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BRIEF OVERVIEW



Microstructures and properties of high-entropy alloy films and coatings: a review

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ABSTRACT

In the past 14 years, as a branch of high-entropy alloy (HEA) materials, HEA films and coatings have exhibited the attractive and unique properties, relative to the conventional film and coating materials. The recent research and development of HEA films and coatings are reviewed in this paper. At first, the basic concept of HEAs films and coatings are introduced. Then, their preparation technologies, microstructures and appealing properties are summarized. Moreover, the possible reasons and design criteria for achieving the excellent properties are discussed. Finally, the suggested future research work for the HEA films and coatings are outlined.



IMPACT STATEMENT

Preparation technologies, microstructures, and properties of HEA films and coatings are reviewed in this paper. The design criteria and suggested research directions are further discussed and proposed.

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KEYWORDS

High-entropy alloys; films and coatings; preparation technologies; microstructure; properties

1. Introduction

In the last 14 years, high-entropy alloys (HEAs) proposed through the work of Yeh et al. [1] and Cantor et al. [2] in 2004, comprised of at least five principal metal elements with the concentration of each element varying from 5 at.% (atomic percent) and 35 at.%, have attracted an increasing attention for their appealing properties and potential uses [3–16]. As a new type of multicomponent metallic alloys, HEAs, also named as complex concentrated alloys (CCAs) [17], multi-principal element alloys (MPEAs) [18], multicomponent alloys [2], compositionally complex alloys (CCAs) [19], baseless alloys [17], or metal buffets (MBs) [20], have inspired the exploration of the vast composition space. Owing to the combined influences of high-entropy effects, sluggish diffusion, and severe lattice distortion, HEAs can easily form the simple solid-solution phases with face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal

close-packing (HCP) structures rather than the inter-metallic compounds. Extensive research has been carried out on numerous HEAs, and many attractive properties have been achieved, such as high hardness and strength [4–6], high fatigue resistance [14,21] and fracture toughness [8], high-temperature oxidation resistance [22,23], high corrosion resistance [24–26], unique electrical and magnetic properties [27–29], which are potentially suitable for applications as structural and functional materials. The research progress on HEAs has already been reviewed by several papers [3,17,30–33].

Currently, most reports on HEAs prepare the alloys through arc melting and casting. However, since the sizes of HEAs prepared by arc melting are limited, and the cost of HEAs could be higher than most of conventional alloys due to the inclusion of more expensive elements (such as Nb, W, Cr, V, Ni, Ti, and Co),

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investigations concerning the high-performance HEA films and coatings on low-cost metal substrates have also aroused more and more interests among the material scientists and engineers. As far as the conception is concerned, a film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness, while a coating is a covering that is applied to the surface of an object, usually referred to as the substrate, which is generally thicker than a film. From the science and application aspects, however, films have many overlaps with coatings. Up to now, a number of technologies have been applied to fabricate HEA films and coatings, e.g. magnetron sputtering [34–36], laser cladding [37,38], spraying [39], electrodeposition [40], plasma-transferred arc cladding [41], and others. The present experimental results have proved that HEA films and coatings can show excellent mechanical and physical properties, such as the high hardness and elastic modulus [42,43], superior wear resistance [44], corrosion [45] and temperature resistance [46], as well as the appealing electrical [47] and magnetic properties [48].

Relative to the HEA bulk materials, the review paper of HEA films and coatings has rarely been documented during the past 14 years. Until 2016, Yeh et al. [19] first reviewed the research progress in the area of the HEA coatings in their book chapter, which included the preparation methods, properties and applications of the HEA coatings and other HEA-Based coatings. In 2017, Yan et al. [49] reported a review of the high-entropy films, which briefly discussed the preparation methods, phase structure, and various properties of the high-entropy films. Relative to the two published literatures, this paper will more deeply discuss the relationships between microstructures and properties, more extensively summarize the properties including corrosion resistance, physical characteristics, etc., which the published ones rarely involved, further bring forward the design criteria for achieving the excellent properties, and generalize the research progress of modeling and simulations for HEA films and coatings, which is expected to shed a light on the future research of the high-performance HEA films and coatings. The present paper is organized into the following major topics. Section 1 introduces the basic concept of HEAs and their films and coatings. The preparation technologies of HEA films and coatings are summarized in Section 2. Sections 3 and 4 discuss the microstructures and appealing properties of the HEA films and coatings. Section 5 includes several reasons and design criteria of HEA films and coatings for achieving the excellent properties, as well as the modeling and simulations. This review ends with the suggested future work (Section 6) and concluding remarks (Section 7).

2. Preparation technologies

In the recent years, several technologies have been applied to manufacture HEA films and coatings, including magnetron sputtering [34–36], laser cladding [37,38], spraying [39], electrodeposition [40], plasma-transferred arc cladding [41], and other techniques. Relative to the preparation technologies of the HEA bulk materials, such as the arc-melting technology or casting methods, the synthetic methods of HEA films and coatings are more easily to achieve the rapid cooling rate, the so-called ‘rapid quenching’ effect, owing to their smaller thickness, which is very important as HEA may undergo various phase transformations while slow cooling due to the reduction in the thermodynamic driving force at lower temperatures. Moreover, a rapid cooling rate can restrict the diffusion of the elements and also restrain the nucleation and growth of the intermetallic compounds, which is in favor of the formation of the HEA solid-solution phase [36,50].

2.1. Sputter deposition

Sputter deposition is the most common technique to fabricate the HEA films. Stoichiometry can be easily controlled by varying the chemical composition of a given target and the process parameters during sputtering. Moreover, due to the convenience of the incorporation of the reactive gas during deposition, such as N_2 , O_2 , or C_2H_2 , the nitride, oxide, or carbide films of the HEAs are easily synthesized, which provides us an effective way to explore new HEA systems.

According to the different forms of sputtering targets, HEA films are usually deposited by sputtering in three different ways. First, the HEA film can be directly prepared by a HEA target, which has a good control over the film stoichiometry and thus, a most often-used way to synthesize the HEA films. The deposited films are easy to have the same stoichiometry as the original target alloy even though the individual elements have different sputtering yields, because the surface composition of the target equilibrates after a pre-sputter step. Moreover, the energetic atoms can quench condensation rapidly ($\sim 10^9$ K/s) for thin films, hence minimizing concentration fluctuations in the films. However, the production of the HEA target is a time-consuming process. Cheng et al. [42] deposited the (AlCrMoTaTiZr)N films at different nitrogen flow ratios [R_N , $N_2/(Ar + N_2)$] by reactive sputtering from an AlCrMoTaTiZr equimolar alloy target. The films consisted of a single FCC solution phase, and the typical cross-sectional microstructure was shown in Figure 1. The superhigh hardness of 40.2 GPa was achieved in this (AlCrMoTaTiZr)N film.

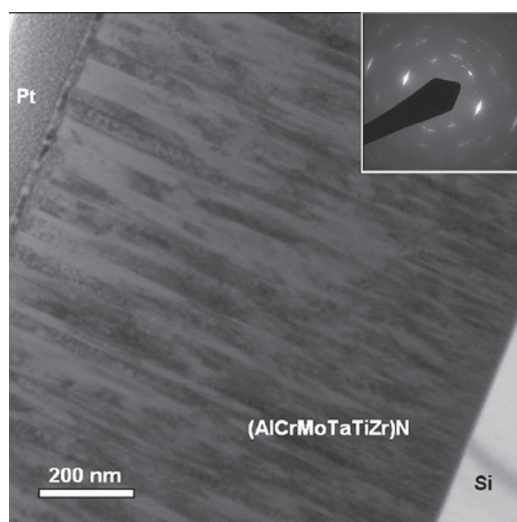


Figure 1. Cross-sectional TEM image and selected-area diffraction pattern of the AlCrMoTaTiZr nitride film deposited by reactive-magnetron sputtering at the nitrogen flow ratio (R_N) = 50% [42].

Second, HEA films can be fabricated by co-deposition with multiple metal targets and mosaic targets. This technique allows the deposition of HEA films in a wide range of chemical compositions by avoiding the complex target preparation process. Stoichiometry can be controlled by changing the target powers and the relative surface fraction of each element on a given target. However, it is more challenging to obtain a desired film composition by altering the deposition parameters. Feng et al. [51] deposited the ZrNbTaTiW films by unbalanced magnetron co-sputtering of two alloy targets and a pure target. An amorphous structure has been formed when the Zr content exceeded 35 at.%. The maximum hardness and elastic modulus of the ZrNbTaTiW alloy films reached the values of 11.5 and 190.4 GPa, respectively.

Third, HEA thin films can be deposited using powder targets. A powder target is easily made by selecting the required metallic powders, weighing, mixing, and finally cold pressing the powder mixture. This is a fast and flexible method, since the number of magnetrons is reduced to one, and the target composition is adjustable by simply changing the weight fractions of the individual powders. A drawback of this method is that the powders must be very well mixed to ensure a homogeneous composition throughout the target. Braeckman et al. [52] successfully deposited the AlCoCrCuFeNi high-entropy thin films by sputtering from the pressed powder targets with different compositions and found that the sputtered thin films could be topologically regarded as binary alloys of the form Al-(CoCrCuFeNi). A transition from FCC to BCC phases was found with the increase of the Al content,

which could be attributed to a critical lattice distortion. The critical Al concentration and corresponding atomic size difference were calculated using the atomic-level stress theory.

2.2. Laser cladding

Laser cladding is a rapidly-developed surface-treatment method that presents the excellent advantage of the rapid solidification velocity (10^3 – 10^6 K s $^{-1}$). This type of the laser-solidification process enables non-equilibrium solute trapping and avoids component segregation. The technique can be used to fabricate HEA coatings of about 1–5 mm in thickness, which is much thicker than the films prepared by magnetron sputtering. Laser cladding produces a metallurgical bonding strength between the coating and substrate, which is stronger than that obtained from the thermal spraying technique. Qiu et al. [53] prepared the Al₂CrFeNiCoCuTi_x coatings by laser cladding. The typical microstructure morphologies of the Al₂CrFeNiCoCuTi_x coatings are shown in Figure 2, from which it can be seen that the cladding layer of coatings consist of the cladding zone, bounding zone, heat-affected zone, and substrate zone. The cladding zone is mainly composed of equiaxed crystals away from the substrate and columnar crystals close to the substrate. The coatings were composed of the FCC, BCC, and Laves phase due to the high-entropy affect.

As is well known to us, a common problem encountered in the laser processing to prepare a coating on the substrate with a low melting point is that the significant dilution of elements from the substrate often occurs. For example, Yue et al. [54] fabricated the AlCoCrCuFeNi coatings on pure magnesium substrates by means of laser cladding. The Mg element in the matrix was found to melt into the lower layer of the HEA coatings. Katakam et al. [50] synthesized the AlFeCoCrNi coatings by laser-surface engineering on the Al substrate and found that laser processing resulted in a coating of a composite microstructure of the BCC HEA-rich phase embedded in the Al-rich matrix. Surprisingly, Shon et al. [55] reported that the effective control of dilution effects was achieved with the aid of the combination of the double-layered coating and higher-energy input (25 J mm $^{-2}$) during laser processing. The reduced dilution and formation of the HEA phase throughout the coating on aluminum resulted in superior corrosion resistance.

2.3. Spraying

Thermal-spray technology is commonly used for producing the protective films or coatings on the surfaces of the

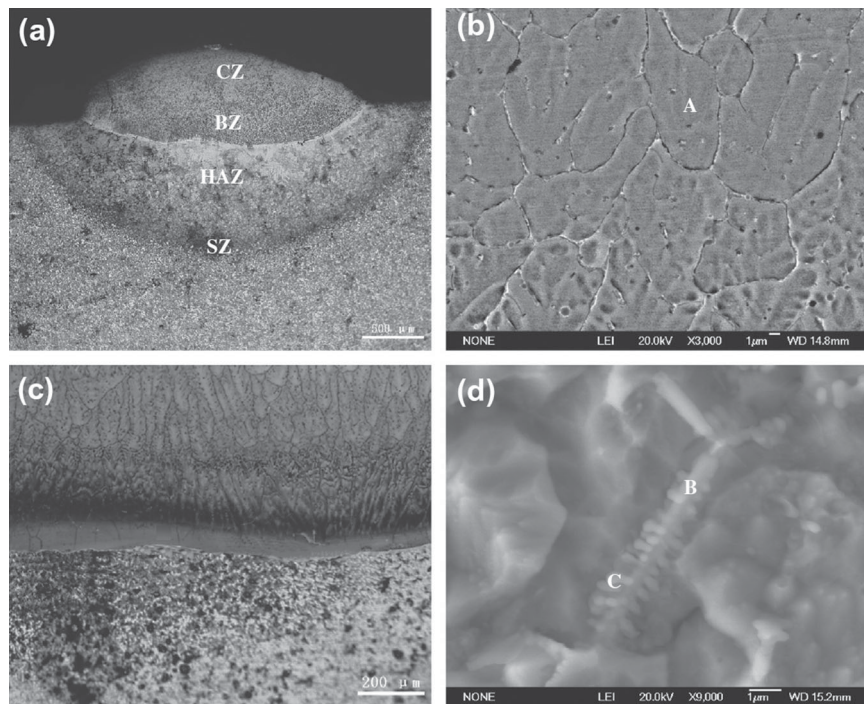


Figure 2. Microstructure morphologies of the $\text{Al}_2\text{CrFeNiCoCuTi}_x$ coatings. (a) Macroscopic feature. (b) Cladding zone. (c) Bounding zone. (d) High-magnification SEM micrograph of the cladding zone [53].

structural components. Huang et al. [56] first prepared the $\text{AlCrFeMo}_{0.5}\text{NiSiTi}$ and $\text{AlCoCrFeMo}_{0.5}\text{NiSiTi}$ coatings with a thickness of around $200\text{ }\mu\text{m}$ by thermal spray, which were in a supersaturated state of a primary BCC phase. Both as-sprayed coatings possessed about half the hardness of the as-cast bulk and hardened significantly at high temperature because of the precipitation of the Cr-silicide phase. For example, the hardness of both coatings reached around 925 HV after heat treatment at 800°C for 1 h. Wang et al. [57] successfully synthesized the $\text{Ni}_x\text{Co}_{0.6}\text{Fe}_{0.2}\text{Cr}_y\text{Si}_z\text{AlTi}_{0.2}$ coatings by thermal spraying and found that the hardness of coatings undergoing a heat treatment ($1100^\circ\text{C}/10\text{ h}$) could be significantly increased to 1045 HV, close to that of the casted state.

The atmospheric-plasma-spraying (APS) technology has been applied to fabricate HEA films and coatings by some researchers, which has many advantages, such as the high-flame temperature, concentration of energy, high bonding strength, lower dilution of the coating, high deposition efficiency, and low cost. Yue et al. [39] reported the fabrication of the AlCoCrCuFeNi coating on a Mg substrate by a two-step method utilizing plasma spraying and laser-surface melting. The as-sprayed coating was found to contain micro-porosity with sizes on the order of $50\text{ }\mu\text{m}$. After laser remelting, however, no apparent porosity was observed in the coating. The X-ray diffraction (XRD) results showed that both the

as-sprayed and the laser-remelted coatings were composed primarily of a BCC phase with a small amount of an FCC phase.

Tian et al. [58] prepared the AlCoCrFeNiTi coating by APS, using mechanically-alloyed powders as the feed-stock. The typical cross-sectional microstructure of the as-sprayed coating is shown in Figure 3. The coating was mainly composed of fully-melted splats, unmelted particles, and particles with irregular shapes and dark gray contrasts. An outstanding bonding strength of higher than $50.3 \pm 8.5\text{ MPa}$ was obtained. The average microhardness of the as-sprayed coating was 642 HV, which was about four times of that of the 316 stainless steel (173 HV).

2.4. Electrochemical deposition

Electrochemical deposition can deposit HEA films on substrates with a complex geometry, and it can be carried out at low-processing temperatures and with low-energy consumption. Since it does not require the complex equipment and expensive raw materials, electrochemical deposition provides a possibility of the low-cost synthesis of HEA films. Furthermore, through altering the deposition parameters, electrodeposition can easily control the composition, morphology, and thickness of the films [59–61].

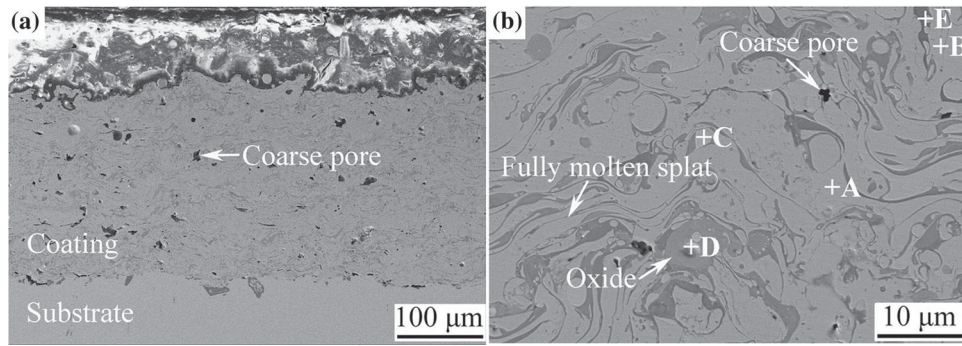


Figure 3. Field emission scanning electron microscopy (FESEM) images of the cross-section of the as-sprayed AlCoCrFeNiTi coating: (a) low-magnification and (b) high-magnification [58].

Yao et al. [40] prepared the amorphous BiFeCoNiMn HEA films by potentiostatic electrodeposition. The surface of the film was composed of compact and uniform particles with triangular cone shapes and a particle size of 100–200 nm. A simple FCC structure was identified by XRD patterns after the films were annealed in the Ar atmosphere. The as-deposited films show soft magnetic behavior, and the annealed films exhibit hard magnetic properties. Soare et al. [60] prepared the AlCrFeMnNi and AlCrCuFeMnNi films by potentiostatic electrodeposition. The as-deposited films were amorphous, and the BCC structures were identified after the films were annealed at various temperatures under inert Ar atmosphere. Li et al. [59] deposited the amorphous MgMnFeCoNiGd films by electrodeposition. The hollow microspheres and core-shell microspheres were obtained. They found that the core-shell-structured MgMnFeCoNiGd amorphous alloy exhibited an abnormal magnetic first-order transition from ferromagnetism to diamagnetism.

2.5. Plasma-transferred-arc cladding

The plasma-transferred arc-cladding process has many advantages to synthesize the HEA films and coatings, such as the high-energy exchanging efficiency, low thermal distortion of the part, low dilution of the substrate material, and a good metallurgical bonding with the substrate [62,63]. Cheng et al. [44] fabricated CoCrCuFeNiNb coatings consisted of the FCC solid-solution and ordered Laves phases by the plasma-transferred arc-cladding process. The CoCrCuFeNiNb coating displays excellent wear and corrosion resistance. They also prepared the CoNiCuFeCr coatings by the plasma-transferred arc-cladding process [64]. The coatings were found to form an FCC solid-solution phase, which had a higher microhardness and better wear resistance than that of the Q235 steel substrate with a mass percent of

elements of 0.18 C, 0.22 Si, 0.60 Mn, 0.02 S, and 0.016 P under the same testing conditions.

2.6. Other techniques

Li et al. [65] successfully clad the AlCoCrFeNi HEA coatings on the American Iron and Steel Institute (AISI) 1045 carbon steel by electrospark deposition. The relationship between the microstructures and corrosion properties of the HEA-coated specimens was studied and compared with that of the copper-molded cast HEA material. Huo et al. [66] synthesized the CoCrFeMnNbNi coating on the AISI 304 steel by tungsten inert gas cladding, which consisted of the FCC solid-solution and Nb-rich Laves phase, and presented the excellent wear resistance under the condition of dry sliding wear. Pogrebnjak et al. [67] prepared the TiHfZrVNb nitride coatings by the cathodic-arc-vapor deposition method, which exhibited a single FCC-structured nitride phase. The maximum hardness of 44.3 GPa was achieved, making this coating system reach the superhard grade (≥ 40 GPa).

3. Microstructures

Like the HEA bulk materials, the HEA films and coatings are composed of more than five elements, resulting in the high mixing entropy, which tends to form random solid-solutions, rather than intermetallic compounds [3,30,32]. To evaluate the entropy of the metallic-alloy formation, Boltzmann's hypothesis can be made, and the mixing entropy, ΔS , can be expressed as:

$$\Delta S = -R \ln \left(\frac{1}{n} \right) = R \ln (n) \quad (1)$$

where R is the ideal gas constant, and n the number of mixed elements. From $n = 6$, ΔS becomes higher than the mixing enthalpy of most intermetallic compounds, which leads to the preferential formation of

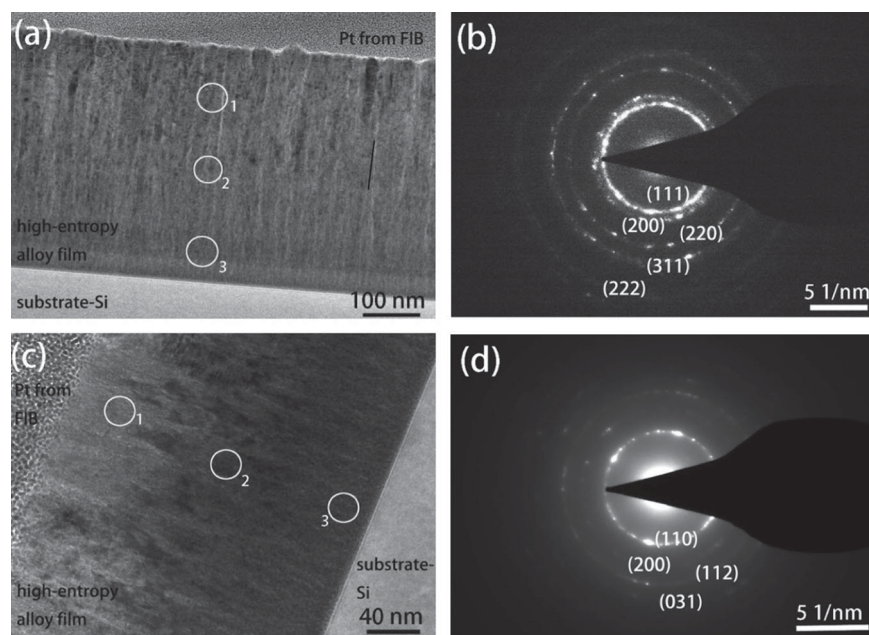


Figure 4. (a) TEM bright-field image and (b) selected-area diffraction pattern for the CoCrCuFeNi film (Al-0), revealing an FCC-like crystalline structure. (c) TEM bright-field image and (d) selected-area diffraction pattern for the Al_{2.5}CoCrCuFeNi film (Al-2.5), revealing a BCC-like crystalline structure [69].

solid-solutions. Due to the remarkable ‘rapid quenching’ effect of the preparation methods of the HEA films and coatings, the FCC or BCC solid-solution phase or amorphous phase are commonly formed because of the restraint effects on the elemental diffusion and nucleation of the intermetallic compounds.

3.1. HEA films and coatings

The quinary CoCrCuFeNi and the senary AlCoCrCuFeNi alloys are two of the most studied HEA bulk materials [6,13–15]. Their corresponding HEA thin films are also investigated by some researchers. Zhang et al. [68] fabricated the CoCrCuFeNi HEA coating by laser cladding onto a Q235 steel, which presented a single FCC solid-solution phase. Wu et al. [69] fabricated the CoCrCuFeNi (at.%) (Al-0) and Al_{2.5}CoCrCuFeNi (at.%) (Al-2.5) HEA films by a sputter technique. The TEM bright-field images and selected-area diffraction patterns are shown in Figure 4, indicating that the as-deposited Al-0 film exhibits an FCC structure, while the as-deposited Al-2.5 film presents a BCC structure.

It is generally believed that the increase of the aluminum content favors the FCC to BCC phase transition, which can be mainly explained by two arguments [70]. First, the incorporation of Al atoms into the FCC lattice increases the lattice distortion whereas the BCC lattice has a lower packing fraction and is more open to accommodate the larger Al atoms. Second, the peculiar

electronic structure of Al favors bonds between the Al and transition metals with an incompletely filled d-shell. Dolique et al. [71,72] deposited three AlCoCrCuFeNi thin films by magnetron co-sputtering. Through tuning the target powers, chemical compositions of the films had been varied in a range close to the equimolar one. Interestingly, they found that three different structures: BCC, FCC solid-solutions, and amorphous (or nanocrystalline) phases were obtained, respectively, suggesting that a tiny variation of the chemical composition could lead to a structure transition.

Braeckman et al. [70] investigated the structural evolution of NbCoCrCuFeNi films with the increase of the niobium concentration deposited by magnetron sputtering. They found that the films changed from a crystalline FCC structure without the Nb addition to an amorphous (or nanocrystalline) structure for higher Nb fractions, as shown in Figure 5, which could be attributed to the largest radius of Nb among all constituent elements. Their group [73] also studied the influence of Ge or In addition on the microstructure of CoCrCuFeNi thin films, and found that when the Ge or In concentration exceeded a certain threshold, the films both transformed from the FCC to amorphous phases, which could be explained by the different reasons. In the In_x-CoCrCuFeNi system, the phase transition could be understood from the lattice distortion, namely, the atomic radius difference between In and the other elements. In the Ge_x-CoCrCuFeNi system, the crystalline to amorphous transition was not topologically driven as the atomic radius of Ge was similar to the base

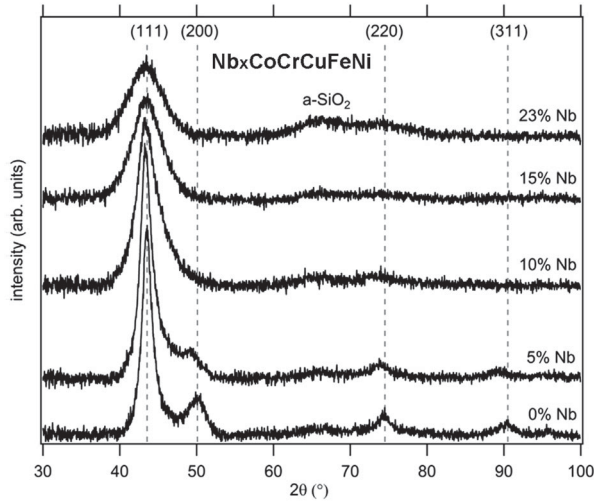


Figure 5. XRD patterns of the Nb_x-CoCrCuFeNi thin films with increasing the Nb fraction deposited at the pressure-distance of 2.8 Pa cm [70].

elements, which could be predicted by a thermodynamic model.

Despite that many HEA films and coatings are composed of only FCC or BCC or a mixed FCC and BCC solid-solutions, some other HEA films and coatings contain the intermetallic compounds. Huang et al. [74] deposited the TiVCrAlSi coatings on the Ti-6Al-4V alloy by laser cladding and reported that the as-clad coating was composed of a BCC solid-solution and (Ti,V)₅Si₃. Jiang et al. [75] reported the laser-cladded CoFeNi₂V_{0.5}Nb_{0.75} and CoFeNi₂V_{0.5}Nb coatings. Both coatings consisted of the FCC solid-solution phase and the Fe₂Nb-type Laves phase, as shown in Figure 6. The mixture of the solid-solution and intermetallic compound helps improve the wear resistance of the coatings.

Based on the previous research, the thermodynamic rules are formulated in order to predict the formation of the HEA phase, such as atomic-radius mismatch (δ), enthalpy of mixing (ΔH_{mix}), entropy of mixing (ΔS_{mix}), electronegativity difference ($\Delta\chi$) and valence electron concentration (VEC), which can be expressed by the following equations [76–80]:

$$\delta = 100 \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (2)$$

where n is the number of components, r_i is the atomic radius, $\bar{r}$ is the average atomic radius given by $\bar{r} = \sum_{i=1}^n c_i r_i$, and c_i is the atomic fraction of the i th element.

$$\Delta H_{\text{mix}} = 4 \sum_{i=1, i \neq j}^n \Delta H_{\text{mix}}^{ij} c_i r_i \quad (3)$$

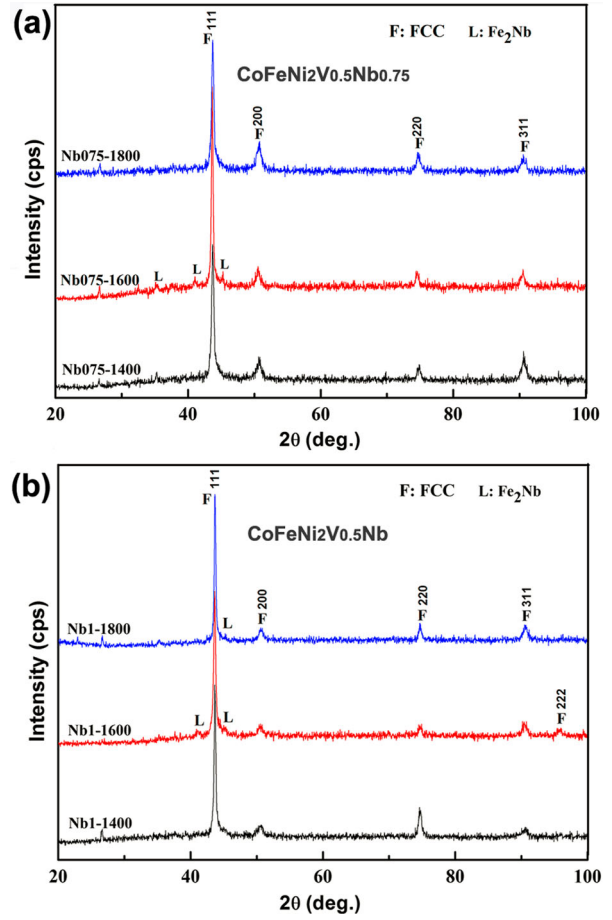


Figure 6. XRD patterns of the laser cladded (a) CoFeNi₂V_{0.5}Nb_{0.75} and (b) CoFeNi₂V_{0.5}Nb coatings synthesized by various laser powers [75].

where $\Delta H_{\text{mix}}^{ij}$ is the mixing enthalpy of the binary liquid ij alloys.

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n c_i \ln c_i \quad (4)$$

where R is the universal gas constant.

$$\Delta\chi = \sqrt{\sum_{i=1}^n C_i (x_i - \bar{x})^2} \quad (5)$$

where $\bar{x} = \sum_{i=1}^n c_i x_i$, x_i being the Pauling electronegativity of i th element.

$$\text{VEC} = \sum_{i=1}^n c_i (\text{VEC})_i \quad (6)$$

where $(\text{VEC})_i$ is the valence-electron concentration of the i th element.

Furthermore, to describe the balance between the entropy of mixing and the enthalpy of mixing, another

parameter, Ω , was also brought forward [7,81], which could be expressed as follows:

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|} \quad (7)$$

where $T_m = \sum_{i=1}^n C_i(T_m)_i$, $(T_m)_i$ represents the melting point of the i th element.

Based on the existing data for HEAs, the empirical criteria for forming disordered solid-solutions in HEAs were suggested to be $-15 < \Delta H_{\text{mix}} < 5 \text{ kJ mol}^{-1}$ and $0\% < \delta < 5\%$, or $\Omega \geq 1.1$ and $\delta < 6.6\%$ [80].

Cai et al. [82] synthesized the NiCrCoTiVAl coating by laser-surface alloying. They suggested that the thermodynamic parameters, δ , ΔH_{mix} , ΔS_{mix} , and $\Delta \chi$, should be used to predict the formation of the BCC solid-solution, which are not the strict criteria. Especially when $\Delta \chi$ reached a high value ($\geq 10\%$), a BCC phase would be partially decomposed, leading to the formation of (Co, Ni)Ti₂ compound phases. Zhang et al. [83] produced a series of FeCoCrAlCuV_xNi coatings by laser-surface alloying, and found that the structures of coatings evolved from the single phase FCC for $0 \leq x \leq 0.2$ to duplex of FCC and BCC structures for $0.5 \leq x \leq 1$. They believed that the formation of a single solid-solution phase was governed by the competition outcome of δ , ΔH_{mix} , ΔS_{mix} , $\Delta \chi$, and VEC.

Generally, similar to the HEA bulks, the HEA films and coatings are composed of more than five elements, resulting in the formation of solid-solution(s), rather than intermetallic compounds. Moreover, relative to the HEA bulks prepared by arc melting and casting, the cooling rate are much higher during the preparation processes of the HEA films and coatings. Therefore, the solid-solution phase(s) or amorphous phase can be more easily produced, while the intermetallic compound can be more difficultly created due to the inhibitory effects on the elemental diffusion and nucleation of the compound.

It is worth noting that the phase transformation behavior and phase stability in nanostructured materials are different from their conventional coarse-grained counterparts [84,85]. For example, the nanostructured Fe-Ni (30 at.% Ni) and Co present the FCC phase at room temperature, while their coarse-grained counterparts present the BCC or HCP phase [86–88], respectively. Some theories have been brought forward to explain this phenomenon, including lack of nucleation sites [89], internal pressure due to particle curvature [90] and surface energy difference [91]. The grain sizes of the HEA films and coatings are generally smaller than those of their HEA bulk counterparts since their grain sizes are usually restrained by their thicknesses [92]. Especially, for the HEA films and coatings synthesized by vapor deposition methods, such as magnetron sputtering, their

grain sizes may decrease to nanoscale. For example, for the CoCrCuFeNi and Al_{2.5}CoCrCuFeNi films in Figure 4 deposited by the sputter technique, the grain sizes in the CoCrCuFeNi and Al_{2.5}CoCrCuFeNi films were found to be as low as about 40–60 and 15–30 nm, respectively. Therefore, the phase structure and stability for the HEA films and coatings are not only affected by their composition but the grain size as well, making the phase transformation behaviors of the HEA films and coatings are more complicated than those of their HEA bulk counterparts.

3.2. HEA nitride, oxide, and carbide films and coatings

Recently, the HEA nitride, oxide, carbide films and coatings have attracted more attentions due to their high hardness, high wear resistance, good oxidation and attractive physical properties [3]. Especially, the HEA nitrides prepared by reactive-magnetron sputtering have been widely investigated as a new type of protective coating materials. Since the nitrogen content in the films has a strong influence on the structure and mechanical performance of the HEA nitrides, many studies reported that the HEA nitride films and coatings deposited under the different nitrogen flow ratios (R_N) by reactive sputtering, such as TiVCrAlZr [93], AlCrMoTaTiZr [42], AlCrNbSiTiV [43], AlCrTaTiZr [94], TiVCrZrHf [95], and AlCrMnMoNiZr [96].

It was found that when depositing with the N₂ flow of 0 SCCM (standard-state cubic centimeter per minute), only one broad peak was found in these XRD patterns, suggesting that the coatings exhibited the amorphous structure. With the increase of the N₂ flow, the HEA nitride coatings with a simple FCC structure could be formed. The XRD spectra of the (AlCrTaTiZr)N [94] and (AlCrMnMoNiZr)N [96] films deposited at the different R_N s are presented in Figure 7. The similar phenomena have also been observed in the TiVCrAlZr [93], AlCrMoTaTiZr [42], AlCrNbSiTiV [43], and TiVCrZrHf [95] nitride films and coatings.

The amorphization tendency of the HEA films and coatings can be due to the high mixing entropy and large atomic size difference. Generally, the high mixing entropy enhances the mutual solubility of various elements in coatings and prevents the phase separation from occurring. Meanwhile, the large atomic size difference causes severe lattice distortion and favors the amorphous structure. The amorphous to FCC structure transition of the HEA nitride films and coatings can be attributed to the high mixing entropy effect, which enhances the mutual solubility of constituent elements and the sluggish long-range diffusion, which help retain a solid-solution structure.

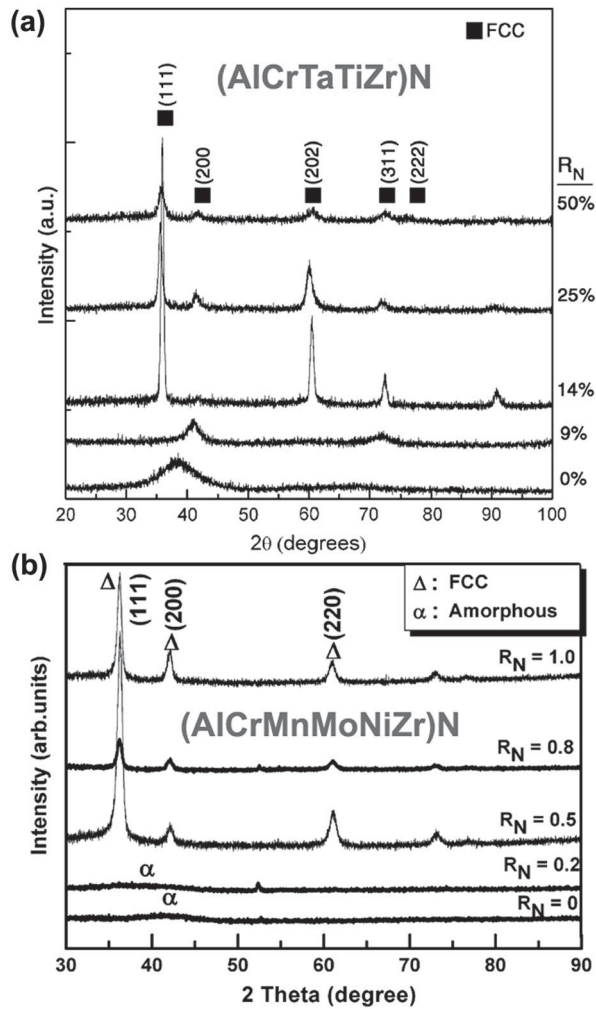


Figure 7. XRD patterns of the (a) (AlCrTaTiZr)N [94] and (b) (AlCrMnMoNiZr)N [96] films deposited at various R_N .

Besides the formation of the FCC solid-solution, Liu et al. [97] reported that the amorphous nitride films of the FeCoNiCuVZrAl HEA deposited by reactive-magnetron sputtering, which were explained by the enhanced glass-forming ability for the multicomponent alloys and the limited diffusion of the elements at the low depositing temperature. Tsai et al. [98] also reported the synthesis of the amorphous AlBCrSiTi nitride film with the high thermal stability up to 700°C for 2 h by reactive DC (direct current) magnetron sputtering. Generally, most of HEA nitride films and coatings present the FCC structure, which can be attributed to the fact that many component binary nitrides have the FCC structure, such as TiN, VN, CrN, ZrN, and HfN. Therefore, it is reasonably believed that the FCC structure dominates the crystal structure of the HEA nitride films and coatings. However, besides the strong nitride-forming elements, some non-nitride-forming elements, such as Co, Cu, Fe, Ni, or Mn included in the HEA nitride films and coatings are difficult to combine with N element and incline

to form the metallic phase, which can disturb the crystalline structure and lead to the amorphization transition. Moreover, Feng et al. [99] prepared the (ZrTaNbTiW)N films by the multi-target magnetron-sputtering deposition and nitrogen-plasma-based ion implantation (PBII). Their results showed the (ZrTaNbTiW)N nitride films were composed of a mixture of BCC and FCC structures. They attributed the formation of the BCC phase to the limited nitrogen content and the BCC structures of the constituent elements, such as Ta, Nb, and W.

Yu et al. [100] deposited the $(\text{ZnSnCuTiNb})_{1-x}\text{O}_x$ films by reactive-magnetron sputtering and found that the $(\text{ZnSnCuTiNb})_{1-x}\text{O}_x$ films were amorphous without any multi-phase structure. Huang et al. [101] deposited the AlCoCrCu_{0.5}NiFe oxide films by a radio-frequency (RF) sputtering system. It was found that the AlCoCrCu_{0.5}NiFe HEA film was amorphous, while the AlCoCrCu_{0.5}NiFe oxide films presented the HCP structure as the oxygen content in the working gas ($\text{C}_{\text{O}_2} = p_{\text{O}_2}/(p_{\text{O}_2} + p_{\text{Ar}})$) was between 10% and 50%. Tsau et al. [102] deposited the amorphous Ti_xFeCoNi, TiFeCoNiCu_x, and Al_xCrFeCoNiCu thin films by sputtering. After being oxidized during annealing, all the oxide films transformed to the FCC structure with very low electrical resistivity. Braic et al. [103] deposited the (TiAlCrNbY)C films by reactive sputtering in (Ar + CH₄) reactive atmospheres. For the film composition close to stoichiometry, a single FCC solid-solution phase with an (111) preferred orientation was detected. The films with higher carbon concentrations (69–82 at.%) exhibited an amorphous structure. The amorphous transition can be attributed to the excessive carbon concentration, which exceeds the standard stoichiometric ratio.

4. Properties

Despite that the HEA films and coatings have been investigated for only 14 years, the extraordinary mechanical, physical, and chemical properties have been already achieved, such as high hardness and elastic modulus, the superior wear resistance, corrosion and temperature resistance, as well as the appealing electrical and magnetic properties.

4.1. Mechanical behavior

4.1.1. Hardness and elastic modulus

Cladding and sputter depositions are two common techniques to fabricate the HEA films and coatings. High hardness values have been achieved among the HEA films and coatings synthesized by both techniques.

Huang et al. [104] prepared the TiVCrAlSi HEA coating on the Ti-6Al-4V alloy surface by laser cladding, which was composed of $(\text{Ti,V})_5\text{Si}_3$ and BCC phases. The microhardness of the TiVCrAlSi coating was found to be close to 1000 HV_{0.2}. Zhang et al. [105] prepared the 6FeNiCoSiCrAlTi HEA coating with a simple BCC solid-solution phase by laser cladding with the microhardness of 780 HV_{0.5}. The microstructure of the coating was mainly composed of equiaxed polygonal grains, discontinuous interdendritic segregation, and nano-precipitates. Zhang et al. [106] fabricated the CoCrNiFeAl_{1.8}Cu_{0.7}B_{0.3}Si_{0.1} HEAs by laser cladding and found that laser-cladding could effectively inhibit the boride precipitation and the laser-cladded alloy was mainly composed of a simple BCC solid solution, with a high hardness about 769 HV_{0.5}. Zhang et al. [107] synthesized the TiZrNbWMo coatings by laser cladding. The microhardness of as-clad HEA coating reached around 700 HV_{0.5}. He et al. [108] prepared the CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y coatings by laser cladding and found that the CoCrFeNiAl_{0.3}Cu_{0.7}Si_{0.1}B_{0.6} coating with a simple FCC matrix had a high hardness of 502 HV_{0.5}. The reported structures, hardness values, and preparation techniques of HEA films and coatings prepared by cladding techniques are summarized in Table 1.

Sputter deposition is another common technique to synthesize the HEA films and coatings. Li et al. [117] deposited the FeAlCuCrCoMn coatings by DC magnetron sputtering, which exhibited a single FCC solid-solution. The hardness and Young's modulus of the coatings were found to be 17.5 and 186 GPa, respectively. Feng et al. [118] fabricated the TaNbTiW films with a simple BCC structure by the combination of the multi-target magnetron sputtering and parallel synthesis method. The films had the residual stresses in the range of -0.1 to -2.63 GPa. Their hardness and modulus

achieved the values of about 5.2 and 127.2 GPa, respectively. After annealing at 500 and 700°C for 90 min in vacuum, the films revealed no phase transformation.

Since the pioneering work by Chen et al. [119], the reactive-sputtered HEA nitride films and coatings have been widely studied. Especially, the superhigh hardness over 40 GPa has been achieved in some HEA nitride films and coatings, making the HEA nitrides become a promising alternative of superhard materials. Cheng et al. [120] deposited multi-element (AlCrTaTiZr)N films on cemented-carbide and M2 steel [C: 0.8% ~ 0.9%, W: 5.5% ~ 6.75%, Mo: 4.5% ~ 5.5%, Cr: 3.8% ~ 4.4%, V: 1.75% ~ 2.2%, Si: 0.2% ~ 0.45%, Mn: 0.15% ~ 0.4%, Ni < 0.3%, Cu < 0.25%, and S < 0.03% (wt.%)] substrates by reactive-magnetron sputtering. The highest hardness (35.2 GPa) and the lowest residual compressive stress (-1.52 GPa) were achieved. Cheng et al. [42] deposited the (AlCrMoTaTiZr)N_x films by reactive-magnetron sputtering and investigated the effect of R_N on the films. They found that the film deposited at $R_N = 40\%$ exhibited the highest hardness of 40.2 GPa, as shown in Figure 8, which achieved the superhard grade (≥ 40 GPa). The main strengthening mechanisms were explained by the grain-size and solid-solution strengthening.

Liang et al. [95] synthesized the (TiVCrZrHf)N multi-component coatings with quinary metallic elements by reactive-magnetron sputtering. The influences of R_N on the compositions, structures, and mechanical properties of the coatings were investigated. By increasing the N₂ flow to 4 SCCM, the hardness and modulus reached a maximum value of 23.8 ± 0.8 and 267.3 ± 4.0 GPa, respectively. Hsieh et al. [121] prepared two AlCrNb-SiTi nitride coatings with the FCC structure by reactive-magnetron sputtering and the maximal hardnesses of 36.1 and 36.7 GPa were obtained at the different substrate biases, respectively.

Table 1. The reported structures, hardness values, and preparation techniques of HEA films and coatings prepared by cladding techniques.

Composition	Structure	Hardness	Preparation method	Ref.
CoNiCuFeCr	FCC	3.64 GPa	Plasma transferred arc cladding	[64]
CoCrFeMnNbNi	FCC + Nb-rich Laves phase	470–500 HV _{0.2}	Tungsten inert gas cladding	[66]
CoCrCuFeNi	FCC	430 HV _{0.5}	Laser cladding	[68]
TiVCrAlSi	BCC + $(\text{Ti,V})_5\text{Si}_3$	965 HV _{0.2}	Laser cladding	[74,104,109]
6FeNiCoSiCrAlTi	BCC	780 HV _{0.5}	Laser cladding	[105,110]
CoCrNiFeAl _{1.8} Cu _{0.7} B _{0.3} Si _{0.1}	BCC + Cr ₂ B	769 HV _{0.5}	Laser cladding	[106]
TiZrNbWMo	BCC + $\beta\text{-Ti}_x\text{W}_{1-x}$	700 HV _{0.5}	Laser cladding	[107]
CoCrFeNiAl _{0.3} Cu _{0.7} Si _{0.1} B _{0.6}	FCC	502 HV _{0.5}	Laser cladding	[108]
FeCoNiCrCu (with Si, Mn and Mo additions)	BCC	450 HV _{0.5}	Laser cladding	[111]
Al ₂ CrFeNiMo _x	two BCC phases	678 HV _{0.25}	Laser cladding	[112]
FeCrNiCoB _{1.25}	FCC + $(\text{Fe,Cr})_2\text{B}$	810–890 HV _{0.2}	Laser cladding	[113]
FeCoCrNiB _x	FCC + M ₃ B phase	4.47–8.48 GPa	Laser cladding	[114]
FeCoNiCrAl ₂ Si	BCC	900 HV _{0.5}	Laser cladding	[115]
FeCoCrNiAlB _{0.75}	FCC + BCC + M ₂ B	726.02 HV _{0.02}	Laser cladding	[116]

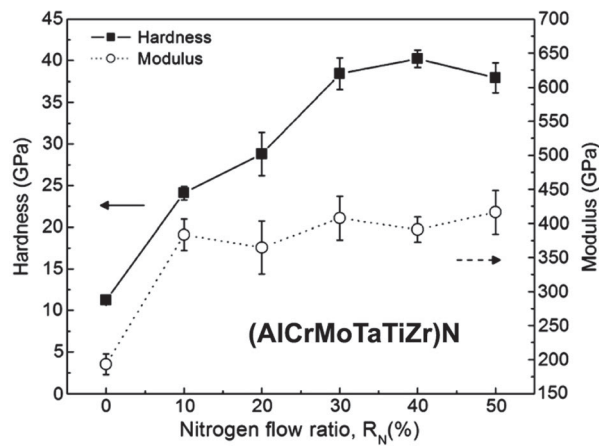


Figure 8. Hardness and modulus of the AlCrMoTaTiZr nitride films as a function of the N_2 flow ratio [42].

Lai et al. [94] prepared the AlCrTaTiZr nitride films by reactive RF-magnetron sputtering. The influences of R_N on the chemical compositions, microstructures, and mechanical properties of the deposited films had been investigated. The hardness and elastic modulus of the nitride films reached the maximum values of 32 and 368 GPa at $R_N = 14\%$. The high hardness was attributed to the solid-solution strengthening effect and dense film structure. They also [122–124] investigated the effects of the substrate temperature (100–500°C) and substrate bias (0 to –200 V) on the chemical compositions, microstructures, and mechanical properties of the (AlCrTaTiZr)N coatings prepared by reactive RF-magnetron sputtering at a constant argon and nitrogen flow. High hardness and elastic modulus around 35 and 350 GPa, respectively, were obtained, nearly independent of the substrate temperature. The highest hardness and elastic modulus of approximately 36 and 360 GPa, respectively, were obtained at a substrate bias of –150 V.

Huang et al. [43,125,126] deposited the AlCrNbSiTiV metallic and nitride films by reactive RF-unbalanced magnetron sputtering. The compositions, microstructures, and mechanical properties of the coatings deposited at different R_N s were studied. The (AlCrNbSiTiV)N coatings had a high hardness and elastic modulus of 41 and 360 GPa, respectively, which placed the coatings in the superhard grade (≥ 40 GPa). The superhardness could be attributed to an overall contribution of the formation of the saturated nitride phase, grain-size strengthening, solution hardening, and residual compressive stress.

Braic et al. [127] synthesized the (TiZrNbHfTa)N and (TiZrNbHfTa)C coatings by co-sputtering of pure metallic Ti, Zr, Nb, Hf, and Ta targets in (Ar + N_2) and (Ar + CH_4) reactive atmospheres, respectively. They

found that the highest hardness value of 33 GPa was obtained for the FCC-structured (TiZrNbHfTa)N coating, while the best wear and friction resistances were achieved for the (TiZrNbHfTa)C coating. Firstov et al. [128] reported the TiVZrNbHf nitride coatings by vacuum-arc deposition with the application of pulsed implantation. The TiVZrNbHf nitride coating was composed of a simple FCC solid-solution phase, and the high hardness ranging from 60.0 to 66.0 GPa was achieved, which is the highest hardness value reported among the existed HEA films and coatings.

The reported structure, hardness, elastic modulus, and preparation technique of HEA nitride films and coatings, along with the relevant HEA films and coatings, are summarized in Table 2. It can be seen from the Table 2 that some HEA nitride films and coatings possess the high hardness (≥ 30 GPa), while the others present the comparatively low hardness (≤ 20 GPa). Lai et al. [94,124] suggested that the low hardness of the HEA nitride can be attributed to the inclusion of non-nitride-forming elements, which will be discussed in the Section 5.1. Moreover, the nitrogen content of the nitride, the crystallite size, preferred orientation, residual stress, and densification also have significant effects on the hardness of the HEA nitride films and coatings [94,123,124].

4.1.2. Tribological behavior

As mentioned above, the HEA films and coatings can achieve high hardness, which can effectively reduce the wear rate. Generally, the tribological properties of the films and coatings are determined by their mechanical properties. Therefore, the HEA films and coatings are expected to present the excellent wear resistance, which has been verified by the numerous investigations on their tribological behaviors.

Lai et al. [122] studied the influence of the substrate bias voltage, ranging from 0 to –200 V, on the microstructural and tribological properties of the (AlCrTaTiZr)N films prepared by reactive-magnetron sputtering. With an increase of the substrate bias, the wear rate reduced while the friction coefficient almost kept constant at 0.75. The lowest wear rate of 3.65×10^{-6} mm³/Nm was obtained for the coating deposited at the bias voltage of –150 V, which could be explained by the high hardness and cohesive strength due to the enhanced ion-bombarding effect.

Zhang et al. [130] synthesized the FeCoCrAlCu coating with about 800 μ m in thickness on the Q235 steel [C: 0.12, Si: 0.04, Mn: 0.29, P: 0.02, S: 0.03, and Fe: balance (wt.%)] by laser-surface alloying. Both the wear volume and specific wear rate of the coating were an order of magnitude lower than that of the Q235 substrate under a dry-sliding condition. Cheng et al. [120]

Table 2. The reported structures, hardnesses, elastic moduli values, and preparation techniques of HEA nitride films and coatings, together with the relevant HEA films and coatings.

Composition	HEA film or coating (N at.% = 0)			HEA-nitride film or coating			Preparation method	Ref.
	Structure	Hardness (GPa)	Elastic modulus (GPa)	Structure at the maximal mechanical properties	Maximal hardness (GPa)	Maximal elastic modulus (GPa)		
(AlCrMoTaTiZr)N	Amorphous	11.2	193	FCC	40.2	420	Magnetron sputtering	[42]
(AlCrNbSiTiV)N	Amorphous	10.4	177	FCC	41	360	Unbalanced magnetron sputtering	[43]
(AlCrSiTiZr)N	Amorphous	11.5	–	FCC + Amorphous	19.6	227.5	Magnetron sputtering	[45]
(NbTiAlSiW)N	–	–	–	Amorphous	13.6	154	Magnetron sputtering	[46]
(TiHfZrVNb)N	–	–	–	FCC	44.3	384	Cathodic arc vapor	[67]
(TiVCrAlZr)N	Amorphous	8.2	128.9	FCC	11	151	Magnetron sputtering	[93]
(AlCrTaTiZr)N	Amorphous	9.3	140	FCC	32	368	Magnetron sputtering	[94]
(TiVCrZrHf)N	Amorphous	8.3 ± 1.3	104.7 ± 3.1	FCC	23.8 ± 0.8	267.3 ± 4.0	Magnetron sputtering	[95]
(AlCrMnMoNiZr)N	Amorphous	7.2	172	FCC	11.9	202	Magnetron sputtering	[96]
(FeCoNiCuVZrAl)N	Amorphous	8.6	153	Amorphous	12	166	Magnetron sputtering	[97]
(AlBCrSiTi)N	Amorphous	–	–	Amorphous	23	256.6	Magnetron sputtering	[98]
(ZrTaNbTiW)N	Amorphous	4.7	120.0	FCC + BCC	13.5	178.9	Magnetron sputtering + PBI	[99]
(FeCoNiCrCuAlMn)N	FCC + BCC	4.2	–	Amorphous	11.8	–	Magnetron sputtering	[119]
(FeCoNiCrCuAl _{0.5})N	FCC	4.4	–	Amorphous	10.4	–	Magnetron sputtering	[119]
(AlCrTaTiZr)N	Amorphous	–	–	FCC	35.2	–	Magnetron sputtering	[120]
(AlCrNbSiTi)N	–	–	–	FCC	36.7	–	Magnetron sputtering	[121]
(AlCrTaTiZr)N	–	–	–	FCC	36	360	Magnetron sputtering	[123]
(AlCrTaTiZr)N	–	–	–	FCC	35	350	Magnetron sputtering	[124]
(TiZrNbHfTa)N	FCC + compounds	5.4 ± 0	–	FCC	32.9 ± 1	–	Magnetron sputtering	[127]
(TiVZrNbHf)N	BCC	8.1	–	FCC	66.0	–	Vacuum arc deposition	[128]
(AlCrTaTiZrSi)N	–	–	–	FCC	30.2	258	Magnetron sputtering	[129]

investigated the influence of the interlayer thickness on the tribological properties of the (AlCrTaTiZr)N films deposited by reactive-magnetron sputtering. They found that the optimal interlayer thickness was 100–200 nm for the 1 μ m-thick (AlCrTaTiZr)N film. The friction coefficient and wear rate were 0.82 and 4.9×10^{-6} mm³/Nm, respectively.

Jiang et al. [75] fabricated the CoFeNi₂V_{0.5}Nb_{0.75} and CoFeNi₂V_{0.5}Nb coatings by laser cladding on the 304 stainless steel substrate. Compared with the 304 steel substrate, the wear resistance of the coatings had been greatly improved, attributing to the combination of the hard Fe₂Nb-type Laves phase and ductile FCC solid-solution matrix. The Fe₂Nb type Laves phase played a dominant role in resisting the abrasive wear, while the FCC solid-solution phase helped avoid brittle fracture. Huo et al. [66] synthesized the CoCrFeMnNbNi coating on the AISI 304 steel by tungsten-inert-gas cladding, which consisted of the FCC solid-solution and Nb-rich Laves phase. The coating presented the excellent wear resistance under the condition of dry-sliding wear, which was due to the fact that a hard Laves phase resisted destructive action during sliding and protected the surface against severe plastic deformation, and the tough FCC phase protected the surface against the brittle fracture.

Tian et al. [58] prepared the AlCoCrFeNiTi coating by APS, which was composed of the BCC matrix, minor FCC, and ordered BCC solid-solution phases. The wear behavior of the AlCoCrFeNiTi coating changed

significantly with the increase in the wear temperature. At 25°C, the volume wear rate of the coating was $(0.77 \pm 0.019) \times 10^{-4}$ mm³/Nm, which was much lower than those of the 316 stainless steel and conventional flame-sprayed NiCrBSi coating. As the temperature rose to 500°C, the coating suffered more severe adhesive wear, and the wear rate increased to $(0.93 \pm 0.029) \times 10^{-4}$ mm³/Nm. However, the wear resistance of AlCoCrFeNiTi coating was still better than that of the laser-cladded NiCrBSi coating at the same temperature.

Wu et al. [112] synthesized a series of Al₂CrFeNiMo_x ($x = 0$ to 2.0 at.%) coatings on the stainless steel by laser cladding. Compared with the stainless steel, the wear resistance of the coatings had been greatly improved. The wear mass loss of the Al₂CrFeNiMo coating was 9.8 mg, which was much less than that of the substrate (18.9 mg). Cheng et al. [62] fabricated the TiC-TiB₂-reinforced CoCrCuFeNi(Ti,B₄C)_x (x in molar ratio, $0.1 \leq x \leq 0.5$) coatings by the plasma-transferred arc-cladding process. As the x content increased, the hardness (H), elastic properties, H/E ratio (E is the elastic modulus), and H³/E² of the coatings were gradually enhanced. The best wear resistance was obtained for the CoCrCuFeNi(Ti,B₄C)_{0.5} coating.

Huang et al. [109] prepared the TiVCrAlSi coating by laser cladding on the Ti-6Al-4V alloy. They found that the TiVCrAlSi coating was composed of precipitates of (Ti,V)₅Si₃ dispersed in a BCC matrix, which greatly

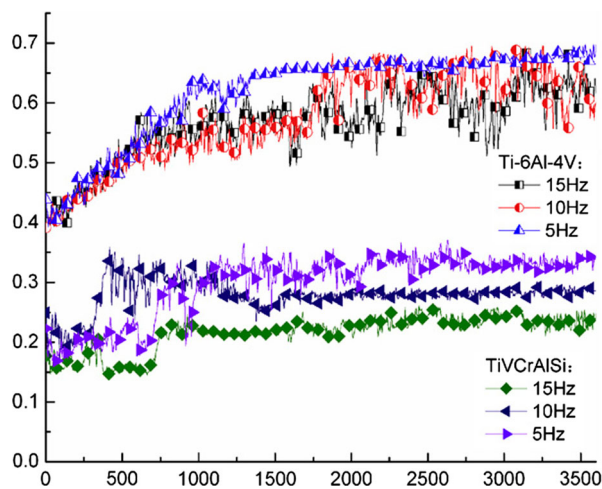


Figure 9. Variation of friction coefficient vs. test time for the laser-cladded TiVCrAlSi coating and the Ti-6Al-4V alloy under different frequencies during the dry-sliding wear test [109].

improved the wear resistance of Ti-6Al-4V during the dry sliding wear tests. The friction coefficients of the TiVCrAlSi coating and the Ti-6Al-4V alloy under different frequencies during the dry-sliding wear test were presented in Figure 9. The enhancement of the wear resistance was explained by the high hardness and the presence of the hard silicide phase dispersed in a relatively ductile BCC matrix, which allowed the sliding wear to occur in the mild oxidative regime for a wide range of testing conditions.

4.2. Corrosion resistance

Previous studies show that the HEAs can present the superior corrosion resistance [33,131]. Owing to the high-entropy effect and the ‘rapid quenching’ effect during the preparation processes, the HEA films and coatings tend to form a single FCC or BCC solid-solution phase or amorphous phase with the more homogeneous microstructure than their bulk counterparts, which contributes to the improvement of the corrosion resistance. Additionally, the incorporation of some elements, such as Cr, Ni, Co, and Cu, can also enhance the corrosion resistance of the HEA films and coatings.

Hsueh et al. [45] studied the effects of R_N and substrate bias on the corrosion properties of the (AlCrSiTiZr)N films deposited by DC reactive-magnetron sputtering. Under the condition of no applied substrate bias, (AlCrSiTiZr)N films deposited at $R_N = 30\%$ gave the best corrosion resistance. The substrate bias of -100 V effectively improved the corrosion resistance of the amorphous film of (AlCrSiTiZr)N, which could be attributed to the densification effect and compressive stress of the film, resulting from the substrate bias. Zhang et al. [111] compared the

corrosion resistance of the FeCoNiCrCu coating with Si, Mn, and Mo additions and Ni60 [C: 0.9, Fe: 4.2, Si: 4.1, Cr: 16.3, B: 3, and Ni: balance (wt.%)] coating. The results indicated that the FeCoNiCrCu coating was easier to be passivated and had higher corrosion resistance in the H_2SO_4 solution, because the alloying elements of Co, Ni, Cr, and Cu had good corrosion resistance, and the protective film could be easily formed on the surface of the coating.

Li et al. [65] produced the AlCoCrFeNi coatings on the AISI 1045 carbon steel (0.45 weight percent carbon) by the electrospark deposition. They found that unlike the cast HEA material, no obvious Cr-rich interdendritic segregation and nano-sized precipitate were found to distribute within the dendrites of the HEA coating. The corrosion current of the HEA-coated specimen was significantly lower than those for the 1045 steel and the cast HEA material, as indicated in Figure 10, which was attributed to the coating specimen having a relatively-high Cr-oxide and Al-oxide contents at the surface. Furthermore, the absence of the Cr-rich interdendritic phase and second-phase precipitation resulted in a more uniform microstructure than the cast specimen. Zhang et al. [113] prepared the FeCrNiCoB_x coatings by laser cladding. They found that the coatings comprised an FCC solid-solution with boride precipitation. When $0.5 \leq x \leq 1.0$, the hardness and corrosion resistance of the coatings were enhanced by increasing the B content. As x approached 1.25, the borides changed from the orthorhombic (Cr,Fe)₂B to tetragonal (Fe, Cr)₂B, which deteriorated the corrosion resistance of the coatings. All of the coatings showed better corrosion resistance than the ASTM 304L stainless steel [C: ≤ 0.03 , Si: ≤ 1.00 , P: ≤ 0.035 , Ni: 9.00–13.00, Mn: ≤ 2.00 , S: ≤ 0.03 , Cr: 18.00–20.00, and Fe: balance (wt.%)].

Qiu et al. [53] prepared the Al₂CrFeNiCoCuTi_x coatings by laser cladding, which consisted of the FCC, BCC, and Laves phases. With increasing the Ti content, the corrosion resistance of Al₂CrFeNiCoCuTi_x coatings was enhanced in the 0.5 mol/L HNO_3 solution. Compared with the Q235 steel [C: 0.16, Si: 0.22, Mn: 0.35, P: 0.021, S: 0.024, and Fe: balance (wt.%)], the free-corrosion current density of Al₂CrFeNiCoCuTi_x coatings was reduced by 1–2 orders of magnitude. Dou et al. [132] deposited the FeAlCoCuNiV coatings with different thicknesses by DC magnetron sputtering, which exhibited a single FCC solid-solution. All coatings exhibited better electrochemical corrosion resistance than the 201 stainless steel in acidic alkali and salt corrosion media. They attributed the superior corrosion resistance of the coatings to no segregation in the simple FCC structures and more corrosion resistance elements (such as, Co, Cr, and Ni) in the coating.

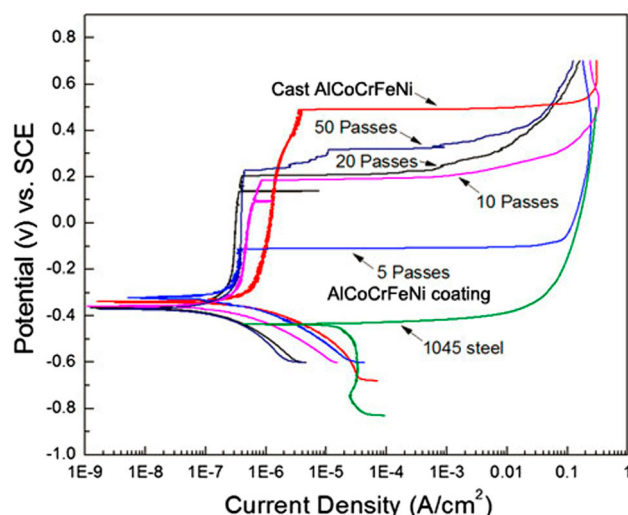


Figure 10. Experimental-polarization curves of the AISI 1045 carbon steel substrate, cast AlCoCrFeNi HEA, and AlCoCrFeNi HEA coatings prepared by electrospray deposition with different passes [65].

4.3. Temperature and oxidation resistance

The existing experimental results have indicated that like the HEA bulk materials, the HEA films and coatings can also present the excellent temperature and oxidation resistance, exhibiting the high phase stability, excellent oxidation resistance, and high mechanical properties at elevated temperatures. The high temperature and oxidation resistance can be attributed to the high mixing entropy of the constituent elements, the lower diffusion coefficients and re-distribution of solute elements during the annealing treatment, relative to the conventional films and coatings. Furthermore, the incorporation of Al, Cr, Ta, and Zr can also improve the oxidation resistance due to the formation of the dense oxide films.

Huang et al. [126] deposited the (AlCrNbSiTiV)N superhard film by reactive sputtering and found that the film presented an excellent thermal stability in both its nanostructure and superhard feature, and retained a simple FCC structure even when annealed at 1000°C for 5 h, which could be explained by the high entropy effect and the inhibition of grain coarsening resulting from severe lattice distortion. Cheng et al. [42] deposited the FCC-structured (AlCrMoTaTiZr)N films. After annealing at 1000°C for 10 h, the nitride films retained a single FCC structure, demonstrating that the FCC solid-solution was thermodynamically stable at least up to 1000°C, which was due to the high mixing entropy effect. Feng et al. [118] prepared a series of TaNbTiW alloy films by the combination of the multi-target magnetron sputtering and parallel synthesis methods. They found that after being annealed at 500 and 700°C for 90 min in vacuum,

respectively, the films revealed no phase transformation. By annealing at 900°C, only a few oxides peaks came out. The better oxidation resistance could be attributed to the more positive mixing enthalpy of W-O and more compact structure resulting from the additions of Ti and W.

Dolique et al. [72] studied the thermal stability of AlCoCrCuFeNi HEA thin films by the in-situ XRD analysis at temperatures in the range 110–810°C. They found that the AlCoCrCuFeNi films were stable until 510°C, which were inferior to their bulk counterpart (until 800°C) in the thermal stability. Sheng et al. [46] prepared the NbTiAlSiN and NbTiAlSiWN films by the magnetron-sputtering method. All the as-deposited films presented an amorphous structure, which remained stable at 700°C for over 24 h. After the heat treatment at 1000°C, the films began to crystalize, after which the NbTiAlSiN films exhibited an FCC structure, while the NbTiAlSiW metallic films showed a BCC structure and then transited into an FCC structure composed of nanoscaled particles with increasing nitrogen flow rate. Zhang et al. [107] synthesized the TiZrNbWMo coatings by laser cladding and found that the coatings showed the high phase stability and softening resistance. The microhardness of as-clad coating reached up to 700 HV_{0.5}, which remarkably increased after heat treatment and reached the maximum of about 1300 HV_{0.5} at 800°C. The hardening was attributed to the solid solution strengthening of BCC matrix and the enhanced fraction of β -Ti_xW_{1-x} precipitation.

Zhang et al. [68] prepared the CoCrCuFeNi coating with an FCC structure onto a Q235 steel by the laser-cladding method. The coating possessed an excellent thermal stability, and no phase transformations occurred up to 1000°C (0.86T_m), and the dendritic morphology of the as-solidified microstructure could be kept to higher than 750°C (0.7T_m), as shown in Figure 11. Although the annealing-induced relaxation of the lattice strain caused a moderate decrease of hardness, a high level of hardness could be retained even after annealing at 1000°C for 5 h. They also [111] investigated the influences of Si (1.2 mol.%), Mn (1.2 mol.%), and Mo (2.8 mol.%) additions on the laser-cladded FeCoNiCrCu coating after annealing at temperatures ranging from 550 to 950°C for 5 h. They found that the microhardness of the coating was almost no change when the coatings were annealed below 750°C, which was attributed to the slower diffusion coefficients and re-distribution of solute elements during annealing.

Wang et al. [57] studied the thermal stability of the thermal-sprayed Ni_xCo_{0.6}Fe_{0.2}Cr_ySi_zAlTi_{0.2} coating. The results showed that even after the heat treatment at 1100°C for 10 h, the high hardness (935 HV) could be obtained, and the coating presented the excellent

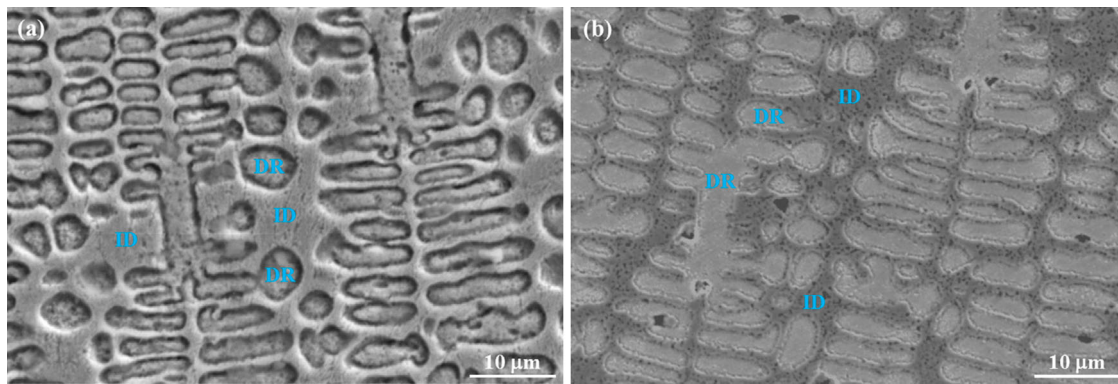


Figure 11. Secondary-electron images for (a) as-solidified and (b) 750°C/5 h annealed CoCrCuFeNi coatings (DR and ID stand for the dendritic and inter-dendritic regions, respectively) [68].

coarsening resistance, which could be attributed to the nanosized Cr_3Si and other unidentified precipitates. Zhang et al. [110] fabricated the 6FeNiCoCrAlTiSi coatings by laser cladding. The coating had a simple BCC solid-solution phase with high microhardness and good resistance to softening. After annealing below 750°C, the coating showed the high thermal stability, the electrical resistivity decreased slightly, and the microhardness almost remained unchanged. After annealing above 750°C, the microhardness of the coating slowly decreased with the decomposition of the BCC solid-solution. The good resistance to softening resulted from the fact that the high-mixing entropy in the multiprincipal elements made the diffusion coefficients and re-distribution of solute elements much slower than those in the conventional coatings.

The oxidation resistance is the core issue of the temperature resistance for the films and coatings at high temperatures. Huang et al. [56] produced the $\text{AlCrFeMo}_{0.5}\text{NiSiTi}$ and $\text{AlCoCrFeMo}_{0.5}\text{NiSiTi}$ coatings by thermal spray and found that both coatings exhibited the good oxidation resistance, which could be mainly attributed to the formation of a dense aluminum oxide layer on the top surface. The weight gains of $\text{AlCrFeMo}_{0.5}\text{NiSiTi}$ and $\text{AlCoCrFeMo}_{0.5}\text{NiSiTi}$ coatings maintained at 1100°C for 150 h were about 8.2 and 9.2 mg/cm^2 , respectively, which were comparable with that of commercial oxidation-resistant NiCrAlY alloys. Huang et al. [74] studied the thermal stability and oxidation resistance of laser-cladded TiVCrAlSi coatings on Ti-6Al-4V alloy, which was composed of $(\text{Ti},\text{V})_5\text{Si}_3$ and a BCC solid-solution. The oxidation testing of the coating and Ti-6Al-4V alloy showed that the laser-cladded TiVCrAlSi coating could effectively improve the oxidation resistance of Ti-6Al-4V at 800°C in air. The formation of a thin and adherent mixed scale consisting of SiO_2 , Cr_2O_3 , TiO_2 , Al_2O_3 and a small amount of V_2O_5

was supposed to be responsible for the improvement of the oxidation resistance. Cai et al. [133] synthesized a Ni-Cr-Co-Ti-V-Al coating by laser surface alloying on a Ti-6Al-4V substrate. After remaining at 900°C for 8 h, the constituent phases remained unchanged. The thermoanalysis results showed that the coating was stable below 1005°C. The oxidation resistance of this HEA coating could be due to the existence of NiO and the alloying elements Al, Cr, and Co.

Shen et al. [134] studied the oxidation resistance of $(\text{Al}_{0.34}\text{Cr}_{0.22}\text{Nb}_{0.11}\text{Si}_{0.11}\text{Ti}_{0.22})_{50}\text{Ni}_{50}$ coating prepared by reactive magnetron sputtering. The thickness of the oxide layer on the coating surface was 290 nm after 50 h annealing at 900°C. The weight gain after thermal ramping to 1300°C was merely 0.015 mg/cm^2 . Such oxidation resistance was superior to other nitride coatings, which could be seen in Figure 12. The superior oxidation resistance was owing to the protection of the dense Al_2O_3 layer and inner Si-rich amorphous network. Tsai et al. [135] prepared the $(\text{AlCrMoTaTi})\text{-Si}_x\text{-N}$ coatings through a reactive magnetron sputtering system and found that the addition of Si into $(\text{AlCrMoTaTi})\text{N}$ coatings significantly improved the oxidation resistance. A Si content of 7.51 at.% could decrease the oxide layer thickness from 1590 nm to approximately 202 nm after oxidation at 900°C for 2 h. The good anti-oxidation performance could be attributed to the protective $\alpha\text{-Al}_2\text{O}_3$ surface layer and $\alpha\text{-SiO}_2$ phase that existed in the inner oxide layer.

4.4. Physical characteristics

The physical properties of the HEA bulk materials have been reviewed by Tsai et al. [31], from which the unique magnetic, electrical, and thermal properties have been presented. Especially, the extremely low-temperature coefficient of resistance (TCR) and favorable soft magnetic properties have been illuminated in the HEA bulk

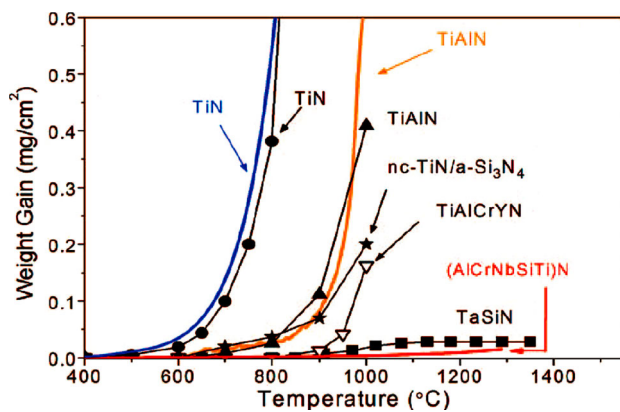


Figure 12. Thermo-gravimetric oxidation rate measurements of TiN, TiAlN, and $(\text{Al}_{0.34}\text{Cr}_{0.22}\text{Nb}_{0.11}\text{Si}_{0.11}\text{Ti}_{0.22})_{50}\text{N}_{50}$ coatings in comparison to other coating systems [134].

materials. As for the HEA films and coatings, the reports on their physical behaviors are comparatively limited. However, the literatures still exhibit the extraordinary electrical and magnetic properties.

Cheng et al. [47] deposited the amorphous BNbTa-TiZr thin films by magnetron sputtering, and the high electrical resistivity of $246 \mu\Omega\text{-cm}$ was obtained. Lin et al. [136] prepared the NiCrSiAlTa thin films by direct-current magnetron co-sputtering. The NiCrSiAlTa film deposited at 100 W and annealed at 300°C exhibited the higher resistivity of $2215 \mu\Omega\text{-cm}$ with $-10 \text{ ppm}/^\circ\text{C}$ of TCR. The observed high electrical resistance of high-entropy thin films could be attributed to several factors [136]. First, the severe lattice distortion increases the degree of electron scattering by lattice. Second, there are inherent highly-concentrated point defects in HEA films and coatings. Third, a large number of grain boundaries exist due to the nano-grained structure, which act as scattering centers.

Compared with the HEA films, their oxide films present the different electrical performance. Tsau et al. [102] found the low electrical resistivity of TiFeCoNi, TiFeCoNiCu, and AlCrFeCoNiCu oxide thin films. Huang et al. [101] deposited the oxide films of AlCoCrCu_{0.5}NiFe by a RF-sputtering system. They found that the resistivity of the oxide film decreased with the increase of the oxygen content, which could be attributed to the more metal vacancies generated when oxygen in the oxide was a surplus. The resistivity of the oxide film increased with the annealing temperature, which was mainly relevant to its lower density. Yu et al. [137] deposited the (TiVCrZrTa)-based oxide and oxynitride films by reactive-magnetron sputtering, respectively. The $(\text{TiVCrZrTa})_{1-x}\text{O}_x$ film was found as insulators, with an indirect band gap of 2.38 eV, while

the $(\text{TiVCrZrTa})_{1-x-y}\text{N}_y\text{O}_x$ film was an n-type semiconductor, with an indirect band gap of 1.95 eV, and a carrier concentration (N) and conductivity (σ) of $1.01 \times 10^{19} \text{ cm}^{-3}$ and $2.75 \times 10^{-2} (\Omega \text{ cm})^{-1}$, due to an increased number of the valence electrons after the introduction of nitrogen atoms. Yu et al. [100] investigated the effect of the oxygen content on the structures and optoelectronic properties of the $(\text{ZnSnCuTiNb})_{1-x}\text{O}_x$ films. The film with the 50.3 at.% oxygen content was an opaque conductive material. When the oxygen contents ranged between 51.6 at.% and 56 at.%, the film was an optoelectronic semiconductor. As the oxygen content was 59.2 at.%, the film became transparent and insulating.

Lin et al. [48] fabricated the FeCoNiCrAlSi thin films and reported the excellent soft magnetic properties. The film had a simple BCC structure under as-deposited and post-annealing conditions at 400°C and below. The optimized magnetic properties of thin films obtained by field-annealing at 200°C for 1 h were the M_s (saturation magnetization) of $9.13 \times 10^5 \text{ A/m}$, H_c (coercivity at the hard axis) of 79.6 A/m, and H_k (out-of-plane uniaxial anisotropy field) of $1.59 \times 10^3 \text{ A/m}$, respectively, as shown in Figure 13. Qiu et al. [53] prepared the Al₂CrFeNiCoCu HEA coating by laser cladding and also found that the coating, with the small coercive force, was a good soft magnetic material. Yao et al. [40] prepared the BiFeCoNiMn HEA films by electrodeposition and found that the as-deposited films showed the soft magnetic behavior, while the annealed films exhibited the hard magnetic properties.

Due to the limited literatures, our knowledge on the physical properties of HEA films is very preliminary. The mechanisms governing the relationship among compositions, structures, and physical properties are still unclear. Therefore, more investigations in this field are highly

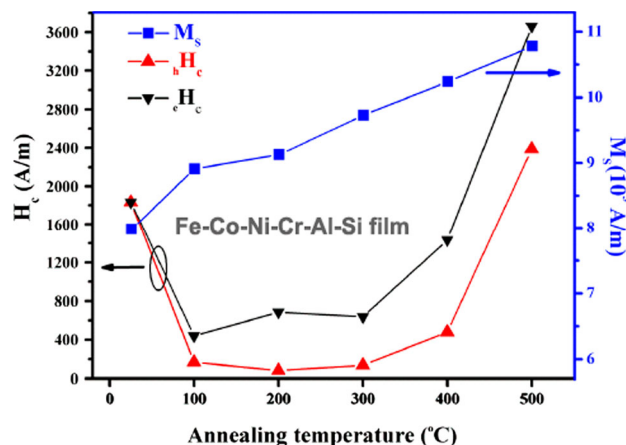


Figure 13. The saturation magnetization (M_s), coercivity at the hard axis (H_c), and coercivity at the easy axis (H_k) of the Fe-Co-Ni-Cr-Al-Si thin film versus field-temperature [48].

needed, which is expected to develop new types of HEA films with the unique physical properties and reveal the intrinsic mechanisms behind them.

4.5. Diffusion retardation and biocompatible properties

The HEA nitride films and coatings have been attempted as diffusion barrier materials. Chang et al. [138] synthesized an ultrathin (AlCrTaTiZr)N film of only 10 nm in thickness as a diffusion barrier layer for Cu interconnects and suggested that the (AlCrTaTiZr)N film was constructed of nanocrystallites embedded in an amorphous matrix. At an extremely high temperature of 900°C, the Si/(AlCrTaTiZr)N/Cu film stack remained thermally stable. The nanocomposite structure and severe lattice distortions were expected as the dominant factors for the superior diffusion resistance of the (AlCrTaTiZr)N film. Chang et al. [139] developed a (AlCrTaTiZr)N/(AlCrTaTiZr)N_{0.7} bilayer structure of about 15 nm in thickness as a diffusion barrier material for Cu interconnects. At a high temperature of 900°C, the bilayer structure remained thermally stable. Neither interdiffusion of Si and Cu through the bilayer structure occurred nor did silicides form, indicating an excellent diffusion resistance of the bilayer structure.

Chang et al. [140] examined the diffusion resistance of six thin solid-solution alloy films (a thickness of about 7 nm), from unitary Ti to senary TiTaCrZrAlRu and characterized the failures of six film barriers against the interdiffusion of Cu and Si. Their experimental results indicated that, with more elements incorporated, the failure temperature of the barriers increased from 550 to 900°C. The activation energy of Cu diffusion through the alloy barriers was determined to increase from 110 to 163 kJ/mol. Mechanistic analyses suggested that, structurally, severe lattice distortion strains and a high packing density caused by different atom sizes, and, thermodynamically, a high cohesive energy, were believed to be the dominant factors of suppressed interdiffusion kinetics through the multi-component barrier materials.

Chang et al. [141] prepared the nitride barriers with different numbers of metallic elements, from unitary TiN to senary high-entropy (TiTaCrZrAlRu)N (with the same FCC structure and a thickness of 5 nm) and found that with more components incorporated, the failure temperature of the nitrides was found to markedly increase from 550 to 900°C, and the activation energy of Cu diffusion was effectively raised from 107 to 161 kJ/mol. Severe lattice distortions and random cohesions were suggested as the dominant factors for the improved diffusion-resistant ability of the HEA nitrides. Chang et al. [142] synthesized the AlCrTaTiZr and 20 at.% Ru-incorporated

AlCrTaTiZrRu films as diffusion barrier layers to inhibit Cu diffusion. Under annealing at 700°C, the interdiffusion of Cu and Si through the AlCrTaTiZr layer of 50 nm in thickness occurred. In comparison, at 800°C, the interdiffusion was still effectively retarded by the Ru-incorporated AlCrTaTiZrRu layer of only 5 nm in thickness. They attributed the high diffusion resistance of the Ru-incorporated barrier layer to the large lattice distortions caused by the addition of extra-large-sized Ru atoms.

Several groups also reported that the HEA films and coatings for biomedical applications. Braic et al. [143] deposited the (TiZrNbHfTa)N and (TiZrNbHfTa)C coatings on Ti-6Al-4V alloy by co-sputtering technique, which consisted of only FCC solid solutions. Biocompatibility tests showed that the investigated coatings did not induce any cytotoxic response by osteoblasts (24 and 72 h), and good morphology of the attached cells was observed. Cell viability analysis showed a very high ratio of live cells compared with the dead cells. Vladescu et al. [144] examined the possibility to improve the biocompatibility of the (TiZrNbTaHf)C through the replacement of either Ti or Ta by Si, and found that the replacement of either Ti or Ta by Si in the (TiZrNbTaHf)C coating led to an enhanced surface electrical charge, as well as to superior biocompatible properties. The (TiZrNbSiHf)C coating, with low electrical potential and the high work function, exhibited the best biocompatible properties.

5. Discussion

5.1. Strong and non-nitride-forming elements—design criteria of HEA nitrides with high hardness

From the aforementioned reports, the HEA nitride films and coatings have attracted an increasing number of attentions due to their high hardness, high wear resistance, and excellent corrosion resistance. Especially, the superhigh hardness (≥ 40 GPa) has been achieved in several HEA nitride film systems [42,43,128], making the HEA nitride becomes an alternative of superhard material. It can be seen from Table 2 that some HEA nitride films with a single FCC structure possess the high hardness (≥ 30 GPa), while the other films with a mixture of BCC and FCC structures or other structures present the comparatively low hardness (≤ 20 GPa). Obviously, the hardness of the HEA nitride has a close correlation with its structure.

All the elements included in the HEA nitride can be divided into the strong nitride-forming elements (such as Al, Cr, Nb, Ti, V, Zr, Hf, Mo, and Ta) and non-nitride-forming elements (such as Co, Cu, Fe, Ni, and

Mn). Lai et al. [94,124] suggested that the low hardness of the HEA nitride can be attributed to the addition of non-nitride-forming elements. As for the HEA nitrides with the hardness over 40 GPa, such as (AlCrNbSiTiV)N [43], (AlCrMoTaTiZr)N [42], (TiVZrNbHf)N [128] and (TiHfZrVNb)N [67] systems, it is easy to find that these HEA nitrides are composed of the strong nitride elements and exhibit a single FCC structure. Actually, for the strong nitride-forming elements, their binary and ternary nitrides, such as TiN, ZrN, CrN, TiAlN, and CrAlN, have high melting points, hardness values, and wear resistance due to their strong bonding, which have already been extensively used as the protective-coating materials in industry [145–147]. Therefore, it is reasonable to believe that the HEA nitrides consisted of the strong nitride elements are more easily to achieve the high hardness.

With respect to the existence form of non-nitride-forming elements within the HEA nitride, Ren et al. [96] believed that the non-nitride-forming elements could be incorporated in the FCC crystalline lattice of MeN (Me: the strong-nitride forming elements) and expected to randomly distribute according to the statistic occupancy probability. Lai et al. [94] discussed that even for

the (AlCrTaTiZr)N film entirely consisted of the strong nitride forming elements, the nitrides of Al, Ta, Ti, and Zr had much greater negative heats of formation than that of Cr. Therefore, under a low nitrogen flow ratio, the nitrogen would preferentially combine to Al, Ta, Ti, and Zr atoms rather than Cr, leading to the formation of the Cr-rich metallic phase.

In fact, the ternary nitride films containing both strong and non-nitride-forming elements have been investigated, such as TiNiN [148], CrCuN [149], and ZrYN [150], in which the non-nitride-forming elements, Ni, Cu, and Y, could encapsulate the TiN, CrN, and ZrN nanocrystallites as an interfacial phase, resulting in the formation of the nanocomposite structure. The cross-sectional high-resolution TEM (HRTEM) images of TiN/Ni film are shown in Figure 14, from which it can be observed that the TiN nanocrystallites marked by the red A, B, C, D, E, F, G, and H are encapsulated with the Ni interfacial phase denoted by the blue a, b, c, d, e, f, g and h. The formation of the nanocomposite structure can lead to high hardness at the specific composition. In the HEA nitride, however, the non-nitride-forming elements may not be segregated as an interfacial phase, but

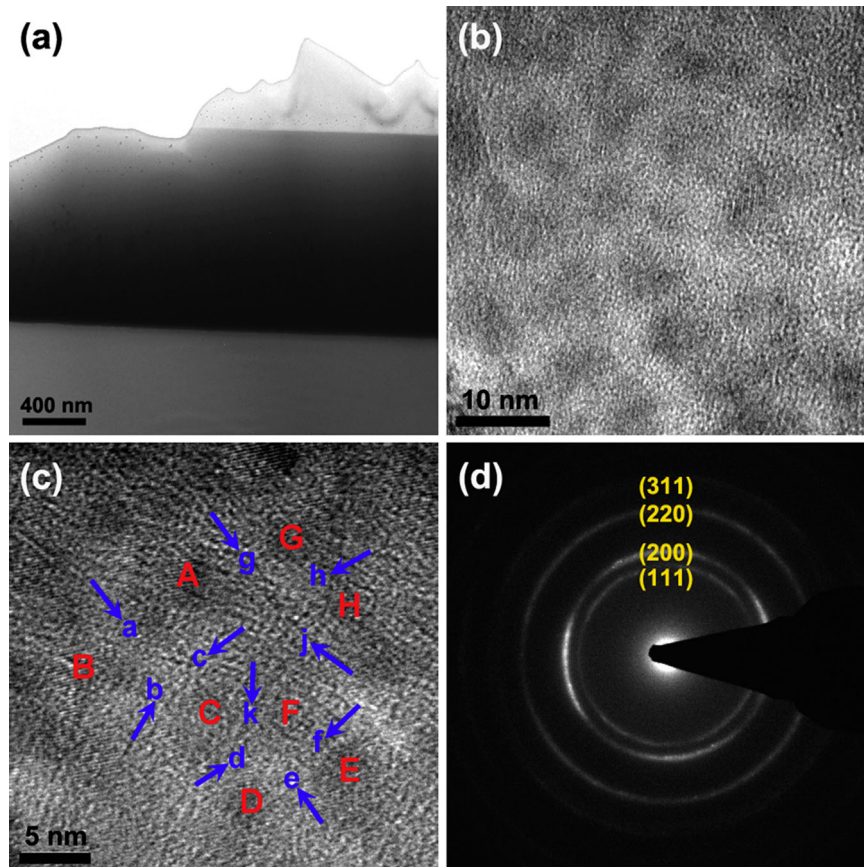


Figure 14. Cross-sectional HRTEM images of the TiN/Ni nanocomposite film (Ni:Ti = 5:20): (a) low-magnification, (b) medium-magnification, (c) high-magnification, and (d) selected-area-diffraction patterns [148].

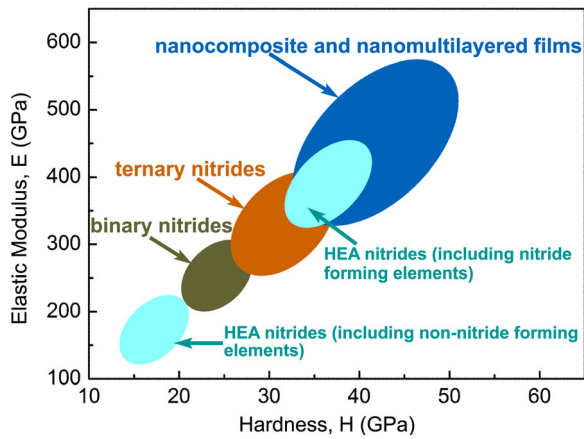


Figure 15. Schematic illustration showing elastic modulus as a function of hardness for the HEA nitrides in relation to other hard film systems.

highly incorporated in the FCC crystalline lattice of MeN due to the high mixing-entropy effect, which promotes the mutual solubility of constituent elements. Therefore, the nanocomposite structure may not form, and thus, the strengthening effect resulting from it may not emerge in the HEA nitrides. The nanocomposite structure will be further discussed in the Section 5.4 by taking the Si-containing HEA nitride as an example.

The elastic modulus as a function of hardness for the HEA nitrides in relation to other hard film systems can be schematically illustrated in Figure 15. Based on the existing literatures, the HEA nitride films, including non-nitride-forming elements, present the low mechanical properties, even lower than the binary nitrides, such as TiN, CrN, and ZrN, while those composed of the strong nitride-forming elements can achieve the high hardness and elastic modulus, higher than those of the ternary nitrides and even comparable with nanomultilayered or nanocomposite films. Therefore, the design of the HEA nitride with the expecting high hardness should avoid the inclusion of the high quantity and content of non-nitride-forming elements. Moreover, besides the formation of Me-N bonding in a stoichiometric ratio, Lai et al. [94,123,124] suggested that the crystallite size, preferred orientation, residual stress, and densification also have the important influence on the hardness of the HEA nitride films and coatings. The small crystallite size, a (111) preferred orientation in the FCC structure, the comparatively high residual stress, and the densification of the film can all contribute to the improvement of the high hardness.

5.2. Reasons for the high wear resistance

From the above-mentioned reports in Section 4.1.2, it can be seen that the HEA films and coatings can

exhibit the excellent wear resistance. Their attractive wear resistance can be attributed to the following four possible reasons, which are more easily present in the HEA films and coatings than the conventional films and coatings. First, some HEA films and coatings, especially the HEA nitride films, have the extremely high mechanical properties. According to Table 2, many HEA nitride films possess the high hardness over 30 GPa. For the (AlCrNbSiTiV)N [43], (AlCrMoTaTiZr)N [42], (TiVZrNbHf)N [128], and (TiHfZrVNb)N [67] films, their hardness values are reported to be above 40 GPa. The mechanical properties of the films basically determine its tribological properties. Especially, the higher hardness is more resistant to plastic deformation under certain applied loads. According to Leyland [151], the tribological properties of the coatings could be evaluated by the value of H/E and H^3/E^2 (H and E represent the hardness and elastic modulus, respectively.), which presented the long elastic strain to failure and the contact yield pressure in a rigid ball on the elastic/plastic plate contact condition, respectively. Therefore, high hardness can bring the appealing wear resistance of the HEA films and coatings.

Second, the mixture structures of solid-solution(s) and intermetallic compound(s) in the HEA films and coatings are beneficial to the improvement of the tribological behavior. For example, Jiang et al. [75] fabricated the $\text{CoFeNi}_2\text{V}_{0.5}\text{Nb}_{0.75}$ and $\text{CoFeNi}_2\text{V}_{0.5}\text{Nb}$ coatings with the high wear resistance consisted of FCC and Fe_2Nb -type Laves phase. Huo et al. [66] also reported the excellent wear behavior of the CoCrFeMnNbNi coating under the condition of dry sliding wear, which was composed of the FCC solid-solution and Nb-rich Laves phase. In the combined structures of solid-solution(s) and intermetallic compound(s), the ductile solid-solution matrix can help protect the surface against the brittle fracture, while the hard intermetallic compound phase can effectively resist abrasive wear and protect the surface against severe plastic deformation. The jointed effects of solid-solution(s) and intermetallic compound(s) can remarkably enhance the wear resistance of the HEA films and coatings.

Third, the compressive residual stress generated by some preparation process for the HEA films and coatings can also contribute to the improved wear resistance. Lai et al. [122] studied the influence of the substrate bias voltage on the tribological properties of the (AlCrTaTiZr)N films prepared by reactive-magnetron sputtering. The lowest wear rate was obtained for the films deposited at the bias voltage of -150 V, which could be attributed to the high compressive residual stress by the application of the substrate bias. The microcrack is generally produced by the tensile stress, which can be effectively restrained by the residual compressive stress within the

coating. Thus, the resistance of crack formation and growth can be enhanced by the compressive residual stress.

Fourth, the inclusion of some elements, such as Mo or W, can reduce the coefficient of friction and the wear rate of the films. Cheng et al. [42] synthesized the (AlCr-MoTaTiZr)N films by reactive RF-magnetron sputtering and attributed the excellent wear resistance to their high hardness and the addition of Mo, which formed the lubricious MoO_3 during the sliding process. Since the HEA films and coatings consist of more than six elements, it is more likely to contain some lubricious elements. These elements or their compounds can help decrease the friction resistance between the sliding components, which also makes the HEA films and coatings exhibit superior wear resistance.

It is worth noting that the high wear resistance of HEA films and coatings cannot be attributed to one reason alone, but the combination of some reasons. The above four possible reasons can be jointly responsible for the excellent wear resistance of the HEA films and coatings. It is suggested that the above aspects should be considered when designing the new HEA films and coatings with the excellent wear resistance. Moreover, it can be seen that the four mechanisms can also exist in the conventional wear-resistant films and coatings. However, it is believed that, relative to the conventional films and coatings, these four mechanisms can more easily exist in the HEA films and coatings due to their unique composition, structure, preparation process and properties, leading to their superior wear resistance. Unfortunately, there are few reports on the new wear-resistant mechanism in the HEA films and coatings. Lin et al. [152] prepared AlCoCrNiW coating by gas tungsten arc welding method, which was composed of a W-based phase, a NiAl-based phase, and a Cr-Fe-C carbide phase and attributed its high wear resistance to the stronger mechanical interlocking between the complex phases and microstructure of the AlCoCrNiW clad layer. The revelation of new wear-resistant mechanisms for the HEA films and coatings is highly needed, which is expected to develop new types of wear-resistant HEA films and coatings.

5.3. Superior corrosion resistance

Based on the aforementioned reports in Section 4.2, the HEA films and coatings exhibit the superior corrosion resistance. A comparison of the corrosion behavior between HEA films (coatings) and other corrosion-resistant alloys, including stainless steels, Al alloys, Ti alloys, Cu alloys, Ni alloys and the HEAs [33,131,153–159], in salt water (3.5 wt.% NaCl) is shown

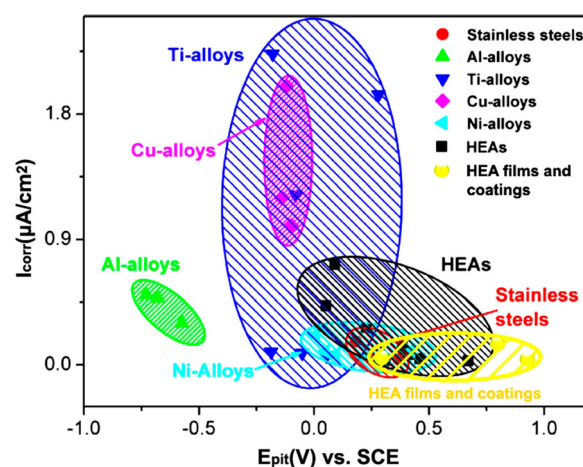


Figure 16. A reproduction of Figure 4 of Shi et al. [33], showing a comparison of the corrosion current density (I_{corr}) and pitting potential (E_{pit}) between the HEA films (coatings) and other materials in the 3.5 wt.% NaCl solution at room temperature.

in Figure 16. E_{pit} is the parameter, which can represent the resistance to pitting corrosion, and I_{corr} is relevant to the corrosion rate obtained through polarization tests in the 3.5 wt.% NaCl solution at room temperature. It can be seen that the HEA films and coatings are located in the lower right part of the figure. The I_{corr} values of the HEA films and coatings are comparable with those of the stainless steels and Ni alloys, while the E_{pit} values of the HEA films and coatings are much higher than those of Al alloys, Cu alloys, and some Ti alloys, and are comparable with those of the stainless steels, and Ni alloys, representing their excellent corrosion resistance. It is worth pointing out that the HEA films and coatings even have the lower I_{corr} values and comparable E_{pit} values relative to the HEAs, suggesting that the HEA films and coatings have more outstanding resistance to corrosion than their bulk counterparts.

The excellent corrosion resistance of the HEA films and coatings can be attributed to the three aspects. First, comparing with the conventional films and coatings, a single solid-solution phase or amorphous phase is easily formed in the HEA ones. The amorphous structure is well known to be more anticorrosive than the crystalline structure, since it has no grain boundaries, which is considered more chemically unstable in the aggressive medium. The formation of a single solid-solution phase can decrease the action of galvanic corrosion and the number of micro-batteries, resulting in the improvement of corrosion resistance. Dou et al. [132] deposited the FeAlCoCuNiV coatings with a single FCC structure by direct-current magnetron-sputtering, which exhibited better electrochemical corrosion resistance than the 201 stainless steel in acidic alkali and salt corrosion media.

Zhang et al. [111] studied the corrosion resistance of the FeCoNiCrCu coating with a simple FCC solid-solution and found that the coating presented the excellent corrosion resistance in a 5 vol.% (volume percent) H₂SO₄ solution.

The reason for the formation of simple solid-solutions in the HEA films and coatings is attributed to the thermodynamics. The relationship of the Gibbs free energy of mixing (ΔG_{mix}), enthalpy (ΔH_{mix}), and mixing entropy (ΔS_{mix}) of the disorder solid-solution can be described as follows:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (8)$$

where T is the temperature value. It can be calculated that the high entropy of mixing can significantly lower the free energy of the solid-solution with multiprincipal elements, therefore lowering the tendency to order and consequently making the random solid-solution more stable than intermetallics.

Second, the corrosion-resistant elements and strong bonding between elements are present in the HEA films and coatings. The main metallic elements satisfying the HEA-formation criteria are reported as Al, Co, Cu, Cr, Fe, Ni, Nb, W, Ti, V, Mo, and Zr [160]. Among them, Cr, Ni, Co, and Cu are commonly used to synthesize HEAs, which have good corrosion resistance, and their protective film can be easily formed on the surface of the HEA films and coatings. Moreover, the excellent corrosion resistance of the HEA nitride films and coatings can be due to the fact that Me-N bonding is more chemically-inert than Me-Me bonding. Hsueh et al. [45] studied the effect of R_N on the corrosion properties of the (AlCrSiTiZr)N films deposited by DC reactive-magnetron sputtering. They found that the (AlCrSiTiZr)N film deposited at $R_N = 30\%$ presented the best corrosion resistance, which was attributed to the full stabilization of Me-N bonding in a stoichiometric ratio.

Third, relative to the HEA bulks, more homogeneous microstructures can be obtained in the HEA films and coatings. Owing to the ‘rapid quenching’ effect during the preparation processes, the diffusion of elements can be more effectively inhibited in the HEA films and coatings. Therefore, a more uniform composition distribution can be achieved. An et al. [36] synthesized the sputtered CrCoCuFeNi film and the cast CrCoCuFeNi HEA bulk. They found that the as-deposited CrCoCuFeNi film consisted of a uniform single-phase solid-solution, which was confirmed by the high-energy synchrotron XRD, wavelength-dispersive spectroscopy and transmission electron microscopy, while the as-cast CrCoCuFeNi alloy was composed of the Cu-poor dendritic and Cu-rich interdendritic phases. The high-energy synchrotron XRD patterns and elemental distributions determined by

EDS of the as-deposited CrCoCuFeNi film and as-cast CrCoCuFeNi alloy are displayed in Figure 17, respectively, which suggests that the as-deposited CrCoCuFeNi film has a more homogeneous microstructure than the as-cast alloy. Li et al. [65] compared the corrosion resistance between the AlCoCrFeNi coatings deposited by the electrospark and the cast AlCoCrFeNi HEA bulk. The corrosion current of the HEA-coated specimen was significantly lower than the cast HEA material, which was attributed to the absence of the Cr-rich interdendritic phase and second-phase precipitation detected in the cast HEA material.

It is worth noting that the dense structure can also contribute to the enhanced corrosion resistance of the HEA films and coatings. Grain boundaries or column boundaries could provide preferential channels for corrosive agents due to their disorder structures. Elimination or decrease of these structure defects can effectively improve the corrosion resistance. Hsueh et al. [45] studied the effect of the substrate bias on the corrosion properties of the (AlCrSiTiZr)N films deposited by the DC reactive-magnetron sputtering. They found that the substrate bias could effectively increase the corrosion resistance of films by weakening the columnar boundaries and micro-pores, which eliminated the diffusion channel for corrosion agents. Due to the above characteristics, the HEA films and coatings can be the promising novel corrosion-resistant material, which may replace the conventional ones. The new type of the corrosion-resistant HEA films and coatings can be designed according to the above characteristics or considerations.

5.4. Si-containing HEA nitride films and nanocomposite structures

The Si-containing nitride films with the nanocomposite due to the thermodynamically-driven phase separation, such as TiSiN [161,162], NbSiN [163], CrAlSiN [164], TiAlSiN [165], and TiSiCN [166], have been extensively studied due to their high hardness, high wear resistance, and excellent thermal stability in the past decades [167–169]. The TiSiN (TiN/Si₃N₄) is a representative film among these films due to the strong thermodynamic incompatibility between TiN and Si₃N₄, which exhibits high hardness ranging from 32 to 105 GPa deposited by different methods [170–172]. Despite the strengthening mechanism of the nanocomposite film is still in dispute, the superhigh hardness over 40 GPa originating from the nanocomposite structure has already been achieved in many film systems [167–169].

During the studies of the HEA films and coatings, some researchers have tried to explore the Si-containing HEA nitride films with an expectation of acquiring the

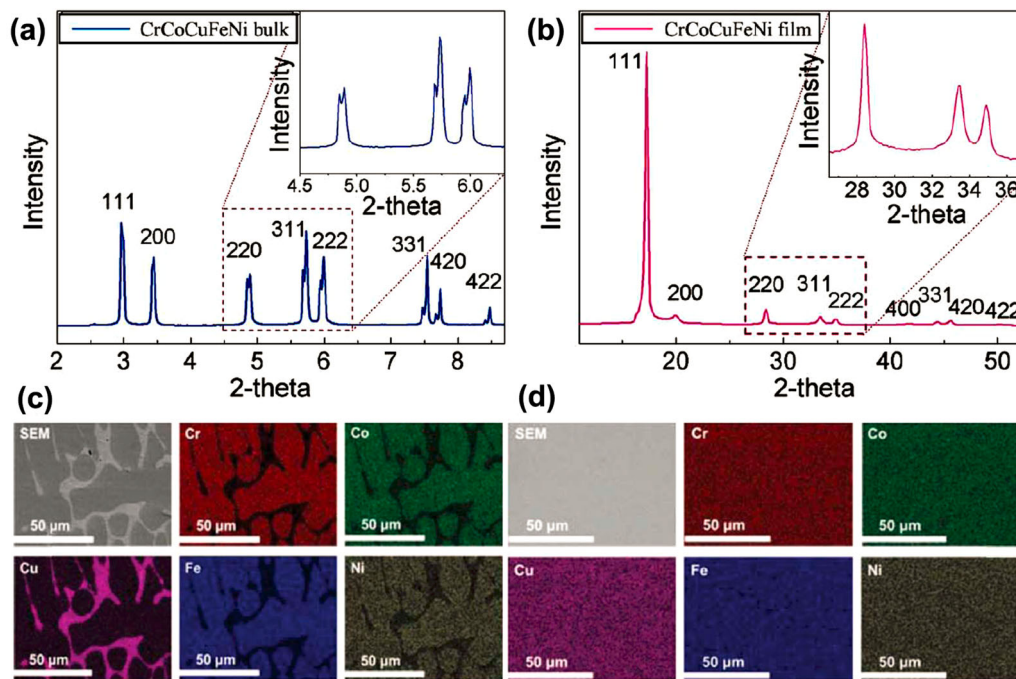


Figure 17. High-energy synchrotron XRD patterns of (a) as-cast CrCoCuFeNi alloy and (b) as-deposited CrCoCuFeNi film; elemental distributions determined by EDS of (c) as-cast CrCoCuFeNi alloy and (d) as-deposited CrCoCuFeNi film [36].

nanocomposite structure. However, the reported results are not very optimistic. Hsueh et al. [45] deposited the Si-containing (AlCrSiTiZr)N films by the DC reactive-magnetron sputtering. The maximal hardness of the film was only 19.5 GPa, and no nanocomposite structure could be observed. Sheng et al. [46] prepared the (NbTiAlSi)N and (NbTiAlSiW)N films by the reactive-magnetron sputtering, and the nanocomposite structure was similarly not detected within the films. The maximal hardness values of those two films were measured as 20.5 and 13.6 GPa, respectively. Tsai et al. [173] investigated the effects of silicon content (0%–7.51 at.%) on the (AlCrMoTaTi)N coatings by reactive-magnetron sputtering, and no formation of the nanocomposite structure had been reported. Especially, the formation of the SiN_x phase was not observed even after the Si content was increased to 7.51 at.%. They attributed the extended solubility of Si to the high entropy effect.

Although Huang et al. [43,125,126] reported that the high hardness of 41 GPa was achieved in the (AlCrNbSiTiV)N coating deposited by the reactive RF-unbalanced magnetron sputtering. However, even after annealing at 1000°C for 2 h, the nano-Augur line-scan and HRTEM elemental analysis indicated no detectable second phase or significant elemental segregation, such as SiN_x , could be observed, which can be seen in Figure 18 [43], suggesting that the nanocomposite structure was not created within the coating. They attributed the high hardness to the formation of the saturated nitride phase,

grain size strengthening, solution hardening, and residual compressive stress.

Surprisingly, based on the HRTEM observations, Cheng et al. [174] and Lin [129] et al. reported the formation of the nanocomposite structure in the (AlCrTaTiZr)SiN coatings produced by the reactive RF-magnetron sputtering, and the hardness values of 34.5 and 30.2 GPa were obtained, respectively. The HRTEM images of the (AlCrTaTiZr)Si_{0.15}N_{1.07} coating were displayed in Figure 19 [129]. However, it can be seen that the nanocrystalline phase is elongated, rather than equiaxed, which is a typical feature of the nanocomposite films, as shown in Figure 14. Moreover, the lattice can be observed within the denoted ‘amorphous regions’ in Figure 19, suggesting the probable crystallized feature in these regions. More importantly, the composition distribution had not been provided in these investigations, which is difficult to verify the phase segregation within the coatings. Therefore, the formation of the nanocomposite structure deserves to be further deliberated.

The difficulty for the formation of the nanocomposite structure within the HEA nitride films and coatings may lie in the high mixing entropy effect, which enhances the mutual solubility of constituent elements. As a result, the Si atoms may be inclined to be incorporated in the crystalline lattice of the HEA nitride, rather than be segregated as the SiN_x phase, which can serve as the interfacial phase of the nanocomposite structure. The nanocomposite structure of Si-containing HEA nitride films is an

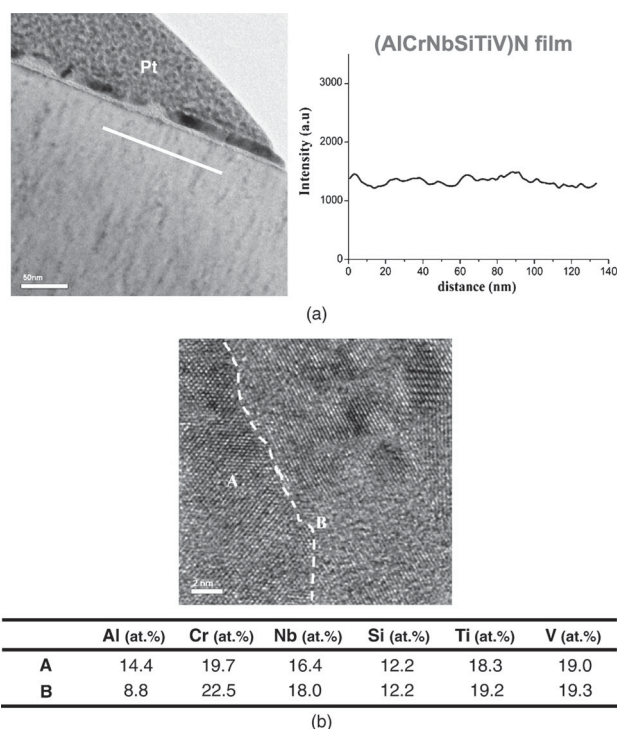


Figure 18. The elemental analyses of the (AlCrNbSiTiV)N films after annealing at 1000°C for 2 h: (a) line-scan for the Si concentration crossing a number of grains in the annealed film by the nano-Auger analysis; and (b) HRTEM images and analyses at point A in the grain interior and point B on the grain boundary (vertical to the image) of the annealed film by EDS of high resolution TEM [43].

interesting and important issue in the HEA films and coatings, which will lay the foundation for the discovery of new HEA nitride protective coatings with improved mechanical properties. More research should be carried out on studying the phase-segregation behavior of the

Si-containing HEA nitride films by the advanced techniques, such as the HRTEM elemental analysis, atom-probe tomography, and Auger-electron spectroscopy.

5.5. Modeling and simulations

Currently, various computational modeling methods have been applied to study the structure, thermodynamics, kinetics, and properties of the HEA bulks in spite of the complexity of the multi-component system and the disordered solid-solution structure, such as molecular-dynamics (MD) simulation [11,175], acronym of calculation of phase diagram (CALPHAD) [80,176,177] and first-principles density functional theory (DFT) calculation [178–181]. However, owing to the non-equilibrium characteristic and the ‘rapid quenching’ effect during the preparation process, the predictive computational modeling of the HEA films and coatings is more challenging than the HEA bulks. Therefore, the theoretical reports on HEA films and coatings have rarely been documented in the open literature.

The MD simulation is a powerful tool in the computational materials science, which can provide a deep insight into the atomic mechanism of ordering of HEAs. Using MD simulations, Xie et al. [182–184] studied the sputtered AlCoCrCuFeNi thin film growth with three compositions on a silicon (100) substrate. Input data were chosen to fit with experimental operating conditions of the magnetron-sputtering deposition process. Simulation snapshots for three AlCoCrCuFeNi thin films are displayed in Figure 20 [182]. It is clear that the atoms, in the $\text{Al}_2\text{Co}_9\text{Cr}_{32}\text{Cu}_{39}\text{Fe}_{12}\text{Ni}_6$ (sample 1) and $\text{Al}_3\text{Co}_{26}\text{Cr}_{15}\text{Cu}_{18}\text{Fe}_{20}\text{Ni}_{18}$ (sample 2) films, are arranged in a crystalline structure. For the

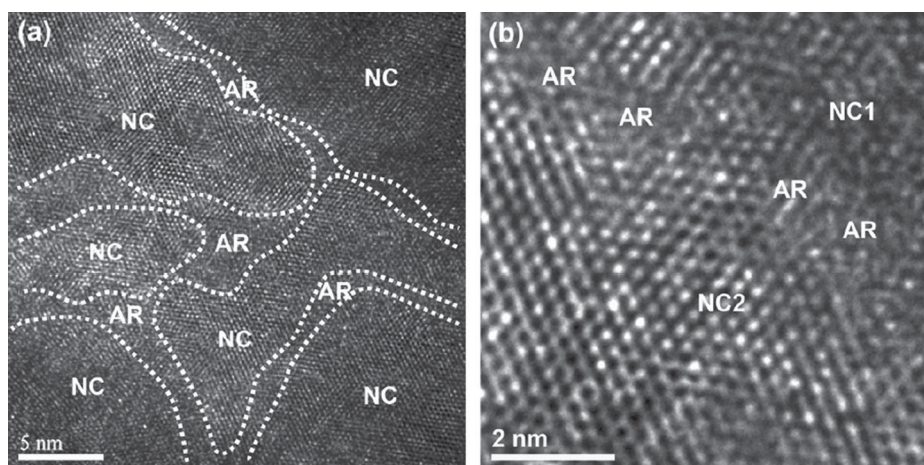


Figure 19. (a) TEM lattice image of the (AlCrTaTiZr) $\text{N}_{1.07}\text{Si}_{0.15}$ coating deposited at a substrate bias of 100 V and a Si-target power of 50 W (NC: nanocrystalline, AR: amorphous regions). (b) Magnified image of (a), showing ARs between NC1 and NC2 of small-angle misorientation [129].

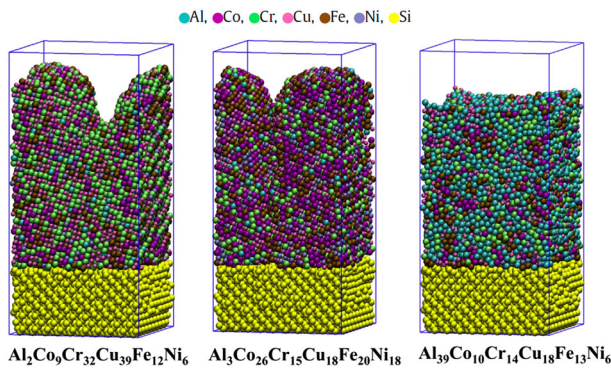


Figure 20. Snapshots of three AlCoCrCuFeNi thin films deposited on the Si (100) substrate with a large substrate [182].

$\text{Al}_{39}\text{Co}_{10}\text{Cr}_{14}\text{Cu}_{18}\text{Fe}_{13}\text{Ni}_6$ (sample 3) film, however, an amorphous structure is formed on the overall thickness.

As for the growth of sample 1, they found that small clusters were formed at the first step ($t = 0.5$ ns), which left the substrate partly uncovered. As the number of deposited atoms increased, a continuous film was formed (from 2.5 ns). Furthermore, the film was amorphous in the first 2.5 ns and changed into a crystalline structure after 3.5 ns. For sample 2, the various crystalline clusters with the same lattice orientation were formed at 2.5 ns, which was different from the continuous amorphous film of sample 1, implying that the film in sample 2 had the strongest ability of crystallization. After several crystalline clusters had been formed, they grew in size, and interfaces were formed. Finally, the different crystalline cluster joined together by rearranging and rotating the lattice. They suggested that the different structures were determined by the chemical composition and atomic size mismatch [182]. Their simulated results were in good agreement with the solid-solution formation rules proposed by Zhang et al. [7].

So far, the literatures of modeling and simulations on the HEA films and coatings are very limited. More investigations on the predictive computational modeling of the HEA films and coatings need to be explored, which will help illuminate the relationship among the preparation processes, microstructures, and properties, and develop new types of the HEA films and coatings.

6. Suggested future work

The extensive work has been done in exploring the HEA films and coatings during the past 14 years. The attractive properties, such as high hardness and elastic modulus, superior wear, corrosion, and temperature resistance, together with the appealing electrical and magnetic properties, have already been achieved in various HEA films and coatings. In this section, the future work of the HEA

films and coatings is proposed concerning the aspects of preparation, microstructures, properties, applications, modeling, and simulations.

- (1) The relationships between the process parameters of the existing preparation technologies and the microstructures and properties of the high-quality HEA films and coatings need to be further revealed. New types of preparation processes, which can fabricate high-quality HEA films and coatings with low cost, need to be explored.
- (2) The effects of non-nitride-forming element(s) on the microstructures and mechanical properties of HEA-nitride films and coatings are still not clear, which needs further studies and is helpful to understand the strengthening mechanism of the HEA-nitride films and coatings, and develop the new HEA-nitride film systems with great hardness.
- (3) Based on the design criteria, such as high hardness, the mixture of solid-solutions and intermetallic compounds, the compressive residual stress, and the inclusion of some lubricious elements, new types of HEA films and coatings with the superior wear resistance should be designed, fabricated, and applied.
- (4) According to the design principles, such as those consisting of single solid-solutions, the inclusion of the corrosion-resistant elements and strong bonding, and more homogeneous and densified microstructures, in-depth research should be carried out on the design of HEA films and coatings with the superior corrosion resistance.
- (5) Further work needs to be done on the phase-segregation behavior of the Si-containing HEA-nitride films, especially by the advanced techniques, such as the HRTEM elemental analysis, atom-probe tomography, and Auger electron spectroscopy, which are helpful for developing the new branch of superhard HEA-nitride film systems.
- (6) The nanomultilayered (or superlattice) structures consisted of one or more HEA nitrides should be designed and fabricated. By combining the strengthening mechanism of the HEA nitride films and the coherent-interface mechanism of nanomultilayered structures, the superhard HEA nitride containing nanomultilayered films are expected to be developed.
- (7) Due to the appealing physical properties, such as electrical, magnetic, optical, and other properties, the design and synthesis of the HEA films and coatings with the specific physical behavior are highly needed. The mechanisms governing the relationships among the compositions, structures, and

physical properties of the HEA films and coatings should be illuminated.

- (8) The literatures of modeling and simulations on the HEA films and coatings are very limited, which are helpful for illuminating their relationships among the preparation processes, microstructures, and properties. More investigations related to the predictive computational modeling of the HEA films and coatings need to be explored.

7. Concluding remarks

In the past 14 years, as a branch of HEA materials, HEA films and coatings have exhibited attractive and unique properties, relative to conventional films and coatings. This paper has reviewed the preparation technologies, microstructures, and properties of HEA films and coatings. The possible reasons and design criteria for achieving the excellent properties are discussed, and the suggested research directions of HEA films and coatings are proposed. The main contents of this paper can be summarized as follows:

- (1) A number of technologies for the deposition of the HEA films and coatings are summarized, including magnetron sputtering, laser cladding, spraying, electrochemical deposition, and other methods. Relative to the preparation technologies of the HEA bulk materials, the preparation methods of HEA films and coatings are more easily to achieve the rapid cooling rate owing to their smaller thickness. The characteristics of each preparation technique are discussed.
- (2) Like the HEA bulk materials, the HEA films and coatings are inclined to form the solid-solution phase or amorphous phase due to the high-entropy effect and the 'rapid quenching' effect of the preparation method. The formation of the single solid-solution phase is discussed by the thermodynamic parameters. The microstructures of the HEA-nitride, oxide, and carbide films and coatings are generalized and discussed.
- (3) The mechanical properties of the HEA films and coatings are summarized, which indicates that the HEA films and coatings present the high hardness, elastic modulus, and superior wear resistance. Especially, the superhigh hardness over 40 GPa has been achieved in some HEA-nitride films and coatings, and HEA films and coatings synthesized by different technologies can effectively improve the wear resistance of the metal substrate.
- (4) The corrosion, temperature and oxidation resistances, along with the physical properties, diffusion retardation and biocompatible properties of the HEA films and coatings, are discussed, suggesting that they can exhibit the unique corrosion resistance, high phase stability, excellent oxidation resistance, and mechanical properties at elevated temperatures, as well as the appealing electrical and magnetic, diffusion retardation and biocompatible properties.
- (5) Several critical issues related to the reasons and design criteria for achieving the excellent properties of the HEA films and coatings are suggested, including the effects of strong and non-nitride-forming elements on the hardness of HEA nitrides and their design criteria with high hardness, possible reasons for the superior wear and corrosion resistance, Si-containing HEA-nitride films, and nanocomposite structures, modeling and simulations.
- (6) The future work of the HEA films and coatings is proposed with respect to the preparation processes, microstructures, models, properties, and applications, including the development of new preparation processes, the effects of non-nitride-forming element(s), the design of the HEA films and coatings with the superior wear or corrosion resistance or physical or other behaviors, the phase-segregation characteristic of the Si-containing HEA-nitride films, the design of nanomultilayered structures consisting of the HEA nitrides, and the development of modeling and simulations.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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