

Article

Improvement of the Mechanical Properties and Corrosion Resistance of CSS-42L Steel with a Novel TiAlMoNbW Nitrid Film Deposition

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Abstract: In this work, a novel TiAlMoNbW high-entropy alloy (HEA) film and its corresponding nitrid (HEN) film were deposited on CSS-42L bearing steel by magnetron sputtering technology. The microstructure, microhardness, wear resistance, and corrosion resistance of the coated CSS-42L steel were systematically investigated. With the introduction of nitrogen, the crystal structure of TiAlMoNbW HEA film transformed from BCC into FCC. The microstructure of the deposited film became denser and was accompanied by lower surface roughness. The hardness of the nitride film was further increased from 11.43 to 25.7 GPa due to the formation of saturated metal nitride phases and the solid-solution strengthening of various elements. The tribological results showed that both TiAlMoNbW HEA and HEN films with excellent mechanical properties could improve the wear resistance of CSS-42L substrate, especially for the nitrid film, the mechanical properties of the film are significantly improved, resulting in a substantial reduction in the friction coefficient of about 22% and the wear rate of nearly 79%. In the electrochemical tests, both the TiAlMoNbW HEA and HEN-coated samples exhibited lower current densities and corrosion rates in 3.5 wt.% NaCl and 1 mol/L H₂SO₄ solutions. It was also noticed that the TiAlMoNbW nitrid film possessed a superior corrosion protection effect for CSS-42L steel.

Keywords: high-entropy alloy film; nitriding; magnetron sputtering; wear properties; electrochemical corrosion behavior



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1. Introduction

With the continuous development of aerospace technology, the extreme performance of the equipment continues to make breakthroughs. Bearing is one of the key basic components of modern mechanical equipment. The ideal performance requirements of spindle-bearing materials are high surface hardness, suitable toughness, high corrosion resistance, and high temperature resistance. The third-generation CSS-42L bearing steel is one of the preferred bearing steel materials, which is comprised of high strength, high toughness, and relatively suitable corrosion resistance [1]. However, its wear resistance and corrosion resistance need to be further improved to accommodate the complex and harsh working conditions. Several surface modification methods have been attempted. Qiu et al. [2] found that the corrosion resistance and mechanical properties of CSS-42L-bearing steel could be modified by the duplex treatment of ions implantation and Cr coating. The corrosion rate of the (Ti + C) co-implanted samples was more than 10 times lower than that of the untreated samples. Yang et al. [3] studied the comprehensive properties of CSS-42L specimens after carburizing and nitriding at different quenching temperatures. The results indicated that nitriding treatment can not only improve the hardness and wear resistance of CSS-42L

carburized steel but also improve its corrosion resistance to a certain extent. However, the application of chemical heat treatment techniques is limited due to the high requirements for specific experimental conditions. Available research has indicated that the higher experimental temperature (generally above 600 °C) would deteriorate the mechanical properties of the bearing matrix [4].

High-entropy alloy (HEA) is one sort of novel multi-element alloy with higher mixing entropy, consisting of five or more main elements in equal or unequal molar ratios, discovered by Ye et al. [5] in 2004. HEA film developed on the basis of HEA with low-dimensional morphology exhibits properties similar to those of bulk high-entropy alloys, such as thermodynamic high-entropy effects, kinetic slow diffusion effects, severe distortion effects of lattice structures, and performance cocktail effects, which can be used for hard wear-resistant coatings for cutting tools, corrosion-resistant coatings for components service in a corrosive environment, diffusion barrier layers in the field of Cu interconnects, etc. [6]. Moreover, some properties of HEA coating are even superior to its bulk material, such as hardness [7]. Some researchers have suggested that the introduction of interstitial elements such as C, N, and O can further improve the mechanical properties of HEA films [8–10]. Braic et al. [8] co-sputtered (CuSiTiYZr)C films with different flow ratios in Ar + CH₄ atmosphere. The experimental results showed that (CuSiTiYZr)C coatings with a carbon/metal ratio of about 1.3 had the highest hardness and the best wear and corrosion resistance. Zhang et al. [11] successfully fabricated a FeCrNiCoB_x HEA cladding layer on 304L stainless steel by laser cladding method. The in situ formed orthorhombic (Cr, Fe)₂B phase improves the microhardness and corrosion resistance in 3.5 wt.% NaCl solution when $x \leq 1$. However, when $x = 1.25$, the borides transform into tetragonal (Fe, Cr)₂B phase, contributing to the decreased corrosion resistance. Hwai-Te et al. [12] investigated the effect of nitrogen content and substrate bias on the mechanical properties and corrosion performance of HEN thin films (AlCrSiTiZr)_{100-x}N_x. They found that the (AlCrSiTiZr)_{100-x}N_x deposited film had the best corrosion resistance in 0.1 mol/L H₂SO₄ when $RN = N_2 / (N_2 + Ar) = 30\%$, and its I_{corr} is almost only 10% of the 6061 aluminum alloy matrix, exhibiting excellent corrosion resistance potential. More and more scholars are interested in the study of high-entropy nitride alloy films due to their high hardness, high strength, high wear resistance and high corrosion resistance [10].

Comparison of the current methods commonly used to prepare HEA films, including magnetron sputtering (MS) [13,14], laser cladding [15,16], spraying [17], electrodeposition [18], plasma-transferred arc cladding [19], etc. Among the technologies mentioned above, MS has become the most commonly used technology to process HEA films due to its advantages of higher deposition rate, a more uniform structure, and easier to introduce gas elements in alloys to synthesize nitride, oxide, or carbide. The HEA films obtained by MS are mostly dense in structure and have a significant “quick quenching” effect [20]. The element diffusion and nucleation of intermetallic compounds are inhibited. FCC or BCC solid-solution phase or amorphous phase may be generated, which is beneficial to wear resistance and corrosion resistance. Dou et al. [14] deposited FeAlCoCuNiV HEA coatings by DC magnetron sputtering and tested its electrochemical behavior in various corrosive media. The experimental results displayed that the coating was composed of a single FCC solid solution and exhibited more superior corrosion resistance than 201 stainless steel in acidic, alkaline, and salt corrosive media. Zheng et al. [13] prepared VAlTiCrSi HEA films with excellent corrosion resistance in artificial seawater by DC magnetron sputtering. Diffraction of X-rays (XRD) and Transmission Electron Microscope (TEM) results indicated that HEA film presented a uniform amorphous structure, thereby enhancing the barrier properties of the substrate. In addition, MS can flexibly control sputtering parameters to tune the properties of thin films.

TiAlMoNbW is a novel high-entropy alloy system. A number of previous works have shown that metallic elements, such as Al, Ti, Nb, Mo, and W, have an obvious function in promoting the mechanical properties of different HEAs. In addition, the Al element can also improve the corrosion resistance of the HEAs, which would be facilitated by Nb and

W elements [21,22]. Furthermore, Al, Ti, Nb, and Mo have a strong affinity for nitrogen. The forming nitrides possess higher hardness and chemical inertness, which may further contribute to the wear resistance and corrosion resistance of HEA films [23]. Thus, it is promising to introduce TiAlMoNbW HEA film and its HEN film to improve the wear and corrosion resistance of CSS-42L steel. As far as we know, there is a lack of systematic research on the mechanical and electrochemical properties of coated steel substrates with TiAlMoNbW HEA and HEN films.

In this study, the TiAlMoNbW HEA film and its nitrid film were deposited on the third-generation aerospace-bearing steel CSS-42L by reactive MS technology. The microstructure and surface modification effect of TiAlMoNbW HEA film and HEN film for CSS-42L steel were evaluated. The improvement effects of TiAlMoNbW HEA film and HEN film on the mechanical properties and corrosion resistance of CSS-42L steel were also deeply discussed.

2. Materials and Methods

2.1. Sample Preparation

The composition of CSS-42L steel used in this research is shown in Table 1. The tested steel was firstly prepared by a vacuum induction melting furnace using Fe-4.3C, Fe-20Si, and Fe-50Mn intermediate alloys. Then the CSS-42L steel ingots were obtained according to the ratio, and the matrix specimens of 10 mm × 10 mm × 4 mm were prepared. Before the deposition process, the base steel was ultrasonically cleaned in ethanol and then dried in a drying oven.

Table 1. Chemical composition of CSS-42L alloy (wt.%).

C	Cr	Co	Mo	Ni	V	Nb
0.10–0.25	13.0–19.0	5.0–14.0	3.0–5.0	1.75–5.25	0.25–1.25	0.01–0.1

The TiAlMoNbW target was prepared by using the powder metallurgy method. Primarily, the 99.99 wt.% purity Ti, Al, Mo, and Nb blocks were used to produce Ti-25Al-25Mo-25Nb (in at.%) master alloy by using a skull vacuum furnace after being cleaned and dried with acetone. Then, the TiAlMoNb alloy powder was obtained by using the rotary spray method with a ~200 mesh particle size. After being mixed uniformly with 99.995% purity, 2000 mesh tungsten powder, the disc target with a diameter of 4 inches and thickness of 3 mm was produced ultimately by using the vacuum hot-pressing method (parameters are shown in Table 2). The CSS-42L samples deposited with TiAlMoNbW alloy (HEA) film and TiAlMoNbW nitrid (HEN) film were abbreviated to S-HEA and S-HEN, respectively. The synthesis of HEA film and HEN film were conducted by using M600 magnetron sputtering system in an atmosphere of high-purity gas with a working pressure of 2.5×10^{-3} Pa. The samples were subjected to a 15 min bias cleaning to remove surface contaminants and oxide layers prior to deposition. The specific preparation parameters of the film are shown in Table 3.

Table 2. Parameter of vacuum hot-pressing sintering.

Diameters	Pressure/MPa	Temperature/°C	Time/h
4 inches	50	1600	2

Table 3. Details of deposition parameters.

Film	Working Gas	Deposition Pressure /Pa	Deposition Power/W	Substrate Temperature/K	Deposition Time/s
HEA	Ar	0.8	200	450	2325
HEN	50%Ar + 50%N ₂				

2.2. Sample Characterization

The crystal structure of the films was characterized by grazing-incidence-angle X-ray diffraction (GIXRD, D/MAX-2500/PC, Rigaku, Tokyo, Japan) with a scanning range of 20° – 90° . The film thickness and surface topography were observed using a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI, Tokyo, Japan). The surface roughness and arithmetic mean deviation of the profile (R_a) of each coating were measured using an atomic force microscope (AFM, FM-NanoviewOp, FEISHIMAN, Shaanxi, China) in tapping mode. A nano-indenter (Nano Indenter G200, Agilent, Santa Clara, CA, USA) equipped with a Berkovich diamond probe tip was performed to measure the hardness and elasticity modulus of films using continuous stiffness mode (CSM). Seven points were tested for each film and averaged. The indentation depth was controlled to be 500 nm. The wear resistance of the films was tested by a reciprocating friction and wear apparatus (UMT-3, CETR, Billerica, MA, USA). The frequency is 5 Hz, the load is 5 N, and the friction pair is Si_3N_4 with a diameter of 6 mm. The wear track length and sliding time were 5 mm and 30 min, respectively. The cross-sections of the wear profile were measured by a surface profilometer (Alpha-Step IQ, Milpitas, CA, USA). An electrochemical potentiostat (PARSTAT MC, AMETEK, Berwyn, IL, USA) was used to conduct the corrosion experiments of HEA films and CSS-42L substrates in different corrosive reagents. A three-electrode connection was used to connect a saturated calomel reference electrode (SCE), a platinum counter electrode, and a working electrode.

3. Results

3.1. Chemical Composition and Phase Analysis

The elemental compositions of the target and film were analyzed by Energy Dispersive Spectroscopy (EDS), and the results are displayed in Figure 1. The five alloy elements of the TiAlMoNbW film are evenly distributed inside the coating without any element segregation. The compositional deviation between target and coating may be related to the competing sputtering and re-sputtering behavior resulting from the different sputtering rates of the five elements during deposition. Lighter elements have a higher probability of backscattering during deposition. With the introduction of nitrogen, the target element changes more uniformly in the film, and the W element decreases slightly. This is reasonable because all these elements except W have a strong affinity for nitrogen atoms. Figure 2 shows the XRD patterns of the HEA film and the HEN film. It can be seen that the alloy film has a single-phase BCC structure. With nitrogen introduced, the crystallinity of the film increases, and the crystal structure transforms from the original BCC to FCC.

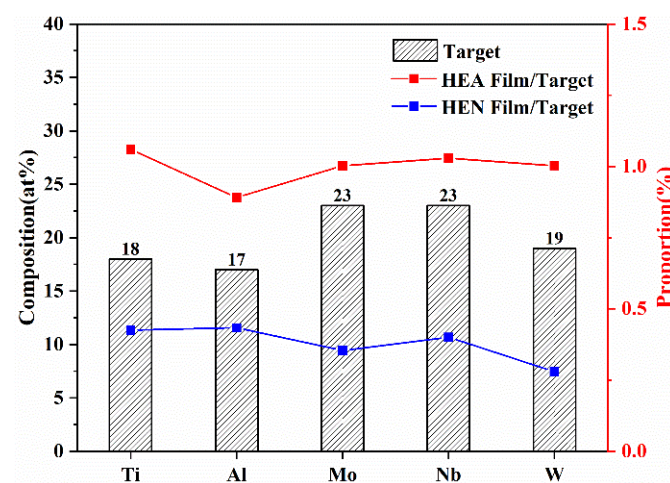


Figure 1. Chemical composition of the target and the composition ratio of different metallic elements in HEA and HEN films compared with that in the target.

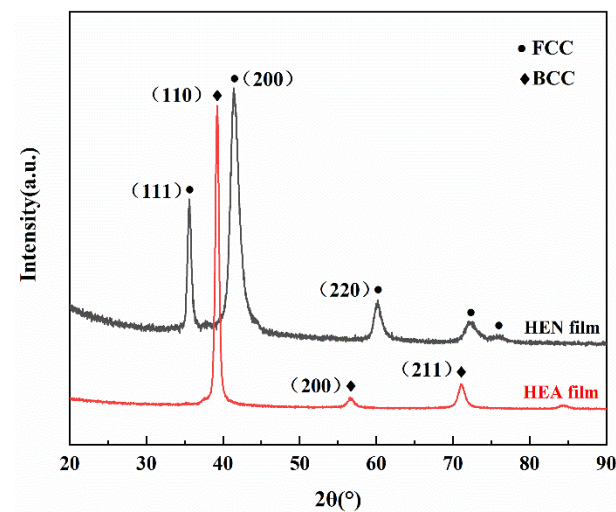


Figure 2. The XRD spectrum of TiAlMoNbW HEA and HEN films.

3.2. Microstructure

The surface and cross-sectional SEM images of HEA and HEN films were demonstrated in Figure 3. The HEA film presents a unique needle-like structure with a uniform film thickness of 952 nm, a uniform texture, and no obvious defects on the surface or inside. After the introduction of nitrogen, the film morphology changes from needle-like to nanoparticle-like, and the surface roughness decreases. As in the cross-sectional view (Figure 3b,d), the thickness of the film decreased to 643 nm. The cross-section morphology of the film changes from a bulk irregular columnar structure to a denser columnar nanocrystalline structure. The AFM surface morphologies of the HEA and HEN films are consistent with SEM results, as displayed in Figure 4. The surface of the HEA film showed a dome-shaped cluster structure, and that of the HEN film showed a stalagmite structure. The calculated values of R_a are 7.31 and 2.70 nm for the TiAlMoNbW HEA film and its HEN film, respectively. Hence, the nitriding treatment can obviously optimize the surface roughness of TiAlMoNbW HEA film, which results in a smoother surface of HEN film.

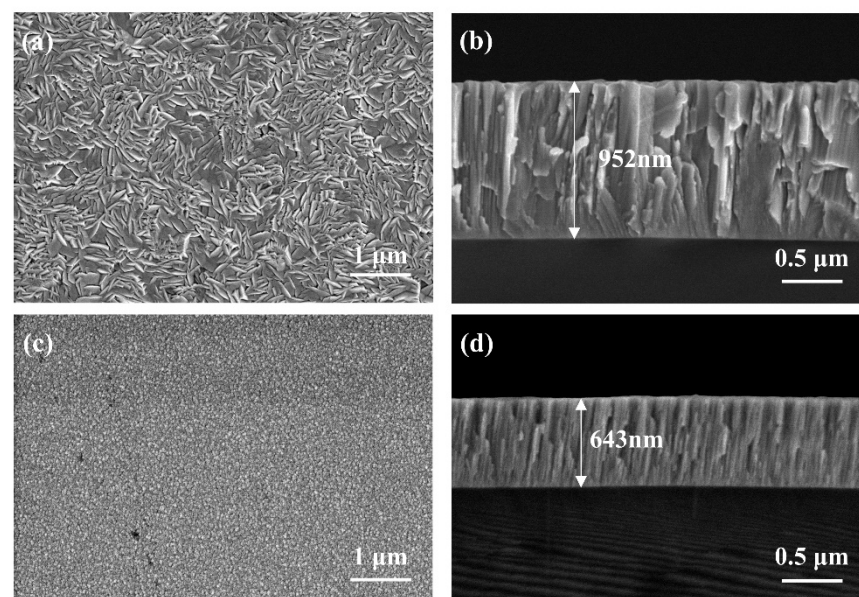


Figure 3. The SEM morphologies of the films: (a) surface of HEA film, (b) cross-section of HEA film, (c) surface of HEN film, and (d) cross-section of HEN film.

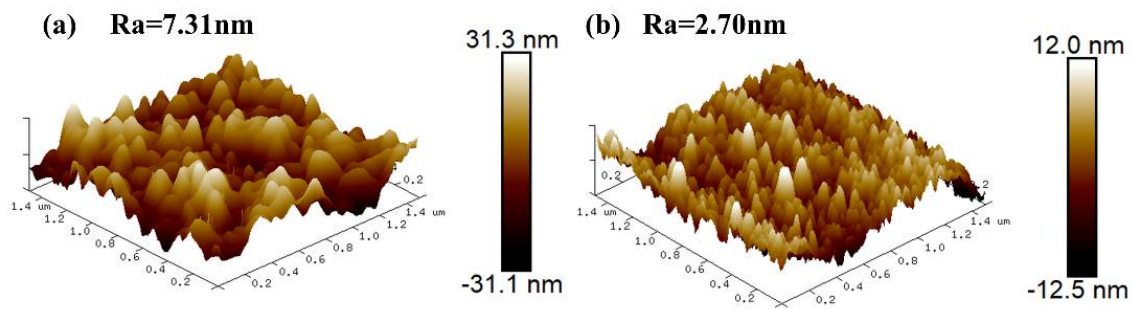


Figure 4. AFM three-dimensional diagrams of (a) HEA film and (b) HEN film.

3.3. Mechanical Properties

The nanoindentation experiment is divided into loading and unloading processes. The load-displacement curve is obtained through the test. The hardness value of the sample can be obtained by measuring and calculating the variable load P , the indentation depth h , and the initial slope S of the unloading curve during the test. The nanoindentation load-displacement curves of S-HEA and S-HEN samples are presented in Figure 5a. The initial slope and peak value of the nitride film curve are significantly larger than the alloy film, which indicates that the nitride film has a higher modulus and hardness. The average value of the nanoindentation hardness and modulus of both films were obtained using the well-known Oliver–Pharr relationship [24]. As exhibited in Figure 5b, the modulus and hardness of the S-HEA sample are 233.1 and 11.43 GPa, respectively. Its hardness value is approximately three times that of the base steel (4.356 GPa). After the introduction of nitrogen, the modulus and hardness of the sample increased to 313.6 and 25.7 GPa, respectively.

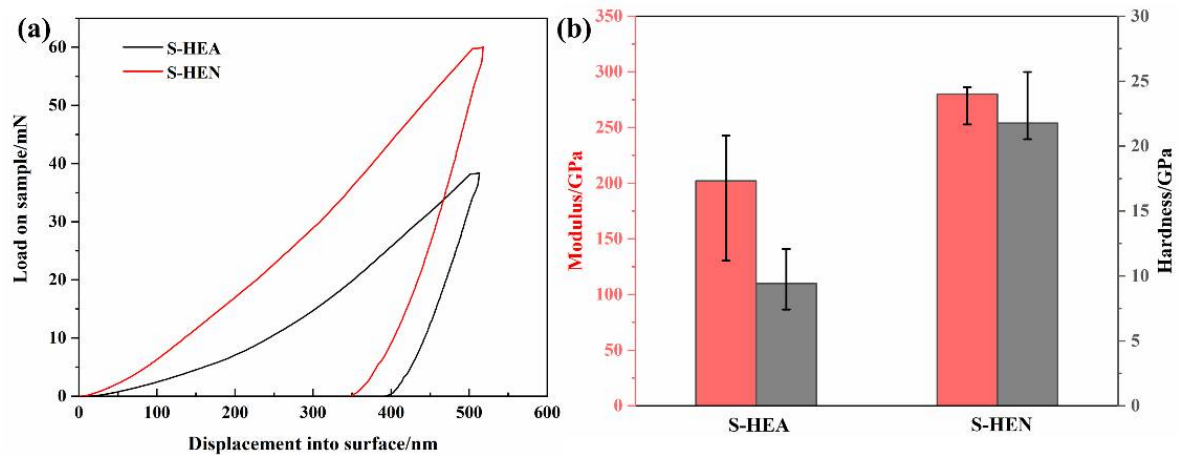


Figure 5. (a) Nanoindentation load-displacement curve of S-HEA and S-HEN samples, (b) hardness and modulus of the S-HEA and S-HEN samples.

In general, the tribological properties of thin films mainly depend on their mechanical properties, and the frictional resistance of materials is also affected by surface roughness. The wear resistance of the specimens was tested using a reciprocating UMT system. The friction coefficient curves of the CSS-42L base steel samples with and without coating are depicted in Figure 6a. After a break-in period of about 100 s, the friction coefficient quickly reaches a steady state and remains at a constant value. The friction coefficient of the base steel was estimated to be 0.73, and the friction coefficient of the S-HEA sample slightly increased to 0.77. After the introduction of nitrogen, the surface roughness of the film decreases, and the hardness increases, so the coefficient of friction of the S-HEN sample decreases to 0.57.

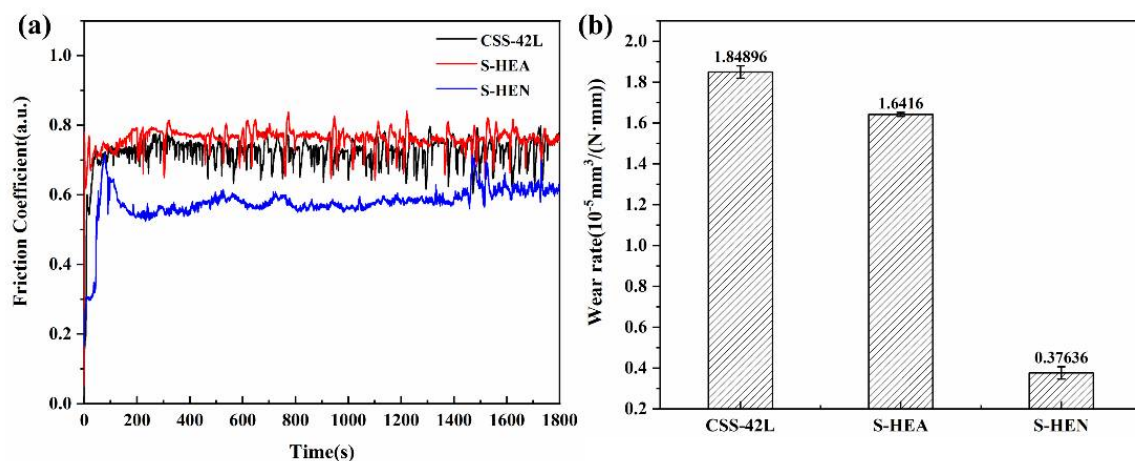


Figure 6. (a) The friction coefficient curve of CSS-42L steel and S-HEA sample, S-HEN sample, (b) wear rate of CSS-42L steel and S-HEA sample, S-HEN sample.

The variations in the wear rate of the CSS-42L steel substrate and S-HEA/S-HEN samples are exhibited in Figure 6b. The wear rate of the sample can be obtained by calculating the volume of the wear loss under the unit load of a fixed length. The calculation formula is as follows [25]:

$$W_s = \frac{C \times S}{F \times L} = \frac{V}{F \times L} \quad (1)$$

where C is the total linear wear (mm), S is the wear surface area (mm²), the product of the two is the wear volume V (mm³), F is the normal load (N), and L is the wear length (mm). After calculation, the wear rate of CSS-42L steel is $1.848 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{mm})$, the wear rate of the S-HEA sample is reduced to $1.642 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{mm})$, and the wear rate of S-HEN sample with high hardness and modulus is only $0.376 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{mm})$, which is only 20% of that of the base steel.

3.4. Electrochemical Corrosion Behavior

The corrosion protection effect of CSS-42L steel sample and S-HEA/S-HEN samples were evaluated in 3.5 wt.% NaCl and 1 mol/L H₂SO₄ solutions. The polarization curve and corrosion parameters obtained by the Tafel curve are presented in Figure 7. It can be found that after sputtering the HEA film, the corrosion rate falls significantly in the NaCl solution. Especially after the nitride film is sputtered, the corrosion rate reduces from 0.493 mpy to 0.033 mpy. The corrosion current also drops from 1544 to 103.481 nA. Obviously, the HEN film has a better corrosion protection effect, and the same tendency in the H₂SO₄ solution also could be concluded. As depicted in Figure 7b, the three groups of samples all displayed passivation areas in the H₂SO₄ solution, and the secondary passivation was not obvious. However, the passivation area of CSS-42L steel appeared later than the high-entropy alloy film, indicating that a stable and dense passivation film is formed on the surface of the high-entropy alloy during the polarization process, which can effectively hinder the corrosion of the acid radical on the substrate. Combined with the SEM image in Figure 8, it can be seen that there are a large number of corrosion pits on the surface of the base steel, while the number and size of the corrosion pits of the S-HEA film are significantly reduced, and the surface of the nitride film is almost not damaged, which can effectively protect the substrate. The corrosion parameters shown in Figure 7c,d express a consistent trend. Both the HEA film and the HEN film show higher corrosion potential (E_{corr}) and lower corrosion current density (I_{corr}), and better corrosion resistance performance was realized in the S-HEN sample compared to the S-HEA sample.

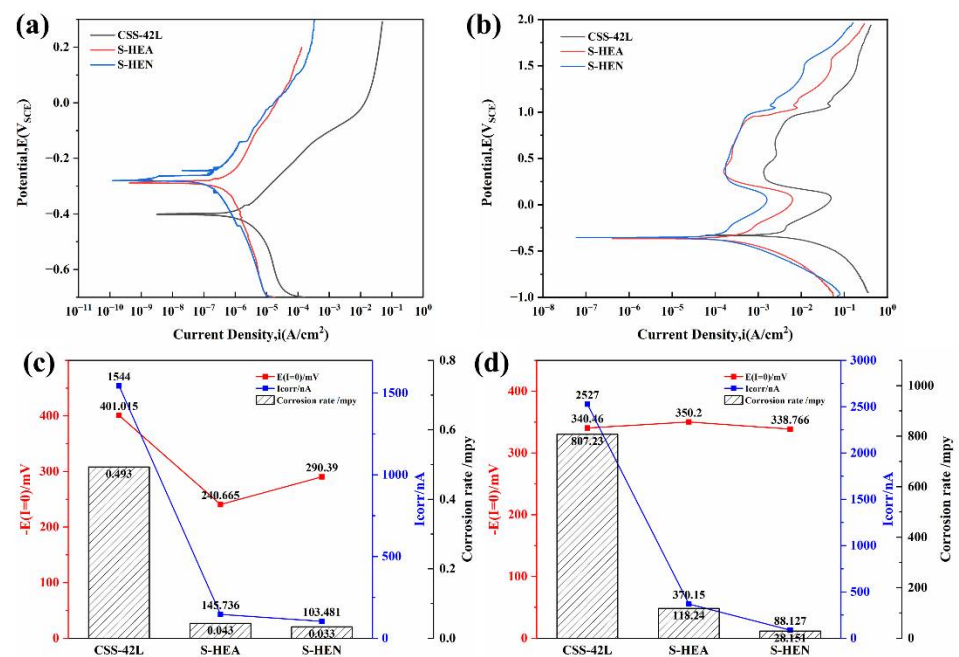


Figure 7. Potentiodynamic polarization curves and fitting parameters of S-HEA/S-HEN and CSS-42L steel samples in different corrosive fluids: (a,b) 3.5 wt.% NaCl, (c,d) 1 mol/L H_2SO_4 .

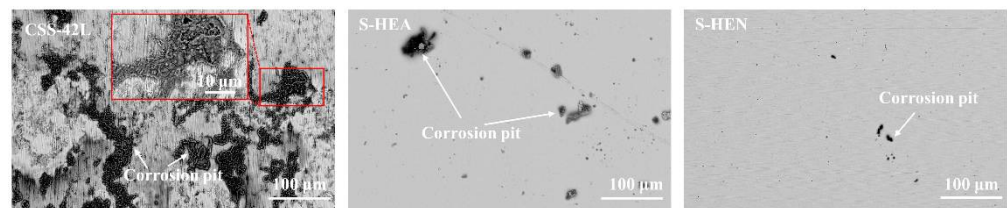


Figure 8. SEM images of CSS-42L and S-HEA/S-HEN after corrosion.

In order to further study the corrosion resistance of samples in 1 mol/L H_2SO_4 solution, electrochemical impedance spectroscopy (EIS) was introduced. Figure 9a presents the evolution of the Nyquist diagram. The curve on the complex impedance plane is approximately a double-arc pattern when exposed to a sulfuric acid solution.

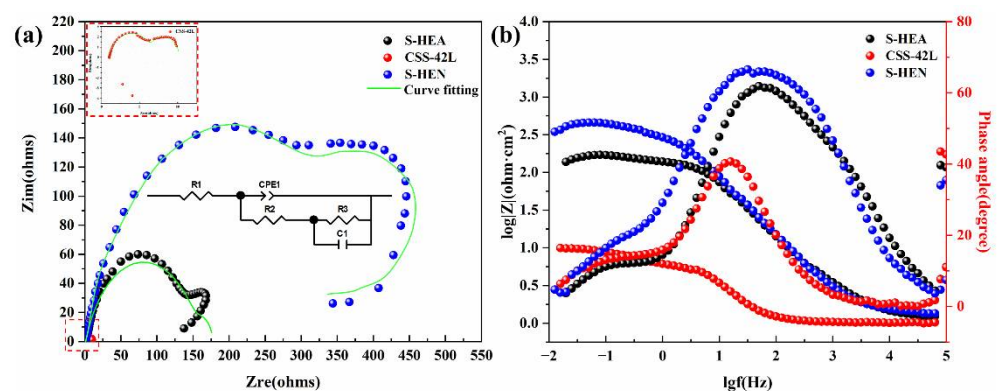


Figure 9. Electrochemical impedance spectroscopy of S-HEA/S-HEN films and CSS-42L steel in sulfuric acid: (a) Nyquist, (b) Bode.

The experimental results demonstrate that the surface passivation layer on the S-HEN sample has the highest interfacial impedance and the best corrosion resistance. All the coated samples exhibit better performance than that of the base CSS-42L steel. The

impedance modulus, phase angle, and frequency function relationship of the substrate steel passivation layer can be clearly observed in the Bode diagram (Figure 9b). The high-frequency region $\log |Z|$ reflects the solution resistance [26]. It can be seen from the figure that the high-frequency zone $\log |Z|$ value of the S-HEA sample is slightly higher than that of the base steel. In the low-frequency region, $\log |Z|$ reflects the passive film resistance of the alloy film. The $|Z|$ value of the S-HEN sample is the largest, which is about 34 times that of the base steel. When the phase angle reaches its maximum value in the intermediate frequency region, the corresponding frequency range indicates the stability of the passivation film during the corrosion process. The results in Figure 9b indicate that the S-HEN sample with the widest intermediate frequency range has the best stability during the corrosion test, while CSS-42L steel has the poorest stability. The peak phase angle of the S-HEA sample is much higher than that of the base steel and shifts to high frequency. With nitriding, the peak phase angle for the S-HEN sample increases further. The high impedance and high peak phase angle indicate that the material has better corrosion resistance.

An equivalent circuit with an impedance diagram was drawn. In this study, two time constants can be used to describe the impedance diagram. The first time constant in the high-frequency region is determined by the resistance of the film (R2) and the capacitance of the film (CPE1). The second time constant is located at mid-low frequency and consists of the charge transfer resistance (R3) and capacitance (C1). The parameters are shown in Table 4. The larger the R2, the more difficult the charge transfer process occurs in the surface passivation film. R3 is usually associated with the surface charge transfer process, and the larger R3 indicates that a protective film forms at this metal-solution interface, the charge transfer process becomes slower, and the passivation film is less likely to receive ion bombardment. The S-HEN sample has a larger R2 and R3, which is consistent with the results of the kinetic potential polarization measurements. It is further proved that both HEA film and HEN film can effectively improve the corrosion resistance of the base steel, and the HEN film is better than the HEA film.

Table 4. The EIS parameters of the CSS-42L and S-HEA/S-HEN in 3.5% NaCl solution.

Sample	R1	CPE1-T	CPE1-P	R2	R3	C1
CSS-42L	1.02	0.00829	0.86799	5.749	3.431	0.3377
S-HEA	1.266	0.00266	0.77124	34.15	11.34	0.1322
S-HEN	1.227	0.00047	0.76342	159.5	17.03	0.0944

4. Discussion

4.1. Formation Mechanism of HEA and HEN Films

HEA thin films form simple single-phase solid solutions due to the high-entropy effect and large atomic differences. From the aspect of thermodynamics, the high-mixing entropy effect results from the increased number of principal component elements. The mutual solubility of the target metal elements is enhanced, and the long-distance diffusion is suppressed. Multi-element solid-solution phase instead of complex intermetallic compounds would be precipitated in HEA [27]. In this system, Mo, W, and Nb are all BCC structures. The BCC structure will become the skeleton for grain growth [28]. It was suggested that the phase composition of HEA was closely associated with their thermodynamic parameters, such as mixing enthalpy (ΔH_{mix}), atomic size difference (δ), valence electron concentration (VEC), and mixing entropy (ΔS_{mix}). The formation criterion for solid-solution phases was described as the following conditions [29]:

$$11 \text{ J/K}\cdot\text{mol} \leq \Delta S_{mix} \leq 19.5 \text{ J/K}\cdot\text{mol} \quad (2)$$

$$-22 \text{ kJ/mol} \leq \Delta H_{mix} \leq 7 \text{ kJ/mol} \quad (3)$$

$$0 \leq \delta \leq 8.5\% \quad (4)$$

The calculated thermodynamic parameters for TiAlMoNbW are depicted in Table 5. The calculation results revealed that the solid-solution phase was preferred to precipitation for the TiAlMoNbW system. In addition, VEC was considered an extremely important parameter used to assess the formation of FCC or BCC solid solutions. BCC phase would be the primary precipitation when $VEC \leq 6.87$. For TiAlMoNbW alloy, the value of VEC was 4.8, indicating the formation of the BCC solid-solution phase, which was verified by XRD analysis (Figure 2).

Table 5. Thermodynamic parameters of TiAlMoNbW system.

Parameters	ΔS_{mix} (J/K·mol)	ΔH_{mix} (J/K·mol)	Δ (%)	VEC
Value	13.38	−6.5	2.77	4.8

With the introduction of nitrogen, the crystallinity of the high-entropy alloy film would increase. Since Ti, Al, Mo, and Nb elements are all strong nitride-forming elements with a strong affinity for nitrogen atoms, nitrides would be preferentially precipitated. Except for Al, the binary nitrides of Ti, Mo, Nb, and W are all FCC structures, so it can be considered that the FCC structure dominates the crystal structure of the film. Therefore, the film has changed from BCC structure to FCC structure, and similar phenomena can be found in previous papers [30,31].

It is clear from the SEM images of HEA and HEN films that after the introduction of nitrogen, the film morphology changes from acicular to nanoparticle-like. The deposition rate decreased from 36.85 to 15.77 nm/min, which is mainly due to the increase in nitrogen partial pressure in the MS process leading to the decrease in peak current and particle density of the sputtering target. Combined with the AFM images, it can also be clearly observed that the HEN film has a smoother surface and less roughness than the HEA film due to the nitrogen atoms that can fill the gaps of the film and the formation of nitride structures. The work of Tsai [32] showed that the film thickness affects the surface roughness; the smaller the film thickness, the smaller the grain size, and the narrower the spacing between the columnar structures, the lower the surface roughness.

4.2. Improvement in Wear and Corrosion Resistance

According to the result of Section 3.3, the S-HEN sample shows the highest micro-hardness. Feng et al. [33] found that solid solution or grain boundary strengthening and grain boundary dislocation density can be affected by grain size, resulting in films with higher hardness. In this work, Ti, Mo, Nb, and W elements have similar atomic radii, making it easier to form stable solid-solution alloys. The additional element Al increases the difference in atomic size and causes serious lattice distortion, thereby improving the performance of the matrix effectively by a solid-solution strengthening mechanism.

After adding nitrogen, the grain size of the film was dramatically decreased. Based on the Hall-Petch effect [25], as the grain size decreases, the refinement and strengthening effect of the grain is significant. Grain boundaries restrict the migration of dislocations, and cracks cannot propagate along the grain boundaries, which further increases the hardness of the film. In addition, the formed nanocrystalline nitride phase and the strong Me-N covalent bonds also affect the hardness of the nitride films. The modulus and hardness of the S-HEN sample increased to 313.6 GPa and 25.7 GPa, respectively, which is higher than the sputtered (CuSiTiYZr)C coatings with a hardness above 20.7 GPa [8] and well beyond the laser-cladded FeCrNiCoB_x high-entropy alloy coatings with a maximum hardness of nearly 1100 HV [11]. The mechanical properties of common high-entropy alloy films in recent years are compiled in Figure 10. It can be seen that the mechanical properties of the S-HEN and S-HEA samples in this study are at a relatively high level compared to other alloy films. In addition to the reasons for the above analysis, this may also be related to alloy compositions and the preparation method for the target, which is processed by powder

metallurgy in this study. Compared with the casting targets used in most studies, the grains of high-purity targets prepared by the powder metallurgy process are relatively fine and uniform, which may be expected to provide better performance for the prepared coatings.

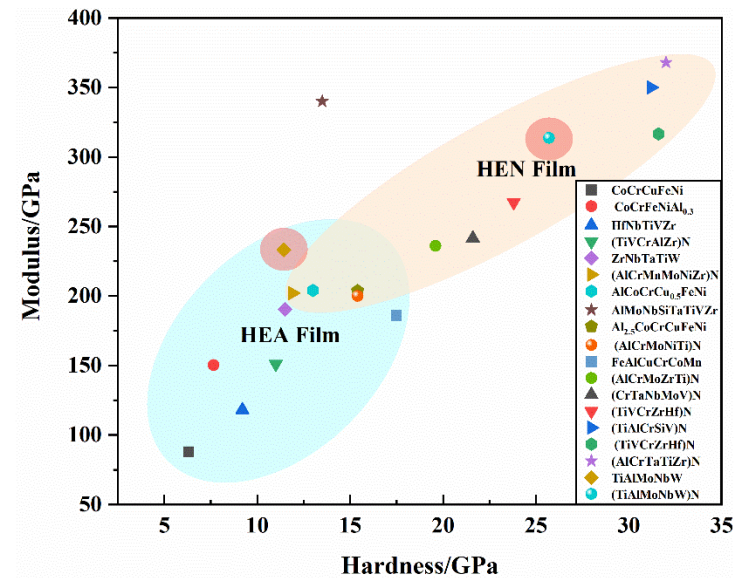


Figure 10. Comparison of mechanical properties of other materials with high-entropy alloy films in this study [6,7,10,34–45].

Research by Archard [46] demonstrated that the hardness of the film is inversely proportional to the amount of wear. The higher hardness and modulus endow the nitride film with higher load-carrying capacity, effectively reducing the wear rate and coefficient of friction. Additionally, the tribological properties of the films can be predicted by the “elasticity index” H/E and the “plasticity index” H^3/E^2 [47], which describe the ability of the film surface to dissipate energy under elastic and plastic strains during loading, respectively. A higher value means better abrasion resistance. The index values of the S-HEA and S-HEN samples in this work are shown in Table 6, which indicates that HEN films have better abrasion resistance.

Table 6. The H/E and H^3/E^2 of HEA and HEN films.

Sample	H/E	H^3/E^2
S-HEA	0.049	0.027
S-HEN	0.083	0.173

To further investigate the wear mechanism, the morphology of the wear trajectory and the wear profile were investigated using SEM and surface profilometer, as described in Figure 11. The wear tracks of S-HEA samples exhibit plowing groove and adhesive wear, which is mainly caused by the large hardness difference between the coating and Si_3N_4 ball. Compared with CSS-42L steel, the area of spalling pits is reduced on the surface of the S-HEA sample, which is due to the hard BCC phase protecting the surface from brittle fracture. The main wear mechanism of the S-HEN sample is mainly abrasive wear, the wear width and wear depth are much smaller than the HEA film, and the wear depth is about 1/3 of that of the S-HEA sample. The cross-sectional view expresses that the peeling only occurs inside the film and barely at the interface between the film and the substrate. Figure 12 graphically illustrates the wear mechanism of HEA and HEN film. The HEN film effectively improves the shear resistance of the contact surface due to its high toughness FCC structure and high hardness nitride phase. As a result, the peeling and chipping caused by adhesive wear were reduced, and the friction coefficient and wear rate were

ultimately decreased. Under the experimentally designed friction conditions, the prepared film can provide a suitable protective effect on the substrate.

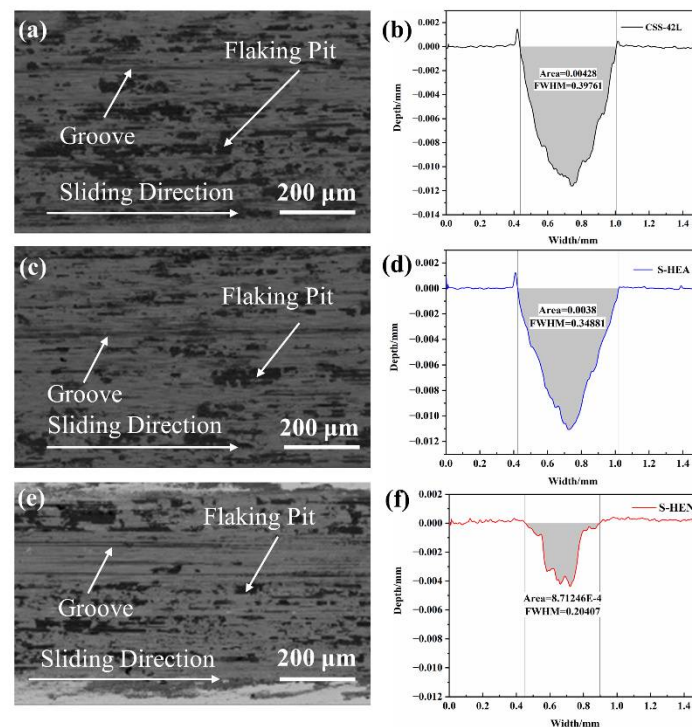


Figure 11. The surface topography and cross-sectional profile of wear track: (a,b) CSS-42L, (c,d) S-HEA sample, (e,f) S-HEN sample.

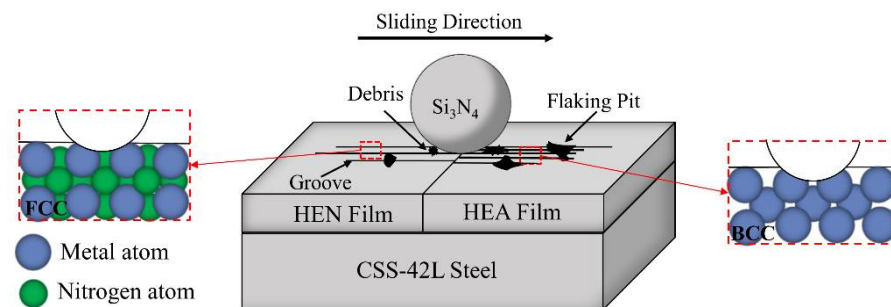


Figure 12. Three-dimensional schematic diagram of wear mechanism of HEA and HEN films.

The corrosion resistance of the S-HEA and S-HEN samples in this study was greatly improved in NaCl solution and H₂SO₄ solution, which is primarily due to the high-entropy effect and rapid quenching effect. During the deposition process, the films are easy to form FCC or BCC solid-solution phase with a more uniform microstructure, which can significantly reduce the effect of galvanic corrosion and the number of microcells. Subsequently, the passivation film with a dense packing structure is formed spontaneously, and, eventually, the corrosion resistance is greatly improved. Furthermore, the addition of corrosion-resistant elements such as Al, Nb, and W can also improve the corrosion resistance of HEA films. Affected by grain refinement, the bonding force between metal atoms and nitrogen atoms is stronger than that between metal atoms [12], and nitrides have higher inertness and stability. Thus, the corrosion resistance of the S-HEN sample is better than that of the S-HEA sample.

5. Conclusions

The effects of TiAlMoNbW high-entropy alloy films and corresponding nitride films on the mechanical properties and wear and corrosion resistance of CSS-42L bearing steel were comparatively studied. The HEN film with excellent performance was obtained. The conclusions are summarized below:

1. The films prepared by the TiAlMoNbW target have excellent mechanical properties. Affected by the solid-solution strengthening effect and the saturated nitride phase, the hardness, and modulus of the HEN film are higher than those of the HEA film, increasing from 11.42 GPa and 233.1 GPa to 25.7 GPa and 313.6 GPa, respectively.
2. Benefiting from the high toughness nanoparticle-like FCC structure, lower surface roughness, and formed nitride phase with high hardness of the HEN film, the friction coefficient of the HEN film-coated samples is reduced from 0.73 to 0.57, and the wear rate is decreased from $1.848 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{mm})$ to $0.376 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{mm})$.
3. In the neutral and acidic environments of this experiment, the HEN films have lower Icorr and an order of magnitude lower corrosion rate than the CSS-42L steel substrate. The corrosion rate is as low as 0.033 mpy and 28.151 mpy, respectively, indicating that the presence of HEN films effectively improves the corrosion resistance of the base steel.

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References

1. Ragen, M.A.; Anthony, D.L.; Spitzer, R.F. A comparison of the mechanical and physical properties of contemporary and new alloys for aerospace bearing applications. *Bear Steel Technol.* **2002**, *1419*, 362–374.
2. Qiu, Z.F.; Wang, F.F.; Li, Q.S.; Zheng, L.J.; Zhang, F.X.; Zhang, H. Corrosion and mechanical properties for Cr-coated CSS-42L bearing steel after Ti and C ions co-implantation. *Appl. Surf. Sci.* **2020**, *509*, 145293. [\[CrossRef\]](#)
3. Yang, C.Y.; Xu, J.H.; Fu, Y.C.; Ding, W.F.; Song, H.H. Investigation on the Grindability of CSS-42L Stainless Steel. *Trans. Nanjing Univ. Aeronaut. Astronaut.* **2016**, *33*, 706–713.
4. Darisuren, S.; Park, J.H.; Pyun, Y.S.; Amanov, A. A Study on the Improvement of the Fatigue Life of Bearings by Ultrasonic Nanocrystal Surface Modification Technology. *Metals* **2019**, *9*, 1114. [\[CrossRef\]](#)
5. 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.* **2004**, *6*, 299–303. [\[CrossRef\]](#)
6. Tsai, D.C.; Chang, Z.C.; Kuo, B.H.; Lin, T.N.; Shiao, M.H.; Shieu, F.S. Interfacial reactions and characterization of (TiVCrZrHf)N thin films during thermal treatment. *Surf. Coat. Technol.* **2014**, *240*, 160–166. [\[CrossRef\]](#)
7. Feng, X.G.; Zhang, K.F.; Zheng, Y.G.; Zhou, H.; Wan, Z.H. Chemical state, structure and mechanical properties of multi-element (CrTaNbMoV)N_x films by reactive magnetron sputtering. *Mater. Chem. Phys.* **2020**, *239*, 121991. [\[CrossRef\]](#)
8. Braic, M.; Balaceanu, M.; Vladescu, A.; Zoita, C.N.; Braic, V. Deposition and characterization of multi-principal-element (CuSiTiYZr)C coatings. *Appl. Surf. Sci.* **2013**, *284*, 671–678. [\[CrossRef\]](#)
9. Huang, Y.S.; Chen, L.; Lui, H.W.; Cai, M.H.; Yeh, J.W. Microstructure, hardness, resistivity and thermal stability of sputtered oxide films of AlCoCrCu_{0.5}NiFe high-entropy alloy. *Mat. Sci. Eng. A-Struct.* **2007**, *457*, 77–83. [\[CrossRef\]](#)
10. Ren, B.; Yan, S.Q.; Zhao, R.F.; Liu, Z.X. Structure and properties of (AlCrMoNiTi)N_x and (AlCrMoZrTi)N_{1-x} films by reactive RF sputtering. *Surf. Coat. Technol.* **2013**, *235*, 764–772. [\[CrossRef\]](#)
11. Zhang, C.; Chen, G.J.; Dai, P.Q. Evolution of the microstructure and properties of laser-clad FeCrNiCoB_x high-entropy alloy coatings. *Mater. Sci. Technol.* **2016**, *32*, 1666–1672. [\[CrossRef\]](#)

12. Hsueh, H.T.; Shen, W.J.; Tsai, M.H.; Yeh, J.W. Effect of nitrogen content and substrate bias on mechanical and corrosion properties of high-entropy films (AlCrSiTiZr)_(100-x)N_x. *Surf. Coat. Technol.* **2012**, *206*, 4106–4112. [\[CrossRef\]](#)
13. Zheng, S.J.; Cai, Z.B.; Pu, J.B.; Zeng, C.; Chen, S.Y.; Chen, R.; Wang, L.P. A feasible method for the fabrication of VAlTiCrSi amorphous high entropy alloy film with outstanding anti-corrosion property. *Appl. Surf. Sci.* **2019**, *483*, 870–874. [\[CrossRef\]](#)
14. Dou, D.; Li, X.C.; Zheng, Z.Y.; Li, J.C. Coatings of FeAlCoCuNiV high entropy alloy. *Surf. Eng.* **2016**, *32*, 766–770. [\[CrossRef\]](#)
15. Ji, X.L.; Duan, H.; Zhang, H.; Ma, J.J. Slurry Erosion Resistance of Laser Clad NiCoCrFeAl₃ High-Entropy Alloy Coatings. *Tribol. Trans.* **2015**, *58*, 1119–1123. [\[CrossRef\]](#)
16. Zhang, H.; Wu, W.F.; He, Y.Z.; Li, M.X.; Guo, S. Formation of core-shell structure in high entropy alloy coating by laser cladding. *Appl. Surf. Sci.* **2016**, *363*, 543–547. [\[CrossRef\]](#)
17. Rajaram, G.; Jain, A. Characteristics of alumina coating on SAE 52100 bearing steel with Ni-Cr bond coat. *Int. Mater. Eng. Innov.* **2018**, *9*, 20–33. [\[CrossRef\]](#)
18. Yao, C.Z.; Zhang, P.; Liu, M.; Li, G.R.; Ye, J.Q.; Liu, P.; Tong, Y.X. Electrochemical preparation and magnetic study of Bi-Fe-Co-Ni-Mn high entropy alloy. *Electrochim. Acta* **2008**, *53*, 8359–8365. [\[CrossRef\]](#)
19. Liu, D.; Cheng, J.B.; Ling, H. Electrochemical behaviours of (NiCoFeCrCu)₉₅B₅ high entropy alloy coatings. *Mater. Sci. Technol.* **2015**, *31*, 1159–1164. [\[CrossRef\]](#)
20. Li, W.; Liu, P.; Liaw, P.K. Microstructures and properties of high-entropy alloy films and coatings: A review. *Mater. Res. Lett.* **2018**, *6*, 199–229. [\[CrossRef\]](#)
21. Zhang, W.J.; Qi, Y.F.; Zhang, L.X.; Tang, Y.H.; Qi, C.; Shen, Q.; Ma, Y.T.; Wang, B. The effect of alloy elements on corrosion and oxidative resistance of W-based alloy films. *Surf. Coat. Technol.* **2022**, *434*, 128165. [\[CrossRef\]](#)
22. Braeckman, B.R.; Boydens, F.; Hidalgo, H.; Dutheil, P.; Jullien, M.; Thomann, A.L.; Depla, D. High entropy alloy thin films deposited by magnetron sputtering of powder targets. *Thin Solid Films* **2015**, *580*, 71–76. [\[CrossRef\]](#)
23. Yan, X.H.; Li, J.S.; Zhang, W.R.; Zhang, Y. A brief review of high-entropy films. *Mater. Chem. Phys.* **2018**, *210*, 12–19. [\[CrossRef\]](#)
24. Liu, K.Q.; Ostadhassan, M.; Xu, X.M. A comparison study of the unloading behavior in shale samples in nanoindentation experiments using different models. *Pet. Sci. Eng.* **2020**, *186*, 106715. [\[CrossRef\]](#)
25. Yu, L.H.; Luo, H.; Bian, J.G.; Ju, H.B.; Xu, J.H. Research on Microstructure, Mechanical and Tribological Properties of Cr-Ti-B-N Films. *Coatings* **2017**, *7*, 137. [\[CrossRef\]](#)
26. Zhang, X.; Cui, H.Z.; Wang, M.L.; Zhao, Y.Q.; Sun, K. Effect of Al content on microstructure and corrosion resistance of Al_xCoCrFeNi high entropy alloys. *Trans. Mater. Heat Treat.* **2018**, *39*, 29–36.
27. Cheng, K.H.; Lai, C.H.; Lin, S.J.; Yeh, J.W. Structural and mechanical properties of multi-element (AlCrMoTaTiZr)_{N-x} coatings by reactive magnetron sputtering. *Thin Solid Films* **2011**, *519*, 3185–3190. [\[CrossRef\]](#)
28. Wang, J.J.; Kuang, S.F.; Yu, X.; Wang, L.Q.; Huang, W.J. Tribo-mechanical properties of CrNbTiMoZr high-entropy alloy film synthesized by direct current magnetron sputtering. *Surf. Coat. Technol.* **2020**, *403*, 126374. [\[CrossRef\]](#)
29. Guo, S.; Liu, C.T. Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase. *Prog. Nat. Sci. Mater. Int.* **2011**, *21*, 433–446. [\[CrossRef\]](#)
30. Huang, P.K.; Yeh, J.W. Effects of nitrogen content on structure and mechanical properties of multi-element (AlCrNbSiTiV)_N coating. *Surf. Coat. Technol.* **2009**, *203*, 1891–1896. [\[CrossRef\]](#)
31. Cui, P.P.; Li, W.; Liu, P.; Zhang, K.; Ma, F.C.; Chen, X.H.; Feng, R.; Liaw, P.K. Effects of nitrogen content on microstructures and mechanical properties of (AlCrTiZrHf)_N high-entropy alloy nitride films. *J. Alloys Compd.* **2020**, *834*, 155063. [\[CrossRef\]](#)
32. Tsai, D.C.; Huang, Y.L.; Lin, S.R.; Jung, D.R.; Chang, S.Y.; Shieu, F.S. Diffusion barrier performance of TiVCr alloy film in Cu metallization. *Appl. Surf. Sci.* **2010**, *257*, 4923–4927. [\[CrossRef\]](#)
33. Feng, X.B.; Zhang, J.Y.; Wang, Y.Q.; Hou, Z.Q.; Wu, K.; Liu, G.; Sun, J. Size effects on the mechanical properties of nanocrystalline NbMoTaW refractory high entropy alloy thin films. *Int. J. Plast.* **2017**, *95*, 264–277. [\[CrossRef\]](#)
34. Lu, T.W.; Feng, C.S.; Wang, Z.; Liao, K.W.; Liu, Z.Y.; Xie, Y.Z.; Hu, J.G.; Liao, W.B. Microstructures and mechanical properties of CoCrFeNiAl_{0.3} high-entropy alloy thin films by pulsed laser deposition. *Appl. Surf. Sci.* **2019**, *494*, 72–79. [\[CrossRef\]](#)
35. Fritze, S.; Koller, C.M.; Fieandt, L.v.; Malinovskis, P.; Johansson, K.; Lewin, E.; Mayrhofer, P.H.; Jansson, U. Influence of Deposition Temperature on the Phase Evolution of HfNbTiVZr High-Entropy Thin Films. *Materials* **2019**, *12*, 587. [\[CrossRef\]](#)
36. Li, X.C.; Zheng, Z.Y.; Dou, D.; Li, J.C. Microstructure and Properties of Coating of FeAlCuCrCoMn High Entropy Alloy Deposited by Direct Current Magnetron Sputtering. *Mater. Res.* **2016**, *19*, 802–806. [\[CrossRef\]](#)
37. Wu, Z.F.; Wang, X.D.; Cao, Q.P.; Zhao, G.H.; Li, J.X.; Zhang, D.X.; Zhu, J.J.; Jiang, J.Z. Microstructure characterization of Al_xCo₁Cr₁Cu₁Fe₁Ni₁ (x=0 and 2.5) high-entropy alloy films. *J. Alloys Compd.* **2014**, *609*, 137–142. [\[CrossRef\]](#)
38. Ren, B.; Shen, Z.; Liu, Z. Structure and mechanical properties of multi-element (AlCrMnMoNiZr)_{N_x} coatings by reactive magnetron sputtering. *J. Alloys Compd.* **2013**, *560*, 171–176. [\[CrossRef\]](#)
39. Feng, X.G.; Tang, G.Z.; Sun, M.R.; Ma, X.X.; Wang, L.Q.; Yukimura, K. Structure and properties of multi-targets magnetron sputtered ZrNbTaTiW multi-elements alloy thin films. *Surf. Coat. Technol.* **2013**, *228*, S424–S427. [\[CrossRef\]](#)
40. Liang, S.C.; Tsai, D.C.; Chang, Z.C.; Sung, H.S.; Lin, Y.C.; Yeh, Y.J.; Deng, M.J.; Shieu, F.S. Structural and mechanical properties of multi-element (TiVCrZrHf)_N coatings by reactive magnetron sputtering. *Appl. Surf. Sci.* **2011**, *258*, 399–403. [\[CrossRef\]](#)
41. Lin, C.H.; Duh, J.G.; Yeh, J.W. Multi-component nitride coatings derived from Ti-Al-Cr-Si-V target in RF magnetron sputter. *Surf. Coat. Technol.* **2007**, *201*, 6304–6308. [\[CrossRef\]](#)

42. Lai, C.H.; Lin, S.J.; Yeh, J.W.; Chang, S.Y. Preparation and characterization of AlCrTaTiZr multielement nitride coatings. *Surf. Coat. Technol.* **2006**, *201*, 3275–3280. [[CrossRef](#)]
43. Khan, N.A.; Akhavan, B.; Zhou, H.; Chang, L.; Wang, Y.; Sun, L.; Bilek, M.M.; Liu, Z. High entropy alloy thin films of AlCoCrCu_{0.5}FeNi with controlled microstructure. *Appl. Surf. Sci.* **2019**, *495*, 143560. [[CrossRef](#)]
44. Shen, W.J.; Tsai, M.H.; Chang, Y.S.; Yeh, J.W. Effects of substrate bias on the structure and mechanical properties of (Al_{1.5}CrNb_{0.5}Si_{0.5}Ti)N_x coatings. *Thin Solid Films* **2012**, *520*, 6183–6188. [[CrossRef](#)]
45. Chang, Z.C.; Liang, S.C.; Han, S.; Chen, Y.K.; Shieu, F.S. Characteristics of TiVCrAlZr multi-element nitride films prepared by reactive sputtering. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2010**, *268*, 2504–2509. [[CrossRef](#)]
46. Wu, H.; Ian, B.; Liu, Y.; Wu, X.L. Dry sliding tribological behavior of Zr-based bulk metallic glass. *Trans. Nonferrous Met. Soc. China* **2012**, *22*, 585–589. [[CrossRef](#)]
47. Leyland, A.; Matthews, A. On the significance of the H/E ratio in wear control: A nanocomposite coating approach to optimised tribological behaviour. *Wear* **2000**, *246*, 1–11. [[CrossRef](#)]