Topical Review

A review on microstructures and properties of high entropy alloys manufactured by selective laser melting

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Abstract
High entropy alloys (HEAs) with multi-component solid solution microstructures have the potential for large-scale industrial applications due to their excellent mechanical and functional properties. However, the mechanical properties of HEAs limit the selection of processing technologies. Additive manufacturing technology possesses strong processing adaptability, making it the best candidate method to overcome this issue. This comprehensive review examines the current state of selective laser melting (SLM) of HEAs. Introducing SLM to HEAs processing is motivated by its high quality for dimensional accuracy, geometric complexity, surface roughness, and microstructure. This review focuses on analyzing the current developments and challenges in SLM of HEAs, including defects, microstructures, and properties, as well as strengthening prediction models of fabricated HEAs. This review also offers directions for future studies to address existing challenges and promote technological advancement.

Keywords: high entropy alloys, selective laser melting, microstructure, property, strengthening model

(Some figures may appear in colour only in the online journal)

1. Introduction
High entropy alloys (HEAs) are a class of unique metals consisting of approximately equal amounts of five or more metal elements [1–4]. The formation of the single solid solution structures in HEAs is attributed to the higher mixing entropy.

The four core effects include the high-entropy effect, sluggish diffusion effect, severe lattice distortion effect and cocktail effect [1–3, 5]. HEAs are featured with ideal mechanical and functional properties due to their unique multi-principal element compositions [6, 7]. Therefore, HEAs provide a main direction for designing next-generation metal materials, and are expected to have a wide range of industrial applications.

The most remarkable feature of HEAs is their high mechanical performance, and their ability to easily achieve a balance between strength and toughness. Ding’s latest research [8] showed sharp fluctuations in the distribution of HEA elements, which caused a significant room-temperature interstitial slip...
and a continuous movement of dislocations. The high stresses were reduced and divided to dispersive lower stresses, which gave the HEAs excellent strength and toughness properties. Compared to CrMnFeCoN, CrFeCoNiPd alloy has a more heterogeneous distribution and is 50% stronger than under the same plasticity [8]. Other characteristics of HEA mechanical performances are high strength and high toughness under extreme conditions, such as high or low temperatures, owing to the sluggish diffusion effect [9, 10]. The excellent elevated-temperature mechanical properties of HEAs produce outstanding wear resistance, while the superior oxidation resistance of HEAs is also improves their wear resistance, according to the mild oxidational wear mechanism [3]. HEAs exhibit excellent fatigue performance [11]. In addition, HEAs can also achieve excellent specific strength. Youssef et al [12] combined lithium, magnesium, titanium, aluminum and scandium to make a nanocrystalline Al29Li20Mg10Sc20Ti30 that had a higher strength-to-weight ratio than any other existing metal or alloy. Combining nanoparticles with microelement alloying enhances the mechanical properties to a new level [13, 14].

HEAs can also be used as functional materials that provide excellent physical and chemical properties, including catalysis, hydrogen storage, high-temperature semiconductors, and gradient magnetism. Xie et al [15] demonstrated that a superb catalyst for breaking ammonia into nitrogen and hydrogen atoms was composed of CoMoFeNiCu HEAs nanoparticles, which provided a promising method of producing hydrogen for fuel cells and powering future electrical vehicles. Kunc et al [16] obtained a maximum hydrogen capacity of 1.81 wt.% in ZrTiFeCrNi, while Edalati et al [17] declared that TiZrCrMnFeNi was able to quickly absorb and desorb 1.7 wt% of hydrogen at room-temperature without activation treatment. The lattice strain made the HEAs favorable to absorb hydrogen in both tetrahedral and octahedral interstitial sites, which enhanced the hydrogen capacity [18]. This research demonstrates the potential of HEAs for hydrogen fuel cells. Solgade et al [19] synthesized a layered composite made of bismuth sulfide (BiS2) and an HEA oxyfluoride containing five rare earth elements, which exhibited superconducting properties over a wider range of lattice parameters than BiS2 without HEA. This work presents an exciting new strategy for designing layered superconductors for high-temperature applications. Chaudhary et al [20] discovered that compositionally graded FeNiAlCoCr1−x (0 ≤ x ≤ 1) HEA featured tunable, functionally graded magnetic properties, including non-monotonic saturation magnetization, coercivity, and Curie temperature behavior, which offered unique potential for permeability engineering applications, such as electrical machines.

Lightweight structural design is vital for energy saving and carbon emission reduction in aerospace, railway, and vehicle fields, which has led to a large number of applications for topology optimization of complex structures with high-strength. Functional materials, such as catalysts and hydrogen absorbing materials, often require a porous structure with a high specific surface area to improve performance. Therefore, HEAs need suitable forming technology to meet these complex structure-manufacturing requirements. At present, the manufacturing of HEAs mainly uses casting and spark plasma sintering. However, these methods can only produce rough parts in simple shapes, because the high strength and high toughness make HEAs difficult to machine. Manufacturing complex HEA structures by traditional technology is a challenge. Metal additive manufacturing has the advantage of synchronizing synthetic materials with material forming and overcoming the limitations of traditional processing methods. The additive manufacturing of difficult-to-machine materials, such as additive manufacturing of titanium alloys and super alloys, has always been a research hotspot [21–24]. Recently, additive manufacturing has becoming an important technology in the field of HEA processing. The major metal additive manufacturing processes for HEAs currently include laser melting deposition (LMD), selective laser melting (SLM) and selective electron beam melting (SEBM) [14, 25–28].

These additive manufacturing technologies have distinctive characteristics. LMD is an additive manufacturing method based on the powder feeding process, which is primarily used to manufacture large parts and surface structures. LMD is also called laser engineered net shaping (LENS), laser cladding deposition (LCD), direct laser fabrication (DLF) or direct metal deposition (DMD). At present, there are many research efforts focused on LMD of HEAs [29–45]. Due to the limitation of technical principles, LMD typically produces workpieces with low dimensional accuracy and geometric complexity. SLM and SEBM are based on powder bed fusion methods [46]. SLM is also called laser powder bed fusion (LPBF), laser beam melting (LBM), laser metal fusion (LMF) or direct metal laser sintering (DMLS). Due to the supporting effect of powder, complex structures such as cantilever, hollow, and complex arrays can be manufactured. The components manufactured by SLM and SEBM have minimal surface roughness and high dimensional accuracy. SEBM works in a vacuum environment [47–51]. Conversely, SLM does not require a vacuum environment, and its equipment is simpler than SEBM, which is conducive to its application. SLM provides cooling rates of up to 10⁴–10⁵ K s⁻¹, while the cooling rate of conventional melting processes (casting, welding etc) are typically less than 100 K s⁻¹. Therefore, SLM can generate finer grains and substructures within the grain, which improves of overall mechanical performance of the final components [52]. The advantages of SLM make it the most widely used technology in additive manufacturing. Research efforts on SLM of HEAs are increasing, making it a hotspot in the both fields of HEAs materials and additive manufacturing. Summarizing the existing research results and clarifying the bottlenecks and fundamental scientific problems will help lay the foundation for researchers to uncover the ultimate solution to the forming problems of HEAs. Unfortunately, the current review of HEAs additive manufacturing does not separately summarize the characteristics of SLM-processed HEAs [14, 25–28]. We will review the defects, characteristic microstructures, mechanical properties, microstructure-property relationships and theoretical models of SLM-processed HEAs respectively and propose new directions and opportunities for future research.
2. SLM procedure setup and powder preparation

Typical SLM equipment is shown in figure 1. The main components include a laser, a beam movement device, a shielding gas chamber, a forming cylinder, and a powder feeding system. At present, fiber lasers with a wavelength of about 1064 nm are generally used for SLM of HEAs. Since the green and blue lasers, with shorter wavelengths, can increase the energy absorption rate of metals, they are powerful candidate heat sources for future SLM. The galvanometer is the most common beam movement device, and its moving speed is relatively fast, so that the molten pool can rapidly melt and cool. An X-Y motor is a low-cost alternative. Powder feeding cylinders were often used in early powder spreading mechanisms. The current powder feeding method is powder dropping, which improves the quality of powder spreading and reduces powder consumption. The shielding gas is generally Ar gas. In addition, there are auxiliary devices that preheat the substrate and powder which helps reduce stress and improve the quality of the final materials. The SLM workflow consists of the following steps: three-dimensional modeling; model slicing; laser motion path planning; control code generation; processing cycle: powder laying, laser melting material, forming cylinder descending; laser processing completion; post-processing [53].

At present, the methods of preparing HEA powder mainly include mechanically mixing and prealloying. Tailored HEA powder can be obtained by mechanical mixing at a free ratio. Zhang et al [54] printed a WTaMoNb HEA mixed with four elemental powders. Due to its lower melting point and lower density, the Nb elements floated to the surface, where they absorbed more energy and evaporated. Moreover, the SLM-processed sample had a large gap between the dendrites and its relative density did not exceed 90%, which greatly reduced its performance. The prealloyed powder was more evenly distributed than the mechanically mixed powder, which prevented the separation of components, resulting in a sample with uniform structure and consistent performance. Therefore, prealloyed powders were commonly used in current research about SLM of HEAs.

In the SLM process, the powder morphology and size influences the processing quality. The densest SLM-processed samples were obtained from spherical particles rather than elongated ones due to the increased fluidity of spherical powder. Using spherical powder reduces spatter, which reduces microstructure defects [55]. Jin et al [56] prepared CoCrFeMnNi HEA powder with an average particle size of 34 µm by aerosol jet and most of the particles were spherical or nearly spherical. Yim et al [57] prepared CoCrFeMnNi HEA powders with four particle sizes by the water phase atomization method. Smaller CoCrFeMnNi powders have higher sintering activity, which lead to denser parts. Moreover, the span of particle size distribution also had a significant effect on powder fluidity. When the span was smaller, the fluidity was better and the relative density of the sample was higher [58]. Therefore, similar to other alloys, the use of HEA powder with circular shape and uniform size is more conducive to improving the quality of SLM.

3. Defects and their suppression

3.1. Void

Void type defects, such as unfused particles and pores, are the most common defects in SLM. As a new material with complex compositions, HEAs are prone to pore defects. Pore defects are the leading cause of density loss. Luo et al [59] found that spherical and irregular pores formed in
SLM-processed AlCrCuFeNi. The pores or voids occurred in interfaces, such as the interlayer of deposited layers, grain boundaries, and cell walls [60]. The main sources of pores in SLM of other metals are the interstitial space between the unfused powder particles and the impurity elements from the protective gas and the powder. The mechanism of pore generation in HEAs may also be related to these sources. Process optimization can suppress pore defects and increase the density of the final material. Zhou and Wu et al [61, 62] discovered that the density of SLM-processed HEAs increases with higher laser power and slower scan speed. Li et al [63] further refined the above parameters so that higher energy density reduced porosity as shown in figure 2. Li et al [63] also found that the densification was improved from 98.2% before hot isostatic pressing (HIP) to 99.1% after HIP. Brif et al [64] demonstrated that the density with the layer thickness of 20 µm was higher than that of 50 µm, indicating that smaller layer thickness was also beneficial to reducing the porosity of SLM-processed HEAs. Studies on reducing porosity through material composition modification have not yet appeared, and this is an important technical route to suppress pores. The unique microstructure of HEAs presents a new challenge in suppressing pores through material modification.

3.2. Residual stress and crack

The complex temperature cycle in SLM with a rapid cooling rate of above 10^6 K s^{-1} causes thermal residual stress in the solidification substructure, which induces cracks. Therefore, inhibiting cracking is the main challenge of SLM, and there is no exception for HEAs. Karlsson et al [65] investigated the cracking of SLM-processed AlCoCrFeNi within a wide process parameter window and failed to obtain crack-free samples due to the stresses. Luo et al [59] reported several vertical microcracks in SLM-processed AlCrCuFeNi. Li et al [63] clarified that microcracks appeared on the surface of SLM-processed CoCrFeMoNi owing to the thermal stress and were reduced with decreasing residual stress. Park et al [66] proved that increasing the processing speed of SLM reduced the thermal residual stress of (CoCrFeMnNi)_{35}C_{1}. The annealing treatment was able to decrease residual stress, which suggests that heat treatment is also a promising way to reduce cracking [67]. Therefore, optimization of the processing parameters and heat treatment are effective methods to reduce residual stress and may solve the cracking problem. However, related research on reducing stress to suppress cracks is still limited. More importantly, increasing Ni content in AlCrCuFeNi led to a crack-free AlCrCuFeNi_{3.0} as shown in figure 3 [68], which proves that optimization of the alloy composition was beneficial to reduce cracks directly. In addition to controlling stress, refining grains and reducing dendrite arm size are the key metallurgical factors to suppress cracks according to the crack mechanism [69, 70]. Thus, adding appropriate grain refining elements or nucleating agents to melt pool is an important methods of suppressing cracks in SLM-processed HEAs.

3.3. Element segregation

Solidification segregation often occurs in HEAs, which are composed of a large variety of alloying elements. Despite the Mn element segregation at the interfaces between two deposited layers or along the melt pool boundaries in SLM as-processed CoCrFeMnNi [60, 63], the HIP heat treatment rendered a more homogeneous distribution of Mn and eliminated the previous segregation [63]. However, annealing heat treatment at 550 °C intensified Cr segregation in the FeCr-rich zone of SLM-processed AlCoCrFeNi, which confirmed that spinodal decomposition occurred after annealing [65]. Segregation deteriorates the microstructure and decrease the performance of traditional single-principal alloys. However, according to the latest HEA toughening mechanism [8], local elemental fluctuation may improve the toughness of HEAs. The influence of element segregation on the microstructure and properties of SLM-processed HEAs requires further investigation.

Intergranular eutectic segregation often occurs in laser melting deposition additive manufacturing of HEAs [29–45], but no related phenomenon has yet been reported in SLM. Considering the current research literature, this may be because related research has not been carried out in depth. The intergranular eutectic segregation also needs to be investigated and suppressed by researchers in the future.

3.4. Slag inclusion

Inclusion is not the main defect in SLM of HEAs. So far, only Mn_3O_5 oxides with an average size of 27.3 nm were found in
SLM-processed CoCrFeMnNi [71]. Clean powder and strict process protection can prevent these types of defects.

3.5. Summary of defect suppression methods

According to the above research results, both the SLM processing parameters and chemical compositions of HEAs contributed to the formation of voids, cracks and segregation, while the slag inclusion was primarily related to chemical composition. When the ability of the element to absorb impurities is weak, the source of the impurity gas element is reduced, and the porosity decreases. Thin layer thickness, narrow hatching space, small powder size, and high laser power keeps the powder molten and thereby suppress unfused voids [55, 58]. The above conditions can be achieved through the optimal adjustment of element composition and process parameters. In addition, preheating powder to eliminate water content and heat treatment such as hot isostatic pressing can also reduce porosity [63]. Cracks are mainly due to the non-equilibrium solidification of the molten pool and the stress concentration. Adjusting the alloy composition to reduce the solid-liquid transition zone and grain size of the molten pool, reducing the laser energy to decrease the heat input, and preheating the metals to reduce the temperature gradient improve solidification and relax stress concentration, which suppresses cracks. Element segregation also comes from the non-equilibrium solidification process of the molten pool. Therefore, most of the existing methods for suppressing defects in SLM of HEA adopt methods such as screening appropriate powder morphology, optimizing process parameters, and adjusting alloy elements.

Introducing an assisting method in SLM to suppress defects is also an important development direction. Zhang et al [72] used ultrasonic assisted SLM to process Ti-6Al-4V alloy. They found that the ultrasonic process reduced spatter, optimized the surface shape of the material, and reduced the tensile residual stress, which prohibited defects. Kang et al [73] used an electromagnetic field to stir the molten pool of SLM pure Ti. Stirring the molten pool accelerated the molten flow and the heat transfer, which prevented pores from forming in the molten pool and eliminated solidification cracks. Although these methods have not been applied to SLM of HEAs, they have important reference significance.

4. Microstructures

4.1. Lattice structure

In general, the lattice structure of an SLM-processed HEA is consistent with that of casting or arc melting. A series of face-centered cubic (FCC) HEAs such as FeCoCrNi, CoCrFeMnNi, C-containing FeCoCrNi, and AlCrFeNiV were still FCC crystal structures after SLM [60, 63, 64, 74, 75]; and the NbMoTaW with body-centered cubic (BCC) maintained BCC [76].

However, there are exceptions, such as the lattice of the Al-containing HEAs, which changes depending on the Al content. This phenomenon is due to the fact that Al is the BCC stabilizer, and the lattice is more likely to change as the Al content increases [77]. When the Al content is low, taking Al_{0.3}CoCrFeNi as an example, the lattice of the SLM as-processed parts is FCC [78]. When the Al content increased
to 0.5, the extreme heating and cooling rates transformed the BCC lattice of Al₈₀FeCoCrNi powders to the FCC lattice of the SLM-processed sample [79]. As the Al content increased to the equal amount with other elements in SLM-processed AlCoCrFeNi, single BCC was observed [65]. Ni element has the ability to change the lattice structure. The increase of Ni in SLM-processed AlCrCuFeNi promoted FCC phase formation [68]. The valence electron concentration (VEC) criterion showed that when the VEC of an element in an HEA exceeds 8.0, the FCC phase forms in the HEA [80]. The VEC of Ni is 10 which explains why increasing Ni facilitated the generation of FCC phase. The FeCoCrNiMn reinforced by Fe-based metallic glass generated a new HEA phase after the SLM process [81]. In addition to the previously mentioned elements and alloys, the promotion of lattice transformation in other elements is also an important research topic.

There is another exception, a unique kind of HEA called interstitial solute strengthened HEA (iHEA). The lattice of FeMnCoCr0.5 iHEA processed using conventional methods was a dual phase consisting of FCC γ phase and hexagonal close-packed (HCP) ε phase, while the SLM-processed iHEA consisted of a single FCC phase [82].

In addition to alloy elements, heat treatment has an important effect on the transformation of the lattice of SLM-processed HEAs. SLM-processed AlCoCuFeNi and AlCrCuFeNi consisted of a single BCC solid solution [59, 83]. The heat treatment promoted precipitation of the FCC phase rich in Cu inside the metastable BCC matrix, which produced a dual phase structure and the fraction and the size of the FCC phase increased with increasing heat treatment temperatures, as shown in figure 4 [83].

4.2. Grain morphology and size

Columnar grains aligned towards the build direction are the most common morphology in SLM-processed HEAs, such as FeCoCrNi [67], CoCrFeMnNi [71, 84]. C-containing FeCoCrNi [61, 62, 78], AlCrFeNiV [75]. In addition to columnar grains, microtextures were also produced. Zhang and Peyrouzet et al [78, 83] both found that the fiber texture along the build direction possessed the typical characteristics of grain orientation in different SLM as-processed HEAs. The epitaxial growth of the existing grains under rapid cooling of SLM induces columnar grain growth, and competitive growth derived from remelting under the repeated deposition of metal leads to grain orientation selection. Thus, columnar grains and microtextures are readily produced. This is an inherent feature of SLM processing.

Different alloy compositions determine the grain size of SLM-processed HEAs due to the fact that some elements can refine grains. C-containing FeCoCrNi and AlCrFeNiV have larger grain sizes (40–70 µm) [61, 62, 75]. SLM-processed Mn-containing HEAs have an average grain size range of 10–16 µm [60, 71, 76, 82]. The grain size increased as a result of Mn evaporation and high volume energy density [84]. Kim et al [71] further revealed that the average grain sizes of SLM-processed CoCrFeMnNi on the cross-section perpendicular to the scanning direction (SD), transverse direction (TD), and building direction (BD) were 15.66 µm, 12.93 µm, and 5.98 µm, respectively. Cu has stronger grain refinement abilities, such that the average grain size of SLM-processed AlCrCuFeNi was 4.39 ± 2.96 µm [59]. The nano-ceramic phase also has a strong influence on grain size/structure. Li et al [85, 86] claimed that 12 wt% nano-TiN particle reinforced CoCrFeNiMn has an isotropic grain structure, with an average grain size less than 2 µm.

Process parameter optimization and post heat treatment are other important factors affecting grain structure. The grain size of the SLM-processed HEAs was positively correlated the scanning power and inversely correlated to the scanning speed [61, 62]. The reciprocating scanning pattern promoted the generation of columnar grains and an alternating pattern of crystal orientation appeared in different deposition layers [74]. Moreover, annealing above 1173 K for 2 h transformed the grains of SLM-processed FeCoCrNi from columnar to equiaxed, and the curved grain boundaries became straight, as shown in figure 5, all of which were mainly due to the generation of recrystallization and nanotwins [67].

4.3. Dislocation and sub-grain microstructure

SLM-processed metals involve high density dislocation due to the complex thermal cycle with a cooling rate of above 10⁶ K s⁻¹. High density dislocations are a common
nanostructure in SLM-processed HEAs, such as FeCoCrNi [67], CoCrFeMnNi [60, 63, 71], C-containing FeCoCrNi [61, 62, 66], FeMnCoCrC0.5 [82], Al0.3CoCrFeNi [78], and AlCrFeNiV [75]. The accumulation of dislocation pile-ups results from stress in the SLM process, which further increases the dislocation density [63, 67]. However, the annealing heat treatment decreased the dislocation density [67]. This is due to the fact that dislocations with high distortion energy tend to transform into a regular lattice structure with low energy states under high temperature annealing processes.

The high dislocation density is related to the generation of the solidification substructure (or sub-grain) in the grain [66]. These substructures are usually cellular- or columnar-type structures, as shown in figure 6, whose boundaries consist of dislocation walls and dislocation networks [71]. The interior of some substructures contained almost no dislocations, while others were filled with high density dislocations [63, 75]. The size of the substructures is usually less than 1 µm. Interestingly, after heat treatment the cellular substructure nearly disappeared and exhibited a much lower dislocation density [60], whose mechanism is consistent with the mechanism of dislocation elimination in annealing. It was believed the SLM-processed HEAs contained unstable substructures, which altered their properties under high temperature environment.

4.4. Precipitates

Precipitates are derived from solid-state phase transformation, and their essential mechanism is atomic diffusion. The sluggish diffusion effect of HEAs endows slow diffusion to the atoms of HEAs, which inhibits the solid-state phase transformation. The precipitating process within heat treatment takes a long time in HEAs manufactured by traditional methods, which is supported by the fact that the \( \sigma \) phase in the casted CoCrFeMnNi precipitated after quenching in water and aging at 700°C for 1000h [87].

However, precipitates were widely observed in several SLM-processed HEAs [59, 63, 65, 66, 75, 88]. Li et al [63] found that tetragonal \( \sigma \) phase precipitated as an
orientation relationship [011]fcc/[167]σ in the SLM-processed CoCrFeMnNi matrix, while either cast or deformed CoCrFeMnNi never precipitated when the true strain was below 3.7%. Park et al. [66] detected precipitates with an average size of 30–70 nm including Mn-rich oxide, Mn-rich sulfide, and Cr-rich carbide at the subgrain boundaries in SLM-processed 1% CoCrFeMnNi. Karlsson et al. [65] observed NiAl-rich B2 precipitates with an average size of 20–30 nm in the BCC matrix of SLM-processed AlCoCrFeNi. Luo et al. [59, 68] found chain-like Cu-rich precipitates at the high angle grain boundaries (HAGBs) in SLM-processed AlCrCuFeNi. Granular Cu-rich precipitates formed at the low angle grain boundaries (LAGBs). The lamellar or cellular FCC + B2 dual-phase and A2 + B2 dual-phase appeared as the Ni content increased, as shown in figure 7 [68]. Yao et al. [75] discovered Ni$_3$Al phase with a length of 5–10 nm in SLM-processed AlCrFeNiV. Yang et al. [88] found most of the Ti-rich precipitates in SLM-processed Ni$_6$Cr$_4$WFe$_9$Ti at the grain boundaries and a minimal amount of unknown phase with a size of 30–50 nm at the intragranular boundaries. Overall, most of the precipitates appeared at the interfaces.

The as-processed precipitates were generated because the SLM-processed HEA possessed a large number of fine grains, substructures, and dislocations. Those microstructures suggest that there were abundant grain boundaries with high levels of energy, which enhanced atomic diffusion. As a result, precipitations were facilitated during the fast heating-cooling cycle of SLM [63]. This also explains why precipitates appeared at the grain boundaries, subgrain boundaries, and other interfaces.

The heat treatment after SLM processing promotes precipitation, and the appropriate heat treatment time is shorter than the HEAs produced by traditional methods with slow solidification rates. Fujieda et al. [89] discovered that SLM-processed CoCrFeNiTi had a uniform elemental distribution. Ni–Ti rich particles that precipitated after water-quenching and air cooling had diameters of 20 nm and 60 nm, respectively. Zhou et al. [90] found that SLM-processed CoCrFeNi$_{0.05}$ annealed at 800 °C rendered Cr$_{23}$C$_6$-type carbide precipitates whose volume fraction rose with annealing time. The heat-treatable characteristic makes improving the microstructures and mechanical properties of HEAs easier.

4.5. Nanotwins

Nanotwins are generated under high stress that originating from heat treatment or pressure processing. Lin et al. [67] discovered that the recrystallization-induced shrinkage stress produced numerous annealing nanotwins in SLM-processed FeCoCrNi; and raising the annealing temperature increased the amount of nanotwins, as shown in figures 8(a)–(c). Zhu et al. [82] observed deformation nanotwins in SLM-processed FeMnCoCr$_{0.5}$ after 12% strain. The nanotwins combined with HCP to form a lamella composite lattice, as shown in figure 8(e). The severely distorted B2/A2 phase interfaces of SLM-processed AlCrCuFeNi$_{3.0}$ during tension promoted the generation of nanotwins [68]. Nanotwins also appeared in
SLM-processed CoCrFeMnNi, as shown in figure 8(d), which had never been found in traditional samples [63]. This means that high stress induced by quick heating and cooling in SLM can generate nanotwins directly.

5. Performances

5.1. Strength properties

The statistical results of the tensile strength of SLM-processed HEAs are listed in table 1. FeCoCrNi is a type of HEA that was discovered earlier and is also the earliest HEA processed by SLM. The maximum yield strength (YS), ultimate tensile strength (UTS), and elongation of the as-built samples reached 600 MPa, 745 MPa and 32%, respectively, which are significantly higher than that of stainless steel [64]. CoCrFeMnNi (also known as Cantor alloy) is formed by adding Mn based on FeCoCrNi. It is the most widely studied SLM-processed HEA [60, 63, 71, 74]. Its UTS ranges between 600–650 MPa. Its elongation is up to 47%, higher than that of SLM-processed FeCoCrNi. The σ phase and ultra-fine grain size enhanced the mechanical properties of SLM-processed CoCrFeMnNi [63].

HEAs based on FeCoCrNi or CoCrFeMnNi series are formed by adding Ti, nano-ceramic particles, C, and Al. These alloys show significant improvements in tensile strength. The Ti-containing SLM-processed HEAs are the strongest followed by the alloys containing ceramic nanoparticles [63, 89]. They all exhibited UTSs over 1000MPa. The YS of solution-treated SLM-processed CoCrFeNiTi depended on the size and number of the Ni- and Ti-containing nano-particles [89]. The dispersion strengthening of nano-TiN particles and the fine grain strengthening were the strengthening mechanisms for SLM-processed TiN-CoCrFeMnNi, and a uniform dispersion of particles and a particle-matrix coherent relationship were also important [85]. The UTS of the HEAs with C and Al were close to 1000MPa. The large Al atom enhanced the strengthening effect of solid solution and promoted the precipitation of BCC structure with high hardness, which brought higher strength for Al-containing HEAs [65, 78, 79]. The solid solution strengthening, fine grain strengthening, and submicron cellular structure were the mechanisms underlying the improvements in strength that were observed after adding Al and C [61, 62]. Furthermore, uniformly dispersed nano-carbides at the cellular structure boundaries maximized the strengthening effect of C-adding (CoCrFeMnNi)0.05C0.5 in SLM [66]. The high YS of SLM-processed FeMnCoCr0.5 was due to the dislocation strengthening and fine grain strengthening [82]. The YS is approximately proportional to the UTS for all above HEAs. However, the addition of Ti, Al, and C reduced the ductility of the HEAs. The Ti-rich nano-precipitates that formed along the grain boundaries and intragranular boundaries of the SLM-processed Ni6Cr4WFe9Ti led to intergranular fractures during the tensile test, which indicates poor ductility [88]. SLM-processed FeCoCrNiC0.05 showed the lowest elongation (10.3%) [90].

Table 2 shows the statistical results of the strength compressions of SLM-processed HEAs. Kim et al [71] found anisotropy in the compressive fracture strength of SLM-processed CoCrFeMnNi, which resulted from different Taylor factors and grain sizes in different directions of the parts.
Table 1. Tensile properties of the SLM-processed HEAs. P is the laser power (W), v is the scan speed (mm s\(^{-1}\)), h is the hatching space (\(\mu\)m), and t is the layer thickness (\(\mu\)m).

| Alloy type                         | Lattice | YS (MPa) | UTS (MPa) | Elongation (%) | Hardness (HV) | Density(%) | Processing parameters                     | Ref. |
|-----------------------------------|---------|----------|-----------|----------------|---------------|------------|------------------------------------------|------|
| FeCoCrNi                          | FCC     | 600      | 745       | 32             | 238           | –          | P = 200 W, v = 300 mm s\(^{-1}\), t = 20 \(\mu\)m | [64] |
| CoCrMnNi                          | FCC     | 402      | 480       | 8              | 205           | –          | P = 200 W, v = 300 mm s\(^{-1}\), t = 50 \(\mu\)m | [64] |
| FCC                               | 581.9   | 707.9    | 20        | 218            | 99.71 ± 0.25  | P = 200 W, v = 740 mm s\(^{-1}\), t = 40 \(\mu\)m, h = 40 \(\mu\)m | [67] |
| FCC                               | 221     | 633.2    | 45        | 138            | 99.71 ± 0.25  | Ditto. Annealed at 1573 K for 2 h | [67] |
| FCC                               | 671     | 402      | 80        | 8              | 205           | Ditto. HIP temp 1150 °C, time 3 h and pressure 150MPa | [63] |
| FCC                               | 581.9   | 707.9    | 20        | 218            | 99.71 ± 0.25  | Ditto. HT. at 900 °C for 1 h in Ar atmosphere | [60] |
| FCC                               | 221     | 633.2    | 45        | 138            | 99.71 ± 0.25  | Ditto. Air cooling | [89] |
| FCC                               | 671     | 402      | 80        | 8              | 205           | Ditto. Water quenching | [89] |
| TiNp-CoCrFeNiMn                   | FCC     | 773.0    | 1178      | 25.8 ± 0.6     | –             | 99.3       | P = 200 W, h = 85 \(\mu\)m | [74] |
| FeCoCrNi                          | FCC     | 897.5 ± 65.8 | 1291.0 ± 29.7 | 26.7 ± 2.3     | –             | –          | Ditto. Annealed at 1073 K for 0.5 h | [90] |
| (CoCrFeMnNi)_{0.1}Ni_{0.4}C (at%)| FCC     | –        | –1100     | –              | –             | –          | P = 250 W, v = 450 mm s\(^{-1}\), t = 30 \(\mu\)m, h = 20 \(\mu\)m | [85] |
| FeCoCrNiC_{0.05}                  | FCC     | –        | 1036      | –12            | –             | –          | P = 200 W, v = 400 mm s\(^{-1}\), t = 30 \(\mu\)m, h = 20 \(\mu\)m | [86] |
| FCC                               | –        | –        | –         | –              | –             | –          | Ditto. HIP temp 1150 °C, time 3 h and pressure 150MPa | [63] |
| FCC                               | –        | –        | –         | –              | –             | –          | Ditto. HT. at 900 °C for 1 h in Ar atmosphere | [60] |
| FCC                               | –        | –        | –         | –              | –             | –          | Ditto. Air cooling | [89] |
| FCC                               | –        | –        | –         | –              | –             | –          | Ditto. Water quenching | [89] |
| NbMoTaW                           | –        | 787      | 950       | 10.3           | 337           | –          | Ditto. Annealed at 1073 K for 0.5 h | [90] |
| Ni_{6}Cr_{4}WFe_{9}Ti             | FCC     | –        | –         | –              | –             | –          | P = 180 W, v = 3000 mm s\(^{-1}\), t = 30 \(\mu\)m, h = 20 \(\mu\)m | [82] |
| Al_{0.5}Co_{9}Cr_{13}Co_{0.5}     | FCC     | –470     | 1000      | 28             | –             | –          | P = 150–170 W, v = 3000 mm s\(^{-1}\), t = 20–30 \(\mu\)m, h = 45 \(\mu\)m | [78] |
| Al_{0.5}CoFeNi                    | FCC     | 730      | 896       | 29             | –             | –          | P = 200 W, v = 1600 mm s\(^{-1}\), t = 30 \(\mu\)m, h = 90 \(\mu\)m | [79] |
| Al_{0.5}CoFeNi                    | FCC     | 579      | 721       | 22             | 262 ± 5       | –          | P = 140 W, v = 900 mm s\(^{-1}\), t = 30 \(\mu\)m, h = 50 \(\mu\)m | [75] |
| NbMoTaW                           | –        | –        | –         | 826            | –             | –          | P = 400 W, v = 250 mm s\(^{-1}\), t = 100 \(\mu\)m | [76] |
| Ni_{6}Cr_{4}WFe_{9}Ti             | –        | 742      | 972       | 12.2           | –             | –          | P = 300 W, v = 2500 mm s\(^{-1}\), t = 100 \(\mu\)m, h = 80 \(\mu\)m | [88] |
Fe-based amorphous alloy reinforced FeCoCrNiMn possessed a strength above 1000 MPa and an excellent fracture toughness over 100 MPa m$^{1/2}$ due to the dispersion strengthening of new particles [81]. Similar to its effects on tensile strength, the addition of Al can significantly enhance the compression strength beyond that of the Mn-containing HEA. The superior compressive properties of SLM-processed AlCrCuFeNi were due to ultrafine grains and BCC with high hardness and nanoscale structures [59, 83]. However, the brittle BCC deteriorated the ductility [59, 81, 83].

The laser power (P), scan speed (v), hatching space (h), and layer thickness (t) are the core parameters influencing microstructure and mechanical properties. The laser power and scan speed determine the heat input and has an important influence on the temperature gradient (G) of the molten pool. The scan speed also determines the growth rate (R) of the solid phase of the molten pool. High heat input will always deteriorate the microstructure and reduce the strength. A lower G/R ratio means that the grain morphology is equiaxed. A higher cooling rate (G × R) indicates a finer microstructure. Appropriately small hatching space and layer thickness can increase the dilution rate and ultimately reduce void defects [64]. The combination of these four parameters determines the concept of volumetric energy density (VED), which is defined as: VED = P/vht. VED plays a key role in the SLM process. As VED increases, the relative density, tensile strength, and elongation also increases [61, 63].

Heat treatment is another key factor that influences the mechanical strength. The HIP heat treatment increased the UTS of the SLM-processed CoCrFeMnNi from 601 MPa to 649 MPa; in contrast, the elongation decreased [63]. The solution heat treatment improved the YS of the SLM-processed CoCrFeNiTi which rose with the square root of the size and volume fraction of the uniform Ni- and Ti-containing nanoparticles [89]. However, the annealing heat treatment decreased strength and increased ductility compared to the SLM-processed sample. The annealing treatment facilitated precipitation, softening the FCC phase and reducing dislocation, which toughened the brittle BCC in the SLM-processed AlCoCuFeNi, resulting in a strength-ductility trade-off [83]. The microhardness, tensile strength, and ductility of SLM-processed FeCoCrNi demonstrated similar regularity, while higher annealing temperatures increased the impact toughness, as shown in figure 9 [67]. The annealing eliminated both residual stress and dislocation networks, which induced a strain hardening effect and improved the mechanical properties.

Some SLM-processed HEAs possess the capability of work hardening. The EBSD results of the SLM-processed FeMnCoCrC0.5 showed that the kernel average misorientation (KAM) values increased with the degree of strain, while deformation nanotwins and nanotwin-HCP lamella composite structures were occasionally observed, as shown in figure 10 [82]. A high KAM value suggests a rising density of geometrically necessary dislocations (GND). The high ductility is due to the united deformation mechanisms involving dislocation slip, deformation twinning and phase transformation which maintains the ability of work hardening at high stress levels. When the deformation twins are absent, the interactions between dislocations also induce work hardening, such as in SLM-processed C-containing FeCoCrNi [61, 62].

In addition, defects are also a key factor affecting mechanical properties. When the layer thickness of CoCrFeNi powder

---

Table 2. Compression properties of the SLM-processed HEAs. P is the laser power (W), v is the scan speed (mm s$^{-1}$), h is the hatching space (µm), and t is the layer thickness (µm).

| Alloy type | Lattice | YS (MPa) | Compression fracture strength (MPa) | Strain (%) | Hardness (HV) | Processing parameters | Ref. |
|------------|---------|----------|------------------------------------|------------|--------------|-----------------------|------|
| CoCrFeMnNi | FCC | 778.4 scanning 676.4 transverse 703.5 building | – | – | – | P = 90 W, v = 600 mm s$^{-1}$, t = 25 µm, h = 80 µm | [71] |
| Metallic glass reinforced FeCoCrNiMn | FCC | 916 | 1517 | 39 | – | P = 185 W, v = 600 mm s$^{-1}$, t = 0.1 mm, h = 40 µm | [81] |
| AlCoCuFeNi | BCC | 1342 | 1471 | 0.9 | 541 | P = 205 W, v = 1000 mm s$^{-1}$, t = 30 µm, h = 40 µm | [83] |
| BCC + FCC | 766 | 1292 | 6.4 | 406 | | heat treated at 900 °C for 10 h | [83] |
| BCC + FCC | 744 | 1600 | 13.1 | 399 | | heat treated at 1000 °C for 10 h | [83] |
| AlCrCuFeNi | BCC | – | 2052.8 ± 123.6 | 6.8 ± 1.3 | – | P = 300 W, v = 600 mm s$^{-1}$, t = 40 µm, h = 80 µm | [59] |
was 20 μm, the parts with this thickness were stronger than those with a thickness of 50 μm. This is due to the fact that the thicker powder layer was not fully melted, resulting in incomplete fusion defects [64]. Li et al [63] found that the pore and crack defects in SLM-processed CoCrFeMnNi with 1 μm average grain size decreased the UTS to 601 MPa, despite the Hall–Petch calculation that showed the theoretical strength with the fine grain size should have been about 900 MPa.

5.2. Creep resistance

Conventional creep experiments using different temperature ranges have not yet been performed on SLM-processed HEAs. Creep tests at room temperature based on nanoindentation has been used in studies on HEAs due to its experimental convenience [91, 92]. Xu et al [92] proposed the hypothesis that the mechanism of nanoimprint creep for SLM-processed CoCrFeMnNi was related to dislocation motion, rather than diffusion creep or grain boundary creep. SLM processing produces high-density dislocations, which provide a path for atomic diffusion and facilitate the movement of dislocations. Of course, the identified mechanism requires additional observational verification.

5.3. Corrosion resistance

Most HEAs contain at least one corrosion-resistant element, such as Ni, Cr, Co, W. The corrosion resistance observed in SLM-processed HEAs was higher than that of conventional high-corrosion-resistant alloys. Zhang et al [76] revealed that the SLM-processed NbMoTaW HEA showed stronger corrosion resistance than 316 l steel. Both the SLM-as-processed CoCrFeNiTi and its solution-treated samples exhibited superior pitting resistance. The pitting potential of the heat treated samples decreased with the size and volume fraction of the Ni- and Ti-containing nanoparticles [89].
Figure 10. Effect of strain on microstructure; (a1)–(a4) grain boundaries (GBs) maps at different strain levels, (b1)–(b4) kernel average misorientation maps. [82] Taylor & Francis Ltd.

Table 3. The microstructure features and mechanical properties of different processing mothed.

| Alloy type        | Process                                           | Microstructure features                                                                 | YS (MPa) | UTS (MPa) | Elongation (%) | Ref.  |
|-------------------|---------------------------------------------------|----------------------------------------------------------------------------------------|----------|-----------|----------------|-------|
| FeCoCrNi          | As-cast                                           | FCC phase with the average width of 100–150 µm and average length of 200–300 µm      | 188      | 457       | 50             | [64]  |
|                   | Cast, heat treated 1000 K for 1 h, 92% hot rolling, | FCC phase with average grain size of 60–80 µm, annealing twins                        | 205      | 580       | 70.3           | [94]  |
|                   | Powder extrusion                                  | Equiaxed FCC phase with average grain size of 34.5 µm, a large number of twins      | 359      | 712.5     | 56             | [95]  |
| CoCrFeMnNi        | As-cast                                           | FCC phase with average grain size of 300–400 µm                                        | 215      | 491       | 71             | [96]  |
|                   | Cast, 87% cold rolling, 1073 K anneal for 1 h      | FCC phase with grain size of 4.4 µm, annealing twins                                  | 350      | 650       | 60             | [97]  |
|                   | Laser melting deposition                          | FCC phase with the average width of 50–200 µm and average length of 500–1000 µm     | 290      | 535       | 55             | [39, 44] |
| Al0.3CoCrFeNi     | As-cast                                           | Single FCC phase                                                                       | 175      | 350       | 57             | [98]  |
|                   | Cast and 900 °C aging for 72 h                     | FCC phase, precipitated B2 phase                                                       | 250      | 500       | 45             | [98]  |
|                   | Laser melting deposition                          | FCC phase with the average width of about 250 µm and average length of 1250 µm       | 194      | 230       | 38             | [99]  |
| Al0.5CoCrFeNi     | As-cast                                           | FCC and BCC phases                                                                     | 355      | 714       | 41.6           | [100] |
|                   | Cast, 900 °C heat-treatment for 8 h and water-quenching | B2 phase both in the FCC and BCC                                                    | 834      | 1220      | 25             | [100] |

5.4. Wear resistance and machinability

In general, a material’s wear resistance performance is closely related to its, therefore HEAs are widely used in surface cladding. SLM parts are expected to possess excellent wear resistance. Li et al [85] found that the dry-sliding friction coefficient (DSFC) of SLM-processed 12 wt% TiN nanoparticle-reinforced CoCrFeNiMn was 0.53, higher than the DSFC of micron-sized TiN<sub>P</sub> particle-reinforced sample (less than 0.4). The excellent wear resistance is due to its ultra-refined microstructure and the dispersed nano-TiN<sub>P</sub> particles.
The SLM process improves the performance of HEAs, making them difficult to be machined, so Guo et al. [93] studied the machinability of the SLM-processed CoCrFeMnNi. Due to the high hardness of HEAs, tool marks appeared after traditional contact machining, such as milling and grinding; and the surface hardness and the residual stress increased. Wire electric discharge machining produced a heat affected zone with high residual stress and hardness. Electro polishing prevented stress and hardening issues. It can be seen that both mechanical processing and high-energy beam processing are relatively difficult for HEAs, as opposed to chemical processing, which provides a reference for the selection of subsequent machining operations after additive manufacturing.

5.5. Comparison with other processes

Other processing methods commonly used for HEA forming are casting, laser melting deposition, powder extrusion, etc. The microstructure characteristics and mechanical properties of commonly used HEAs processed by these methods are shown in Table 3. Compared with previous SLM data, the strength of HEA components manufactured by these methods is lower but the elongation is higher than those manufactured by SLM. The HEAs processed by these methods usually consist of a simple solid solution phase with coarse grain size without precipitated phases, sub-micron cellular structures, dislocations, twins, and other structures. Due to the lack of various strengthening mechanisms and coarse grain size, the yield strength and ultimate tensile strength are far lower than the performance of the SLM samples. Due to the small number of interface defects and the absence of strengthening phases, the lattice slip band of the materials forms unimpeded movement during plastic deformation, significantly improving the ductility of the material, which is generally higher than that of SLM samples. If these materials continue to undergo complex heat treatment or plastic processing after as-forming, microstructures such as precipitated phases, dislocations, and twins also appear, which greatly improves the strength, but it is still lower than the performance of SLM samples. This comparison shows that SLM has the advantage of improving the strength of HEAs. The complex microstructure under high-speed thermal cycling of SLM provides multiple strengthening paths, which is the most important reason for this advantage.

6. Strengthening prediction models

The strengthening mechanism of HEAs is different from other metals, and the most prominent features are the friction stress of the lattice and unusual solid-solution strengthening. The multi-principle characteristics of HEAs make traditional models unsuitable for predicting the degree of solid-solution strengthening in HEAs. At the same time, the extremely high heating and cooling rate of SLM, generate a large number of dislocations. The dislocations are so concentrated that they can almost be regarded as grain boundaries. This blurs the boundary between grain-boundary strengthening and dislocation strengthening. The following section reviews various strengthening mechanisms in order to obtain a strength prediction model suitable for SLM of HEAs. The strengthening mechanism associated with special microstructures of SLM-processed HEAs is the focus.

The main strengthening mechanisms are summarized into five different aspects: friction stress of the lattice, solid-solution strengthening, grain-boundary strengthening, dislocation strengthening and precipitation strengthening. The YS of an HEA can be calculated by the sum of the contributions of the above five strengthening mechanisms [66, 78, 90]:

\[
\sigma_y = \sigma_f + \sigma_{ss} + \sigma_{GB} + \sigma_p + \sigma_{or} \tag{1}
\]

where \( \sigma_y \) is YS, \( \sigma_f \) is the friction stress of the lattice, \( \sigma_{ss} \) is the intensity of solid-solution strengthening, \( \sigma_{GB} \) is the intensity of grain-boundary strengthening, \( \sigma_p \) is the intensity of dislocation strengthening, and \( \sigma_{or} \) is the intensity of precipitation strengthening. Kim et al. [71] revised the above formula as follows considering the interaction between the strengthening mechanisms under external forces:

\[
\sigma_y = \sigma_f + \sigma_{ss} + \sqrt{\sigma_{GB}^2 + \sigma_p^2 + \sigma_{or}^2}. \tag{2}
\]

6.1. Lattice friction stress and solid-solution strengthening

In conventional alloys, the lattice friction stress of the solvent and the solid-solution strengthening of the solute are calculated separately. However, the solvent and the solute are not distinguished in HEAs due to the multi-principle alloy feature. Because both of these strengthening methods were caused by the mismatch of atomic and modulus, they were combined in terms of \( \sigma_0 \) in the model used in most literatures [94, 97, 101–104]. Otto et al. [97] obtained \( \sigma_0 \) by experimental data fitting in the as-cast FeCoNiCrMn almost without defects. The calculation model of \( \sigma_0 \) on the basis of nickel alloys was as follows [102–105]:

\[
\sigma_0/E = Y_0 + A \cdot \exp(B \cdot \sqrt{\varepsilon^2}) \tag{3}
\]

where \( E \) is the elasticity modulus; \( \varepsilon \) is residual strain; \( Y_0 \), \( A \), and \( B \) are fitting parameters which are 27.81, 35.57, and

| Alloys          | \(< \varepsilon^2 >\) | Elastic modulus, GPa | Intrinsic YS, MPa |
|-----------------|-----------------|----------------------|-------------------|
| CoCrFeMnNi     | 0.01451         | 201.6                | 147               |
| CoCrFeNi       | 0.01337         | 215.0                | 123               |
| CoFeMnNi       | 0.01454         | 187.9                | 131               |
| CoFeNi         | 0.01043         | 162.0                | 161               |
| FeMnNi         | 0.01511         | 181.0                | 176               |
| CoMnNi         | 0.01601         | 189.4                | 178               |
| FeNi           | 0.01220         | 166.2                | 139               |
| CoNi           | 0.00290         | 216.7                | 59                |
| Ni             | 0               | 199.1                | 10                |
202.28 respectively. The calculated value was consistent with the experimental value, as shown in figure 11. In addition, the root mean square (RMS) residual strain, elastic modulus, and experimentally measured intrinsic YS of HEAs and Ni-based alloys are shown in table 4.

The lattice structure of HEAs is usually a displacement of solid solution. Interstitial solid solution forms when small atoms (such as carbon) are doped in HEAs, causing more greater lattice distortion than atomic displacement. At present, there is no accurate model to calculate the contribution of interstitial solution strengthening; most of the existing studies are measured by systematic experiments. For example, Wang et al [106] tested the effects of different elements on strength. YS increases linearly with C element content, as shown in figure 12.

6.3. Dislocations strengthening

The SLM process forms complex dislocation networks in HEAs. Cellular and columnar structures are key strengthening factors. The dislocation strengthening model is as follows [108]:

$$\sigma_\rho = \alpha MgB\sqrt{\rho}$$

(5)

where $\alpha$ is constant, $M$ is the Taylor factor, $G$ is shear elasticity, $b$ is the Burgers vector, and $\rho$ is dislocation density. There are different methods to determine the dislocation density. Kim et al [71] obtained it with the convolutional multiple whole profile method. Pevrouzet et al [78] estimated the dislocation density from the projection area of dislocations in the TEM image. Zhu et al [60] used the following equation to calculate dislocation density:

$$\rho^{1/2} = c/\lambda$$

(6)

### Table 5. The $k$ values of several HEAs.

| Ingredient          | $k$          | Ref.  |
|---------------------|--------------|-------|
| Fe$_{49.5}$Mn$_{10}$Cr$_{10}$Co$_{0.5}$ | 573 MPa mm$^{1/2}$ | [107] |
| CoCrFeNiMn          | 490 MPa $\mu$m$^{1/2}$ | [101] |
| CoCrFeMnNi          | 494 MPa $\mu$m$^{1/2}$ | [97]  |
| FeCoCrNiC$_{0.05}$  | 226 MPa $\mu$m$^{1/2}$ | [95]  |

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**Figure 11.** Calculated and experimental lattice friction stress values of the YS of each alloy. Reprinted from [105], Copyright (2018), with permission from Elsevier.

**Figure 12.** (a) Engineering stress-engineering strain curves of HEAs with different C contents, (b) the relationship between YS and C content. Reprinted from [106], Copyright (2016), with permission from Elsevier.
6. Precipitation strengthening

During SLM of HEAs with more components, second phase particles are often precipitated and dispersed in the matrix. These precipitated second phases contribute to the enhancement of strength. The Orowan equation is the most widely used predictive model, which is as follows [112]:

\[ \sigma_{\text{Orowan}} = \frac{0.4M\sqrt{\pi\lambda}}{\pi\sqrt{1-\nu}} \frac{Gb}{L} \ln \frac{\sqrt{4d_p}}{b} \]  

with

\[ L = \frac{\pi}{3} \cdot d_p \left( \frac{\sqrt{\pi}}{4v_p} - 1 \right) \]  

where \( \alpha = \) constant and \( \lambda = \) size of cellular dislocation. According to the strain gradient theory [28, 29], the density of geometrically necessary dislocations (GND) is functionalized in the following equation [83, 109, 110]:

\[ \rho^{\text{GND}} = \frac{2\theta}{\mu b} \]  

where \( \theta = \) local misorientation angle, which can be obtained via the kernel average misorientation method based on EBSD data, \( \mu = \) unit length of the selected point, which is 400 nm, and \( b = \) Burgers vector (about 0.25 nm [111]). Zhou et al. [90] regarded the pile-up of dislocations in SLM-processed FeCoNiCrC0.05 as the grain boundary and calculated the strength by the Hall–Petch equation.

6.4. Precipitation strengthening

6.5. Model application examples

Park et al. [66] printed FeCoNiCrMn containing 1% C at different scanning speeds by SLM and calculated its YS using equation (1). The experimental results were consistent with the expected values. Changes in scan speed altered the microstructure and composition of the HEA and affected the contribution rate of each strengthening mechanism. Zhou et al. [90] annealed the SLM-processed FeCoNiCrC0.05 at different times and calculated its YS using equation (1). The contribution of each strengthening mechanism changed as the annealing time increased. Kim et al. [71] used the equation (2) to calculate the YS of SLM-processed FeCoNiCrMn, which was close to the experimental value, as shown in figure 13. Kim also found that different processing directions produced significantly different Taylor factors, grain sizes, and properties. The value pairs of model calculations and experiments from the literature are shown in table 8.

In addition, some SLM-processed HEAs undergo phase transformation after heat treatment and form double phases, which affect the properties. However, the existing model does not account for phase transformation [68, 75, 83]. Current models only consider the effects of dislocation reinforcement on the reinforcement mechanism. However, researchers also found that the effects of nanotwins on strength have not been considered by the existing models [71].

### Table 6. Parameter values of some HEAs for precipitation strengthening.

| Ingredient                  | \( \alpha \) | M   | G/GPa | b/\( \mu m \) | \( \nu \) | Ref.  |
|-----------------------------|--------------|-----|-------|--------------|---------|-------|
| FeCoCrMn                   | 0.2          | 3.06| 76    | 0.262        | –       | [113, 114] |
| CoCrFeNiMn                 | –            | 3.06| 80    | 0.2536       | –       | [60]  |
| CoCrFeMnNi                 | 0.33         | –   | Table 7 | 80.85      | 0.255  | 0.26  | [108, 115–117] |
| 1%C-CoCrFeMnNi             | 0.2          | 3.06| 81    | 0.254        | 0.265   | [118, 119] |
| Al0.3CoCrFeNi              | 0.2          | 3.30| 83.88 | 0.254        | 0.3     | [120, 121] |

### Table 7. Taylor factor of the planes at scanning, transverse, and building directions (SD, TD, BD) [71].

| Loading axis | BD plane | TD plane | SD plane |
|--------------|----------|----------|----------|
| SD           | 3.328    | 3.113    | –        |
| TD           | 3.340    | –        | 3.143    |
| BD           | –        | 3.012    | 3.050    |

Figure 13. Calculated and experimental YS of the SLM-processed FeCoNiCrMn in different direction (scanning direction: BD). Reprinted from [71], Copyright (2019), with permission from Elsevier.
7. Simulation models

Warping/deformation and cracking often occur during the SLM process due to thermal residual stress. So far, only Zhang et al. [54] built a multiphysics model that includes the heat transfer and solid mechanics of SLM of HEA by the hybrid finite difference (FD) and finite element (FE) approach. The model has been proved to be successful for simulating and improving the SLM process.

The first principles method is another effective method of predicting the properties of SLM-processed HEAs. Sar-swat et al. [122] used this method to reveal that hybrid HEAs, including AlCoCrFeNi0.9Sm0.1, AlCoFeNiSm0.1TiV0.9, and AlCoFeNiSm0.05TiV0.95Zr, exhibited excellent mechanical and corrosion-resistance properties.

8. Conclusions and outlook for future researches

The existing research efforts of SLM-processed HEAs have focused on analyzing microstructures and static mechanical properties. The majority of samples were simple block parts. The characteristics of the rapid melting and cooling rates in SLM processing improved the microstructures of HEAs, including grain refinement, increased dislocation density, phase precipitation, and nanotwin generation. These characteristics increased the mechanical strength of SLM-processed HEAs beyond that of other commonly used forming methods. Similar to traditional alloys, process optimization, addition of alloying elements, and heat treatment of SLM-processed HEA remained the main methods of regulating microstructure and improving performance.

However, defects such as pores and cracks still exist in the SLM-processed components. These defects may have minimal effects on static strength but are fatal to dynamic fatigue performance. Eliminating these defects may further enhance the mechanical performance of SLM-processed HEAs. Therefore, research on defects deserves future efforts. These future studies should investigate mechanisms of defects generation, effective methods of defect suppression, theoretical models of metallurgy processes, and simulations of heat transfer, flow, and stress in SLM of HEAs.

Present research efforts on mechanical strength focus on tensile strength, compressive strength, and hardness. However, limited research focusing on the impacts of experimental fatigue, strength, and life prediction on the final application has been conducted. This research gap hinders the acceptance of SLM of HEAs for broader applications beyond the space industry with one time use and without critical components. An important feature of HEAs is their excellent stability under high- and low-temperature strength. The mechanical properties of SLM-processed HEAs under extreme environments have not been reported in the existing literature. Future research must focus on the fatigue performance, high-temperature strength, low-temperature strength, high-temperature creep, and fatigue properties of SLM-processed HEAs.

The theoretical predictive models of mechanical strength are primarily based on single-component alloys. However, considering the characteristics of HEA microstructures, we believe that the strengthening model of HEAs should have its own features. In order to improve the current understanding of HEA strengthening methods, future research should include advanced simulation methods of various scales, such as density functional theory and molecular dynamics. Modeling validation tools also need to be developed. Ideally, these tools should be able to monitor processing steps in terms of microstructures, environments, stress/deformation evolution, and defect initiation and control.

The functional properties of the SLM-processed HEA parts with complex geometric structures and composition of composite materials possess vital research value for chemical, energy storage materials, electronic functional devices, electromagnetic shielding, and stealth applications. Until now, no studies in this field have been reported. It will become the focus of future research considering the demand for new high-performance materials in aforementioned areas.

Existing research on SLM of HEAs focuses on FeCoNiCrMn and AlFeCoNiCr series alloys. The SLM of lightweight HEAs has not been reported. Using lightweight alloys is an important method of weight reduction and carbon emission reduction. Research on SLM of lightweight HEAs has the potential for significant industrial applications.

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