samples facing Zr, TiNb and CrV targets sequentially. The periodic thickness of the multilayered CrVTiNbZrN was about 15 nm. Coatings with such multilayer architecture, which is capable of dispersing energy and deflecting cracks at layer interfaces, may enhance mechanical properties such as hardness and toughness, and therefore improve tribological properties [27]. Similar results by A. Kameneva et al. [41] showed that the two- and three-component multilayer nitride coatings containing TiN and ZrN had exceptional corrosion resistance in both 5% NaOH and 3% NaCl solutions and superior tribological properties.

![Cross-sectional TEM image of the CrVTiNbZrN coating deposited with 165 sccm nitrogen flow rate (HEAN-N165). The right figure shows the corresponding selective area electron diffraction (SAED) pattern of the top CrVTiNbZrN layer.](image1)

![Cross-sectional TEM micrograph of the top layer of the HEAN-N165 coating which shows the multilayer architecture of dark layer (ZrN), gray layer (TiNbN) and bright layer (CrVN).](image2)
Table 2. The EDS results of the dark layer (ZrN), gray layer (TiNbN) and bright layer (CrVN) in Figure 3b.

| Element | Chemical Content (at.%) |
|---------|-------------------------|
|         | Dark Layer (#1) | Gray Layer (#2) | Bright Layer (#3) |
| N       | 31.12            | 32              | 27.46            |
| Zr      | 36.37            | 14.42           | 16.40            |
| Ti      | 7.36             | 16.68           | 7.73             |
| Nb      | 4.93             | 14.43           | 4.19             |
| Cr      | 9.03             | 10.98           | 19.01            |
| V       | 11.19            | 11.49           | 25.21            |

3.2. Mechanical and Tribological Properties

The Rockwell indentation test was used to evaluate adhesion strength of the HEA and HEA nitride coatings. This destructive test exhibited the interfacial adhesion strength between the substrate and the coatings. Figure 4 shows the optical images of the indented contours of the CrVTiNbZr(N) coated specimens with different nitrogen flow rates. According to ISO 26443 [42], the adhesion strength of HEA is identified as class 0, HEAN-N50 is class 2 and HEAN-N165 is class 1. In the case of class 2, small coating delamination was observed, and the adhesion is not so good. The radial cracks without delamination indicated strong and good adhesive strength between coating and substrate, and the adhesion strength in this case was evaluated to class 1, as shown for HEAN-N165. Therefore it can be seen from the results that the coating becomes hard and brittle by adding nitrogen, and brittle failure will occur under concentrated load, while the coating without nitrogen is relatively ductile (the adhesion strength of HEA is class 0). The coating with composition-gradient interlayers can improve the adhesion strength compared to the single-layer coating [27,43]. The result indicates that composition-gradient interlayers and multilayer structure in the hard HEA nitride coatings are beneficial for increasing adhesion strength.

Figure 5 exhibits the hardness (H) and the \( H^3/E^{*2} \) of the CrVTiNbZr(N) coatings with different nitrogen flow rates (HEA, HEAN-N50 and HEAN-N165). Effective elastic modulus \( E^{*} = E/(1-\nu^2) \), where \( \nu \) is the Poisson’s ratio. The \( H^3/E^{*2} \) ratio is an indicator of resistance to plastic deformation which dominates the abrasion wear resistance [44]. The hardness of the HEA coating was ~8.2 GPa. When nitrogen was introduced to form nitrides, the hardness increased higher than 24 GPa. The highest hardness (25.2 GPa) was obtained for the HEAN-N165 with nitrogen content higher than 50 at.%. The HEAN-N50 and HEAN-N165 possessed higher hardness than that of binary and ternary nitride coatings such as CrN (~18 GPa) and CrVN (~17 GPa). The hardness of the coatings can be generally improved due to the enhancement of multicomponent solution strengthening effect to form nitride materials after the introduction of nitrogen atoms. The result could be ascribed to the multilayer structure in nano scale with relatively small periodic thickness of 15 nm of the HEAN-N165 coatings. The multilayer structure revealed more grain boundaries to hamper slip of dislocations [45]. In addition, the HEAN-N165 possessed the best ability to resist the plastic deformation where \( H^3/E^{*2} \) was 0.2 GPa. It is known that the metals, such as Cr, V, Ti, Nb, Zr, Ta and Mo, which belong to transition element groups are easy to form binary and ternary compounds with nitrogen that are metastable solid solution with fcc structure. Interface is one of the most important characteristics for nanoscale multilayer coatings, which can act as the source for dislocations. If multilayer coatings are subjected to external loading, plastic deformation can be activated and the dislocation slip is confined in the layer between two adjacent nitride interfaces. Therefore, multilayer architecture of HEAN-N165 allows to achieve higher resist the plastic deformation comparing with HEA coatings due to the obstacle of dislocation slip across the multilayer interfaces [46].
Table 2. The EDS results of the dark layer (ZrN), gray layer (TiNbN) and bright layer (CrVN) in Figure 3b.

| Element | Chemical Content (at.%) |
|---------|-------------------------|
| N       | 31.12, 32, 27.46       |
| Zr      | 36.37, 14.42, 16.40    |
| Ti      | 7.36, 16.68, 7.73      |
| Nb      | 4.93, 14.43, 4.19      |
| Cr      | 9.03, 10.98, 19.01     |
| V       | 11.19, 11.49, 25.21    |

Figure 4. Optical images of the indentation crater of the CrVTiNbZr(N) coatings with different nitrogen flow rates: (a) HEA, (b) HEAN-N50 and (c) HEAN-N165.
Figure 5. Hardness (H) and the $H^3/E^2$ values of the CrVTiNbZr(N) coatings with different nitrogen flow rates (HEA, HEAN-N50 and HEAN-N165) measured by nano-indentation.

Figure 6 shows the variation of average friction coefficient and wear rate of the CrVTiNbZr(N) coatings with different nitrogen flow rates. The wear rate of the CrVTiNbZr(N) (HEAN-N50 and HEAN-N165) decreased substantially compared to that of the HEA. The HEAN-N165 had lowest wear rate of $3.23 \times 10^{-7} \text{mm}^3/\text{Nm}$, which was much lower than that of HEA ($1.46 \times 10^{-5} \text{mm}^3/\text{Nm}$) and HEAN-N50 ($7.29 \times 10^{-6} \text{mm}^3/\text{Nm}$). The average friction coefficients of HEA and HEAN-N50 coatings were about 0.84 and 0.81, respectively. The average friction coefficient of the HEAN-N165 decreased to ~0.72, which was lower than that of HEA and HEAN-N50. Compared with the results of hardness test, it can be found that the wear resistance and hardness of the coating are positively correlated with $H^3/E^2$, and the HEAN-N165 coating with the highest hardness (25.2 GPa) and $H^3/E^2$ (0.2 GPa) possessed the best wear resistance. The increase of hardness and $H^3/E^2$ values of CrVTiNbZr(N) coatings indicated the enhancement of anti-wear capability of abrasion wear [47]. The nanolayer and nanocrystalline HEAN-N165 coating based on cubic CrVN, TiNbN and ZrN may have good fracture toughness and resistance to abrasive wear [10,48]. The multiplex interfaces in the multilayers can result in an increase of hardness and toughness. The improved physical-mechanical and tribological properties of the HEAN-N50 multilayer coatings are originated from the gradient of coating structure, phase and elemental composition [18,41,49].

Figure 7 shows the 3D optical profilometry images (bottom), SEM images (middle) and EDS Iron (Fe) element mapping (top) of the wear track of the CrVTiNbZr(N) coated high speed steel samples (HEA, HEAN-N50 and HEAN-N165). As shown in the Figure 7a,b for the HEA and HEAN-N50, the long wear scars indicated abrasive wear. Iron (Fe) signal was observed on the wear track surface of the HEA and HEAN-N50 coated samples. The observation of plowing grooves and wear debris indicated that abrasion wear dominated the wear behavior of the coatings. The hardness of the HEA was lower than that of WC-Co ball (~15 GPa), and abrasive wear occurred. Although the HEAN-N50 had higher hardness than that of WC-Co ball, the adhesion strength was not good enough (class 2, small coating delamination was observed in the Rockwell indentation test). During the wear process, the decrease of adhesion strength between the coating and the substrate led to the formation of wear debris from the coating. The abrasive wear resulted from the abrasion between wear debris and the substrate [18]. Similar to the HEA, TiAlN and ZrN families, the coefficients of friction wear relatively high for the HEA and HEAN-N50 coatings, reflected that friction was highly influenced by the deformation of asperities [50–53]. The HEAN-N165 coated sample showed smoother morphology, where no obvious substrate iron (Fe) material was observed, as shown in the Figure 7c. As mentioned above, the trend of the wear rate was inversely related to the hardness and $H^3/E^2$ values, which showed the resisting capability of abrasion wear. As a result, the nanolayer and nanocrystalline HEAN-N165 multilayer coatings overcome the shortcomings of HEA, and showed greatly improved
tribological properties [54]. Similarly, in the tribological study of nanostructured hard nitride coatings by E. C. Romero et al. [55], it showed the multilayer structure provided the ability to dissipate energy, especially in tangential direction, due to the numerous interfaces generated between multilayers. In addition, compared to the friction behavior of CrN, addition of V and Nb may remarkably improve the tribological properties as seen in CrVN and CrN/NbN coatings [56,57]. Therefore, the decrease in friction coefficients and wear rates of the HEA nitride coatings can be attributed to the high $\frac{H^3}{E^2}$ values and architecture of multilayers, which can improve the energy dissipation associated with the tribological contact and in turn the observed enhancement of wear resistance.

Figure 6. Wear rate and friction coefficient of the CrVTiNbZr(N) coatings (HEA, HEAN-N50 and HEAN-N165).

Figure 7. Cont.
Figure 7. (a) 3D optical profilometry images (bottom), SEM images (middle) and EDS Fe element mapping (top) of the wear track of the HEA coated high speed steel samples; (b) 3D optical profilometry images (bottom), SEM images (middle) and EDS Fe element mapping (top) of the wear track of the HEAN-N50 coated high speed steel samples; (c) 3D optical profilometry images (bottom), SEM images (middle) and EDS Fe element mapping (top) of the wear track of the HEAN-N165 coated high speed steel samples.
4. Conclusions

CrVTiNbZr high entropy alloy and nitrogen contained CrVTiNbZr(N) coatings were deposited using a high ionization cathodic-arc deposition system to study the effect of nitrogen content in coatings’ microstructure, as well as to understand the influence of the nitrogen content and microstructure on mechanical and tribological properties of HEA and HEA nitride coatings. Multi-arc sources containing a chromium-vanadium alloy target, a titanium-niobium alloy target and a pure zirconium target were used for the deposition. The main finding are as followed:

1. In this study, the characteristics of CrVTiNbZr(N) coatings fabricated using cathodic arc deposition by changing nitrogen flow rates was addressed. When no nitrogen was introduced, the contents of five metal elements in the CrVTiNbZr HEA coating were between 14.13–26.8 at.%, and the HEA coating conforms to the high entropy alloy definition. Increase in the nitrogen content led to the transformation from single-phase bcc to fcc structure. When the nitrogen flow rate increased to 165 sccm, the HEAN-N165 coating exhibited reflections corresponding to fcc NaCl-type phases of TiNbN, CrVN and ZrN while bcc diffraction peak disappeared.

2. The CrVTiNbZrN coating (HEAN-N165) had columnar structure growth from the CrV and CrVN bottom layers to the top CrVTiNbZrN layer without interruption. The top layer exhibited multilayered structures containing CrVN, TiNbN and ZrN. The design of multilayered CrVTiNbZrN coatings showed good adhesion strength. Improvement of adhesion strength was obtained with composition-gradient interlayers.

3. The CrVTiNbZr(N) HEAN-N165 coating with nitrogen content higher than 50 at.% possessed the highest hardness and $H^2/E^2$, and therefore the lowest wear rate was obtained because of high abrasion wear resistance. The strengthening effect was mainly attributed to the formation of multilayered metal nitride structure and the solid solution strengthening of multicomponent elements.

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