High-temperature wear mechanisms of TiNbWN films: Role of nanocrystalline oxides formation

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Abstract: Refractory high/medium entropy nitrides (HENs/MENs) exhibit comprehensive application prospects as protective films on mechanical parts, particularly those subjected to sliding contacts at elevated temperatures. In this study, a new MEN system TiNbWN, forming a single fcc solution, is designed and its wear performance at temperatures ranging from 25 to 750 °C is explored. The wear mechanisms can be rationalized by examining the subsurface microstructural evolutions using the transmission electron microscopy as well as calculating the phase diagrams and interfacial adhesion behavior employing calculation of phase diagram (CALPHAD) and density functional theory (DFT). To be specific, increased wear losses occur in a temperature range of 25–600 °C, being predominantly caused by the thermally-induced hardness degradation; whereas at the ultimate temperature (750 °C), the wear loss is refrained due to the formation of nanocrystalline oxides (WnO3n−2, TiO2, and γ-TiOx), as synergistically revealed by microscopy and CALPHAD, which not only enhance the mechanical properties of the pristine nitride film, but also act as solid lubricants, reducing the interfacial adhesion. Thus, our work delineates the role of the in situ formed nanocrystalline oxides in the wear mechanism transition of TiNbWN thin films, which could shed light on the high-temperature wear behavior of refractory HEN/MEN films.

Keywords: high/medium entropy nitrides (HENs/MENs); TiNbWN thin films; wear mechanisms; nanocrystalline oxides

1 Introduction

High/medium entropy alloys (HEAs/MEAs) containing elements in near-equiatomic proportions normally with a single-phase structure have attracted extensive attention as they demonstrate potential combinatorial properties that are not attainable in conventional alloys [1–3]. Recently, incorporation of p-block elements such as nitrogen (N), carbon (C), and boron (B) has led to the development of new high/medium entropy materials, which are high/medium entropy nitrides (HENs/MENs), high/medium entropy carbides (HECs/MECs), and high/medium entropy borides (HEBs/MEBs) [4–7]. The HENs/MENs possess superiorities in terms of high-temperature thermal stability, oxidation resistance, and mechanical properties due to the sluggish diffusion and solid solution strengthening effects, being qualified as protective films on the mechanical parts that operate at varying temperatures [5, 7–9].

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Herein, toward high-temperature applications, we add the refractory metal elements, niobium (Nb) and tungsten (W), into the benchmark binary nitride system, TiNbWN. Even though there is a paucity of studies on the TiNbWN films, the structure–property relationships for the ternary TiNbN and TiWN films have been tackled. For example, Baran [10] reported that the TiNbN film contained a single TiN-type fcc phase, with a microhardness ($H$) value as high as 24 GPa. Serro et al. [11] further compared the wear resistance of TiN, TiNbN, and TiCN thin films for biomedical applications, whereby the TiNbN film performed best in the presence of albumin. For the TiWN films, on the other hand, the phase transformation from βW to an fcc solution was observed with an increasing N concentration [12–14]. Besides, the mechanical properties of the TiWN film also depend on the N and W concentrations. For instance, the hardness values of TiWN films varied from 23 to 50 GPa in a composition range of 30–57 at% N [15]; while they changed from 13.9 to 26.3 GPa in a composition range of 0–50.6 at% W, following the variations in crystallinity [16–18].

The wear failure mechanisms in high-temperature protective films are one of the most fundamental issues to be addressed for a prolonged service lifetime [19–21]. In particular, the sliding-induced oxidation that can significantly influence the tribological performance of materials has been considered to be an interesting topic [19, 22–24]. After their discovery in the 1930s [25], specific types of oxides, formed on metal and alloy surfaces during the course of sliding, have been recognized as important constituents for generating protective tribolayers at elevated temperatures, which could decrease metal–metal contacts and alleviate wear losses [26–29]. For non-oxide ceramics and ceramic coatings in general, however, the generated oxides may play a different role in friction and wear performances [30–33]. For instance, the wear resistance of the transitional metal nitrides strongly depends on their mechanical properties, especially surface hardness [32], whereas the sliding-induced oxidation of transitional metal nitrides would generally decrease the surface hardness due to the formation of an oxide layer, leading to the so-called “oxidational wear” [30]. The generated oxides at elevated temperatures, on the other hand, could act as solid lubricants in certain scenarios and reduce the friction [32, 33]. Specifically, some functional oxides, such as the Magnéli phase [31], can effectively improve the tribological performances of ceramic materials. The Magnéli phases, defined as a homologous series of compounds with closely related lamellar structures [34–36], can serve as effective solid lubricants to improve friction and wear performance when generated in a large quantity [31, 37–39].

In this work, we design and synthesize a new multicomponent TiNbWN thin film with an fcc structure based on the high/medium entropy concept, and subsequently examine its wear resistance by performing the tribological tests at 25, 300, 600, and 750 °C. With an aid of electron microscopy and spectroscopic methods, the wear mechanism transition and nano-oxide formation are identified as a function of temperature. The subsurface microstructures of the worn samples, the phase diagrams of the W–O system, as well as the calculated adsorption energies of relevant interaction counterparts, are further utilized to address the following specific questions: (1) How can the wear behavior of TiNbWN thin films at varying temperatures be described; (2) what is the role of the in situ formed nano-oxides in the wear mechanism transition.

2 Experimental details

2.1 Film deposition

The multicomponent TiNbWN thin film was reactively magnetron sputtered in mixed N$_2$/Ar (20/100 sccm gas flow rate) discharges on 304 stainless steel (304ss) substrates using a custom-built system. Prior to the deposition, the synthesis chamber was first pumped down at 25 °C to a base pressure lower than 5 × 10$^{-4}$ Pa; then, the substrate holder was gradually heated up to 800 °C. A TiNbW alloy target (Ti = 33.3 at%, Nb = 34.9 at%, W = 31.8 at%; purity 99.99%) was used to synthesize the thin film, which was driven by direct current (DC) power supply at a power density of 1.06 W/cm$^2$. The total working pressure (Ar + N$_2$) in the chamber was 1.0 Pa. A pulsed-DC bias voltage of −100 V (at a pulse frequency of 20 kHz and a pulse duty ratio of 50%) was applied on the substrate holder, which rotated at the speed of 20 rpm during the
deposition. The distance between the target and the substrate was 11 cm.

2.2 Tribological testing

The tribological tests of the TiNbWN thin film were conducted against 316 stainless steel (316ss) balls with 6 mm in diameter at temperatures ranging from 25 to 750 °C under ambient atmosphere (~35% relative humidity) using Anton–Paar tribometer (THT1000, Anton-Paar) equipped with a rotational module. An applied normal load of 1 N and a linear sliding speed of 3 mm/s were employed in all the tests, yielding a maximum Hertzian contact pressure of ~800 MPa. The radius of the wear track was 3 mm, and the test time was 20 min that corresponded to a total sliding distance of 18 m. After the completion of each sliding test, the volumetric wear losses were acquired from the surface profile traces across the wear track using surface profilometry.

2.3 Film characterization

The surface and cross-sectional morphologies of the deposited TiNbWN thin film were studied using a field-emission scanning electron microscope (FE-SEM; Quanta FEG 250, FEI), while the elemental compositions of the film were measured by the energy dispersive X-ray spectrometry (EDS). The accelerating voltage of 15 kV was applied. The crystal structure of the film was investigated using the X-ray diffraction analysis (XRD; D8 Advance, Bruker) with Cu Kα radiation (λ = 1.5406 Å). The power settings were 40 mA for the current and 40 kV for the voltage. The H and elastic modulus (E) of the film were determined using a nano-indenter (G200, MTS) with a Berkovich diamond tip within the continuous stiffness measurement mode, following the method by Oliver and Pharr [40]. The reported values of H and E were the average of five measurements. The Poisson ratio (v) of 0.18 was assumed.

After sliding tests, the types of oxides induced by sliding contact were studied using a micro-Raman spectrometer (InVia Reflex, Renishaw) that operated with a laser wavelength of 532 nm. Cross-sections of the worn samples were prepared using a focused ion beam (FIB; Auriga, Zeiss) “lift-out” technique, with the subsurface microstructure evolutions and elemental distributions examined using a transmission electron microscope (TEM; Talos F200, Thermo Fisher) and a high-resolution TEM (HRTEM) equipped with a windowless energy dispersive spectrometer. The accelerating voltage of 20 kV was applied during microscopy.

2.4 Computational methods

The adsorption energy was calculated using ab initio calculations based on density functional theory (DFT) [41], which was carried out in the Vienna ab initio simulation package (VASP) [42]. Projector augmented wave potentials and the generalized gradient approximation were used in all calculations [43, 44]. A total energy cut-off of 500 eV was applied for the adsorption calculations. The Brillouin zone was sampled using gamma-centered Monkhorst–Pack k-point grids. The TiNbWN(001), TiO2(001), and WO3(001) surfaces were modeled as slabs with a vacuum thickness of 10 Å. Supercells containing 24 atoms were constructed for TiNbWN(001) and TiO2(001) surfaces, while a supercell containing 40 atoms was chosen for the WO3(001) surface to enable a suitable slab thickness. The top four-atom layers near the vacuum layer were relaxed until the force on each of them was less than 0.01 eV/Å, while the other atoms were fixed to mimic a bulk behavior. Herein, we assumed that the sliding interfaces comprised of the pristine/oxidized film surface and oxidized the counterpart atoms (stainless steel) being represented by a vertically aligned Fe–O molecule with either the Fe or O atom approaching the coating surface. The adsorption energies (E_{ads}) were calculated by Eq. (1):

$$
E_{ads} = E_{FeO/slab} - E_{slab} - E_{FeO}
$$

where $E_{FeO/slab}$ and $E_{slab}$ are the total energy of the (001) surface of the slab models with FeO and without it, respectively; and $E_{FeO}$ is the total energy of the FeO molecule, calculated in a cell with a dimension of $10 \, \text{Å} \times 10 \, \text{Å} \times 10 \, \text{Å}$.

3 Results and discussion

3.1 Microstructures and properties

The surface and cross-sectional morphologies of the
TiNbWN thin film are shown in Fig. 1. A faceted microstructure is present based on the top-view of the thin film, while its cross-sectional SEM image shows a distinct columnar growth, a common feature for sputtered thin films. The elemental compositions of the thin film measured by EDS confirmed that the Ti, Nb, and W have similar atomic concentrations (Ti = 21 at%, Nb = 19 at%, and W = 23 at%), and the N content is 37 at%. The XRD pattern was obtained over 20°–90° to investigate the constitution of the TiNbWN thin film, as shown in Fig. 1(c). The TiNbWN thin film can be described as a TiN-type single fcc phase (PDF#28-1420), in which the Nb and W atoms occupy the Ti sites. The fact that the TiNbWN film contains a single solution phase can be supported by the structural similarities of the binary nitrides of TiN, NbN, and γWN, which exhibit the same fcc phase with rather similar lattice parameters (a (TiN) = ~0.42 nm, a (NbN) = ~0.44 nm, and a (γWN) = ~0.41 nm) [45–47]. The characteristic peaks in the XRD pattern slightly deviated to smaller values compared with that of the TiN phase, indicating that the interplanar spacing of the fcc solution in the TiNbWN thin film was increased by dissolving Nb and W. The strongest peak corresponded to the (111) crystallographic plane, implying the preferred growth of the film deposited.

3.2 Sliding wear performance

Figure 2(a) shows the wear losses of the TiNbWN film sliding against 316ss as a function of the sliding temperature, as well as the variation in $H$ with the increasing oxidation temperature. In the temperature range of 25–600 °C, the hardness of the thin film sharply decreased while the wear losses increased dramatically with increasing temperature. Interestingly, at a temperature of 750 °C, the hardness of the thin film slightly increased, and the wear losses simultaneously decreased. The $H/E$ and $H^3/(E^*/E)^2$ ratios (where $E^* = E / (1 - v^2)$ is the effective Young's modulus [48]) were then calculated based on the obtained $H$ and $E$, as shown in Fig. 2(b). The $H/E$ value implies the resistance against elastic strain to failure [49], while the $H^3/(E^*)^2$ value indicates the resistance to plastic deformation [48]. Accordingly, with the increase of temperature, the TiNbWN film experiences first a decrease then a slight increase in the deformation resistance. It remains to be explored, but it seems that there is a change in microstructure at a temperature around 750 °C, which in turn may be a cause for the improved mechanical and wear properties of the thin film.

Fig. 1 Morphologies and microstructural features of the as-deposited TiNbWN thin film: (a) surface and (b) cross-sectional SEM images; (c) XRD pattern.

Fig. 2 (a) Volumetric wear losses for TiNbWN films sliding against 316ss stainless steel at an applied load of 1 N for a total sliding distance of 18 m and the change in hardness ($H$) of the films as a function of temperature. (b) $H/E$ and $H^3/(E^*)^2$ ratios of the TiNbWN film plotted against temperature.
Representative SEM images of the worn surfaces of the TiNbWN thin film after sliding against 316ss and the corresponding two-dimensional (2D) line scans of the wear tracks are shown in Fig. 3. The wear tracks generated at 25 °C exhibit a smooth appearance with some transferred materials attached, while those formed at 300 °C contain distinct grooves parallel to the sliding direction. Severe wear damage of the thin film occurred when the sliding temperature increased to 600 °C, as the film was entirely worn out, exposing the bare steel substrate. The thin film after sliding test at 750 °C, however, maintains a relatively intact surface with some grooves generated and the squeeze-out of materials occurring at certain locations. The 2D line scans of the wear tracks are shown in Fig. 3(e), in which the wear track at 600 °C reveals the largest width and depth, followed by the wear track formed at 750 and 300 °C. By analyzing the results presented in Figs. 2 and 3, the wear behavior of the TiNbWN thin film at varying temperatures can be preliminarily depicted as follows: (i) The thin film exhibits a high surface hardness at 25 °C, thus possessing a relatively low wear loss according to the Archard equation [50]; (ii) when temperature increases, plastic deformation occurs during sliding due to the thermally-induced mechanical property attenuation, and as a result, the wear loss monotonously increases up to 600 °C; (iii) further increase of the temperature, however, reduces the wear loss, indicating a transition in the wear mechanisms. Section 3.3 will focus on the subsurface microstructural features at both 25 and 750 °C to unravel this wear mechanism transition.

3.3 Subsurface microstructures at different temperatures

Figure 4 shows the subsurface microstructure of the TiNbWN thin film after sliding at 25 °C. An obvious deformation zone was observed right beneath the top sliding surface of the thin film, where the columnar structure was slightly bent towards the sliding direction under the effect of shear stresses. The equivalent plastic strains were estimated to be 0.202 at a depth of 600 nm from the top surface [51]. Associated with the accumulation of shear strains, plenty of microcracks that penetrated across the columnar structure were observed, which can be understood as the harbinger of catastrophic fracture. In addition, an amorphous oxide layer with a thickness of ~130 nm formed on the contact surfaces, while the elemental distribution mappings in Fig. 4(b) confirmed the high concentrations of O and Ti in the oxide layer, and the selected area electron diffraction (SAED) pattern in Fig. 4(c) further revealed its amorphous nature. The composition of this amorphous layer obtained using the EDS was
Friction

Ti₆.8 Nb₇.3 W₇.6 N₆.3 O₇₂.0 (at%). Thus, the sliding wear of TiNbWN thin films at 25 °C can be characterized by the simultaneous operation of mechanical and oxidational wear mechanisms, and the formation of an amorphous oxide layer is conceivably beneficial to restrain the wear loss, but only to a limited extent.

The subsurface microstructures of the TiNbWN thin film after sliding tests against 316ss for a total sliding distance of 18 m at 750 °C are shown in Fig. 5. As observed, the film at this condition exhibits a homologous morphology with the disappearing of the columnar structure shown in Fig. 4. The film is composed of dark and white nano-size particles in both the near-surface region and the region far from the top surface (Fig. 5(c)). The SAED pattern (Fig. 5(d)) identifies the oxides as a mixture of W₃O₆₋₂ (PDF#05-0386) and TiO₂ (PDF#87-0710) in addition to γTiOₓ (PDF#08-0117). The γTiOₓ oxide is a high-temperature phase with a wide solubility range of composition, which crystallizes in the halite (NaCl-type fcc) structure [52]. EDS mappings of the film confirm (Fig. 5(e)) the occurrence of segregation upon high-temperature oxidation, with the presence of W-rich and Ti-rich nanoparticles. The chemical
compositions of the W-rich and Ti-rich regions (areas) were acquired through the EDS point measurements and are provided in Table 1. The nano-grain boundaries of $W_6O_{12-n}$, TiO$_2$, and $\gamma$TiO$_x$ crystallites are demarcated in the HRTEM images using purple dash lines, yellow dash-dot lines, and cyan-blue dash-dot-dot lines, respectively. Measured interplanar spacing of $W_6O_{12-n}$ (010), TiO$_2$ (110), and $\gamma$TiO$_x$ (101) planes are 3.7, 3.3, and 2.4 Å, respectively.

The formation of nanocrystalline oxides in the TiNbWN thin film during high-temperature sliding (750 °C) resulted in a significant reduction of the grain size and could enhance $H$ in accordance with the Hall–Petch relationship [53]:

$$H = H_0 + k \times d^{-1/2}$$  \hspace{1cm} (2)

where $H_0$ is the hardness value for large grain sizes, $d$ is the average grain size of the material, and $k$ is the strengthening coefficient (a constant specific to each material). According to Eq. (2), the increment of hardness ($\Delta H$) induced by the grain size variation ($\Delta d$) can be calculated using the following Eq. (3):

$$\Delta H = k \times \left(d_1^{-1/2} - d_2^{-1/2}\right)$$  \hspace{1cm} (3)

in which $d_1$ and $d_2$ are the average grain sizes of the material before and after grain refinement, respectively. Here, an experimentally-determined $k$ value of ~10.2 GPa·(nm)$^{1/2}$ for titanium oxide was used for general estimates [54, 55]. The average grain sizes of the as-deposited thin film and the one after high-temperature sliding were determined from Figs. 1 and 5 ($d_m \approx 140$ nm and $d_n \approx 18.1$ nm). Hence, the calculated $\Delta H$ as per the Hall–Petch relationship was ~1.5 GPa. The grain refinement may conceivably cause the slight increment of the hardness of the film at 750 °C.

|                | N (at%) | O (at%) | Ti (at%) | Nb (at%) | W (at%) |
|----------------|---------|---------|----------|----------|---------|
| W-rich region  | 0.0     | 62.8    | 2.1      | 13.8     | 21.3    |
| Ti-rich region | 9.2     | 58.6    | 23.9     | 3.5      | 4.8     |

### 3.4 Formation temperature of nanocrystalline oxides

Figure 6(a) shows the representative Raman spectra taken from the wear tracks of the TiNbWN thin film after the sliding tests at different temperatures. Characteristic peaks at 260, 334, 734, and 805 cm$^{-1}$ indicate the presence of the $W_6O_{12-n}$ phase on the wear track of the thin film generated at 750 °C [56–58], which cannot be detected on the worn surfaces at lower temperatures. One should note that the generated tungsten oxides at 750 °C were possibly the $W_6O_{12-n}$ phase (one of the Magnéli phase) rather than the WO$_3$ phase [34, 36, 59–61]. According to the literature, the $W_6O_{12-n}$ phase with an oxygen deficiency possesses a crystal structure with ordered patterns of edge-sharing octahedra within the ReO$_3$-like network, leading to the emerging of easy crystallographic shear planes [62]. It was found that Magnéli phases could be formed on the surfaces of Ti-, V-, Mo-, W-, or Nb-containing materials upon sliding or oxidation at elevated temperatures [34, 36, 61, 63]. The present results of Raman spectra and TEM observations suggest the formation of $W_6O_{12-n}$ in the film. Besides, the formation
of TiO\textsubscript{2} after sliding at 600 and 750 °C was confirmed by the characteristic peaks at 246, 612, and 825 cm\textsuperscript{-1} in the Raman spectra [23, 64]. The formation temperature of the W\textsubscript{n}O\textsubscript{3n-2} oxides was further rationalized using the W–O phase diagram [59] shown in Fig. 6(b). A threshold temperature at ~585 °C for the formation of the W\textsubscript{3}O\textsubscript{9} and W\textsubscript{6}O\textsubscript{15} series was noted, which was also supported by the relevant literature [37, 63, 65]. For example, Polcar et al. [65] demonstrated the formation temperature of tungsten oxides on the WN film at ~500 °C. Liu et al. [37] argued that the critical oxidizing temperature of WC is between 500 and 550 °C, and the tungsten oxides became detectable at 550 °C. Using differential scanning calorimetric and simultaneous thermo-gravimetric analysis, Gassner et al. [63] found the oxidation threshold of the WN thin film to be ~550 °C. Their experimental results also indicated that a large quantity of oxides could only form when the temperature exceeded ~650 °C [63]. Thus, it can be inferred that the amount of W\textsubscript{3}O\textsubscript{9} phase generated at 600 °C was insufficient to maintain a stable oxide layer to reduce wear, whereas bulk oxidation of the TiNbWN film at 750 °C facilitated a wear reduction as a result of both hardness enhancement and a solid-lubrication effect.

Figure 6(c) shows the phase diagram of the Ti–O system calculated using CALPHAD approach [66–68] based on the well-accepted thermodynamic dataset from the literature [52]. The γTiO\textsubscript{2} phase (marked in orange) is shown in the phase diagram, which exhibits a wide solubility range (from ~ 41.2 to 56.7 at% O) and a threshold formation temperature at ~456 °C. Since it stretches over wide composition and temperature ranges in the phase diagram, γTiO\textsubscript{2} is supposed to possess a high thermal stability, especially at high temperatures. Additionally, there are a number of stoichiometric compounds existing in the Ti–O phase diagram, such as Ti\textsubscript{3}O\textsubscript{4}, αTiO\textsubscript{2}, and Ti\textsubscript{2}O\textsubscript{3}. The G\textsubscript{form} of selected oxides were further obtained to compare their thermodynamic stabilities. G\textsubscript{form} of a compound A\textsubscript{n}B\textsubscript{m} can be calculated using Eq. (4):

\[
G_{\text{form}} = G(A) - \frac{n}{n+m} G(A) + \frac{m}{n+m} G(B)
\]  

in which G(A) and G(B) present the Gibbs energies of Components A and B at their reference states, respectively. G(A) and G(B) can be obtained using the CALPHAD approach. Figure 6(d) shows the calculated G\textsubscript{form} of the selected oxides. Among the selected oxides, TiO\textsubscript{2} contains the lowest G\textsubscript{form} at temperatures below ~600 °C, while γTiO\textsubscript{2} becomes more thermodynamically preferable at higher temperatures. As for tungsten and niobium oxides, it appears that W\textsubscript{1}O\textsubscript{3} contains much lower G\textsubscript{form} than Nb\textsubscript{2}O\textsubscript{5}. The calculated results demonstrated that the TiO\textsubscript{2}, γTiO\textsubscript{2}, and W\textsubscript{1}O\textsubscript{3} binary oxides are thermodynamically preferable to form in the Ti–Nb–W–N–O system, which is highly in agreement with the current experimental observations.

To clarify the effect of TiO\textsubscript{2}, γTiO\textsubscript{2}, and W\textsubscript{1}O\textsubscript{3} formation on the wear performance of TiNbWN film, we investigated the adhesion behavior of the pristine and oxidized TiNbWN films against the sliding counterfaces by employing ab initio calculations. Due to the complexity of wear mechanisms, rough approximations at the DFT level are made to mimic the real physical interactions and provide the general trends. Since the 316ss counterface could easily be oxidized during sliding, FeO instead of pure iron or steel was considered as an adsorbate in all the adsorption calculations. Additionally, the calculations narrowed down to the adsorption on the (001) surface due to its lower surface energy compared with other crystallographic planes in an fcc structure [69], and it is one of the facets obtained in this work (Fig. 1). The calculated adsorption energies of FeO molecule on the WO\textsubscript{3}(001), TiO\textsubscript{2}(001), and TiNbWN(001) surfaces are shown in Fig. 7(a), in which typical slab models with the O atom approaching the surface metal atoms are presented. Although the lateral size of the considered configurations is not the same, only minor deviations in the adsorption energy can be expected based on the previous work [70]. The present results show that the FeO molecules with O end toward the surface of WO\textsubscript{3}(001), TiO\textsubscript{2}(001), and TiNbWN(001) surfaces exhibit lower adsorption energies compared with the FeO molecule with Fe end (notated here as OFe), demonstrating that there are stronger adhesions between O atoms and the metal atoms on crystal surfaces. The TiNbWN(001) surface exhibits the lowest adsorption energy (the strongest interaction) compared with the TiO\textsubscript{2}(001) and WO\textsubscript{3}(001) surfaces, when
Fig. 7  (a) Calculated adsorption energies of iron oxide molecule on the WO₃(001), TiO₂(001), and TiNbWN(001) surfaces with the slab models inserted. Notations FeO and OFe pertain to the orientations of the FeO molecule atop the surfaces. The insets show the FeO case. The VASP code was employed. (b) Summary of the reported adsorption energies of species and molecules on various surfaces [71–83] compared with the currently calculated adsorption energies.

considering both FeO and OFe orientations of iron oxides. This indicates that when the oxides were formed on the surface of TiNbWN films, the interfacial adhesion could be distinctly mitigated, leading to the improved performance of friction and wear.

We further compared our calculation results with the literature pertaining to the adsorption of other substances on various surfaces, as shown in Fig. 7(b). The adsorption energy on the WO₃ surface varied in a range of −1.25 to −0.97 eV/atom, depending on the types of adsorbates (NO, CO, or H₂O) [71–75], while those of NO and CO on the TiO₂ surface were in a narrow range of 0.03 to 0.74 eV/atom [76–78]. As for the nitride surfaces, the adsorption sites obviously impact the adsorption energies [79–81]. The interaction between oxygen/H₂O molecules and the metal atoms in the nitrides was considerably stronger, resulting in a lower adsorption energy [80, 81]. Furthermore, the Fe atom adsorbed strongly on TiN(001) surface, exhibiting the adsorption energies in the range of −5.81 to −4.12 eV/atom at different adsorption sites. The currently calculated adsorption energies of iron oxides with the O end (FeO) varied between −2.73 and −1.30 eV/atom, which was within the adsorption energy range of NO/CO/H₂O on WO₃ and oxygen on nitrides, and slightly lower than the adsorption energy of CO₂/NO on TiO₂. FeO with the Fe end (OFe), however, exhibited slightly weaker interactions with the WO₃(001), TiO₂(001), and TiNbWN(001) surfaces and contained higher adsorption energies (−2.00 to −0.66 eV/atom). Clearly, the TiNbWN outperforms the benchmark coating TiN since the interaction with oxidized steel surfaces (wear counterpart) is considerably weaker. Based on the calculation results, the WO₃ and TiO₂ oxides are expected to achieve an ameliorated adhesion with the iron oxide in comparison with the TiNbWN film, which is consistent with the experimental data. Hence, by combining the CALPHAD and DFT results, the wear mechanism transition of the TiNbWN film between 600–750 °C can be delineated as follows: (i) When the sliding temperature reaches 600 to 750 °C, a large quantity of tungsten and titanium oxides readily form (Fig. 6); (ii) mechanical properties of the film could be slightly enhanced, following the Hall–Petch relationship (Section 3.3), thus increasing the wear resistance; (iii) the tungsten and titanium oxides can obviously alleviate the interface adhesion between the film and the sliding counterparts, as suggested by DFT calculations (Fig. 7). Therefore, the nano-oxides generated at high temperatures could act as solid lubricants to reduce wear losses.

4 Conclusions

We have designed and synthesized a new MEN film, TiNbWN, with a near-equatomic composition and an fcc solution using a reactive magnetron sputtering. The wear performances of the thin film at a temperature range of 25–750 °C were examined. In the temperature range of 25–600 °C, the wear resistance of the film was dependent on the surface hardness, which decreased monotonously as the temperature rose. At a higher temperature (750 °C), the nanocrystalline oxides (WₙO₃ₙ₋₂, TiO₂, and γTiO₃) were formed during sliding, enhancing the hardness of the film and providing solid lubrication, both of which contributed to a reduced wear loss. This is corroborated theoretically on both continuum and atomic level. Thus, the work presented herein delineated the role of the in situ formed nanocrystalline oxides in the wear mechanism transition of TiNbWN thin films, which could in general shed light on the high-temperature wear behavior of refractory HEN/MEN films.
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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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Reference

[1] Yeh J W, Chen S K, Lin S J, Gan J Y, Chin T S, Shun T T, Tsau C H, Chang S Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. Adv Eng Mater 6(5): 299–303 (2004)
[2] George E P, Raabe D, Ritchie R O. High-entropy alloys. Nat Rev Mater 4(8): 515–534 (2019)
[3] Cantor B, Chang I T H, Knight P, Vincent A J B. Microstructural development in equiatomic multicomponent alloys. Mater Sc Sci Eng A 375–377: 213–218 (2004)
[4] Zhang Y. Materials design of high-entropy materials. In: High-Entropy Materials: A Brief Introduction. Singapore: Springer Singapore, 2019: 35–63.
[5] Oses C, Toher C, Curtarolo S. High-entropy ceramics. Nat Rev Mater 5(4): 295–309 (2020)
[6] Moon J, Park J M, Bae J W, Do H S, Lee B J, Kim H S. A new strategy for designing immiscible medium-entropy alloys with excellent tensile properties. Acta Mater 193: 71–82 (2020)
[7] Lewin E. Multi-component and high-entropy nitride coatings—A promising field in need of a novel approach. J Appl Phys 127(16): 160901 (2020)
[8] Shu R, Paschalidou E M, Rao S G, Lu J, Grezynski G, Lewin E, Nyholm L, le Febvrier A, Eklund P. Microstructure and mechanical, electrical, and electrochemical properties of sputter-deposited multicomponent (TiNbZrTa)N, coatings. Surf Coat Technol 389: 125651 (2020)
[9] Shu R, Paschalidou E M, Rao S G, Bakht B, Boyd R, Moro M V, Primetzhofer D, Grezynski G, Nyholm L, le Febvrier A, et al. Effect of nitrogen content on microstructure and corrosion resistance of sputter-deposited multicomponent (TiNbZrTa)N, films. Surf Coat Technol 404: 126485 (2020)
[10] Baran Ö. Manetron Sıçratma Yöntemiyle Kaplanlanmış TiNbN ve TiVN Filmlerin Mekanik ve Tribolojik Özelliklerinin İncelenmesi. Gümüşhane Üniversitesi Fen Bilimleri Enstitüsü Dergisi 7(2): 181–191 (2017) (in Turkish)
[11] Serro A P, Completo C, Colaço R, dos Santos F, da Silva C L, Cabral J M S, Araújo H, Pires E, Saramago B. A comparative study of titanium nitrides, TiN, TiNbN and TiCN, as coatings for biomedical applications. Surf Coat Technol 203(24): 3701–3707 (2009)
[12] Zhou S, Liu W G, Liu H, Cai C L. Structural and electrical properties of Ti–W–N thin films deposited by reactive RF sputtering. Phys Procedia 18: 66–72 (2011)
[13] Shaginyan L R, Mišina M, Zemek J, Musel J, Regent F, Britun V F. Composition, structure, microhardness and residual stress of W–Ti–N thin films deposited by reactive magnetron sputtering. Thin Solid Films 408(1–2): 136–147 (2002)
[14] Kuchuk A V, Kladko V P, Lytvyn O S, Piotrowska A, Minikayev R A, Ratajczak R. Relationship between condition of deposition and properties of W–Ti–N thin films prepared by reactive magnetron sputtering. Adv Eng Mater 8(3): 209–212 (2006)
[15] Cavaleiro A, Trindade B, Vieira M T. Influence of Ti addition on the properties of W–Ti–C/N sputtered films. Surf Coat Technol 174–175: 68–75 (2003)
[16] Jalali R, Parhizkar M, Bidadi H, Naghshara H, Eshraghi M J. Characterization of nano-crystalline Ti–W–N thin films for...
diffusion barrier application: A structural, microstructural, morphological and mechanical study. Appl Phys A 124(12): 810 (2018)

[17] Jalali R, Parhizkar M, Bidadi H, Naghshara H. Correlation between optical, structural and microstructural properties of Ti–W–N thin films. Ceram Int 46(5): 6454–6461 (2020)

[18] Kitamika Y, Shingu H, Tanigawa S, Hasegawa H. Mechanical properties and oxidation resistance of Ti–W–N coatings. J Surf Finish Soc Jpn 69(11): 517–520 (2018)

[19] Lou M, Chen X, Xu K, Deng Z X, Chen L L, Lv J, Chang K K, Wang L P. Temperature-induced wear transition in ceramic–metal composites. Acta Mater 205: 116545 (2021)

[20] Meng Y G, Xu J, Jin Z M, Prakash B, Hu Y Z. A review of recent advances in tribology. Friction 8(2): 221–300 (2020)

[21] Chen X, Han Z. A low-to-high friction transition in gradient nano-grained Cu and Cu–Ag alloys. Friction 9(6): 1558–1567 (2021)

[22] Lou M, White D R, Banerji A, Alpas A T. Dry and lubricated friction behaviour of thermal spray low carbon steel coatings: Effect of oxidational wear. Wear 432–433: 102921 (2019)

[23] Lou M, Alpas A T. High temperature wear mechanisms in thermally oxidized titanium alloys for engine valve applications. Wear 426–427: 443–453 (2019)

[24] Yang R, Ma W, Duan C J, Li S, Wang T M, Wang Q H. Self-lubrication of tribologically-induced oxidation during dry reciprocating sliding of aged Ti–Ni51.5 at% alloy. Friction 9(5): 1038–1049 (2021)

[25] Fink M. Wear oxidation—A new component of wear. T Am Soc Steel Treating 18:1026–1034 (1930)

[26] Stott F H. The role of oxidation in the wear of alloys. Tribol Int 31(1–3): 61–71 (1998)

[27] Cui X H, Wang S Q, Wang F, Chen K M. Research on oxidation wear mechanism of the cast steels. Wear 265(3–4): 468–476 (2008)

[28] Childs T H C. The sliding wear mechanisms of metals, mainly steels. Tribol Int 13(6): 285–293 (1980)

[29] Doeh A, Roher C, Reza–Aria F, Mahayotsan A. Tribology in metal forming at elevated temperatures. Friction 3(1): 1–27 (2015)

[30] Dong X, Jahanmir S. Wear transition diagram for silicon nitride. Wear 165(2): 169–180 (1993)

[31] Zhou Z, Rainforth W M, Luo Q, Hovsepian P E, Ojeda J J, Romero-Gonzalez M E. Wear and friction of TiAlN VN coatings against Al2O3 in air at room and elevated temperatures. Acta Mater 58(8): 2912–2925 (2010)

[32] Javdšák R, Musil J, Soukup Z, Haviar S, Čerstvý R, Houska J. Tribological properties and oxidation resistance of tungsten and tungsten nitride films at temperatures up to 500 °C. Tribol Int 132: 211–220 (2019)

[33] Mohgaddam P V, Prakash B, Vuorinen E, Fallqvist M, Andersson J M, Hardell J. High temperature tribology of TiAlN PVD coating sliding against 316L stainless steel and carbide-free bainitic steel. Tribol Int 159: 106847 (2021)

[34] Magné J. Structures of the ReO3-type with recurrent dislocations of atoms: “Homologous series” of molybdenum and tungsten oxides. Acta Crystallogr B: 495–500 (1953)

[35] Woydt M, Skopp A, Dörfler l, Witke K. Wear engineering oxides/anti-wear oxides. Wear 218(1): 84–95 (1998)

[36] Migas D B, Shaposhnikov V L, Borisienko V E. Tungsten oxides. II. The metallic nature of Magné phases. J Appl Phys 108(9): 093714 (2010)

[37] Liu Y L, Wang Z X, Sun Q C, Yin B, Cheng J, Zhu S Y, Yang J, Qiao Z H, Liu W M. Tribological behavior and wear mechanism of pure WC at wide range temperature from 25 to 800 °C in vacuum and air environment. Int J Refract Met Hard Mater 71: 160–166 (2018)

[38] Lugscheider E, Knotek O, Bobzin K, Bärwulf S. Tribological properties, phase generation and high temperature phase stability of tungsten- and vanadium-oxides deposited by reactive MSIP–PVD process for innovative lubrication applications. Surf Coat Technol 133–134: 362–368 (2000)

[39] Suszko T, Gubinski W, Jagielski J. The role of surface oxidation in friction processes on molybdenum nitride thin films. Surf Coat Technol 194(2–3): 319–324 (2005)

[40] Oliver W C, Pharr G M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res 7(6): 1564–1583 (1992)

[41] Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys Rev A 135(3B): B864–B871 (1964)

[42] Kresse G, Hafner J. Ab initio molecular-dynamics simulation of the liquid–metal–amorphous–semiconductor transition in germanium. Phys Rev B 49(20): 14251–14269 (1994)

[43] Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys Rev B 59(3): 1758–1775 (1999)

[44] Blöchl P E. Projector augmented-wave method. Phys Rev B 50(24): 17953–17979 (1994)

[45] Predel F. Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys. Heidelberg (Germany): Springer Berlin Heidelberg, 2016.

[46] Huang W M. Thermodynamic assessment of the Nb–N system. Metall Mater Trans A 27(11): 3591–3600 (1996)

[47] Miao K F, Wang J, Zhao Q, Wang K W, Wen M, Zhang K. Water-based lubrication of niobium nitride. Friction 10(6): 842–853 (2022)

[48] Lin J L, Moore J J, Mishra B, Pinkas M, Sproul W D. The structure and mechanical and tribological properties of...
Erb U, Palumbo G, McCrea J L. The processing of bulk Li Y, Song K F. Study on manufacture process, micro-
Hampl M, Schmid-Fetzer R. Thermodynamic description of Archard J F, Hirst W. The wear of metals under unlubricated conditions.
Proc Roy Soc A Math Phy Sci 236(1206): 397–410 (1956)
Hutchings I, Shipway P. Tribology: Friction and Wear of Engineering Materials, 2nd edn. Oxford (UK): Butterworth-
Heinemann, 2017.
Hampf M, Schmid-Fetzer R. Thermodynamic description of the Ti–O system. Int J Mater Res 106(5): 439–453 (2015)
Erb U, Palumbo G, McCrea J L. The processing of bulk nanocrystalline metals and alloys by electrodeposition. In: Nanostructured Metals and Alloys: Processing, microstructure, mechanical properties and applications, Whang S H, Ed. Cambridge (UK): Woodhead Publishing, 2011: 118–151.
Li Y, Song K F. Study on manufacture process, micro-hardness and Hall–Petch relation of pure rutile phase TiO2 MAO coating. Appl Mech Mater 738–739: 175–179 (2015)
Bahador A, Umeda J, Hamzah E, Yusof F, Li X C, Kondoh K. Synergistic strengthening mechanisms of copper matrix composites with TiO2 nanoparticles. Mater Sci Eng A 772: 138797 (2020)
Chen J, Lu D Y, Zhang W H, Xie F Y, Zhou J, Gong L, Liu X, Deng S Z, Xu N S. Synthesis and Raman spectroscopic study of W2O58 nanowires. J Phys D Appl Phys 41(11): 115305 (2008)
Sun L, Li Z, Su R, Wang Y L, Li Z L, Du B S, Sun Y, Guan P F, Besenbacher F, Yu M. Phase-transition induced conversion into a photothermal material: Quasi-metallic WO2.9 nanorods for solar water evaporation and anticancer photothermal therapy. Angew Chem Int Ed 57(33): 10666–10671 (2018)
Pirkner L, Višić B, Škapan S D, Dražić G, Kovač J, Remškar M. Multi-stoichiometric quasi-two-dimensional W12O38 nanotubes. Nanoscale 12(28): 15102–15114 (2020)
Wriedt H A. The O–W (oxygen–tungsten) system. Bull Alloy Phase Diagr 10(4): 368–384 (1989)
Kutschej K, Mayrhofer P H, Kathrein M, Polcik P, Mitterer C. A new low-friction concept for Ti1−xAlxN based coatings in high-temperature applications. Surf Coat Technol 188–189: 358–363 (2004)
Reeswinkel T, Music D, Schneider J M. Coulomb-potential-dependent decohesion of magnéli phases. J Phys Condens Matter 22(29): 292203 (2010)
Lugscheider E, Bärwulf S, Barimiani C. Properties of tungsten and vanadium oxides deposited by MSIP–PVD process for self-lubricating applications. Surf Coat Technol 120–121: 458–464 (1999)
Gassner G, Mayrhofer P H, Kutschej K, Mitterer C, Kathrein M. Magnéli phase formation of PVD Mo–N and W–N coatings. Surf Coat Technol 201(6): 3335–3341 (2006)
Zheng J, Li M J, Feng Z C, Chen J, Li C. UV Raman spectroscopic study on TiO2. I. Phase transformation at the surface and in the bulk. J Phys Chem B 110(2): 927–935 (2006)
Polcar T, Parreira N M G, Cavaleiro A. Structural and tribological characterization of tungsten nitride coatings at elevated temperature. Wear 265(3–4): 319–326 (2008)
Xu K, Chang K K, Yu M, Zhou D P, Du Y, Wang L P. Design of novel NiSiAlY alloys in marine salt-spray environment: Part II. Al–Ni–Si–Y thermodynamic dataset. J Mater Sci Technol 89: 186–198 (2021)
Xu K, Chang K K, Zhou X B, Chen L L, Liu J W, Deng Z X, Huang F, Huang Q. Thermodynamic descriptions of the light rare-earth elements in silicon carbide ceramics. J Am Ceram Soc 103(6): 3812–3825 (2020)
Liu S D, Chang K K, Music D, Chen X, Mráz S, Bogdanovski D, Hans M, Primetzhofer D, Schneider J M. Stress-dependent prediction of metastable phase formation for magnetron-sputtered V1−xAlxN and Ti1−xAlxN thin films. Acta Mater 196: 313–324 (2020)
Wang C, Dai Y B, Gao H Y, Ruan X M, Wang J, Sun B D. Surface properties of titanium nitride: A first-principles study. Solid State Commun 150(29–30): 1370–1374 (2010)
Riedl H, Zálešák J, Arndt M, Polcik P, Holec D, Mayrhofer P H. Ab initio studies on the adsorption and implantation of Al and Fe to nitride materials. J Appl Phys 118(12): 125306 (2015)
Zhao L H, Tian F H, Wang X B, Zhao W W, Fu A P, Shen Y Y, Chen S G, Yu S Q. Mechanism of CO adsorption on hexagonal WO3 (001) surface for gas sensing: A DFT study. Comput Mater Sci 79: 691–697 (2013)
Saadi L, Lambert-Mauriat C, Oison V, Ouali H, Hayn R. Mechanism of NO2 sensing on WO3 surface: First principle calculations. Appl Surf Sci 293: 76–79 (2014)
Oison V, Saadi L, Lambert-Mauriat C, Hayn R. Mechanism of CO and O2 sensing on WO3 surfaces: First principle study. Sens Actuat B Chem 160(1): 505–510 (2011)
Hurtado-Aular O, Vidal A B, Sierraalta A, Añez R. Periodic DFT study of water adsorption on m-WO3(001), m-WO3(100), h-WO3(001) and h-WO3(100). Role of hydroxyl groups on the stability of polar hexagonal surfaces. Surf Sci 694: 121558 (2020)
Albanese E, di Valentin C, Pacchioni G. H2O adsorption on WO3 and WO3(001) surfaces. ACS Appl Mater Interfaces 9(27): 23212–23221 (2017)
[76] Sorescu D C, Rusu C N, Yates J T. Adsorption of NO on the TiO$_2$(110) surface: An experimental and theoretical study. J Phys Chem B 104(18): 4408–4417 (2000)

[77] Sorescu D C, Yates J T. Adsorption of CO on the TiO$_2$(110) surface: A theoretical study. J Phys Chem B 102(23): 4556–4565 (1998)

[78] Klyukin K, Alexandrov V. CO$_2$ adsorption and reactivity on rutile TiO$_2$(110) in water: An ab initio molecular dynamics study. J Phys Chem C 121(19): 10476–10483 (2017)

[79] Wang C, Dai Y B, Gao H Y, Ruan X M, Wang J, Sun B D. Ab initio molecular dynamics study of Fe adsorption on TiN (001) surface. Mater Trans 51(11): 2005–2008 (2010)

[80] Kang Q X, Wang G F, Liu Q, Sui X C, Liu Y K, Chen Y Q, Luo S Y, Li Z L. Investigation for oxidation mechanism of CrN: A combination of DFT and ab initio molecular dynamics study. J Alloys Compd 885: 160940 (2021)

[81] Guo F Y, Wang J C, Du Y, Wang J, Shang S L, Li S L, Chen L. First-principles study of adsorption and diffusion of oxygen on surfaces of TiN, ZrN and HfN. Appl Surf Sci 452: 457–462 (2018)

[82] Music D, Schneider J M. Ab initio study of Ti$_{0.5}$Al$_{0.5}$N(001)—residual and environmental gas interactions. New J Phys 15(7): 073004 (2013)

[83] Sanyal S, Waghmare U V, Ruud J A. Adsorption of water on TiN(100), (110) and (111) surfaces: A first-principles study. Appl Surf Sci 257(15): 6462–6467 (2011)

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