Review

High Entropy Alloy Coatings and Technology

Ashutosh Sharma

Department of Materials Science and Engineering, Ajou University, Suwon 16499, Korea; ashu@ajou.ac.kr;
Tel.: +82-31-219-2464; Fax: +82-31-219-1613

Abstract: Recently, the materials research community has seen a great increase in the development of multicomponent alloys, known as high entropy alloys (HEAs) with extraordinary properties and applications. In surface protection and engineering, diverse applications of HEAs are also being counted to benefit from their attractive performances in various environments. Thermally sprayed HEA coatings have outperformed conventional coating materials and have accelerated further advancement in this field. Therefore, this review article overviews the initial developments and outcomes in the field of HEA coatings. The authors have also categorized these HEA coatings in metallic, ceramic, and composite HEA coatings and discussed various developments in each of the categories in detail. Various fabrication strategies, properties, and important applications of these HEAs are highlighted. Further, various issues and future possibilities in this area for coatings development are recommended.

Keywords: coatings; high entropy alloy; thermal spray; electroplating; laser melting; ball milling

Citation: Sharma, A. High Entropy Alloy Coatings and Technology. *Coatings* **2021**, *11*, 372. <https://doi.org/10.3390/coatings11040372>

Academic Editor: Robert Franz

Received: 7 February 2021

Accepted: 20 March 2021

Published: 24 March 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The surface is the most important component of a material that is associated with the performance of material for industrial applications. The application of various surface modification techniques allows an economic substitution of a low-grade base alloy with a coating for better surface characteristics and performance in various demanding conditions, e.g., thermal insulation, erosion, corrosion, and stress [1,2]. The surface quality of materials has a greater impact on durability and performance, which cannot be ignored in design.

In the last few decades, several metallic and organic coatings have been applied for the surface protection of metals against environmental degradation. Thermal insulation coatings have been developed at high-temperature applications in turbine and aerospace applications. Various research activities have been conducted to improve the durability of base alloy components in various gaseous and corrosive atmospheres [3]. For example, highly oxidation-resistant coatings permit the application of various oxidizing or corrosive environments over a wider window of operating conditions. However, there is no solution for the long-term protection of metals when applied in harsh conditions. Although, oil and gas industries have made sufficient progress in novel cathodic protection methods and monitoring systems, these industries also have frequent coating failures [4,5]. The various factors affecting the durability and performance of coatings include the composition and type of substrate, residual stresses, adhesion, toughness, service temperature, humidity, and wear [6]. In this regard, the coating industry has been continuously evolving in technology throughout the last few decades. Various types of ceramic coatings [7,8], powder coatings [9], and composites [10–12] containing novel carbon nanomaterials have shown their potential for oxidation and wear-resistant applications.

For wear-resistant application, the prime goal is to control the surface topography of the base alloy or modifying its mechanical properties to withstand higher weight in dynamic loading applications. This is established by a variety of coating techniques, surface modification, thin film deposition, texturing of deposits, altering the metallurgical bonding, e.g., by micro- or nanojoining of the surface. The underlying principle is to engineer the

surface topography to control friction or outgrowths and adhesion to the substrate. As the contact area of the surface depends on the surface features, surface characteristics can be tuned by an appropriate method for enhanced protection and wear properties in various engineering applications [13,14].

Compared to bulk structural metals and conventional alloy coatings, the last decade has seen a big jump in the field of alloy design and development [15–17]. High entropy alloys (HEAs) were discovered and published independently by Yeh et al. [18], and Cantor et al. [19] in 2004. These novel alloys are also known as multicomponent or multi-principal element alloys (MPEAs), which differ from traditional alloys having a single principal element, such as Al, Cu, Fe, Ti, alloys, etc. HEAs are mostly composed of five or more elements in equiatomic or non-equiatomic ratios where the composition of each element varies from 5–35 at.% [18]. The mixing of elements in this composition produces simple solid solution phases, e.g., face-centered cubic (FCC), base centered cubic (BCC), hexagonal close-packed (HCP) structure, rather than a complex phase or intermetallic compounds (IMCs) [19]. HEAs have been reported to possess exceptional characteristics, such as high mixing entropy, severe lattice torsion, sluggish diffusion, and cocktail effect which give rise to their outstanding mechanical strength, high good thermal stability, wear, and corrosion resistance [20]. Therefore, HEAs have great potential in various engineering applications [20]. Several HEAs have been discovered which are mostly Cantor HEAs (FeCoNiMnCr), refractory alloys (NbMoTaW and VNbMoTaW), or non-Cantor dual-phase AlCuSiZnFe [21–23]. The addition of additive elements has been investigated to control the microstructure. For example, the phase fraction of FCC and BCC solid solution depends upon the Al fraction in AlCoCrFeNi alloy. The FCC to BCC phase transition occurs while increasing the Al atomic fraction in AlCoCrFeNi HEA [24,25].

HEA-based coatings have emerged as a potential surface protective on account of their attractive surface protection ability. Several HEA coatings have been produced by many fabrication routes in the form of thin or thick films for surface protection [16]. The last few years have seen enormous developments in the fabrication methods of high entropy alloys and coatings, microstructural evolution, properties evaluation, and versatile applications. Therefore, this review mainly focuses on the development of HEAs and HEAs as coating materials for demanding and high-performance protection in extreme conditions. The basic understanding of the HEAs and related concepts, classifications, processing methods, properties, and applications of HEA coatings are reviewed. Section 1 covers the introduction and background of HEAs. Section 2 deals with the HEA-based coatings and their classification. Sections 3 and 4 provide more details about the development of various types of HEA coatings, their fabrication methods, and applications. Finally, Section 5 summarizes the basic challenges in the development of the HEAs coatings, and future recommendations for this area have been also addressed systematically.

2. High Entropy Alloy Based Coatings

A huge number of HEAs have also been produced showing precipitation hardenability, lightweight, antioxidation, wear, and corrosion resistance, etc., which further expand their applications in various sectors [26–29]. The superior specific strength of HEAs over various conventional engineering materials shown in Figure 1.

HEA-related alloys and coatings have been widely investigated in various surface engineering applications due to their attractive properties and unique applications in extreme environments. Recently, there have been rapid developments in HEA coatings. For example, N₂ containing HEAs have been seen as a potential candidate to replace conventional Ni-base superalloys exhibiting high oxidation, hardness, and wear characteristics. Consequently, more diverse properties can be obtained by employing several constituent elements, such as transition metals, refractories, nitrides, and carbides systems [30]. The resultant performance of HEA coatings is governed by the type of elements, composition, and microstructures of the coatings. Therefore, based on the prior art, the classification of HEA coating systems can be summarized pictorially as shown in Figure 2.

Figure 1. Yield strength versus density of HEAs (dark dotted circle) compared with other materials, particularly structural alloys. Reproduced with permission from Reference [17]. Copyright 2014 Elsevier.

Figure 2. Various classes of HEA coatings.

The three HEA groups can be possible based on the recent developments in this area [31,32]; (1) Metallic HEAs, (2) ceramic HEAs (or high entropy ceramics), and (3) high entropy composites. The metallic HEA coatings include initially developed Cantor-based HEAs and their derivatives with other lightweight HEA based on Al, Mg, Si, etc structural elements. Refractory alloys are also included in metallic HEAs. The high entropy ceramics include oxides, carbides, nitrides, and other hard refractories coatings (Figure 2). Based on the metallic and ceramic coating, high entropy composite coatings are also in development in the last few years [33–35].

3. Research Trends on HEA Coatings and Technology

3.1. Metallic Coatings

Metallic HEA-related coatings consist of basically FeCoNiMnCr series elements which are generally known as Cantor-based alloys, developed initially by cantor et al. in 2004 [19]. The constituents in this class of HEAs are mostly transition elements such as Al, Cr, Co, Mn, Fe, Ti, Ni, V. Refractory elements have also been developed to improve the mechanical

properties, unlike Cantor alloys. The refractory HEAs are mainly composed of harder refractory elements such as Ta, Mo, Hf, Nb, Zr, W, Ti, V, Cr, etc [22]. These are designed for high-temperature application where oxidation, wear, and corrosion is of utmost importance. Various refractory HEAs developed so far are TaNbCrMo, TaMoNbW, TaNbZrHf, CrNbVZr series [31,32]. Metallic lightweight alloys have also been researched based on light elements to reduce their density for various lightweight structural applications, such as AlCuSiZnFe, AlLiMgScTi, AlCuFeMnMgTi, $\text{Al}_{20}\text{Be}_{20}\text{Fe}_{10}\text{Si}_{15}\text{Ti}_{35}$, etc [23,36–38].

3.2. Ceramic Coatings

Ceramics-related HEA coatings mainly consist of metal nitrides and carbides of transition elements [31]. Several HEA oxides, nitrides, carbides, and perovskite materials have been deposited by various routes such as magnetron sputtering in various atmospheres (nitrogen, oxygen, methane, and combination of nitrogen and methane, as well as hydrogen gas [39–41]. In such hard ceramic HEA coatings, the constituent impurities such as O, C, N, H are present in the solid solution and show a high-entropy effect. Various ceramic forming elements are used for hard ceramic HEA coatings such as Cr, Si, Zr, Ti, Al, etc. Such HEA coatings possess extraordinary surface protection ability, in terms of high strength, thermal stability, anti-corrosion performance, and sluggish diffusion rate [42,43]. Therefore, these coatings have been applied to thermal diffusion barrier, oxidation, and hard radiation resistant coatings applications in nuclear plants [44].

3.3. Composite Coatings

Composites have played a major role in modern alloy developments for versatile applications. In the HEA field, composite fabrication has been frequently tested to further broaden the HEA applications. Similar to conventional composite materials, the HEA composites can be synthesized by reinforcing the HEA matrix with suitable ceramic reinforcements. In the last few years, several ceramic reinforcements, SiC, Al_2O_3 , WC, TiC, TiN, TiB_2 , NbC [33–35] have been developed showing better hardness, wear, chemical stability, and bonding with HEA matrix coatings. Considerable progress has been done in these composite HEA coatings fabricated by laser cladding, plasma-arc cladding, magnetron sputtering, etc. Metallic reinforcements have been also used in HEA coatings. Tian et al. fabricated AlCoCrFeNiTi reinforced Ni powder by plasma spray deposition and demonstrated a significant enhancement in the high-temperature hardness and wear resistance of the final coatings [45–47]. Recently, Guo et al. designed $(\text{TiZrNb})_{14}\text{SnMo}$ refractory HEA by cluster-plus glue atom model and produced it by arc melting and laser cladding. The authors found superior wear and corrosion resistance, as well as better biocompatibility, compared to the conventional Ti-6Al-4V alloy [48].

4. Methods of Fabrication of HEA Coatings

Based on the advancement of HEAs, various fabrication methods have developed concerning the application of these HEA coatings. Most of these methods are based on laser cladding, plasma spray, vapor deposition methods, with a few related to powder metallurgy and chemical bath plating, as shown in Figure 3.

Laser-based methods are the most popular and attractive for HEA coatings due to their attractive features, such as high heat input, rapid process, less material wastage, and eco-friendly process [46–48]. This process contributes to a strong coating substrate bonding, uniform microstructure, formation, but there is smaller thermal damage caused due to rapid heating and cooling rates involved in the process. The major drawbacks of laser surface alloying are the formation of the heat-affected zone, high residual stresses, and elemental dilution of the HEA coating and the substrate [49]. The manufacturing process of high entropy alloys affects their microstructure considerably. Various microstructural features of the HEA coatings are reported, including equiaxed, columnar grains, dendritic and lamellar structures depending upon the thermal history, such as in laser cladding, laser surface alloying, and plasma spray methods. In chemical methods, HEA coatings have

granular and spherical-shaped grainy structures. The developments in the laser-based HEA coatings including the fabrication methods, morphologies, coating thickness, and hardness on different base substrates are given in Table 1.

Figure 3. Methods of fabricating various HEA coatings.

Table 1. The details about HEA-related coatings fabricated by various coating methods.

Base Metal	HEA Coating	Coating Method	Phase	Microstructure	Approx. Thickness	Reference
AA5083	Al _{0.5} FeCu _{0.7} NiCoCr	Laser cladding	FCC + BCC	Equiaxed and columnar grain microstructure	600 µm	Ref. [50]
AZ31Mg	AlCoCrCuFeNiSi _{0.5} /Y ₂ O ₃	Laser cladding	FCC + BCC	Core-shell microstructure	1500 µm	Ref. [51]
Q235 steel	AlCoCrFeNi/NbC	Laser cladding	FCC + BCC + NbC	Rod-like and blocky particles with equiaxed fine structure	1200 µm	Ref. [34]
Q235 steel	Al ₂ CrFeNiCoCuTi _x	Laser cladding	FCC + BCC	Equiaxed grains and columnar crystals	600 µm	Ref. [52]
Q235 steel	FeCoNiCrCu+Si,Mn,Mo	Laser cladding	FCC	Columnar and equiaxed grains	2000 µm	Ref. [53]
AISI 1045	FeCoNiAlCu	Plasma cladding	FCC + BCC	Columnar and equiaxed grains	1000 µm	Ref. [54]
Pure Ti	FeCoCrNiNb _x	Plasma cladding	FCC + BCC	Dendritic microstructure	1500 µm	Ref. [55]
AZ91D Mg	AlCoCrCuFeNi	Laser melt injection	BCC + CuM ₂ g	Dendritic eutectic structure	400 µm	Ref. [56]
H13 steel	FeCoCrBNiSi	Laser cladding	FCC + Amorphous	Equiaxed microstructure	200 µm	Ref. [57]
Q235 steel	FeCoCrAlCu	Laser surface alloying	BCC	Dendritic microstructure	800 µm	Ref. [58]
A36 steel	FeCoNiCrMn	Laser surface alloying	FCC	Dendritic microstructure	2000 µm	Ref. [59]
Ti64	AlCoCrNiTiV	Laser surface alloying	BCC + (Co, Ni)Ti ₂	Dendritic microstructure	800 µm	Ref. [60]
Ni201	FeCoCrAlCuV _x Ni	Laser surface alloying	FCC + BCC	Columnar and equiaxed grains	400 µm	Ref. [61]
Pure Cu	FeCoCrAlCuNi _x	Laser surface alloying	FCC + BCC	Dendritic microstructure	500 µm	Ref. [62]
Al6082	FeCoNiCrMn	Cold spray	FCC	Dislocations and coarse grained.	1500 µm	Ref. [63]

Table 1. Cont.

Base Metal	HEA Coating	Coating Method	Phase	Microstructure	Approx. Thickness	Reference
S235 steel	AlCoCrFeNiTi	HVOF	BCC	Lamellar structure	210 μm	Ref. [64]
Pure Mg	AlCoCrCuFeNi	Plasma spray	BCC + FCC	Lamellar structure	275 μm	Ref. [65]
316 stainless steel	AlCoCrFeNiTi	Atmospheric plasma spray	BCC + FCC	Lamellar structure	240 μm	Ref. [66]
Ti64	TiTaHfNbZr	Magnetron sputtering	Amorphous	Couliflower shaped microstructure	0.8 μm	Ref. [67]
Mild steel	(TiAlCrSiV) _x Ny	Magnetron sputtering	Amorphous + FCC	Columnar microstructure	1.7 μm	Ref. [68]
C45 steel	(TiZrNbHfTa)N	Magnetron sputtering	FCC	Glassy dense and fine grained	2 μm	Ref. [69]
Stainless steel	(TiZrNbAlYCr)N	Vacuum arc evaporation	FCC + BCC	Fine grained droplet type structure	7 μm	Ref. [39]
Q235 steel	CoCrFeNi	Hot press sintering	FCC	Nanoscale grains	700 μm	Ref. [70]
Q235 steel	CoCrFeNiCu	Hot press sintering	FCC	Nanoscale grains	700 μm	Ref. [70]
Ti64	CrMnFeCoMoW/Al	HEBM	FCC + BCC	Lamellar microstructure	210 μm	Ref. [71]
Mild steel	AlCrFeCoNiCu/GO	Electrodeposition	FCC + BCC	Granular microstructure	4 μm	Ref. [72]
Pure Cu	AlCrFeMnNi	Electrodeposition	Amorphous + BCC	Spherical and flaky	350 μm	Ref. [73]
Pure Cu	AlCrCuFeMnNi	Electrodeposition	Amorphous + BCC	Spherical and flaky	400 μm	Ref. [73]

Another widely adopted process for HEA coatings is thermal spraying at high temperatures. Thermal spray is a line-of-sight process, where powder, wire, or rod feedstock is fed into a spray torch and heated at a very high velocity in the form of spray towards the base metal. The process is further categorized into three major categories according to the energy source applied, (1) high-velocity oxygen fuel spray (HVOF); (2) electric plasma/arc formation such as atmospheric plasma spray (APS), and cold spray occurring at a relatively low temperature from gas expansion, as shown in Figure 5 [30]. The various thermal spray processes are categorized based on the source of energy, spray particle size, and velocity, nature of feedstock materials, and phase composition. Thermal sprayed HEA coatings were produced initially by Huang et al. in 2004 [74]. The authors developed AlSiTiCrFeCoNiMo_{0.5} and AlSiTiCrFeNiMo_{0.5} coatings, which exhibited enhanced wear and oxidation resistance. However, the rapid progress in this area happened in the last decade after various thermally sprayed (Ni_xCo_{0.6}Fe_{0.2}Cr_ySi_zAlTi_{0.2}) and plasma sprayed (AlCoCrFeNi and MnCoCrFeNi) coatings were developed by Wang et al. [75].

APS is suitable for porous coatings in the case of bioimplants, while the cold spray is mostly suitable in low-temperature processing of coatings on Al, Mg alloys, or ceramics on Ni-based superalloys. Hushchuk et al. cold sprayed AlNiCoFeCrTi HEA milled powder on the steel substrate. Their results confirmed that HEA coatings were produced with low porosity as a low-temperature process and there was no phase composition change in HEA coating without any phase transformation [76]. The AlNiCoFeCrTi HEA coatings were highly dense and vary from 430–470 μm in thickness. The porosity is around less than 1%, much lower than that of plasma-sprayed HEA coatings (7.4%) obtained by Ajdelsztajn et al. [77], Cai et al. [78]. Lu et al. [79] studied plasma cladded CrCuFe_xNiTi on Q235 and found an increased hardness from 650 to 730HV_{0.2}. Similar results were also shown by laser NiCoFeCrAl₃ HEA reported by Zhang et al. [80]. Wang et al. studied the Ni_xCo_{0.6}Fe_{0.2}Cr_ySi_zAlTi_{0.2} HEA coated on 304 stainless steel by thermal spray technology [75]. The HEA used for thermal spray was prepared by arc melting of the constituent elements. After thermal spray, heat treatment was carried out by the authors at 100 °C for 10 h to study the phase transformation studies. The authors found that, as cast Ni_xCo_{0.6}Fe_{0.2}Cr_ySi_zAlTi_{0.2} HEA revealed nano-size precipitates (5 to 10 nm), atoms segregation, twin structure, and formation of subgrains in the matrix. After thermal spray and heat treatment of coatings, the formation of a semi-coherent interface associated with a series of dislocation networks was found [75].

Another important technique for the HEA coatings is magnetron sputtering where the HEA is atomically sputtered layer-by-layer over a substrate. Most of the HEA coatings deposited by sputtering are HEA nitride, carbide, and boride coatings with excellent wear, oxidation, and irradiation resistance properties [81–85]. Most of these sputtered coatings have BCC or FCC solid solution phases with amorphous structures compared to other thermally sprayed coatings. Tuten et al. [67], fabricated dense (HfNbTiVZr) N_x HEA coating fabricated by sputtering with a maximum thickness of 800 nm (Figure 4).

Figure 4. (a) Wear track profiles of Ti-6Al-4V and (b) AFM images of 800 nm thick TiTaHfNbZr HEA coatings at different loads [67]. Copyright 2019 Elsevier.

The authors found that increasing the load from 1 to 3 N, enhanced the wear depth when a bare Ti-6Al-4V substrate was used (Figure 4a). However, the wear depth was very small and was not detected by the profilometer. The surface topography is shown by the AFM images (Figure 4b). They found that wear loss volume was negligible for TiTaHfNbZr HEA coatings at all loads as compared to the Ti-6Al-4V substrate. It is known that the wear loss was highly dependent on the hardness of tested materials and normal loads [86,87]. In the vacuum deposition process, target material vaporizes on the base metal by the plasma generated from the arc produced. Although, there is a limit on the coating thickness, yet the coatings are very harder and good for wear and antioxidation resistance properties, due to columnar and amorphous structures [67–69,81,85].

Powder metallurgy is now becoming popular for HEAs and HEA-based coatings which do not involve any fusion of the base metal. By using various sources of energy, such as thermal, electrical, or mechanical energy to achieve fine-grained [71,88–90]. Various authors have used mechanically alloyed HEA powder for plasma spraying on a harder substrate [76,91]. Tian et al. ball-milled AlCoCrFeNiSi HEA powder for 10 h to obtain BCC and FCC dual-phase HEA alloy which was further plasma sprayed on 316 stainless

steel substrates. Compared to milled HEA, plasma-sprayed HEA consisted of an ordered BCC phase, devoid of Si after plasma treatment with a grain size of about 30 nm, which enhanced the hardness and wear resistance of the coating [91].

Among liquid state methods, electrodeposition has emerged as a prime route to fabricate HEA coatings at low temperatures. The electrodeposition process has well-established advantages, such as economical processes and lower consumption of energy unlike laser and solid-state processes [92–95]. Following these advantages, few researchers have attempted electrodeposition of HEA coatings such as AlCrFeMnNi and AlCrCuFeMnNi [73], and BiFeCoNiMn [96]. Various bioactive coatings have also been developed on Ti substrates in the past by electrodeposition from non-aqueous chemical baths [97]. Soare et al. [73], produced AlCrFeMnNi and AlCrCuFeMnNi HEA coatings by high entropy alloy thin films potentiostatically using an electrolyte (N, N-dimethylformamide)-CH₃CN with 4:1 volume fraction and individual elemental salts for the first time as shown in Figure 5. The formation of round structures increased with the deposition potential as shown in Figure 5a–d.

Figure 5. Low and high magnification SEM images of the AlCrCuFeMnNi films deposited at (a,b) -2.1 V for 90 min, and (c,d) -2.5 V for 90 min [73]. Copyright 2015 Elsevier.

The size of rounded structures increased slightly with negative potential (Figure 5c,d). The as-deposited coatings were initially amorphous which turned to BCC solid solution phases after annealing at 600 °C. The authors stated that the new HEA produced by this route possesses good corrosion resistance and hence can be used as corrosion protective coatings [73]. Yoosefan et al. studied a thorough parametric study on electrodeposited FCC CoCrFeMnNi HEA. Their results indicated that the surface morphology of the HEA coatings depends on the applied duty cycle and frequency [98]. A higher duty cycle resulted in a decrease in crystal size. Also, at a higher frequency and higher duty cycle, the crystallite size decreased but the higher frequency and lower duty cycle produced opposite results [98].

Yao and his co-workers fabricated BiFeCoNiMn HEA coatings with dense and nanometer scaled surface with conical surface morphology with particle size (100–200 nm). The

authors reported soft magnetic properties which changed to hard magnetic properties after annealing [99]. Aliyu et al. prepared graphene oxide reinforced AlCrFeCoNiCu coatings by electroplating. The authors found a great improvement in corrosion resistance of coatings in the presence of graphene oxide which improved the homogeneity of the HEA coating matrix and prevented localized corrosion [72]. However, despite all this progress, the electroplated HEAs are still in the emerging stage, due to the complexity of processing parameters and multicomponent alloy deposition, which is a tedious task given the interrelated pulse deposition parameters [95,98,100]. Dmitry Moskovskikh et al. produced $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2})\text{N}$, which demonstrated outstanding hardness and fracture toughness (33 GPa, $5.2 \text{ MPa}\cdot\text{m}^{1/2}$), compared to other reported binary and high entropy ceramics coatings [101]. Moreover, post-processing of the coatings is also required to improve adhesion as seen by the various researchers. The following section will provide an overview of various post-processing techniques in the HEAs coatings to improve the final surface properties. Other techniques have been implemented to design the harder high entropy ceramics such as nitrides using combustion synthesis methods.

5. Post-Processing of HEA Coatings

The fabrication of HEAs coatings involves various non-equilibrium processes owing to severe deformation of the matrix, rapid cooling, chemical and solid-liquid phase changes which degrade the adhesion led to premature failure of the substrate [102,103]. Besides, the weak interfacial forces due to the formation of pores/voids and incorporated gaseous elements caused by thermal stress cause anisotropy and interface incompatibility in the long run [104,105]. Therefore, several modification processes are needed to modify the surface characteristics and improve the coating adhesion. The various post-processing techniques of HEA coatings include annealing, friction stir processing, and laser re-melting.

Laser-based methods (laser cladding, laser surface alloying, and laser additive manufacturing) are the most promising methods of HEA coatings, which are associated with large solidification cracks and porosity in the microstructure due to rapid heating and cooling processes [104–106]. A continuous rate of change in the heat energy causes the formation of crystal defects, lattice distortion, and retardation of solubility limits, residual stresses, and composition non-uniformity [103,104]. Also, the layerwise manufacturing processes result in microstructural anisotropy due to the heat gradient [104,105]. Zhang et al. performed annealing of the laser rapid solidified 6FeNiCoCrAlTiSi HEA coating at 500 °C. They found a great improvement in the solidified grain morphology [90].

After annealing, the interdendritic morphology turned into polygonal grains, as in the marked circles (Figure 6). The results indicated that columnar grains transform to the equiaxed after annealing treatment without any appreciable change in microhardness (Figure 6a,b). Similar behavior is also seen in the case of friction stir processing (FSP) modified HEA coatings. FSP has been widely used as a surface modification method for mostly laser alloyed coatings. Li and his co-workers treated laser deposited CrFeCoNiMoWC HEA coatings by FSP. The authors found that the dendritic HEA coatings turned into nanoscale grains (5–100 nm) with dispersed nano precipitates after FSP treatment [107]. Figure 6 shows the morphology of the FSPed plastic zone. Due to the high value of frictional heat produced in FSP, large forging load and severe plastic deformation cause severe grain refinement and homogeneous dispersion of the brittle phases in the HEA coatings [108]. In addition, the process also eliminates the formation of various pores and voids which existed before and enhances the surface performances. The strength and ductility trade-off of the cast HEAs have also been noticed to enhance simultaneously when treated with FSP.

Figure 6. Cross-section microstructure of the 6FeNiCoCrAlTiSi HEA coating. (a) Before annealing, and (b) after annealing [90]. Copyright 2011 Elsevier.

Some researchers have utilized the laser re-melting process to enhance the microstructure of HEA coatings produced by ultrafast melting and solidification. The internal defects can be eliminated and the interfacial interactions with the HEAs constituents can be restricted on the low melting base alloys such as Al, Mg, Zn alloys [109,110]. Such a combination of laser-remelting has been widely used for post modification of various HEA coatings in the past produced by thermal spray, cold spray, laser clad, arc spray, HVOF based coatings. Jin and his co-workers prepared plasma-sprayed $\text{FeCoCrNiAl}_{0.5}\text{Si}_x$ HEA coatings and subsequently subjected them to laser remelting. The authors found a great improvement in the bonding and surface performance [111]. The as-sprayed lamellar, flat, and weakly bonded coatings were changed into a network of dendrites and there was no change in the phase composition of HEAS coating before, and after, laser melting. It was argued that the laser power that controls the heat input primarily determines the life of re-melted coatings [111]. Cai and his co-workers studied the effect of laser power during re-melting of NiCrCoTiV laser clad coatings. There was no change in the morphology and phase composition of the coatings, while the Ti-rich particles segregated at high temperatures during re-melting [112]. Composite HEAs have also been investigated to improve the final strength and wear performance.

Jiang et al. fabricated studied the wear performance of FeCoCrAlCu by laser alloying surface method. The authors also treated the HEA coating with TiC particles. The microstructure consisted of BCC and FCC phase with embedded TiC particles. The authors found that there exists a certain degree of TiC volume fraction (50%) to obtain improved wear and strength properties [113].

Figure 7 shows the EBSD and inverse pole figure maps of TiC reinforced FeCoCrFeCu HEA coating. The different colors present different grain orientations. This investigation suggested that the grain anisotropy can be controlled after the addition of TiC particles in a certain fraction. The inverse pole figures of FeCoCrAlCu and $\text{FeCoCrAlCu-50 wt.\%TiC}$ HEA coatings are shown in (Figure 7c,d). The different colors (red, green, blue) represent anisotropy in different grain orientations ($\langle 001 \rangle$, $\langle 101 \rangle$, $\langle 111 \rangle$). It was noticed that no preferred grain orientation in composite and monolithic HEAs coatings was observed, but the texture intensity of FeCoCrAlCu , containing 50%TiC, was higher (7.17), and compared with FeCoCrAlCu HEA coating (2.90). Authors have used various kinds of composite coatings to improve the wear, corrosion, and strength performance of HEA coatings [72,73]. It can be seen that coatings composed of ceramic particles, heat treatment procedures, laser remelting, and FSP processes are all effective in surface engineering of HEA coatings that improve the coating quality and controls the porosity and defects.

Figure 7. Grain orientations and anisotropy. (a,c) FeCoCrAlCu HEA, (b,d) FeCoCrAlCu-50%TiC HEA coating [113].

6. Summary, Concluding Remarks, and Future Scope

This article briefly discussed the properties of the several HEA coatings, their fabrication, and their application. It can be seen that enough attention has been paid to this area in improving the surface of a material. As indicated, the properties of the HEAs nitride, oxide, or boride coatings, are promising with a few showing impressive performances. In contrast, not all HEA coatings have a better or enhanced surface protection ability. Therefore, there is a great need to develop a fundamental understanding of this class of materials to consistently move forward in developing a HEA coating that can provide superior performance.

- The multi-component HEA, and related coatings, form an attractive class of materials that display a wide potential for competitive applications.
- The full potential of these HEA coatings can be only realized by attempting enough research activities, a combination of new strategies, and data-driven methodology.
- In this article, the background and state of art in HEA-related coatings, their fabrication types, and applications according to their classification based on the previous literature are covered. However, there are several open questions such as stability of the phase, homogeneity of coating concerning metal to N, O, or C ratio, order-disordering in HEA coatings, etc.
- The rapid solidification processes involved in such post modification techniques, especially laser-based methods, need to be further investigated to control the porosity and residual stresses developed due to the high energy density laser beam.
- Despite few good reports on electroplating, chemical-based routes have to be attempted due to a scarcity of such HEAs coatings which can be an economical option when compared with laser and magnetron-based techniques.

Considering a huge constituent composition space and the number of possible permutations and combinations in a solid solution phase, traditional methods of metallurgy may

not be sufficient to deal with these unique concepts. The material composition and design complexity increase with the number of possible combinations and compositions, where the traditional metallurgy principles will not meet the demands and consume time in achieving results. To solve the issues of material design, advanced materials characterization techniques, combined with theoretical simulation, are needed. Further, the combination of traditional metallurgy knowledge-base with new data-driven methodologies/machine learning approaches may be considered.

Funding: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2018R1D1A1B07044706). This research was supported by the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2009-0082580).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2018R1D1A1B07044706). This research was supported by the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2009-0082580).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Evans, C.J.; Bryan, J.B. Structured, textured or engineered surfaces. *Ann. CIRP* **1999**, *48*, 541–556. [\[CrossRef\]](#)
2. Stout, K.J. Engineered surfaces—A philosophy of manufacture. *Proc. Inst. Mech. Eng.* **1998**, *212*, 169–174. [\[CrossRef\]](#)
3. Khodakarami, S.; Zhao, H.; Rabbi, K.F.; Miljkovic, N. Scalable Corrosion-Resistant Coatings for Thermal Applications. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4519–4534. [\[CrossRef\]](#)
4. Yan, M.; Sun, C.; Xu, J.; Ke, W. Anoxic Corrosion Behavior of Pipeline Steel in Acidic Soils. *Ind. Eng. Chem. Res.* **2014**, *53*, 17615–17624. [\[CrossRef\]](#)
5. Koerner, C.M.; Hopkinson, D.P.; Ziomek-Moroz, M.E.; Rodriguez, A.; Xiang, F. Environmentally friendly tannic acid multilayer coating for reducing corrosion of carbon steel. *Ind. Eng. Chem. Res.* **2021**, *60*, 243–250. [\[CrossRef\]](#)
6. Abadias, G.; Chason, E.; Keckes, J.; Marco, S.; Thompson, G.B.; Barthel, E.; Doll, G.L.; Murray, C.E.; Stoessel, C.H.; Martinu, L. Stress in thin films and coatings: Current status, challenges, and prospects. *J. Vac. Sci. Technol. A* **2018**, *36*, 020801. [\[CrossRef\]](#)
7. Chinnusamy, S.; Ramasamy, V.; Venkatajalapathy, S.; Kaliyannan, G.V.; Palaniappan, S.K. Experimental investigation on the effect of ceramic coating on the wear resistance of Al6061 substrate. *J. Mater. Res. Technol.* **2019**, *8*, 6125–6133. [\[CrossRef\]](#)
8. Ramazan, K.; Levent, U.; Ali, C.; Serdar, S.; Fehim, F. Three types of ceramic coating applicability in automotive industry for wear resistance purpose. *Ind. Lubr. Tribol.* **2005**, *57*, 140–144.
9. Kulu, P.; Tarbe, R.; Vallikivi, A. Abrasive wear of powder materials and coatings. *Mater. Sci.* **2005**, *11*, 230–234.
10. Borkar, T.; Harimkar, S. Microstructure and wear behaviour of pulse electrodeposited Ni–CNT composite coatings. *Surf. Eng.* **2011**, *27*, 524–530. [\[CrossRef\]](#)
11. Chen, S.; Brown, L.; Levendorf, M.; Cai, W.; Ju, S.-Y.; Edgeworth, J.; Li, X.; Magnuson, C.W.; Velamakanni, A.; Piner, R.D.; et al. Oxidation Resistance of Graphene-Coated Cu and Cu/Ni Alloy. *ACS Nano* **2011**, *5*, 1321–1327. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Abdel-Aal, H.A. Functional surfaces for tribological applications: Inspiration and design. *Surf. Topogr. Metrol. Prop.* **2016**, *4*, 043001. [\[CrossRef\]](#)
13. Qin, D.; Xu, G.; Yang, Y.; Chen, S. Multiphase ceramic coatings with high hardness and wear resistance on 5052 aluminum alloy by a microarc oxidation method. *ACS Sustain. Chem. Eng.* **2018**, *6*, 2431–2437. [\[CrossRef\]](#)
14. Chen, X.; Han, Z.; Lu, K. Friction and Wear Reduction in Copper with a Gradient Nano-grained Surface Layer. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13829–13838. [\[CrossRef\]](#)
15. Ding, Q.; Zhang, Y.; Chen, X.; Fu, X.; Chen, D.; Chen, S.; Gu, L.; Wei, F.; Bei, H.; Gao, Y.; et al. Tuning element distribution, structure and properties by composition in high-entropy alloys. *Nat. Cell Biol.* **2019**, *574*, 223–227. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Varvenne, C.; Luque, A.; Curtin, W.A. Theory of strengthening in fcc high entropy alloys. *Acta Mater.* **2016**, *118*, 164–176. [\[CrossRef\]](#)
17. Zhang, Y.; Zuo, T.T.; Tang, Z.; Gao, M.C.; Dahmen, K.A.; Liaw, P.K.; Lu, Z.P. Microstructures and properties of high-entropy alloys. *Prog. Mater. Sci.* **2014**, *61*, 1–93. [\[CrossRef\]](#)

18. Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H.; Chang, S.-Y. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303. [\[CrossRef\]](#)
19. Cantor, B.; Chang, I.; Knight, P.; Vincent, A. Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* **2004**, *375–377*, 213–218. [\[CrossRef\]](#)
20. Kuzminova, Y.O.; Firsov, D.G.; Dagesyan, S.A.; Konev, S.D.; Sergeev, S.N.; Zhilyaev, A.P.; Kawasaki, M.; Akhatov, I.S.; Evlashin, S.A. Fatigue behavior of additive manufactured CrFeCoNi medium-entropy alloy. *J. Alloys Compd.* **2021**, *863*, 158609. [\[CrossRef\]](#)
21. Yan, X.; Zhang, Y. Functional properties and promising applications of high entropy alloys. *Scr. Mater.* **2020**, *187*, 188–193. [\[CrossRef\]](#)
22. Senkov, O.N.; Wilks, G.B.; Scott, J.M.; Miracle, D.B. Mechanical properties of Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys. *Intermetallics* **2011**, *19*, 698–706. [\[CrossRef\]](#)
23. Sharma, A.; Oh, M.C.; Ahn, B. Microstructural evolution and mechanical properties of non-Cantor AlCuSiZnFe lightweight high entropy alloy processed by advanced powder metallurgy. *Mater. Sci. Eng. A* **2020**, *797*, 140066. [\[CrossRef\]](#)
24. Wang, W.R.; Wang, W.L.; Yeh, J.W. Phases, microstructure and mechanical properties of Al_xCoCrFeNi high-entropy alloys at elevated temperatures. *J. Alloys Compd.* **2014**, *589*, 143–152. [\[CrossRef\]](#)
25. Wang, W.R.; Wang, W.L.; Wang, S.C.; Tsai, Y.C.; Lai, C.H.; Yeh, J.W. Effects of Al addition on the microstructure and mechanical property of Al_xCoCrFeNi high-entropy alloys. *Intermetallics* **2012**, *26*, 44–51. [\[CrossRef\]](#)
26. Todai, M.; Nagase, T.; Hori, T.; Matsugaki, A.; Sekita, A.; Nakano, T. Novel TiNbTaZrMo high-entropy alloys for metallic biomaterials. *Scr. Mater.* **2017**, *129*, 65–68. [\[CrossRef\]](#)
27. Gludovatz, B.; Hohenwarter, A.; Catoor, D.; Chang, E.H.; George, E.P.; Ritchie, R.O. A fracture-resistant high-entropy alloy for cryogenic applications. *Science* **2014**, *345*, 1153–1158. [\[CrossRef\]](#)
28. Xu, X.D.; Liu, P.; Hirata, A.; Song, S.X.; Nieh, T.G.; Chen, M.W. Microstructural origins for a strong and ductile Al_{0.1}CoCrFeNi high-entropy alloy with ultrafine grains. *Materialia* **2018**, *4*, 395–405. [\[CrossRef\]](#)
29. Xu, X.D.; Chen, S.Y.; Ren, Y.; Hirata, A.; Fujita, T.; Liaw, P.K.; Chen, M.W. Temperature-dependent compression behavior of an Al_{0.5}CoCrCuFeNi high-entropy alloy. *Materialia* **2019**, *5*, 100243. [\[CrossRef\]](#)
30. Tucker, R.C., Jr. Thermal spray coatings. In *ASM Handbook Vol. 5: Surface Engineering*; Cotell, C.M., Sprague, J.A., Smidt, F.A., Jr., Eds.; ASM International: Materials Park, OH, USA, 1994; pp. 497–509.
31. Lee, S.Y.; Byeon, S.; Kim, H.S.; Jin, H.; Lee, S. Deep learning-based phase prediction of high-entropy alloys: Optimization, generation, and explanation. *Mater. Des.* **2021**, *197*, 109260. [\[CrossRef\]](#)
32. Fu, X.; Schuh, C.A.; Olivetti, E.A. Materials selection considerations for high entropy alloys. *Scr. Mater.* **2017**, *138*, 145–150. [\[CrossRef\]](#)
33. Guo, Y.; Shang, X.; Liu, Q. Microstructure and properties of in situ TiN reinforced laser cladding CoCr₂FeNiTi_x high-entropy alloy composite coatings. *Surf. Coat. Technol.* **2018**, *344*, 353–358. [\[CrossRef\]](#)
34. Li, X.; Feng, Y.; Liu, B.; Yi, D.; Yang, X.; Zhang, W.; Chen, G.; Liu, Y.; Bai, P. Influence of NbC particles on microstructure and mechanical properties of AlCoCrFeNi high-entropy alloy coatings prepared by laser cladding. *J. Alloys Compd.* **2019**, *788*, 485–494. [\[CrossRef\]](#)
35. Cheng, J.; Liu, D.; Liang, X.; Chen, Y. Evolution of microstructure and mechanical properties of in situ synthesized TiC–TiB₂/CoCrCuFeNi high entropy alloy coatings. *Surf. Coat. Technol.* **2015**, *281*, 109–116. [\[CrossRef\]](#)
36. Youssef, K.M.; Zaddach, A.J.; Niu, C.; Irving, D.L.; Koch, C.C. A novel low-density, high-hardness, high entropy alloy with close-packed single-phase nanocrystalline structures. *Mater. Res. Lett.* **2015**, *3*, 95–99. [\[CrossRef\]](#)
37. Chae, M.J.; Sharma, A.; Oh, M.C.; Ahn, B. Lightweight AlCuFeMnMgTi High Entropy Alloy with High Strength-to-Density Ratio Processed by Powder Metallurgy. *Met. Mater. Int.* **2020**, *1–10*. [\[CrossRef\]](#)
38. Juan, C.C.; Yeh, J.W.; Chin, T.S. A novel light high-entropy alloy Al₂₀Be₂₀Fe₁₀Si₁₅Ti₃₅. In Proceedings of the E-MRS Fall Meeting, Symposium I, Warsaw, Poland, 14–18 September 2009.
39. Pogrebnjak, A.D.; Beresnev, V.M.; Smyrnova, K.V.; Kravchenko, Y.O.; Zukowski, P.V.; Bondarenko, G.G. The influence of nitrogen pressure on the fabrication of the two-phase superhard nanocomposite (TiZrNbAlYCr)N coatings. *Mater. Lett.* **2018**, *211*, 316–318. [\[CrossRef\]](#)
40. Bagdasaryan, A.A.; Pshyk, A.V.; Coy, L.E.; Konarski, P.; Misnik, M.; Ivashchenko, V.I.; Kempinski, M.; Mediuikh, N.R.; Pogrebnjak, A.D.; Beresnev, V.M.; et al. A new type of (TiZrNbTaHf)N/MoN nanocomposite coating: Microstructure and properties depending on energy of incident ions. *Compos. Part B-Eng.* **2018**, *146*, 132–144. [\[CrossRef\]](#)
41. Chang, S.Y.; Lin, S.Y.; Huang, Y.C.; Wu, C.L. Mechanical properties, deformation behaviors and interface adhesion of (AlCrTa–TiZr)N_x multi-component coatings. *Surf. Coat. Technol.* **2010**, *204*, 3307–3314. [\[CrossRef\]](#)
42. Lin, S.Y.; Chang, S.Y.; Huang, Y.C.; Shieu, F.S.; Yeh, J.W. Mechanical performance and nanoindenting deformation of (AlCrTa–TiZr)N_{Cy} multi-component coatings co-sputtered with bias. *Surf. Coat. Technol.* **2012**, *206*, 5096–5102. [\[CrossRef\]](#)
43. Wan, H.; Song, D.; Shi, X.; Cai, Y.; Li, T.; Chen, C. Corrosion behavior of Al_{0.4}CoCu_{0.6}NiSi_{0.2}Ti_{0.25} high-entropy alloy coating via 3D printing laser cladding in a sulphur environment. *J. Mater. Sci. Technol.* **2021**, *60*, 197–205. [\[CrossRef\]](#)
44. Barron, P.J.; Carruthers, A.W.; Fellowes, J.W.; Jones, N.G.; Dawson, H.; Pickering, E.J. Towards V-based high-entropy alloys for nuclear fusion applications. *Scr. Mater.* **2020**, *176*, 12–16. [\[CrossRef\]](#)

45. Tian, L.; Feng, Z.; Xiong, W. Microstructure, microhardness, and wear resistance of AlCoCrFeNiTi/Ni₆₀ coating by plasma spraying. *Coatings* **2018**, *8*, 112. [\[CrossRef\]](#)
46. Tsai, D.C.; Chang, Z.C.; Kuo, L.Y.; Lin, T.J.; Lin, T.N.; Shieu, F.S. Solid solution coating of (TiVCrZrHf)N with unusual structural evolution. *Surf. Coat. Technol.* **2013**, *217*, 84–87. [\[CrossRef\]](#)
47. Chang, S.Y.; Li, C.E.; Chiang, S.C.; Huang, Y.C. 4-nm thick multilayer structure of multi-component (AlCrRuTaTiZr)N_x as robust diffusion barrier for Cu interconnects. *J. Alloys Compd.* **2012**, *515*, 4–7. [\[CrossRef\]](#)
48. Guo, Y.; Li, X.; Liu, Q. A novel biomedical high-entropy alloy and its laser-clad coating designed by a cluster-plus-glue-atom model. *Mater. Des.* **2020**, *196*, 109085. [\[CrossRef\]](#)
49. Nam, S.; Kim, C.; Kim, Y.M. Recent studies of the laser cladding of high entropy alloys. *JWJ* **2017**, *35*, 58–66. [\[CrossRef\]](#)
50. Ni, C.; Shi, Y.; Liu, J.; Huang, G. Characterization of Al_{0.5}FeCu_{0.7}NiCoCr high-entropy alloy coating on aluminum alloy by laser cladding. *G. Opt. Laser Technol.* **2018**, *105*, 257–263. [\[CrossRef\]](#)
51. Zhang, H.; Wu, W.; He, Y.; Li, M.; Guo, S. Formation of core-shell structure in high entropy alloy coating by laser cladding. *Appl. Surf. Sci.* **2016**, *363*, 543–547. [\[CrossRef\]](#)
52. Qiu, X.W.; Zhang, Y.P.; Liu, C.G. Effect of Ti content on structure and properties of Al₂CrFeNiCoCuTi_x high-entropy alloy coatings. *J. Alloys Compd.* **2014**, *585*, 282–286. [\[CrossRef\]](#)
53. Zhang, H.; Pan, Y.; He, Y.Z. Synthesis and characterization of FeCoNiCrCu highentropy alloy coating by laser cladding. *Mater. Des.* **2011**, *32*, 1910–1915. [\[CrossRef\]](#)
54. Cai, Z.; Wang, Y.; Cui, X.; Jin, G.; Li, Y.; Liu, Z.; Dong, M. Design and Microstructure Characterization of FeCoNiAlCu High-Entropy Alloy Coating by Plasma Cladding: In Comparison with Thermodynamic Calculation. *Surf. Coat. Technol.* **2017**, *330*, 163–169. [\[CrossRef\]](#)
55. Fang, Q.; Chen, Y.; Li, J.; Liu, Y.; Liu, Y. Microstructure and mechanical properties of FeCoCrNiNb_x high-entropy alloy coatings. *Physica B* **2018**, *550*, 112–116. [\[CrossRef\]](#)
56. Meng, G.H.; Lin, X.; Xie, H.; Yue, T.M.; Ding, X.; Sun, L.; Qi, M. The effect of Cu rejection in laser forming of AlCoCrCuFeNi/Mg composite coating. *Mater. Des.* **2016**, *108*, 157–167. [\[CrossRef\]](#)
57. Shu, F.; Yang, B.; Dong, S.; Zhao, H.; Xu, B.; Xu, F.; Liu, B.; He, P.; Feng, J. Effects of Fe-to-Co ratio on microstructure and mechanical properties of laser clad FeCoCrBNiSi high-entropy alloy coatings. *J. Appl. Surf. Sci.* **2018**, *450*, 538–544. [\[CrossRef\]](#)
58. Zhang, S.; Wu, C.L.; Yi, J.Z.; Zhang, C.H. Synthesis and characterization of FeCoCrAlCu high-entropy alloy coating by laser surface alloying. *Surf. Coat. Technol.* **2015**, *262*, 64–69. [\[CrossRef\]](#)
59. Ye, Q.; Feng, K.; Li, Z.; Lu, F.; Li, R.; Huang, J.; Wu, Y. Microstructure and corrosion properties of CrMnFeCoNi high entropy alloy coating. *Appl. Surf. Sci.* **2017**, *396*, 1420–1426. [\[CrossRef\]](#)
60. Cai, Z.; Cui, X.; Jin, G.; Lu, B.; Zhang, D.; Zhang, Z. In situ TEM tensile testing on high-entropy alloy coating by laser surface alloying. *J. Alloys Compd.* **2017**, *708*, 380–384. [\[CrossRef\]](#)
61. Zhang, S.; Wu, C.L.; Zhang, C.H. Phase evolution characteristics of FeCoCrAlCuV_xNi high entropy alloy coatings by laser high-entropy alloying. *Mater. Lett.* **2015**, *141*, 7–9. [\[CrossRef\]](#)
62. Wu, C.L.; Zhang, S.; Zhang, C.H.; Zhang, H.; Dong, S.Y. Phase evolution and properties in laser surface alloying of FeCoCrAlCuNi_x high-entropy alloy on copper substrate. *Surf. Coat. Technol.* **2017**, *315*, 368–376. [\[CrossRef\]](#)
63. Yin, S.; Li, W.; Song, B.; Yan, X.; Kuang, M.; Xu, Y.; Wen, K.; Lupoi, R. Deposition of FeCoNiCrMn high entropy alloy (HEA) coating via cold spraying. *J. Mater. Sci. Technol.* **2019**, *35*, 1003–1007. [\[CrossRef\]](#)
64. Löbel, M.; Lindner, T.; Mehner, T.; Thomas, L. Microstructure and wear resistance of AlCoCrFeNiTi high-entropy alloy coatings produced by HVOF. *Coatings* **2017**, *7*, 144. [\[CrossRef\]](#)
65. Yue, T.M.; Xie, H.; Lin, X.; Yang, H.; Meng, G. Microstructure of laser re-melted AlCoCrCuFeNi high entropy alloy coatings produced by plasma spraying. *Entropy* **2013**, *15*, 2833–2845. [\[CrossRef\]](#)
66. Tian, L.; Wei, X.; Liu, C.; Lu, S.; Fu, M. Microstructure and wear behavior of atmospheric plasma-sprayed AlCoCrFeNiTi high-entropy alloy coating. *J. Mater. Eng. Perform.* **2016**, *25*, 5513–5521. [\[CrossRef\]](#)
67. Tüten, N.; Canadinc, D.; Motallebzadeh, A.; Bal, B. Microstructure and tribological properties of TiTaHfNbZr high entropy alloy coatings deposited on Ti-6Al-4V substrates. *Intermetallics* **2019**, *105*, 99–106. [\[CrossRef\]](#)
68. Lin, C.H.; Duh, J.G. Corrosion behavior of (Ti–Al–Cr–Si–V)_xN_y coatings on mild steels derived from RF magnetron sputtering. *Surf. Coat. Technol.* **2008**, *203*, 558–561. [\[CrossRef\]](#)
69. Braic, V.; Vladescu, A.; Balaceanu, M.; Luculescu, C.R.; Braic, M. Nanostructured multi-element (TiZrNbHfTa)N and (TiZrNbHfTa)C hard coatings. *Surf. Coat. Technol.* **2012**, *211*, 117–121. [\[CrossRef\]](#)
70. Shang, C.; Axinte, E.; Ge, W.; Zhang, Z.; Wang, Y. High-entropy alloy coatings with excellent mechanical, corrosion resistance and magnetic properties prepared by mechanical alloying and hot pressing sintering. *Surf. Interface* **2017**, *9*, 36–43. [\[CrossRef\]](#)
71. Tian, Y.; Shen, Y.; Lu, C.; Feng, X. Microstructures and oxidation behavior of Al–CrMnFeCoMoW composite coatings on Ti-6Al-4V alloy substrate via high-energy mechanical alloying method. *J. Alloys Compd.* **2019**, *779*, 456–465. [\[CrossRef\]](#)
72. Aliyu, A.; Srivastava, C. Microstructure-corrosion property correlation in electrodeposited AlCrFeCoNiCu high entropy alloys-graphene oxide composite coatings. *Thin Solid Films* **2019**, *686*, 137434. [\[CrossRef\]](#)
73. Soare, V.; Burada, M.; Constantin, I.; Mitrica, D.; Badilit, V.; Caragea, A.; Târcolea, M. Electrochemical deposition and microstructural characterization of AlCrFeMnNi and AlCrCuFeMnNi high entropy alloy thin films. *Appl. Surf. Sci.* **2015**, *358*, 533–539. [\[CrossRef\]](#)

74. Huang, P.K.; Yeh, J.W.; Shun, T.T.; Chen, S.K. Multi-principal-element alloys with improved oxidation and wear resistance for thermal spray coating. *Adv. Eng. Mater.* **2004**, *6*, 74–78. [\[CrossRef\]](#)
75. Wang, L.M.; Chen, C.C.; Yeh, J.W.; Ke, S.T. The microstructure and strengthening mechanism of thermal spray coating $\text{Ni}_{10}\text{Co}_{10}\text{Fe}_{10}\text{Cr}_{10}\text{Ti}_{10}\text{Al}_{10}\text{Zr}_{10}$ high-entropy alloys. *Mater. Chem. Phys.* **2011**, *126*, 880–885. [\[CrossRef\]](#)
76. Hushchuk, D.V.; Yurkova, A.I.; Cherniavsky, V.V.; Bilyk, L.I.; Nakonechnyy, S.O. Nanostructured AlNiCoFeCrTi high-entropy coating performed by cold spray. *Appl. Nanosci.* **2020**, *10*, 4879–4890. [\[CrossRef\]](#)
77. Ajdelsztajn, L.; Zúñiga, A.; Jodoin, B.; Lavernia, E.J. Cold gas dynamic spraying of a high temperature Al alloy. *Surf. Coat. Technol.* **2006**, *201*, 2109–2116. [\[CrossRef\]](#)
78. Cai, Z.; Cui, X.; Jin, G.; Liu, Z.; Li, Y.; Dong, M. TEM observation on phase separation and interfaces of laser surface alloyed high-entropy alloy coating. *Micron* **2017**, *103*, 84–89. [\[CrossRef\]](#)
79. Lu, J.; Wang, B.; Qiu, X.; Peng, Z.; Ma, M. Microstructure evolution and properties of CrCuFeNiTi high-entropy alloy coating by plasma cladding on Q235. *Surf. Coat. Technol.* **2017**, *328*, 313–318. [\[CrossRef\]](#)
80. Zhang, H.; He, Y.; Pan, Y.; He, Y.; Shin, K. Synthesis and characterization of NiCoFeCrAl₃ high entropy alloy coating by laser cladding. *Adv. Mater. Res.* **2010**, *97–101*, 1408–1411. [\[CrossRef\]](#)
81. Lai, C.H.; Lin, S.J.; Yeh, J.W.; Chang, S.Y. Preparation and characterization of AlCrTaTiZr multi-element nitride coatings. *Surf. Coat. Technol.* **2006**, *201*, 3275–3280. [\[CrossRef\]](#)
82. Chen, T.K.; Shun, T.T.; Yeh, J.W.; Wong, M.S. Nanostructured nitride films of multi-element high-entropy alloys by reactive DC sputtering. *Surf. Coat. Technol.* **2004**, *188–189*, 193–200. [\[CrossRef\]](#)
83. Ren, B.; Shen, Z.; Liu, Z. Structure and mechanical properties of multi-element (AlCrMnMoNiZr)_{N_x} coatings by reactive magnetron sputtering. *J. Alloys Compd.* **2013**, *560*, 171–176. [\[CrossRef\]](#)
84. Tsai, D.C.; Deng, M.J.; Chang, Z.C.; Kuo, B.H.; Chen, E.C.; Chang, S.Y.; Shieu, F.S. Oxidation resistance and characterization of (AlCrMoTaTi)-Six-N coating deposited via magnetron sputtering. *J. Alloys Compd.* **2015**, *647*, 179–188. [\[CrossRef\]](#)
85. Zhang, W.; Tang, R.; Yang, Z.B.; Liu, C.H.; Chang, H.; Yang, J.J.; Liao, J.L.; Yang, Y.Y.; Liu, N. Preparation, structure, and properties of high-entropy alloy multilayer coatings for nuclear fuel cladding: A case study of AlCrMoNbZr/(AlCrMoNbZr)_N. *J. Nucl. Mater.* **2018**, *512*, 15–24. [\[CrossRef\]](#)
86. Sharma, A.; Bhattacharya, S.; Das, S.; Fecht, H.J.; Das, K. Development of lead free pulse electrodeposited tin based composite solder coating reinforced with ex situ cerium oxide nanoparticles. *J. Alloys Compd.* **2013**, *574*, 609–616. [\[CrossRef\]](#)
87. Sharma, A.; Ahn, B. Dry sliding wear behavior of Sn and NiSn overlays on Cu connectors. *Trib. Lett.* **2018**, *66*, 136. [\[CrossRef\]](#)
88. Chen, C.; Feng, X.; Shen, Y. Oxidation behavior of a high Si content Al–Si composite coating fabricated on Ti–6Al–4V substrate by mechanical alloying method. *J. Alloys Compd.* **2017**, *701*, 27–36. [\[CrossRef\]](#)
89. Zhang, H.X.; Dai, J.J.; Sun, C.X.; Li, S.Y. Microstructure and wear resistance of TiAlNiSiV high-entropy laser cladding coating on Ti–6Al–4V. *J. Mater. Proc. Technol.* **2020**, *282*, 116671. [\[CrossRef\]](#)
90. Zhang, H.; Pan, Y.; He, Y.Z. Grain refinement and boundary misorientation transition by annealing in the laser rapid solidified 6FeNiCoCrAlTiSi multicomponent ferrous alloy coating. *Surf. Coat. Technol.* **2011**, *205*, 4068–4072. [\[CrossRef\]](#)
91. Tian, L.; Fu, M.; Xiong, W. Microstructural evolution of AlCoCrFeNiSi high-entropy alloy powder during mechanical alloying and its coating performance. *Materials* **2018**, *11*, 320. [\[CrossRef\]](#)
92. Sharma, A.; Das, S.; Das, K. Pulse electrodeposition of lead-free tin-based composites for microelectronic packaging. In *Electrodeposition of Composite Materials*; Mohamed, A.M.A., Golden, T.D., Eds.; IntechOpen: Rijeka, Croatia, 2016; pp. 253–274. [\[CrossRef\]](#)
93. Sharma, A.; Das, S.; Das, K. Pulse electroplating of ultrafine grained tin coating. In *Electroplating of Nanostructures*; Aliofkhaeaei, M., Ed.; IntechOpen: Rijeka, Croatia, 2015; pp. 105–129. [\[CrossRef\]](#)
94. Sharma, S.; Bhattacharya, S.; Das, S.; Das, K. Fabrication of Sn nanostructures by template assisted pulse electrodeposition. *Surf. Eng.* **2016**, *32*, 378–384. [\[CrossRef\]](#)
95. Sharma, A.; Bhattacharya, S.; Das, S.; Das, S. A study on the effect of pulse electrodeposition parameters on the morphology of pure tin coatings. *Metall. Mater. Trans. A* **2014**, *45*, 4610–4622. [\[CrossRef\]](#)
96. Zheng, M.; Li, Y.; Hu, J.; Zhao, Y.; Yu, L. Preparation of high entropy alloy thin film fencobimn by electroplating deposition method. *MSAIF* **2014**, *11*, 344–348.
97. Braic, V.; Balaceanu, M.; Braic, M.; Vladescu, A.; Panseri, S.; Russo, A. Characterization of multi-principal-element (TiZrNbHfTa)_N and (TiZrNbHfTa)_C coatings for biomedical applications. *J. Mech. Behav. Biomed. Mater.* **2012**, *10*, 197–205. [\[CrossRef\]](#) [\[PubMed\]](#)
98. Yoosefan, F.; Ashrafi, A.; Vaghef, S.M.M.; Constantin, I. Synthesis of CoCrFeMnNi high entropy alloy thin films by pulse electrodeposition: Part 1: Effect of pulse electrodeposition parameters. *Met. Mater. Int.* **2020**, *26*, 1262–1269. [\[CrossRef\]](#)
99. Yao, C.Z.; Zhang, P.; Liu, M.; Li, G.R.; Ye, J.Q.; Liu, P. Electrochemical preparation and magnetic study of Bi–Fe–Co–Ni–Mn high entropy alloy. *Electrochim. Acta* **2008**, *53*, 8359–8365. [\[CrossRef\]](#)
100. Bhattacharya, S.; Sharma, A.; Das, S.; Das, K. Synthesis and properties of pulse electrodeposited lead-free tin-based Sn/ZrSiO₄ nanocomposite coatings. *Metall. Mater. Trans. A* **2016**, *47*, 1292–1312. [\[CrossRef\]](#)
101. Moskovskikh, D.; Vorotilo, S.; Buinevich, V.; Sedegov, A.; Kuskov, K.; Khort, A.; Shuck, C.; Zhukovskyi, M.; Mukasyan, A. Extremely hard and tough high entropy nitride ceramics. *Sci. Rep.* **2020**, *10*, 19874. [\[CrossRef\]](#)
102. Zhao, J.; Gao, Q.; Wang, H.; Shu, F.; Zhao, H.; He, W.; Yu, Z. Microstructure and mechanical properties of Co-based alloy coatings fabricated by laser cladding and plasma arc spray welding. *J. Alloys Compd.* **2019**, *785*, 846–854. [\[CrossRef\]](#)

103. Lin, Y.; Cho, Y. Elucidating the microstructure and wear behavior for multicomponent alloy clad layers by in situ synthesis. *Surf. Coat. Technol.* **2008**, *202*, 4666–4672. [[CrossRef](#)]
104. Chen, Y.Y.; Hong, U.T.; Yeh, J.W.; Shih, H.C. Selected corrosion behaviors of a Cu_{0.5}NiAlCoCrFeSi bulk glassy alloy in 288 °C high-purity water. *Scr. Mater.* **2006**, *54*, 1997–2001. [[CrossRef](#)]
105. Zhang, H.; Pan, Y.; He, Y.; Jiao, H. Microstructure and properties of 6FeNiCoSiCrAlTi high-entropy alloy coating prepared by laser cladding. *Appl. Surf. Sci.* **2011**, *257*, 2259–2263. [[CrossRef](#)]
106. Sharma, A.; Oh, M.C.; Kim, J.T.; Srivastava, A.K.; Ahn, B. Investigation of electrochemical corrosion behavior of additive manufactured Ti–6Al–4V alloy for medical implants in different electrolytes. *J. Alloys Compd.* **2020**, *830*, 154620. [[CrossRef](#)]
107. Li, R.; Wang, M.; Yuan, T.; Song, B.; Shi, Y. Microstructural Modification of Laser-Deposited High-Entropy CrFeCoNiMoWC Alloy by Friction Stir Processing: Nanograin Formation and Deformation Mechanism. *Metall. Mater. Trans. A* **2017**, *48*, 841–854. [[CrossRef](#)]
108. Huang, Y.; Wang, Y.; Meng, X.; Wan, L.; Cao, J.; Zhou, L.; Feng, J. Dynamic recrystallization and mechanical properties of friction stir processed Mg–Zn–Y–Zr alloys. *J. Mater. Process. Technol.* **2017**, *249*, 331. [[CrossRef](#)]
109. Li, R.; Jin, Y.; Li, Z.; Zhu, Y.; Wu, M. Effect of the remelting scanning speed on the amorphous forming ability of Ni-based alloy using laser cladding plus a laser remelting process. *Surf. Coat. Technol.* **2014**, *259*, 725–731. [[CrossRef](#)]
110. Yilbas, B.S.; Akhtar, S.S. Laser re-melting of HVOF coating with WC blend: Thermal stress analysis. *J. Mater. Process. Technol.* **2012**, *212*, 2569–2577. [[CrossRef](#)]
111. Jin, B.; Zhang, N.; Guan, S.; Zhang, Y.; Li, D. Microstructure and properties of laser re-melting FeCoCrNiAl_{0.5}Si₆ high-entropy alloy coatings. *Surf. Coat. Technol.* **2018**, *349*, 867–873. [[CrossRef](#)]
112. Cai, Z.; Cui, X.; Liu, Z.; Li, Y.; Dong, M.; Jin, G. Microstructure and wear resistance of laser clad Ni–Cr–Co–Ti–V high-entropy alloy coating after laser remelting processing. *Opt. Laser Technol.* **2018**, *99*, 276–281. [[CrossRef](#)]
113. Jiang, P.F.; Zhang, C.H.; Zhang, S.; Zhang, J.B.; Chen, J.; Liu, Y. Fabrication and wear behavior of TiC reinforced FeCoCrAlCu-based high entropy alloy coatings by laser surface alloying. *Mater. Chem. Phys.* **2020**, *255*, 123571. [[CrossRef](#)]