

# High-Entropy Alloys

Subjects: Others

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Microstructural phase evolution during melting and casting depends on the rate of cooling, the collective mobility of constituent elements, and binary constituent pairs. Parameters used in mechanical alloying and spark plasma sintering, the initial structure of binary alloy pairs, are some of the factors that influence phase evolution in powder-metallurgy-produced HEAs. Factors such as powder flowability, laser power, powder thickness and shape, scan spacing, and volumetric energy density (VED) all play important roles in determining the resulting microstructure in additive manufacturing technology. Large lattice distortion could hinder dislocation motion in HEAs, and this could influence the microstructure, especially at high temperatures, leading to improved mechanical properties in some HEAs. Mechanical properties of some HEAs can be influenced through solid solution hardening, precipitation hardening, grain boundary strengthening, and dislocation hardening. Despite the HEA system showing reliable potential engineering properties if commercialized, there is a need to examine the effects that processing routes have on the microstructure in relation to mechanical properties.

Keywords: high-entropy alloy ; powder metallurgy ; melting and casting ; microstructural evolution ; additive manufacturing ; solid solution strengthening

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## 1. Introduction

The discovery and application of alloying and composite technology have made possible the achievement of various categories of materials that exhibit a wide range of properties. An example is a novel alloy system known as high-entropy alloys (HEAs). [1] defined HEAs, by composition, as alloys having at least five principal elements, wherein each has a concentration between 5 and 35 at.%. [2] also categorized HEAs based on elemental composition and configurational entropy.

Some categories of the HEAs studied are lanthanide HEAs [3][4], refractory HEAs (RHEAs) [5], and lightweight HEAs (LWHEAs) [6]. RHEAs are primarily developed for exceptionally high-temperature applications (up to 1400 °C), but with a disadvantage of high density. PGM-HEAs consist of precious elements (Au, Ag, Pt, Ir, Os, and Re), while LWHEAs are composed of low-density elements such as Li, Mg, Be, and Al.

Over the past decade, material scientists have used several techniques in synthesizing HEAs, such as the melting and casting route, the powder metallurgy (PM) route, and additive manufacturing (AM) processing techniques. The PM process involving mechanical alloying (MA) and consolidation by spark plasma sintering (SPS) is usually used in attempts of achieving homogeneous microstructures in HEAs. In contrast, the AM fabrication route in recent years has received more attention in circumventing the flaws of other synthesis processes. The AM process is a flexible manufacturing technique with the capability of producing parts with complex geometries, finer microstructures, mass customization, and efficient material usage [7].

They are the high-entropy effect, sluggish diffusion effect, lattice distortion effect, and cocktail effect. Moreover, a fine precipitate and a controlled grain structure are usually formed as a result of the sluggish diffusion effect. The effect suggests that the pair distribution function directly relates to the distribution of the interatomic spacing on a local atomic level [8]. The properties of HEAs are known to be a result of the overall contributions of the constituent phases influenced by phase shape, phase distribution, and boundaries, as well as the properties of each phase [9].

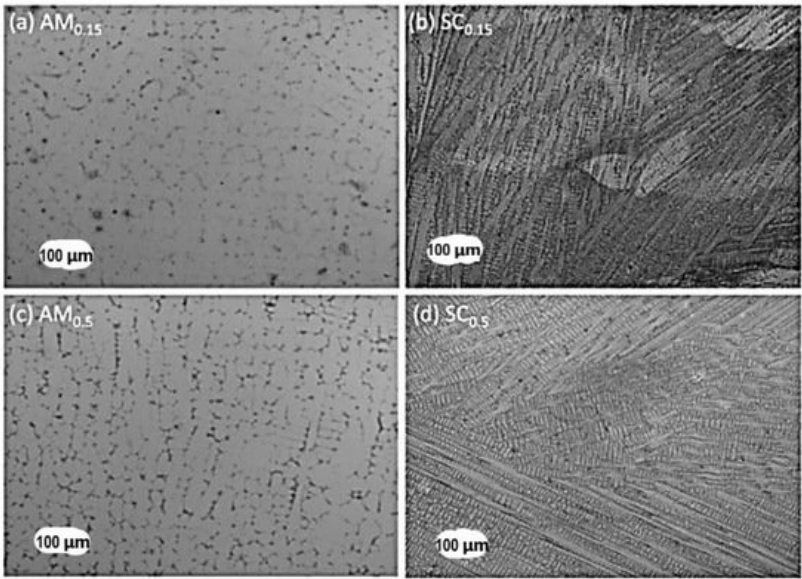
There is no doubt that the basis of HEA design revolves around these so-called core effects. Hence, most HEAs studied have been derived from these basic principles [10][11][12]. Nevertheless, the validity of these core effects has been doubted by some researchers recently.

This makes the prediction of processing–structure relationships quite a challenge. The design approach adopted by most researchers does not follow a specific logic; rather, a number of these alloys are a result of a trial-and-error approach. Although attempts have been made to categorize these alloys according to the intended application, there still exists a

multitude of alloys exhibiting a wide range of properties. This paper will also try to establish a structure–property relationship and link it to the processing route used.

## 2. Microstructural Evolution of HEAs Synthesized through the Melting and Casting Route

HEAs have been fabricated using the melting and casting route. [Table 1](#) is a compilation of some HEAs fabricated using the melting and casting route. In general, the melting and casting route is a liquid-state processing route with equilibrium or non-equilibrium cooling rates. An advantage of processing HEAs using the melting and casting route is the high temperatures that can be realized or needed to melt some elements that make up the HEA alloy [\[13\]](#). Melting and casting can be achieved by a tilt casting furnace or suction casting. During the melting and casting process, the phase transformation of HEAs occurs during solidification (cooling). During solidification, phase evolution depends on the collective mobility or distribution of constituent elements making up the alloy [\[13\]](#). However, the rate of cooling, differences in the local atomic arrangement, and the varying elemental diffusivity can influence the solid phase that is first to form and the microstructure of the alloys [\[14\]\[15\]](#). HEAs fabricated using the melting and casting route usually show dendritic microstructures with interdendritic segregations. For instance, AlCoCrFeNi HEAs fabricated using the melting and casting route have been shown to exhibit BCC + B2 phases with dendritic microstructures [\[16\]\[17\]](#). Tian et al. [\[18\]](#) studied the effect of different cooling rates using arc-melting processing routes in the fabrication of AlCoCrFeNi HEAs. Both studies observed nanoparticles of the B2 phase within the grains of the single-phase BCC structure. Lv et al. [\[19\]](#) compared the effect of cooling rates on the microstructure of Al<sub>x</sub>CoCrFeNi HEAs using arc-melting and suction casting. The higher cooling rate of the suction casting resulted in refined columnar dendrite grains, while the arc-melting process led to a columnar cellular structure (see [Figure 1](#)). However, both processes led to the formation of BCC and FCC phases, with the inclusion of a B2 phase for arc-melting and Laves phases for suction casting. Thus, the melting and casting techniques with faster cooling rates favor the formation of a more dominant single phase and limit the precipitation of secondary phases [\[20\]](#). Several studies have reported the cooling rate effects on HEAs fabricated using melting and casting [\[15\]\[21\]\[22\]](#).



**Figure 1.** OM micrographs of arc-melting (AM<sub>x</sub>) and suction-casting (SC<sub>x</sub>) alloys (x = 0.15 and 0.5). (a) Columnar cellular structure and (c) non-equiaxed columnar dendrite by arc-melting; (b) and (d) columnar dendrite grains by suction casting [\[19\]](#).

**Table 1.** Phase evolution of HEAs fabricated using the melting and casting route.

HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
AlCoCrFeNi	Arc-melting	BCC	A dendritic structure is included.	<a href="#">[16][18]</a>
AlTiVCr	Arc-melting	Single phase consisting of a B2 phase and a disordered BCC phase	The B2 phase is more stable than the disordered BCC phase.	<a href="#">[23]</a>

HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
AlCoFeNiTi	Arc-melting	BCC	A dendritic structure is included.	[24]
TiVZrNbHf	Arc-melting	Single-phase BCC		[25]
AlCrFeNiMo <sub>0.2</sub>	Vacuum Induction	BCC and B2 structure	The BCC phase is FeCrMo-rich, while the B2 phase is a NiAl-rich intermetallic compound.	[26]
NbCrMoTiAl <sub>0.5</sub>	Arc-melting	Simple BCC	Mo segregates to the dendritic region.	[27]
NbCrMoTiVAl <sub>0.5</sub> Si <sub>0.3</sub>			Cr, Ti, Al, and Si segregate to the interdendritic regions.	
Al <sub>x</sub> CoFeNiSi (x > 0.3)	Arc-melting	BCC		[28]
MoNbTaVW	Arc-melting	Single BCC	Dendritic and interdendritic regions are present due to constitutional segregation during solidification.	[29][30]
Al <sub>x</sub> CrFeMnNi <sub>0.5</sub> (x = 0.8–1.2)	Arc-melting	BCC		[31]
Nb <sub>25</sub> Mo <sub>25</sub> Ta <sub>25</sub> W <sub>25</sub>	Arc-melting	BCC phase	There is no dendritic segregation.	[8]
Fe <sub>36</sub> Mn <sub>21</sub> Cr <sub>18</sub> Ni <sub>15</sub> Al <sub>10</sub>	Arc-melting	Dual-phase 2 BCCs/B2	The matrix phase (BCC) is rich in Fe and Cr.  The B2 phase is rich in Ni and Al.	[32]
CoCrCuFeNi	Arc-melting	FCC	The interface morphology would grow in planar, cellular, and dendrite if the solidification rate is increased.	[33][34]
CoCrFeNiV <sub>0.5</sub> C <sub>x</sub> (x = 0.01, 0.02, 0.03, and 0.04)	Arc-melting	FCC	A large number of M <sub>7</sub> C <sub>3</sub> -type interstitial carbides are formed at an annealing temperature of 700 °C and above.	[35]
Fe <sub>40</sub> Mn <sub>40</sub> Co <sub>10</sub> Cr <sub>10</sub>	Vacuum induction	FCC		[36]
CrMnFeCoNi	Arc-melting, Vacuum Induction	FCC	Precipitates of M <sub>23</sub> C <sub>6</sub> and the σ phase exist following prolonged exposure at 700 °C.	[7][37]
Al <sub>x</sub> CoCrFeNi (x = 0–0.65)	Arc-melting	FCC	The FCC phase is transformed to the BCC phase with the presence of a transition duplex FCC/BCC region as Al increases.	[38]
CoCrFeNiTi <sub>0.3</sub>	Arc-melting	FCC	A crystalline structure is present consisting of a mixture of a (Ni, Ti)-rich R phase and a (Cr, Fe)-rich σ phase within the FCC matrix.	[39]
Al <sub>0.5</sub> CoCrCu <sub>0.5</sub> FeNi	Arc-melting	FCC	The BCC phase will evolve from the FCC phase with an increase in the Al content.  FCC + BCC duplex phases will evolve at Al (0.5–1.5).	[40]
CoCrFeNiNb <sub>0.25</sub>	Arc-melting	FCC	Lath-shaped FCC precipitates + nano-basket-weave microstructures are randomly distributed in the proeutectic FCC phase.	[41]
Al <sub>x</sub> CoCrFeNiTi <sub>y</sub>	Arc-melting	FCC	The Al and Ti content strongly affects the phase and microstructure.	[42]
Co <sub>1.5</sub> CrFeNi <sub>1.5</sub> Ti <sub>0.5</sub> Mo <sub>x</sub> (x = 0, 0.1)	Arc-melting	FCC	An interdendritic phase, (Ni, Ti)-rich phase and dendritic (Fe, Cr)-rich phase are present when x = 0, 0.1.	[43]
Mn <sub>22.3</sub> Fe <sub>22.2</sub> Ni <sub>22.2</sub> Ge <sub>16.65</sub> Si <sub>16.65</sub>	Arc-melting	FCC	Magneto-structural first-order phase transition is exhibited.	[44]

HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
AlCrFeMnNi	Arc-melting	BCC (B2) + FCC	The BCC phase is interdendritic and rich in Al + Ni.	[45]
Ni <sub>30</sub> Co <sub>30</sub> Cr <sub>10</sub> Fe <sub>10</sub> Al <sub>18</sub> W <sub>2</sub>	Arc-melting	FCC + BCC	Fine, regular, lamellar eutectic + coarse irregular eutectic hierarchical microstructures are present.	[46]
Al <sub>0.5</sub> CrFeMnNi <sub>0.5</sub>	Arc-melting	FCC + BCC	A dendritic region (higher Al and Cr) and an interdendritic region are present.  Precipitates (AlNi B2 compound) are present.	[47]
Al <sub>x</sub> CoCrFeNi (x = 0.45–0.85)	Arc-melting	FCC + BCC	An AlNi-rich precipitate is formed.	[48]
Cr <sub>2</sub> Cu <sub>2</sub> FeNi <sub>2</sub> Mn <sub>2</sub>	Arc-melting	FCC + BCC	A dendritic and interdendritic phase is present.	[49][50]
Cr <sub>2</sub> Cu <sub>2</sub> NiMn <sub>2</sub>			Cu, Mn, Cr, and Fe are segregated in dendritic/interdendritic regions, while Ni is homogeneously distributed in the alloy.	
CrCu <sub>2</sub> Fe <sub>2</sub> NiMn				
Cr <sub>2</sub> CuFe <sub>2</sub> NiMn				
Al <sub>x</sub> (CoCrFeMnNi) <sub>100–x</sub>	Arc-melting	FCC + BCC	An increase in Al turns the dendritic structure to a lamella-like structure, hence the transit from the FCC to the BCC phase.	[51]
CoCrFeMnNiZr <sub>x</sub> (x = 0–0.3)	Arc-melting	FCC + BCC	Dendritic and interdendritic regions are present.  The interdendritic region increases with an increase in the Zr content.	[52]
AlCoCrCu <sub>x</sub> NiTi (x = 0.5–0.8)	Arc-melting	FCC + BCC	Dendritic (contains compound impurities) and chrysanthemum-shape dendrites are present.  Cu segregates in the interdendritic region.	[53]
CoCu <sub>y</sub> FeNiTi <sub>x</sub>	Arc-melting	2 FCCs + BCC	FCC 1 is Cu rich, and FCC 2 is Co rich (x = 1/3, 3/7, and 3/5).  The BCC phase is β Ti rich (x = 3/5).  A cast-dendritic morphology is present.	[54]
CoCrFeNiCuAl	Arc-melting	FCC + BCC	The BCC phase is an ordered one.  of 2 FCC phases are present.	[55][56]
Fe <sub>50-x</sub> Mn <sub>30</sub> Co <sub>10</sub> Cr <sub>10</sub> B <sub>x</sub> (x = 0, 0.3, 0.6, 1.7 wt%)	Arc-melting	FCC + BCC	The addition of boron promotes the formation of M <sub>2</sub> B-type borides (M = Cr, Fe).	[57]
AlCrCuFeMnNi	Vacuum Induction	2 BCCs (B2 + A2) + FCC	The 2BCC phase is formed by spinodal decomposition, i.e., B2 (NiAl dendrite matrix) and A2 (Cr-Fe rich) embedded precipitate.	[58]
Al <sub>0.5</sub> CoCrFeNi	Arc-melting, Vacuum Induction	FCC + BCC crystalline structures	The presence of the Al-Ni-rich phase decreases as the aging temperature increases and, hence, leads to an increase in the amount of Al-(Ni, Co, Cr, Fe).	[59][60]
NbMoTaTi–(W, V)	Arc-melting	BCC + HCP—with W inclusion	The HEA with “V” shows a dendritic/cellular microstructure rich in Ti and V.	[61]
		BCC—with V inclusion	The HEA with “W” forms a Ti-rich HCP phase.	

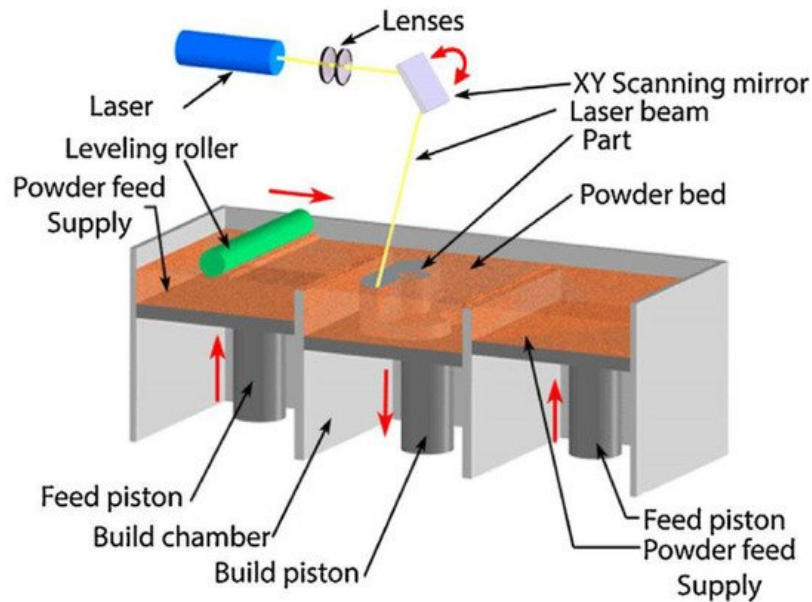
HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
$\text{Al}_{0.5}\text{CrCuNiV}$	Arc-melting	FCC + 2 BCCs + B2	A dendrite rich in Cr and V is present. The incorporation of Cu into the 2-BCC phase differentiates it from the B2 phase.	[62]
$\text{AlCoCrFeNi}_{2.1}$	Vacuum Induction	Dual-phase FCC + BCC (B2)	-	[63]
$\text{AlCrCuFeNi}$	Arc-melting	FCC + BCC	The content of Ni has a significant effect on the HEA microstructure.	[64][65]

From another perspective, HEA phase formation during fabrication via the melting and casting route is suggested to hinge on binary constituent pairs rather than individual constituent elements [66][67]. An HEA system such as the AlCoCrFeNi alloy forms a BCC structure after processing; although among the constituent elements, only Cr and Fe have BCC crystal structures. The AlNi pair, from the possible binaries in the AlCoCrFeNi system, serves as the primary crystal structure in the AlCoCrFeNi HEA. This is due to the similar lattice parameter between AlNi (0.28810 nm) and AlCoCrFeNi (0.289675 nm) [68][69]. In addition, AlNi has the largest negative enthalpy of formation among all the binary pairs in AlCoCrFeNi [70][71][72]. The AlNi binary pair stabilizes over a wide composition field from 1638 °C down to room temperature and can dissolve other constituent elements [73][74]. The other elements, therefore, dissolve into the primary lattice due to their chemical compatibility and mixing entropy effect [75]. During solidification, Cr having the highest melting point is the first element to solidify. Cr remains segregated from the liquid mixture up to 1350 °C at the equiatomic composition [76][77]. In contrast, Al has the lowest melting temperature and thus has the highest diffusivity during solidification. The effect of Al addition on 3d transition metal-based HEAs such as AlCoCrFeNi been studied [78][79][80]. The increasing quantity of Al promotes the formation of the BCC phase [80][81][82]. Moreover, Wang et al. [83] and Rogström et al. [84] observed that the AlCoCrFeNi HEA exhibits a spinodal microstructure of an A2 ((Cr, Fe)-rich) disordered solid solution and a modulated B2 ((Al, Ni)-rich) ordered solid solution. The A2 phase forms at temperatures below 600 °C, while the B2 phase forms at higher temperatures [83].

Some examples of HEAs that exhibit a single-phase FCC structure after melting and casting are the CoCrFeMnNi HEA structure [85][86], the  $\text{Al}_x\text{CoCrCuFeNi}$  alloy system [87][88], the CoCrCuFeNi HEA [89][90], the  $\text{FeCoNiCrCuO}_{0.5}\text{Al}_x$  HEA [40], and the  $\text{Al}_x\text{CoCrFeNiTi}_y$  HEA [42][91]. The binary constituents in these HEAs encourage the formation of the FCC phase. In addition, the addition of elements such as Cu and Ti stabilizes the FCC phase [92][93]. In the  $\text{Al}_x\text{CoCrFeNi}$  alloy system, the addition of Ti promotes phase evolution from the BCC to an FCC phase [72]. Furthermore, when Al in AlCoCrFeNi is replaced with Cu to form the CoCrCuFeNi alloy, the FCC phase forms instead of an A2 + B2 structure associated with AlCoCrFeNi. CuCo, CuNi, CoNi, FeNi, and CoFe, which make up the binary constituents in the CoCrCuFeNi alloy, all have an FCC structure and promote the FCC phase. In addition, the use of Mn to form CoCrFeMnNi also leads to a single-phase FCC structure [94].

### 3. Microstructural Evolution of HEAs Fabricated by Additive Manufacturing (AM)

AM has become a mainstream manufacturing process because of its flexible design optimization and processing advantages. The production of customized parts and the ability to control the microstructure in a specific site are possible in this processing route. The higher heating and cooling rates associated with AM promote chemical homogeneity in alloys by restricting diffusion to avoid undesired multiple phase transformations during cooling [95]. Solidification mainly takes place along the building direction and is predominantly epitaxial. The successive building process in thin layers by local heat input characterizes the microstructures as a result of rapid and directional solidification. Factors such as powder flowability, laser power, powder thickness and shape, scan spacing, and volumetric energy density (VED) all play an important role in determining the resulting microstructure in AM technology. [Figure 2](#) below shows the schematic representation of additive manufacturing techniques.



**Figure 2.** Schematic representation of additive manufacturing techniques [96].

Table 2 presents some HEAs fabricated using the AM route. The AlCrFeCoNi HEA system has also been synthesized by Kuwabara et al. [97] and Fujieda et al. [98] using the selective electron beam melting (SEBM) AM technique. The microstructure of the SEBM HEA exhibited a BCC and a B2 phase, same as that reported when processed through the melting and casting route, despite the rapid solidification of the SEBM process [99][10]. In addition to the BCC microstructure, an FCC phase was observed at the bottom of the SEBM-fabricated HEA. The precipitation of the FCC phase could have resulted from the BCC or B2 phase in a lower temperature range during building. Moreover, the phase evolution could have also occurred during the preheating process, which is associated with the SEBM AM technology. The coexistence of BCC and FCC phases in AlCrFeCoNi was confirmed when Ji et al. [100] fabricated the same HEA using the powder metallurgy (MA + SPS) approach.

**Table 2.** Phase evolution of HEAs fabricated using different additive manufacturing routes.

HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
CoCrFeMnNi	Laser 3D printing	FCC (major) + BCC	An equiaxed-to-columnar transition structure was discovered in the melt pool.	[101]
CoCrFeMnNi	Laser powder bed fusion (LPBF)	FCC + $\sigma$ phase	Nanotwins were present in the printed sample.	[102]
CoCrFeMnNi	Laser directed energy deposition	FCC solid solution	Mn segregates at the boundary of the weld pool due to its volatility.	[103]
AlCrFeCoNi	Selective electron beam melting (SEBM)	FCC + BCC	No phase transformation occurred	[97][98]
AlCrFeCoMnNi	LPBF	BCC (B2, A2)	Lattice strain and grain refinement occurred.	[104]
Al <sub>0.3</sub> CoCrFeNi	LPBF	Supersaturated FCC phase	Phase evolution occurred during the preheating process	[105]
AlCoCrFeNiTi <sub>0.5</sub>	Laser-engineered net shaping (LENS)	2 BCC (B2, A2)	B2 (Ni-Al rich) and A2 (Fe-Cr rich)	[106]
			Due to liquid-phase spinodal decomposition and cubic nature of the HEA	
			Fine columnar grains were present due to rapid solidification and anisotropic heat removal.	
			A fully equiaxed grain microstructure was exhibited rather than a columnar microstructure associated with alloys fabricated with AM.	

HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
AlCrCuFeNi	LPBF	2 BCC (B2, A2)	Unique columnar grains were present containing multiple ultrafine sub-grain structures.	[107]
AlCrFeNiV	LPBF	FCC	Rapid cooling rate and solidification resulted in the formation of sub-grains in every columnar grain and L1 <sub>2</sub> nano-phase.	[108]
AlCrFe <sub>2</sub> Ni <sub>2</sub>	LPBF	BCC	Columnar BCC of spinodal decomposed B2 and A2 structures was exhibited. Cracks were present at the intergranular site.	[109]
FeCoCrNi	LPBF	FCC	After annealing at 1373 K, columnar grains and equiaxial grains were found to co-exist.	[110]
AlCoCrFeNi	Direct laser fabrication (DLF)	BCC (B2)	Intergranular needle-like and plate-like FCC phase precipitates and wall-shaped FCC phase precipitates were present along grain boundaries after aging at 800, 1000, and 1200 °C.	[111]
MoNbTaW	Direct energy deposition (DED)	BCC		[112]
Al <sub>0.5</sub> Cr <sub>1.0</sub> Mo <sub>1.0</sub> Nb <sub>1.0</sub> Ta <sub>0.5</sub>	SEBM	BCC	Two phases were present: TaMoNbCr and (TaMoNbCr) <sub>Al</sub> solid solutions.	[113]
CoCrCuFeNiAl	LENS	BCC (B2, A2)	Dendritic grains were present. An ordered interface transition region was present between the two phases.	[114][115]
AlCoCrFeNi <sub>2.1</sub>	LENS	Ordered FCC (L1 <sub>2</sub> ) + BCC	Co, Cr, and Fe stabilize L1 <sub>2</sub> . L1 <sub>2</sub> and BCC are rich in nickel.	[116]
Fe <sub>38.5</sub> Mn <sub>20</sub> Co <sub>20</sub> Cr <sub>15</sub> Si <sub>5</sub> Cu <sub>1.5</sub>	LPBF	FCC	Deformation-induced phase transformation of γ (FCC) to ε (HCP) occurred in the vicinity of microcracks.	[117]
CoCrFeNi	3D extrusion printing	FCC	There was complex structural evolution, from loosely packed oxide particles in the green body to fully-annealed, metallic CoCrFeNi.	[118]
AlCrFeMoV <sub>x</sub> (x = 0 to 1)	LENS	BCC	The high solubility of V offers a broad range of solid solution strengthening of a compositionally complex but structurally simple BC matrix.	[118]
ZrTiVCrFeNi	LENS	C14 Laves phase (major) + α-Ti solid solution	The C14 Laves phase becomes stable on exposure to annealing and hydrogen influence.	[119]
6FeNiCoSiCrAlTi	Laser cladding	BCC	Equiaxed polygonal grains, discontinuous interdendritic segregation, and nano-precipitates are present.	[120]
MoFeCrTiW	Laser cladding	BCC	Cellular crystals are formed on which dispersion precipitates exist.	[121]
TiZrNbMoV	LENS	FCC (δTiH <sub>x</sub> -type) + BCC (NbH <sub>-0.4</sub> -type)	αZr-rich precipitates are present, in addition to the phases formed.	[122]
Al <sub>0.5</sub> FeCu <sub>0.7</sub> NiCoCr	Laser cladding	FCC + BCC + Al phases	A laser rapid cooling rate facilitates the formation of a simple structure and prohibits the formation of undesired intermetallic compounds.	[123]



HEA Composition	Processing Method	Observed Phase(s)	Microstructures and Comments	Reference
TiZrNbHfTa	Laser metal deposition (LMD)	BCC	An equiaxed grain shape is present.	[124]
Al <sub>0.5</sub> CrMoNbTa <sub>0.5</sub>	Electron beam melting (EBM)	BCC	Intermetallic phases C14, C36, C15, and 6H are present.	[125]
Ni <sub>6</sub> Cr <sub>4</sub> WFe <sub>9</sub> Ti	LPBF	FCC	Tiny precipitates of an unknown phase are present.	[126]
FeCoCrNiC <sub>0.05</sub>	LPBF	FCC	Nano-scale Cr <sub>23</sub> C <sub>6</sub> -type carbides can precipitate under annealing conditions.	[127]

## 4. Recommendations for Future Studies

Large differences in the melting temperatures of the constituent elements due to compositional complexity result in elemental segregation, dendritic structure, and residual stress in HEAs fabricated using the melting and casting route. To address these discrepancies, the rate of cooling, differences in the local atomic arrangement, and the varying elemental diffusivity must be taken into consideration in future studies. Faster cooling routes such as suction casting, injection casting, melt spinning, or splat cooling suppress the precipitation of the secondary phase and thereby form a predominantly stable single-phase structure. Hence, induction remelting can reduce microsegregation, reduce the inhomogeneity challenge, and refine the grain size.

Most of the studies on HEAs fabricated by MA are focused on varying the milling duration in achieving a homogeneous solid solution of the elements. However, since the parameters of the MA process are not independent of each other, it is imperative to know that other parameters such as milling speed, the BPR, grinding media, and the milling environment are given some attention in future studies. These other parameters also significantly influence the heat generated during milling and the diffusion of elements in the solid solution process. A lower sintering temperature (depends on the melting temperatures of constituent elements) should also be considered.

There is no adequate information to better understand how, where, and why voids and porosity were formed in most AM-fabricated materials. More attention is needed in this area as controlling their distribution or avoiding them is crucial and requires a better understanding; hence, these defects are undesirable in certain engineering applications. Therefore, there is a need for the development and standardization of economically viable and printable materials for engineering applications in the AM fabrication technique spectrum to complement its processing advantages. Urgent attention is needed in developing computer-aided design tools and predictive models of both the printing process and the post-printing material properties in future studies.

[128], and more researchers have used the combinatorial approach in processing multicomponent alloys, more attention is still needed on this method owing to the possibility of exploring composition space. Thus, observations suggest that proper selection of the chemical composition and an appropriate processing route combined with appropriate thermomechanical treatment may offer an opportunity to manipulate the strengthening mechanism to enhance HEAs' mechanical properties. An optimal composition with required properties could be more efficient. Therefore, more research with modeling and simulations is required, in addition to computational tools and integrated computational material engineering available.

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