

Article

Effect of Modulation Period on the Cavitation Erosion Resistance of TiSiN/AlCrTiVNbN Nanomultilayer Films

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Highlights

- All films exhibit a single-phase face-centered cubic (FCC) structure with a (200) preferred orientation; the λ_6 sample has the highest interface density.
- The 6 nm-period film achieves a maximum hardness of 38.9 GPa and superior plastic deformation resistance indexes.
- The λ_6 coating obtains the lowest mass loss of 0.8 mg and best integrity under 3.5 wt% NaCl cavitation erosion tests.

Abstract

Cavitation erosion severely limits the service life of marine hydraulic components. Magnetron sputtering was utilized to fabricate TiSiN/AlCrTiVNbN high-entropy nitride nanomultilayer films, whose modulation periods ranged from 4 nm to 23 nm. The effects of modulation period on the microstructure, mechanical properties, and cavitation erosion resistance were systematically investigated. All films exhibited a single-phase face-centered cubic structure with a preferred orientation (200) plane. The film with a 6 nm layer period reached the highest hardness (38.9 GPa) and elastic modulus (214.1 GPa), which is due to the many closely fitting interfaces that effectively stopped line defect movement; in cavitation erosion tests in 3.5% salt water, this film had the lowest mass loss (0.8 mg) and its surface stayed in the best condition. Its superior cavitation erosion resistance originates from the synergistic effects of high-density coherent interfaces that obstructed crack propagation, enhanced mechanical properties that provided excellent resistance to plastic deformation, and the formation of a protective oxide layer during cavitation. As this work shows, optimizing the layer period is an effective strategy; it allows the design of strong protective films for ocean use.

Keywords: high-entropy nitride nanomultilayer films; TiSiN/AlCrTiVNb high-entropy nitride nanomultilayer (HENM) films; modulation period; anti-cavitation erosion performance



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1. Introduction

High-pressure micro-jets, generated by collapsing bubbles, continuously strike marine hydraulic equipment such as seawater pumps and propellers over extended periods. This easily initiates cracks and surface peeling, greatly shortening the service life of these components [1,2]. Type 304 stainless steel possesses low processing cost and wide applicability. However, its base hardness is somewhat low, and after ultrasound cavitation, many erosion pits and cracks that go right through appear. This makes it hard to meet the needs for

long-term ocean protection [3,4]. An effective strategy to improve the base material's resistance to cavitation damage is to use nitride coatings; these coatings are applied by magnetron sputtering and can form dense protective layers without harming the substrate's performance [5].

Monolayer nitride coatings such as TiN and CrN suffer from drawbacks including coarse grain size and insufficient corrosion resistance. In contrast, nanomultilayer films can use many interfaces to make grains smaller and pin line defects, resulting in much better overall performance than single-layer coatings [6,7]. The CrAlN/TiSiN multilayer coatings prepared by Wang et al. exhibited a hardness of 34.2 GPa. However, the system lacks multi-principal elements. Because of this, its ability to passivate in seawater is limited [8]. Lothrop et al. prepared (AlCrTiVZr)N coatings, which contain multiple principal elements. These coatings exhibit a hardness of 27.5 ± 2.1 GPa and a stiffness of 284 ± 23 GPa, and the presence of multiple components helps form complex protective oxide layers [9]. Yet the multi-component design is not limited to oxide formation; it also aims to enhance mechanical performance to withstand cyclic cavitation impact. Although binary and ternary oxides may possess good corrosion resistance, they generally lack sufficient mechanical stability under repeated impact loading.

The layer period is a key process factor; it sets the interface amount and grain size in TiSiN/AlCrTiVNbN nanomultilayer films [10]. Zhu et al. found that a too large layer period makes interfaces less restrictive and grains coarser. Too small a one tends to accumulate stress from misfit, and both reduce the films' mechanical performance and cavitation erosion resistance [11,12]. Yan et al. investigated the tribological properties of multilayer films within the same material system. However, the study did not include any cavitation erosion tests [10]. Another study carried out cavitation erosion experiments on TiSiN/NiTiAlCoCrN multilayer films. Yet, V and Nb elements are not included in the system, and this results in a rather singular oxidation protection mechanism [13]. Monolithic TiSiN coatings can attain high hardness but generally suffer from insufficient fracture toughness, and cracks tend to initiate followed by rapid material spallation under cyclic cavitation impact loading. Although monolithic AlCrTiVNbN high-entropy nitrides exhibit favorable multi-element oxidation-resistance capacity, they show unconstrained grain coarsening and limited crack-arresting capability under repeated impact stress [14].

For marine corrosion and cavitation-erosion-resistant coatings applied to 304 stainless-steel components, several key performance criteria must be met. A multi-element system containing no fewer than four metallic elements is desirable to activate high-entropy effects and stabilize solid-solution microstructures [15]. Sufficient hardness (typically >15 GPa for hard ceramic protective coatings) is required to withstand plastic deformation induced by cavitation impact. In addition, reliable coating–substrate adhesion, a dense microstructure free of through-thickness pinholes, and the ability to form stable protective oxide passive films are essential for long-term service in seawater [16]. Guided by these criteria, this work designs TiSiN/AlCrTiVNbN nanomultilayer films.

TiSiN/AlCrTiVNbN nanomultilayer films with modulation periods of 4 nm, 6 nm, 8 nm, 10 nm, and 23 nm were prepared by magnetron sputtering in this study. The regulation effects of modulation period on the microstructure, mechanical properties, and cavitation erosion resistance of the films were systematically investigated by XRD, SEM, AFM, nanoindentation, ultrasonic cavitation, and XPS. The synergistic protection mechanism involving coherent interfaces, solid solution strengthening, and multi-component oxide layers was elucidated, providing an experimental basis for the design and development of protective films for marine cavitation erosion resistance.

2. Experimental Materials and Film Deposition

2.1. Experimental Materials

304 stainless steel substrates with dimensions of $\Phi 20 \text{ mm} \times 3 \text{ mm}$ and mirror-polished surfaces, together with single-crystal silicon wafers of $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ with single-side polished surfaces, were selected as the substrate materials. Prior to deposition, the substrates were ultrasonically cleaned sequentially in acetone and anhydrous ethanol for 20 min each, dried with a dryer, and then fixed onto the rotatable sample stage in the vacuum chamber.

Three targets were employed in the experiments: a Ti cathode with 99.99% purity, a TiSi alloy sputtering source containing 10 at.% silicon, and an AlCrTiVNb high-entropy alloy target with equimolar elements. The targets uniformly measured 50.8 mm in diameter and 4 mm in thickness, the size tolerance fell within 0.1 mm, and their purity reached 99.99%.

2.2. Film Deposition

TiSiN/AlCrTiVNbN high-entropy nitride nanomultilayer (HENM) films were synthesized via magnetron sputtering in a multi-cathode high-vacuum JCP-350M2 sputtering apparatus (manufactured by Beijing Taikono Tech. Co., Ltd., Beijing, China). The substrates were mounted on a rotatable stage positioned atop the deposition chamber, which was evacuated to a base pressure of $3 \times 10^{-5} \text{ Pa}$. Prior to deposition, the substrates were first subjected to 15 min Ar^+ ion etching to remove surface oxide and contaminants. Pure Ar gas was supplied at 40 sccm during etching, with a substrate bias voltage of 600 V and the chamber pressure maintained at 0.8–1.2 Pa. After substrate cleaning, 10 min target pre-sputtering was performed to eliminate target-surface impurities and native oxide layers. During this step, the substrate bias voltage was set to 100 V, the chamber pressure was kept within 0.3–0.5 Pa, and the N_2 -to-Ar flow ratio was adjusted to 3:4. During coating, the working gas argon and reactive gas nitrogen were introduced, the N_2 -to-Ar flow ratio was kept at 3:4, and the chamber working pressure was maintained at 0.6 Pa. All coatings were deposited at room temperature, without any extra heating of the substrates. The structural schematic diagram was drawn using OriginPro 2022 software. Figure 1 presents a schematic illustration of the sputtering system and the resulting HENM architecture. In this figure, the pink dots denote sputtered AlCrTiVNb particles, and the green dots represent sputtered TiSi particles.

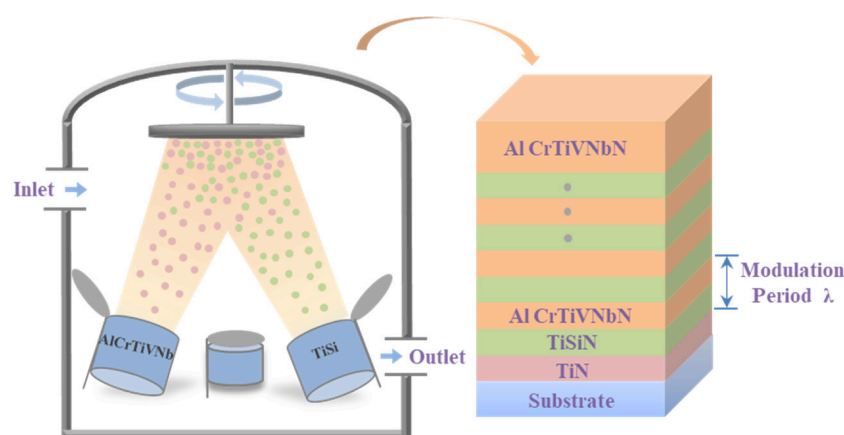


Figure 1. Schematic illustration of the magnetron sputtering apparatus and the HENM structure.

To improve the bonding of the film to the base materials, a TiN interlayer was first deposited for 30 min. The TiN interlayer is widely adopted to mitigate interfacial residual stress and enhance film substrate adhesion between 304 stainless steel and hard nitride coatings [17]. According to cross-sectional SEM observations, the resulting TiN interlayer

thickness ranged from 94 nm to 106 nm. The Ti target was operated in direct current (DC) mode with a sputtering power of 110 W under an N₂-to-Ar flow ratio of 1:4. This pretreatment procedure was performed prior to the deposition of HENM films. A constant substrate bias voltage of 100 V was applied throughout the subsequent formal deposition process. During sputtering, a 100 W RF source powered the TiSi target and a 110 W DC source powered the AlCrTiVNb target. The deposition rates of the TiSiN and AlCrTiVNbN sublayers were measured as 0.044 nm·s^{−1} and 0.1 nm·s^{−1}, respectively. The thickness of the TiSiN layer was fixed at 3 nm, corresponding to a deposition time of 68 s. The AlCrTiVNbN layer coating time was changed, and HENM films with layer periods of 4, 6, 8, 10, and 23 nm were deposited in turn on the TiN interlayer, and finally, a top AlCrTiVNbN layer is deposited for 30 min, using only the AlCrTiVNb target, to serve as the working layer. The detailed deposition parameters and the corresponding bilayer numbers for each modulation period are presented in Table 1.

Table 1. Deposition parameters of the TiSiN/AlCrTiVNbN HENM films.

Abbr.	TiSiN Sublayer Thickness/nm	AlCrTiVNbN Sublayer Thickness/nm	Single Modulation Cycle Time/s	Cycles/N	Overall Film Thickness/μm
λ4	3	1	78	455	1.211
λ6	3	3	98	304	1.352
λ8	3	5	118	228	1.405
λ10	3	7	138	182	1.464
λ23	3	20	268	80	1.605

2.3. Thin Film Characterization

The crystallographic phases of the as-deposited films were identified using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, Japan), which operated with Cu Kα radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA. Diffraction data were collected over a 2θ interval of 20–80° at a scanning step of 5°·min^{−1}. Morphological observations of the surface and cross-section were carried out using a Carl Zeiss Sigma-300 field-emission SEM (Carl Zeiss Microscopy GmbH, Jena, Germany). The elemental distributions on the as-deposited and post-cavitation surfaces were subsequently mapped with an Oxford Instruments Ultim Max EDS detector (Oxford Instruments plc, Abingdon, UK) fitted to this microscope. Surface roughness was characterized by atomic force microscopy (AFM; Bruker MultiMode 8, Bruker Corporation, Santa Barbara, CA, USA) in tapping mode over a scan area of 5 μm × 5 μm. For each sample, three different regions were measured to obtain the average roughness (Ra) and root-mean-square roughness (Rq) values, and the corresponding standard deviations were calculated. Hardness and elastic modulus were assessed using an Anton Paar UNHT nanoindentation system (Anton Paar GmbH, Graz, Austria) fitted with a Berkovich diamond indenter (tip radius: 100 nm). The loading and unloading rates were both kept at 20 mN·min^{−1}. Three independent indentations were performed on each sample surface, and the average hardness and elastic modulus together with standard deviations were calculated. Cavitation erosion testing was performed using a 3.5 wt% NaCl electrolyte maintained at 25 ± 5 °C. The experiments employed an ultrasonic vibratory device (Wuhan Corrttest Instruments Corp., Ltd., Wuhan, China) set to a power of 600 W, a frequency of 20 kHz, and an amplitude of 15 μm. The cavitation-erosion test was performed referring to the ASTM G32-16 standard [18]. The total cavitation exposure duration for all samples was 120 min. The chemical composition and bonding configurations of the film surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha⁺ system (Thermo Fisher Scientific, East Grinstead,

UK) equipped with a monochromatic Al K α source (1486.6 eV). The binding energy scale was calibrated using the C 1s line at 284.8 eV as a reference.

3. Results and Discussion

3.1. Microstructure

X-ray diffraction (XRD) was used to examine the crystal structure of the TiSiN/AlCrTiVNbN HENM films, which were deposited at different modulation periods. Figure 2 presents both the survey spectra and the corresponding enlarged regions of the principal diffraction peaks. Regardless of the modulation period, all films displayed a single FCC phase with a pronounced (200) preferred orientation and relatively weak (111) reflections. The identified phases were indexed as solid solutions of CrN, AlN, and Ti₂N, among other nitrides. No extra phases were found in the films, which suggests that coherent crystal growth between the TiSiN and AlCrTiVNbN layers is well set up during the repeated coating [10]. Bragg's law [19] and the Scherrer equation [20] are used:

$$d = \frac{\lambda}{2 \cdot \sin \theta} \quad (1)$$

$$D = \frac{K\lambda}{\beta \cdot \cos \theta} \quad (2)$$

where d is the interplanar spacing, λ represents the wavelength of the X-ray source, θ is the Bragg diffraction angle, D is the average crystallite size, K is the shape factor, and β is the full width at half maximum (FWHM) of the diffraction peak.

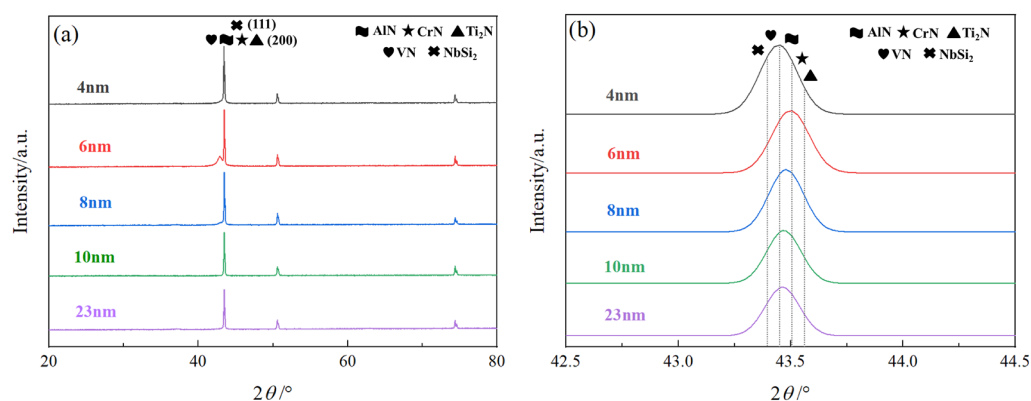


Figure 2. X-ray diffractograms recorded for the HENM films: (a) full patterns; (b) a magnified portion.

It should be noted that instrumental broadening was not corrected for in the present work. Therefore, the calculated crystallite sizes represent apparent values that contain contributions from both material microstrain and the instrumental broadening.

The calculated interplanar spacing and grain size for each group of films are summarized in Table 2. When the modulation period was increased from 4 nm to 6 nm, the diffraction peak shifted toward higher angles, accompanied by a decrease in interplanar spacing from 0.20819 to 0.20797 nm, along with a broadening of the full width at half maximum (FWHM). When the layer period was further increased to 23 nm, the diffraction peak is shifted slightly back to lower angles, the plane spacing was gradually recovered to 0.20810 nm, the half-width was found to decrease continuously, and the grain size was progressively increased to 8.23 nm [21]. These variations can be attributed to the evolution of interfacial stress states. At smaller modulation periods, coherent compressive stress was generated at the TiSiN/AlCrTiVNbN interfaces, leading to lattice contraction and a higher interface density. When the layer period was larger, each sublayer became thicker and this

weakens the interface pinning, allowing misfit strain release and lattice relaxation [22]. As a result, the λ_6 sample has the smallest plane spacing, the highest interface density, and the strongest layer matching, which effectively blocked line defect movement [10].

Table 2. Diffraction angles, interplanar spacings, and full widths at half maximum (FWHMs) of the HENM films.

Abbr.	λ/nm	2θ Diffraction Angle/ $^\circ$	Interplanar Spacing/nm	FWHM/rad	Crystallite Size/nm
λ_4	4	43.43	0.20819	0.19546	7.55
λ_6	6	43.48	0.20797	0.19567	7.55
λ_8	8	43.46	0.20806	0.18288	8.07
λ_{10}	10	43.45	0.20810	0.17958	8.21
λ_{23}	23	43.45	0.20810	0.17935	8.23

Figure 3 presents typical surface and cross-sectional SEM images for the TiSiN/AlCrTiVNbN HENM films at various modulation periods. A distinct three-layer structure is observed in each film, which is composed of the substrate, a TiN interlayer (94–106 nm thick), and the overlying HENM film, and a clear columnar structure standing perpendicular to the substrate is seen across all films, along with sharp interfaces between the individual layers. The overall film thickness increased monotonically from 1.105 to 1.502 μm with increasing modulation period. A typical cauliflower-like morphology is displayed on the surfaces of all films, the grains are arranged tightly, and no large defects are observed. As the modulation period rises, a gradual coarsening of the surface grains becomes evident, and this coarsening is mainly attributed to the lower interface density, which makes the suppression of grain growth weaker [10,23].

It is worth noting that the adhesion performance of nitride coatings can be sensitive to the thicknesses of both interlayers and sublayers [24]. An excessively thick TiN interlayer or TiSiN sublayer could induce high residual stress and potentially cause interfacial spallation [25,26]. In the present work, all samples were prepared with identical TiN interlayer thickness (94–106 nm) and a fixed TiSiN sublayer thickness of 3 nm. Accordingly, the observed variations in adhesion and cavitation erosion resistance originated primarily from the change in modulation period instead of differences in TiN or TiSiN thickness.

Besides the sublayer and interlayer factors discussed above, total coating thickness and interface density represent a pair of coupled experimental variables. As listed in Table 1, total coating thickness increases monotonically with modulation period. Nevertheless, the thickness discrepancy among specimens is limited, ranging merely from 1.211 μm to 1.605 μm . Previous reports reveal that moderate thickness growth exerts negligible effects on hardness and cavitation-erosion resistance for nitride protective coatings above 1 μm in thickness [27,28]. In this work, the λ_6 sample achieved optimal mechanical and cavitation-erosion performance without possessing the maximum total thickness. This finding demonstrates that property variations are predominantly governed by modulation period (i.e., interface density), rather than differences in overall coating thickness.

Figure 4 presents the elemental compositions of the TiSiN/AlCrTiVNbN HENM films deposited at different modulation periods. Nitrogen was the most abundant element across all films, with contents ranging from 44 to 47 at.% and exhibiting only minor fluctuations. A decrease in titanium, which is mainly from the TiSiN sublayers, was observed from 20.8 to 18.6 at.% as the modulation period was increased, and this decrease was attributed to the growing volume fraction of the AlCrTiVNbN high-entropy layers in each bilayer. The Cr content showed a gradual upward trend with increasing modulation period, while the other elements varied only slightly. The observed compositional evolution was consistent with the designed layer thickness ratios of the HENM films.

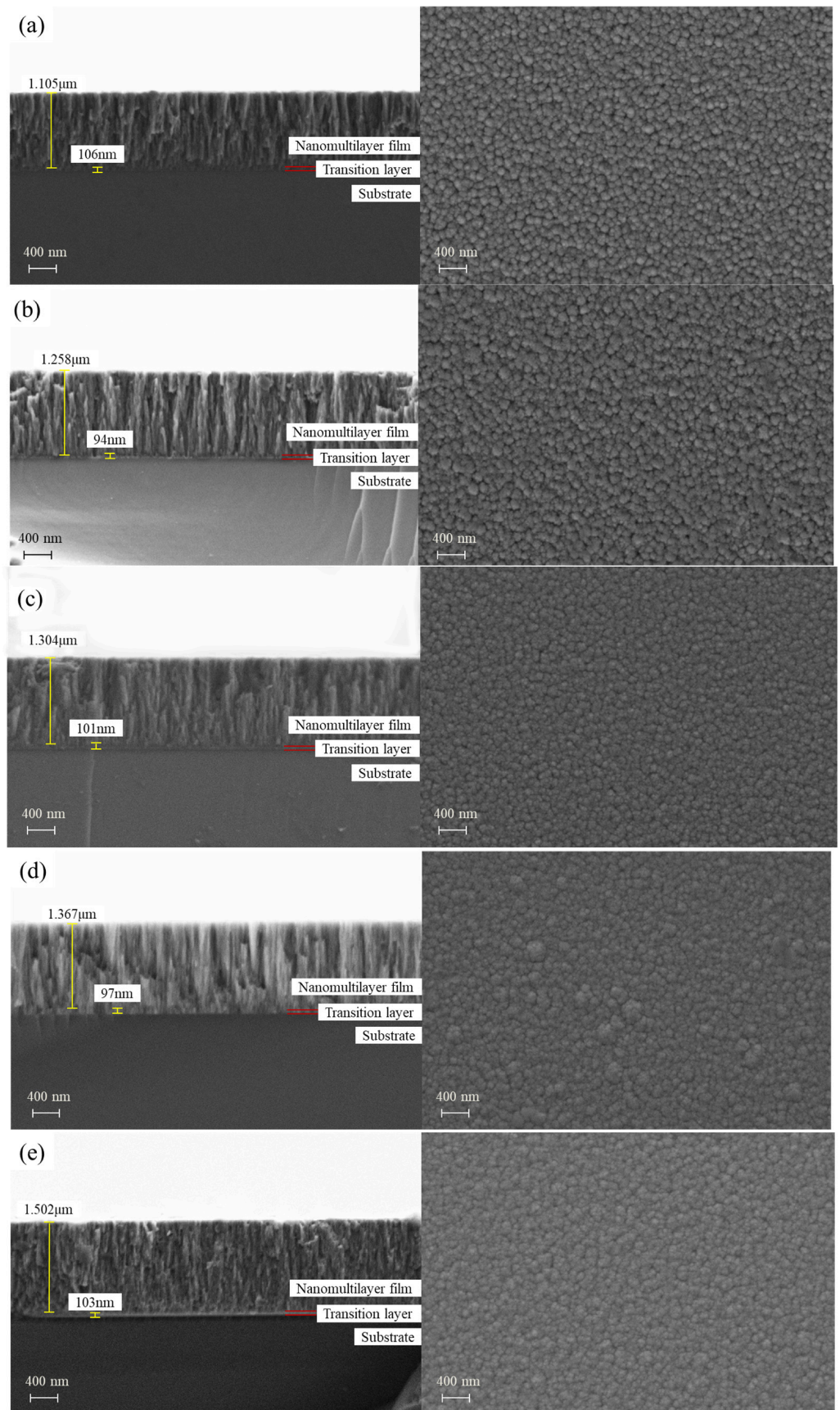


Figure 3. The cross-sectional and surface morphologies of the HENM films: (a) λ_4 , (b) λ_6 , (c) λ_8 , (d) λ_{10} , (e) λ_{23} .

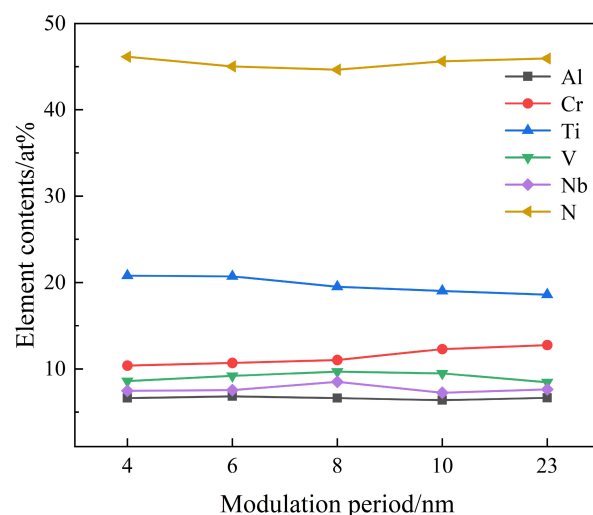


Figure 4. The elemental distribution for the HENM films.

Figure 5 displays the three-dimensional surface topographies of the TiSiN/AlCrTiVNbN HENM films at various modulation periods. All films exhibited dense and continuous surfaces, free from visible pores or macro-scale cracks. At smaller modulation periods ($\lambda = 4$ and 6 nm), the surfaces were characterized by fine grains and relatively low roughness. As the modulation period further increased, larger protruding grains gradually emerged, accompanied by a moderate increase in surface undulation.

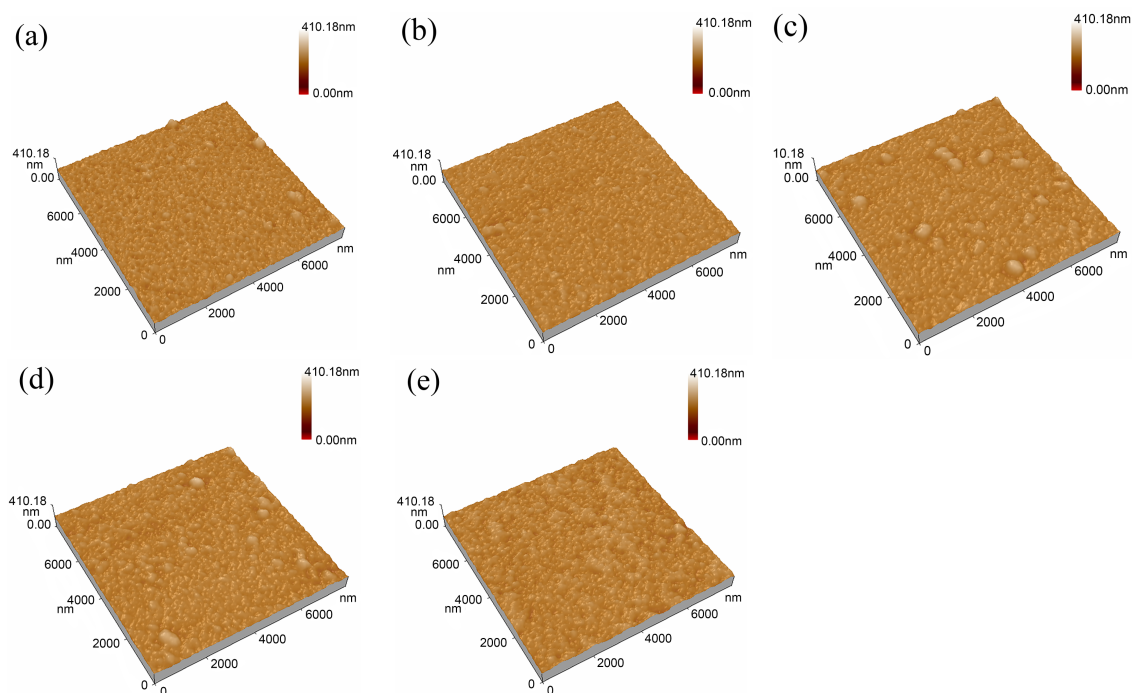


Figure 5. Surface topographies of the HENM films: (a) $\lambda 4$, (b) $\lambda 6$, (c) $\lambda 8$, (d) $\lambda 10$, (e) $\lambda 23$.

Figure 6 shows the variation in the average roughness and root-mean-square roughness of the HENM films as a function of modulation period. The roughness exhibited an initial decrease followed by a continuous increase with increasing modulation period, reaching its minimum value at $\lambda = 6$ nm. At smaller modulation periods, the multilayer interfaces effectively constrained grain growth, resulting in a smoother surface. When the modulation period was further increased, the interface pinning effect was weakened by the thicker high-entropy sublayers, grain coarsening was caused, and a rise in sur-

face roughness was observed [29]. This trend was consistent with the three-dimensional morphological observations.

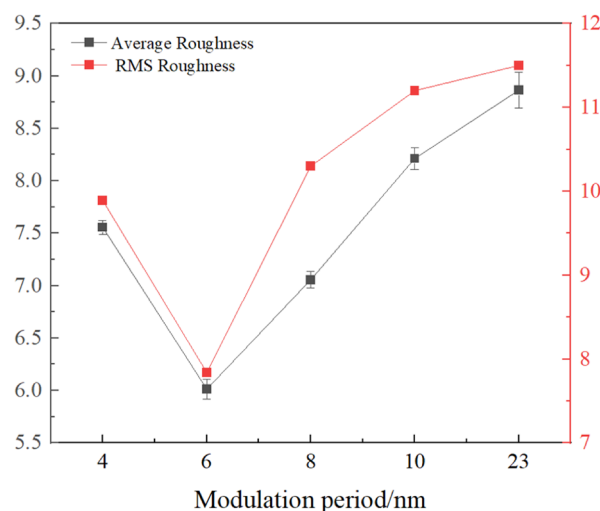


Figure 6. Surface roughness values obtained for the HENM films.

3.2. Mechanical Characteristics

The hardness and elastic modulus of the HENM films are plotted against modulation period in Figure 7a. Both properties initially increased with increasing modulation period, attaining peak values of 38.9 GPa (hardness) and 214.1 GPa (elastic modulus) at a period of 6 nm, then decreased to a minimum at $\lambda = 10$ nm, followed by a subsequent rebound after the modulation period was further raised to 23 nm. Among all the films, the one with $\lambda = 6$ nm had the highest interface density, and the many phase boundaries there effectively blocked dislocation movement, making the interface strengthening effect, which is typical of HENM structures, the strongest [30]. Beyond 6 nm, the reduced number of interfaces per unit thickness weakened this strengthening mechanism, leading to a hardness decline. However, at $\lambda = 23$ nm, the AlCrTiVNbN sublayers became significantly thicker, which may partly activate the solid-solution strengthening of the high-entropy phase, which made up for the reduced interfacial effect and led to a renewed hardness increase [31].

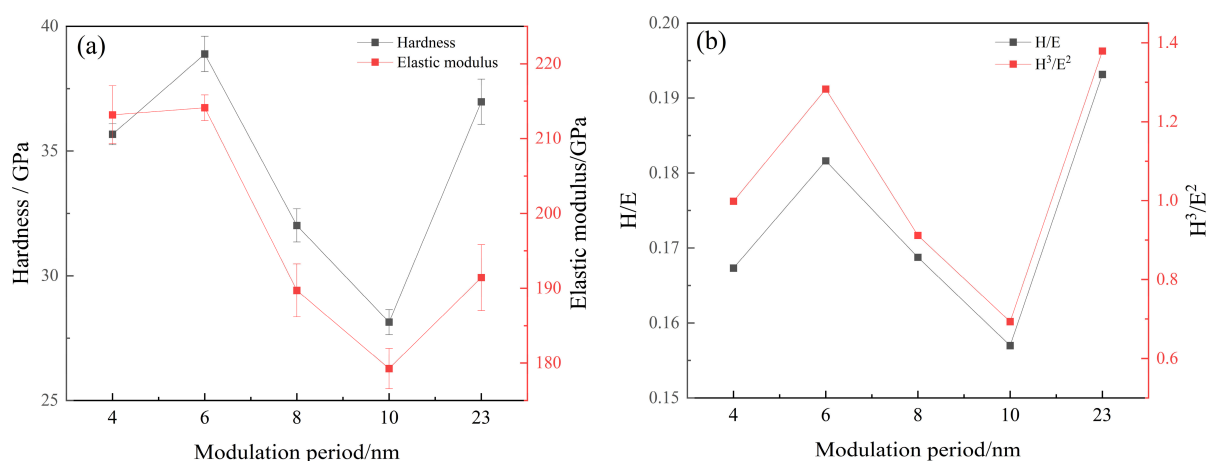


Figure 7. (a) Hardness and elastic modulus; (b) H/E and H^3/E^2 ratios of the HENM films.

In Figure 7b, the H/E and H^3/E^2 ratios are presented, where H is the hardness and E is the elastic modulus. These parameters are frequently employed to assess the elastic recovery capability and plastic deformation resistance of the films. Both parameters

exhibited an evolution consistent with that of hardness and elastic modulus, following an initial increase, then a decrease, and finally a rebound with increasing modulation period. Higher H/E and H^3/E^2 ratios signify better resistance to plastic deformation [32]. The mechanical property changes that are observed show a strong link with the changes in interface density and microstructure of the films.

3.3. Cavitation Erosion Properties

Figure 8 presents the mass loss evolution curves of the TiSiN/AlCrTiVNbN HENM films with different modulation periods during cavitation erosion. As the cavitation time is prolonged, a continuous increase in mass loss is observed for all films, and this increase reflects the accumulated erosion damage that is caused by micro-jet impacts, with these impacts being generated by bubble collapse [33]. Throughout the entire testing period, the $\lambda 6$ film consistently exhibited the lowest mass loss, whereas the $\lambda 23$ film showed localized spallation as early as 20 min into cavitation. The experimental findings indicated that the modulation period strongly dictated the resistance to cavitation erosion, and the $\lambda 6$ film outperformed all other specimens [34].

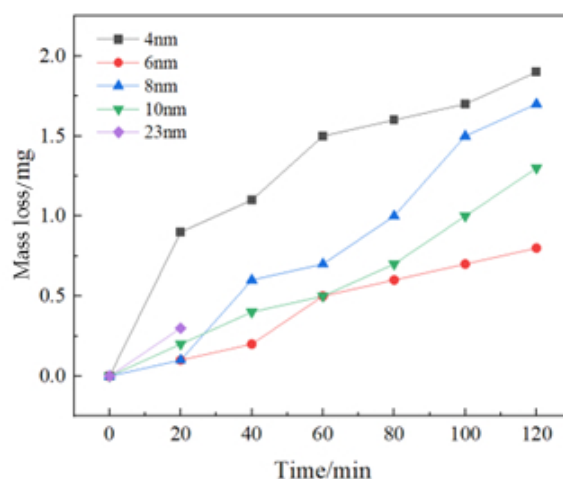


Figure 8. Mass loss for HENM films.

Figure 9 shows the surface topographies of the TiSiN/AlCrTiVNbN HENM films with different modulation periods after cavitation erosion testing. Typical damage features, including cavitation pits, impact cracks, and film spallation, were observed on all sample surfaces. However, the degree of damage varied markedly with modulation period. The $\lambda 6$ film exhibited the smallest pit size (approximately $0.8 \mu\text{m}$), sparse surface cracks, the most limited spallation area, and thus the best surface integrity. As the modulation period is increased, the pits get larger, reaching up to $1.9 \mu\text{m}$ across, and more cracks that spread out appear, along with clearly worse peeling of the film.

Bubble collapse keeps generating micro-jets that strike the coating surface again and again, this causes stress to build up, which helps pits start to form, and then cracks begin and grow, finally making the film peel off [35]. The microstructural observations were consistent with the mass loss trends shown in Figure 8. The mechanical properties discussed above show that the $\lambda 6$ film has a rather high hardness, along with high H/E and H^3/E^2 ratios, and its strong ability to resist permanent deformation effectively reduces stress buildup, holds back the growth of pits and cracks, and thereby delays the peeling of the film [36]. It should be noted that all films were deposited under identical conditions with the same TiN interlayer, so the initial coating–substrate adhesion was comparable for all specimens. Therefore, the observed film peeling under cavitation loading originates mainly from cumulative fatigue damage induced by repeated micro-jet impacts.

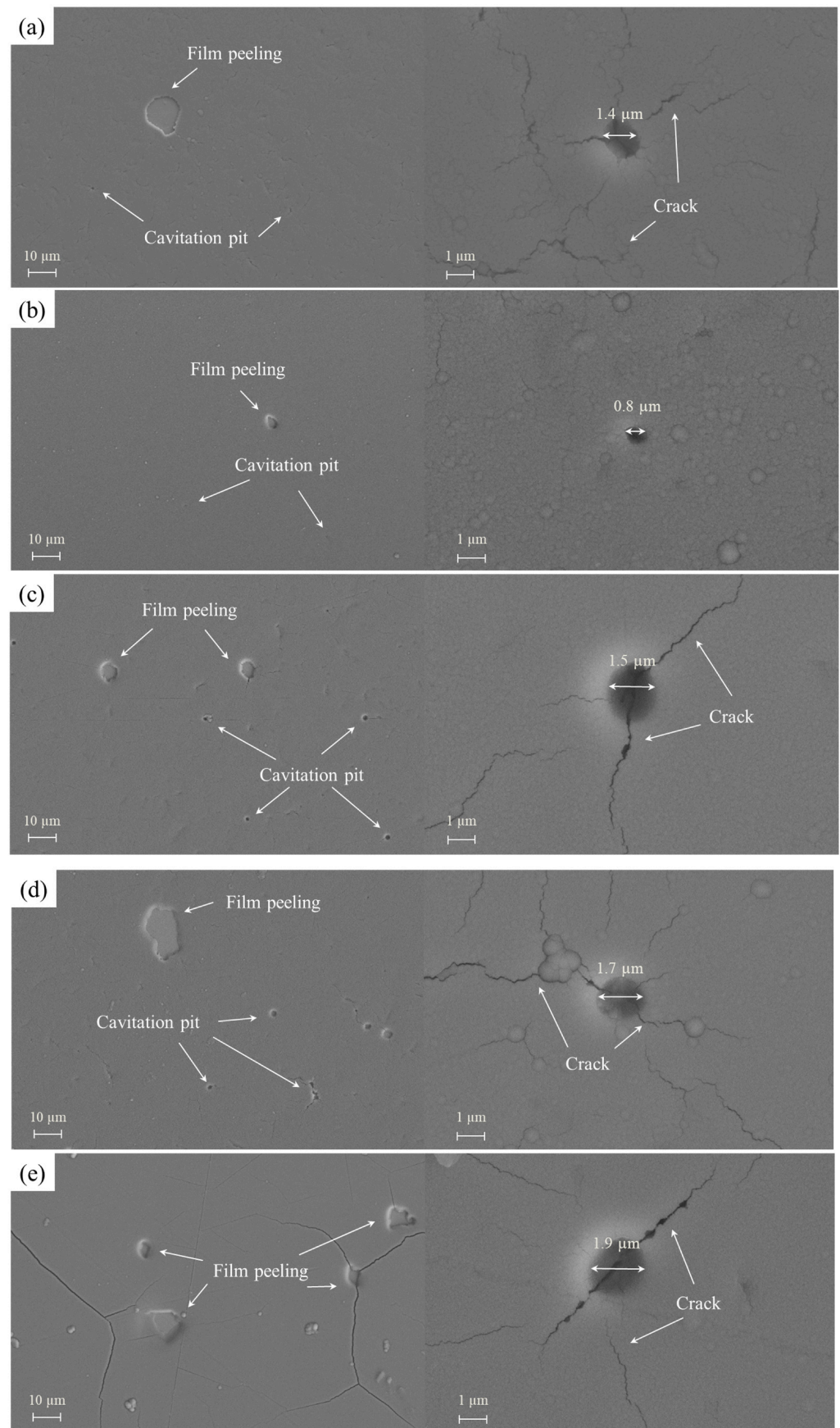


Figure 9. Post-cavitation surface morphologies and pits of the HENM films: (a) $\lambda 4$, (b) $\lambda 6$, (c) $\lambda 8$, (d) $\lambda 10$, (e) $\lambda 23$.

Elemental distribution maps acquired from an individual cavitation pit on the surface of the $\lambda 6$ film are displayed in Figure 10. The constituent elements of the film matrix, including Al, Cr, Ti, V, Nb, and N, were uniformly distributed over the intact surface, while their signal intensity decreased markedly within the pit region. In contrast, oxygen enrichment was observed at the pit site, along with a trace amount of Fe.

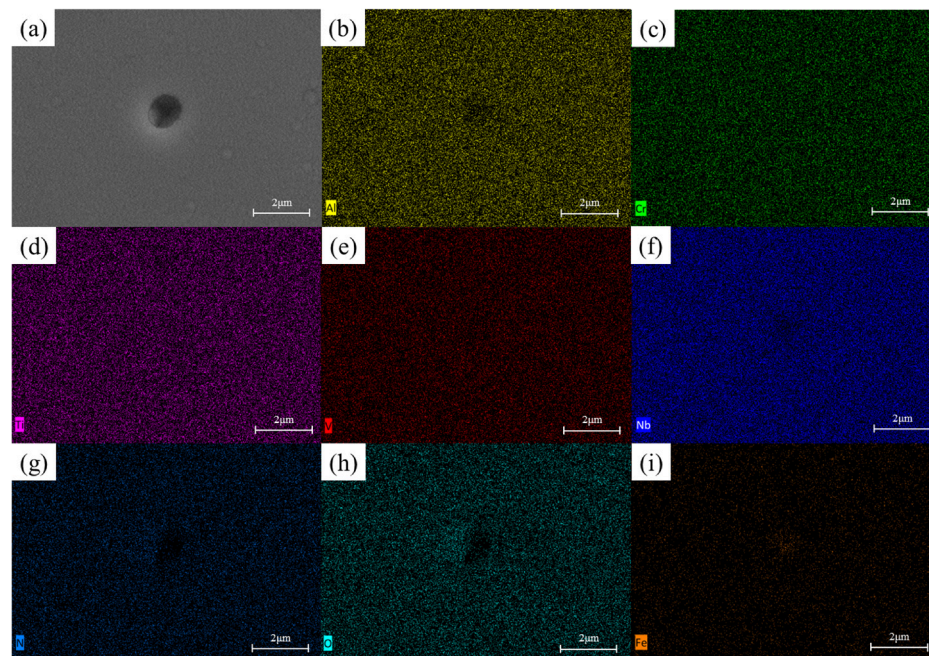


Figure 10. Elemental mapping results for the cavitation erosion craters on the $\lambda 6$ film: (a) Cavitation erosion pits, (b) Al, (c) Cr, (d) Ti, (e) V, (f) Nb (g) N, (h) O, (i) Fe.

During cavitation, the cyclic impact of micro-jets induced localized plastic deformation and material removal, accounting for the attenuated film element signals in the pit area. At the same time, the protective film on the surface was disrupted by the impact, and the water environment promotes localized oxidation, which creates zones rich in oxygen [37]. The film was locally perforated under severe impacts, and this was shown by a small amount of iron found inside the pit area.

Elemental mapping provides only the spatial distribution of elements without distinguishing their chemical valence states or phase types. To further identify the oxide species formed during cavitation erosion, XPS analysis was performed on the surface of the $\lambda 6$ film. In the survey spectrum of Figure 11a, peaks for Al 2p, Cr 2p, Ti 2p, V 2p, Nb 3d, N 1s, O 1s, and C 1s are observed, and from this, strong oxidation of the film surface caused by cavitation erosion was confirmed, which matches the oxygen enrichment seen in the elemental maps [13].

The high-resolution spectra were deconvoluted for each element. The open circles in the XPS spectra represent raw experimental data, and the coloured solid lines denote the fitted individual peak components. In Figure 11b, the Al 2p spectrum is fitted with two components; the component at 73.5 eV is attributed to Al-N bonds, and the component at 74.7 eV is attributed to aluminum oxide (Al_2O_3) [38]. In the Cr 2p spectrum of Figure 11c, two characteristic signals are detected at 576.1 eV and 585.3 eV, which match the Cr^{3+} features of chromium oxide (Cr_2O_3), and this indicates that the chromium oxide formed during cavitation is mainly Cr_2O_3 [39,40]. In the Ti 2p spectrum of Figure 11d, a peak at 456.3 eV is found and it corresponds to Ti-N bonds in the TiN phase, while peaks at 458.3 eV and 463.9 eV are observed, which confirm the formation of titanium dioxide, and the former peak is characteristic of the Ti^{4+} oxidation state [41]. In the V 2p spectrum

of Figure 11e, signals from V-N bonds are observed at 514.8 eV and 521.7 eV, and peaks belonging to vanadium pentoxide are also found at 516.9 eV and 523.5 eV [42]. In the Nb 3d spectrum of Figure 11f, a peak at 204.8 eV is observed, and it is from Nb-N bonds in NbN, whereas the signals at 206.8 eV and 209.4 eV correspond to Nb⁵⁺ species within Nb₂O₅ [37].

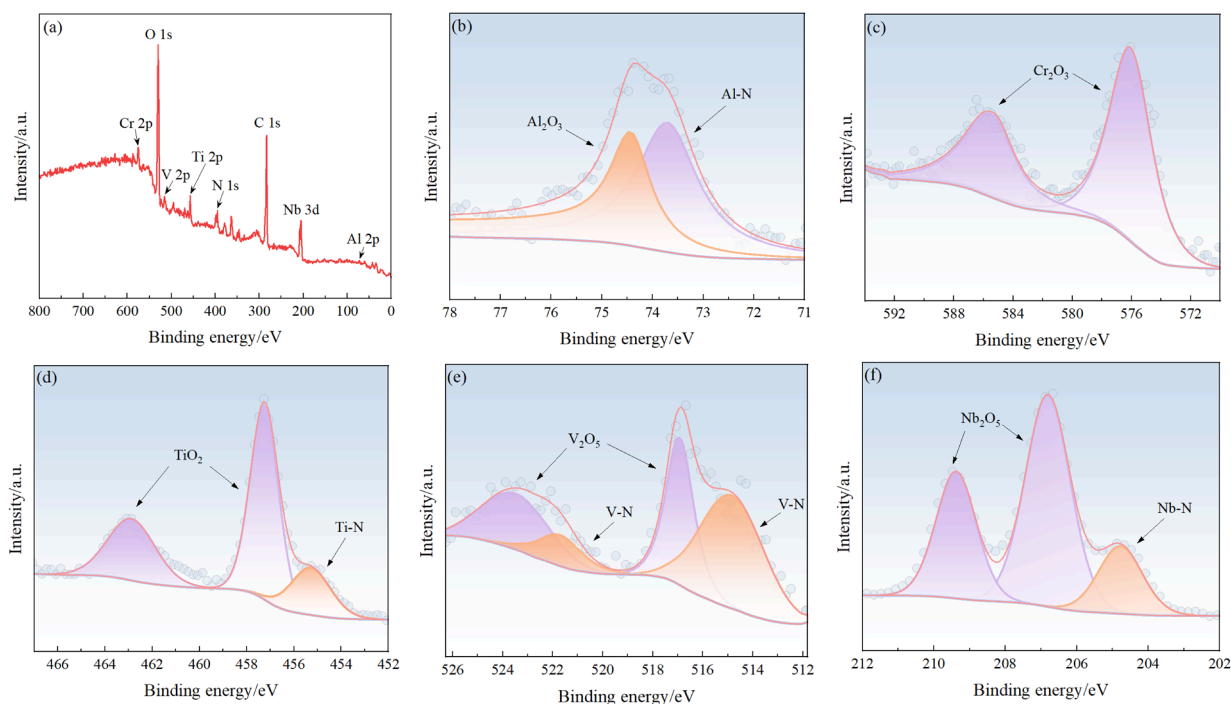


Figure 11. XPS spectra recorded from the $\lambda 6$ films: (a) survey spectrum; (b) Al 2p, (c) Cr 2p, (d) Ti 2p, (e) V 2p, (f) Nb 3d.

For the $\lambda 23$ sample with poor cavitation-erosion resistance, characteristic signals of Al, Cr, Ti, V, Nb, O, and N are detected in the full-survey X-ray photoelectron spectrum, confirming the generation of oxide products on the coating surface following cavitation-induced impact. In Figure 12, The high-resolution Al 2p spectrum is deconvoluted into two fitted peaks at 73.80 eV and 75.26 eV, which are assigned to Al-N and Al₂O₃, respectively [38]. Two dominant peaks located at 576.68 eV and 586.38 eV are observed in the Cr 2p spectrum, corresponding to Cr₂O₃ [39,40]. The Ti 2p signals centered at 458.18 eV and 463.88 eV originate from TiO₂ [41]. For the V 2p spectrum, fitted components at 515.76 eV and 522.37 eV are attributed to V-N bonds, whereas peaks at 516.90 eV and 523.99 eV correspond to V₂O₅ [41]. Two characteristic peaks of Nb₂O₅ appear in the Nb 3d spectrum at 206.69 eV and 209.46 eV [41].

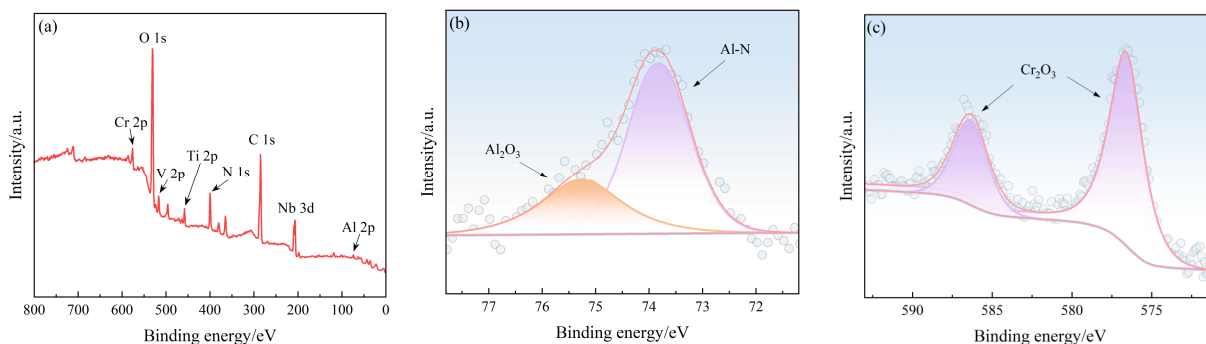


Figure 12. Cont.

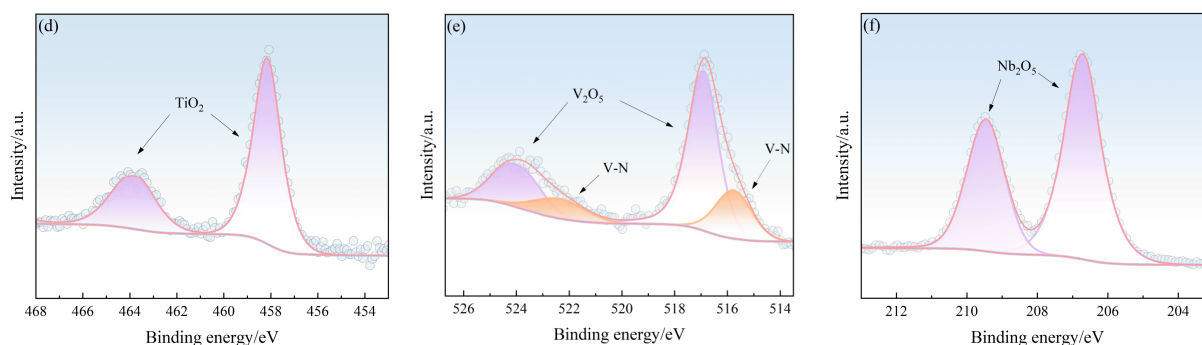


Figure 12. XPS spectra recorded from the λ_{23} films: (a) survey spectrum; (b) Al 2p, (c) Cr 2p, (d) Ti 2p, (e) V 2p, (f) Nb 3d.

4. Conclusions

Magnetron sputtering was employed to deposit TiSiN/AlCrTiVNbN HENM films possessing different modulation periods. The effect of modulation period on the evolution of microstructure, mechanical properties, and resistance to cavitation erosion was systematically studied.

1. The TiSiN/AlCrTiVNbN HENM films all possessed an FCC single-phase structure featuring a (200) preferred orientation. With increasing modulation period, the diffraction peak initially shifted toward higher angles and then reversed to lower angles, accompanied by a corresponding decrease and subsequent recovery in interplanar spacing. In the λ_6 film, the smallest plane spacing, the strongest compressive stress from layer matching, and the highest number of interfaces are observed, and through these, grain refining is promoted and surface roughness is lowered. When viewed in cross-section, a columnar structure that grows upward from the substrate is seen in the films, and on the surfaces, a typical cauliflower-like shape is found.
2. The variation in film hardness and elastic modulus with modulation period followed a non-monotonic trend, first rising, then declining, and finally rebounding. The λ_6 film achieved the highest values among all samples, with hardness reaching 38.9 GPa and elastic modulus 214.1 GPa, accompanied by consistently superior H/E and H^3/E^2 ratios. This optimal mechanical performance was attributed to the high-density coherent interfaces that effectively impeded dislocation motion. A renewed enhancement in mechanical properties was achieved after the modulation period was further raised to 23 nm, because the high-entropy nitride sublayers become much thicker, and this thickening activates solid-solution strengthening, which makes up for the diminished interfacial effect.
3. The cavitation mass loss of the films exhibited a decrease–increase–decrease trend with increasing modulation period. Among all samples, the λ_6 film showed the best cavitation erosion resistance, with the lowest mass loss of only 0.8 mg, a pit size of approximately 0.8 μm , and the least severe cracking and spallation. Protective oxides, including Al_2O_3 , Cr_2O_3 , TiO_2 , V_2O_5 , and Nb_2O_5 , were formed during cavitation and effectively mitigated the sustained impact of micro-jets. The outstanding cavitation erosion resistance of the λ_6 film originated from the synergistic effects of multiple mechanisms, which are the obstruction of crack propagation by high-density coherent interfaces, the combined contribution of high hardness and superior resistance to plastic deformation, and the formation of a protective surface oxide layer.

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Abbreviations

The following abbreviations are used in this manuscript:

HENM	Institute high-entropy nitride nanomultilayer
XRD	X-ray diffraction
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
XPS	X-ray photoelectron spectroscopy

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