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Chapter 4

Magnetic Characteristics of High Entropy Alloys

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Additional information is available at the end of the chapter

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Abstract

High entropy alloy (HEA) is a multi-principal alloy having at least five principal elements in the concentration range of 5–35 at.%. HEAs having excellent mechanical properties and further these properties can be altered by the addition of different alloying element. For example with the addition of Al in base alloy make them a ductile and the addition of Co, Ti, etc. transforms base alloy to brittle material. This characteristic of HEAs makes them a promising technologically important material. A soft magnetic material should have good mechanical property, structural stability at high temperature and low coercivity with high magnetization. Recently, reported $FeCoNiMn_{0.25}Al_{0.25}$ and CoCrFeNiM (M = Cu, Mn) HEAs got attention as a better soft magnetic material because these HEAs having good soft magnetic characteristics along with good mechanical and excellent structural stability at high-temperature. Recent reports described that the mechanical as well as magnetic characteristics of these alloys can be tuned by the variation and/or the addition of alloying element in the base alloys. The magnetic characteristics of these alloys basically depend on the alloying element and compositional variation of the magnetic element present in particular HEAs. We have summarized the key results of magnetic characteristics of some recently investigated promising high entropy alloys.

Keywords: high entropy alloy, magnetic properties, soft magnetic materials, alloying

1. Introduction

For centuries alloy design has been a hot topic for metallurgists and material scientists. The design concepts of alloys is based on only one or two principle elements, while minor fraction of other elements are added for property enhancement. This classical definition has been broken by the Yeh et al. in 2004 by the suggestion of a new alloy design concept, referred as multicomponent alloys named as high entropy alloys (HEAs) [1]. They defined the HEAs in two ways one is based on composition and other on entropy. Under the

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compositional definition, HEAs are defined as those alloys having at least 5 principle elements [4]. The each with a concentration range of 5–35 at.% [1–4]. From the entropic point of view, the HEAs are defined as those alloys having configurational entropy larger than 1.5R (where R is the gas constant) [1–4]. Moreover, it should be noted that rather than the principle element in HEAs, some minor element (having concentration less than 5 at.%) have also been added to optimize the properties presence of multiple principal elements in HEAs is not merely a compositional difference compared to the conventional alloys, but it has a fundamental effect on the system characteristics that leads four core effects: high entropy, severe lattice distortion, sluggish diffusion and cocktail effects [2–4]. Due to these characteristics it has been reported that HEAs are a good candidate of structural as well as functional engineering materials that have high strength and hardness, excellent corrosion and wear resistance, as well as great fatigue resistance [2–6].

Previous studies discovered that HEAs generally exhibit simple solid solution structures such as body centered cubic (BCC), face centered cubic (FCC), hexagonal close packed (HCP) or mixture of the above rather than the intermetallic compounds due to the high entropy effect. However, minor fractions of intermetallic phases are observed in some HEAs [7]. The formation of solid solution phases in HEAs are governed by several thermodynamic parameters. These are entropy of mixing (ΔS_{mix}), enthalpy of mixing (ΔH_{mix}) and atomic size difference (δ) [8]. These parameters are defined as follows:

$$\Delta S_{mix} = -R \sum_{i=1}^{n} Ci \ln Ci \tag{1}$$

Here, R is the gas constant and C_i is the molar fraction of ith element.

$$\Delta H_{mix} = \sum_{i=1}^{n} 4\Delta H_{ij}{}^{mix} CiCj \tag{2}$$

Here, $\Delta H_{ij}{}^{mix}$ is the enthalpy of mixing of the binary liquid between the i^{th} and j^{th} element and C_i, C_j are the atomic fraction of i^{th} and j^{th} elements.

$$\delta\% = 100\% \sqrt{\sum_{i=1}^{n} Ci \left(1 - \frac{r_i}{\sum_{j=1}^{n} C_j r_j}\right)^2} \tag{3}$$

Here, C_i and r_i denotes the atomic fraction and atomic radius of the i^{th} element respectively.

Guo et al. reported that HEAs forms simple solid solution phases when $-22 \le \Delta H_{mix} \le 7$ kJ/ mol, $11 \le \Delta S_{mix} \le 19.5$ J/K mol and $\delta \le 8.5\%$. Moreover, it has been found that the most critical factor that decides whether the formed simple solid solution phases are FCC or BCC in HEAs is the valence electron concentration (VEC) [9]. It has been observed that for VEC < 6.87 and VEC ≥ 8.0 BCC and FCC phases are formed respectively, while both phases (i.e., mixture of FCC and BCC) will coexist when $6.87 \le VEC \le 8.0$ [9].

The typical synthesis routs used for traditional alloys can also be applied for the synthesis of HEAs. On the dependence of how the constituent elements are mixed, the processing routs are classified into four categories [10–13]: (1) from the liquid state (arc melting), (2) from solid state (mechanical alloying), (3) from the gas state (sputtering), and (4) from electrodeposition process. It has been found that for the same composition of the alloys, different synthesis rout produced distinct microstructure that leads different properties. For example, CoCrFeNiTi HEA synthesized through arc melting has mixture of FCC, BCC and minor fraction of an intermetallic phase [14]. However, when it was synthesized through mechanical alloying (MA), it has only single FCC phase [15]. In addition to the synthesis rout, selection and composition of constituent elements also plays a critical role in deciding the microstructure and phase composition that influenced the properties of the HEAs [16–18]. Addition of Ti into CoCrFeNi leads the formation of intermetallic phases such as Laves and σ-phases and enhanced the hardness and compressive strength [16]. Moreover, Shun et al. reported that as the content of Mo increased from 0 to 0.85 into $CoCrFeNiMo_x$, the crystal structure changed from single FCC to mixture of FCC with (Mo, Cr)-rich σ and μ phases, correspondingly the hardness and compressive strength of the system increased up to 68 and 40% as compared to initial sample [17]. Liu et al. also reported that addition of Nb into CoCrFeNi changes the microstructure from the initial single FCC to mixture of FCC+ Nb-rich Laves phase. It has been found that the fracture and yield strength of the system increased from 413 to 1004 MPa and 147 to 637 MPa with the addition of Nb [18]. Apart from the mechanical property of the HEAs, functional properties of HEAs such as magnetic property, electrical resistance, etc. attracted great attention during last 5 years [19]. Recent reports showed that the soft magnetic characteristics along with optimal mechanical behaviour of HEAs can be obtained through carefully selection of constituent elements [20–22]. The magnetic characteristics of the alloys are sensitive to the base alloy, addition of alloying elements, resulting phases and their volume fractions [23, 24]. For example, Zuo et al. reported that the addition of Si in CoFeNi reduced the value of Ms more significantly from 151.3 to 80.5 emu/g than Al (from 151.3 emu/g to 101.8 emu/g) [23]. Moreover, Kao et al. reported that the magnetic nature of $Al_xCoCrFeNi$ HEA turned from paramagnetic to ferromagnetic, when the crystal structure changed from FCC (at x = 0) to BCC (at x = 2.0) [24]. Thus as a consequence the selection of alloying elements, their composition and the type of resultant crystal structure are the dominant factor for controlling the mechanical as well as magnetic properties of HEAs. In this chapter we have discussed and described the magnetic behaviour of recently developed multicomponent HEAs.

2. Effects of constituent elements on magnetic characteristics of different HEAs

Soft magnetic materials are widely used in the electrical power generation and transmission, electric motors, electromagnets, etc. However, conventional alloys have certain limitations, such as brittleness, weak mechanical behaviour and low electrical resistivity of Fe—Ni alloys. However, some FeCoNi based HEAs have better soft magnetic characteristics along with

excellent mechanical properties [20–22, 25]. These combined properties of FeCoNi based HEAs are rarely seen in conventional alloys. Moreover, it has been found that the optimal balance of magnetic and mechanical properties of HEAs is dominantly affected by the alloying elements and their composition [20–22, 25]. Among all the studied alloys the ternary equiatomic FeCoNi alloy having single FCC structure exhibits higher saturation magnetization (Ms) (151 emu/g) with low coercivity (Hc) (1.52 Oe) [23]. Any addition of other paramagnetic or diamagnetic elements will affect its resultant magnetic characteristics. Since, it is well known that the magnetic characteristics of the alloys are very sensitive to the composition, alloying elements and the resultant phase structure [26]. For example, addition of Cr in FeCoNi base alloy changed its magnetic nature from ferromagnetic to paramagnetic. However, further addition of Al or Pd in CoCrFeNi alloy, the paramagnetic nature of base alloy changed to ferromagnetic. It has been reported that FeCoCrNiAl alloy has the value of the Ms = 13 emu/g and value of Ms for $FeCoCrNiPd_2$ alloy was found to be 34 emu/g [26]. In addition to the increase in saturation magnetization, Lucas et al. also found that with the addition of Al and Pd in CoCrFeNi alloy, the Curie temperature increased up to 157 and 230°C respectively. Enhancement of Curie temperature with Pd addition makes this alloy useful for magnetic refrigeration near room temperature [26].

Zhang et al. investigated the magnetic and mechanical properties of most widely studied equiatomic AlCoCrCuFeNi HEA in as cast and annealed state [27]. They reported that both alloys exhibit soft magnetic characteristics. Moreover, after annealing, the value of Ms and Hc decreased from 38.18 to 16.08 emu/g and 45 to 15 Oe respectively. The decrement of Ms is associated to the structure coarsening and phase transformation [27]. For detail study, Singh et al. investigate the microstructure of AlCoCrCuFeNi HEA in three different states (splat-quenched, as cast and aged at 600°C) [28]. They reported that the ferromagnetic characteristic of HEAs is correlated to the decomposition of the Cr—Fe—Co rich regions into Fe—Co-rich and Cr-rich regions. It has been found that splat-quenched alloy exhibit better soft magnetic characteristic than the as cast and aged HEAs. This was associated to the initial stage decomposition of Cr—Fe—Co region, resulting in clustering of Fe-rich and Cr-rich domain. However, the aged alloy exhibit high value of Ms, Hc and remanence ratio as compared to the as cast HEA due to a higher degree of decomposition in Cr—Fe—Co rich regions. Additionally, they also pointed out that the aged alloy exhibits no ferromagnetic phase transition up to temperature of 400 K at 1 T [28].

Wang et al. investigated the effect of milling duration and composition on microstructure and magnetic properties of FeSiBAlNi and FeSiBAlNiNb HEAs [29]. Initially amorphous HEA has been synthesized by MA method. They found that the addition of Nb enhanced the milling duration for the formation of full FeSiBAlNiNb amorphous phase and also decreased the glass forming ability. Moreover, the resultant alloy has higher thermal stability and heat resistance properties. They reported that as milled FeSiBAlNiNb powders have low coercivity and, hence behave as a soft-magnetic material. As the milling duration increases Ms decreased and become lowest when the amorphous HEAs are formed. It is found that as milled products with solid solution phase having better soft magnetic characteristics as compared to fully amorphous phases. Moreover, the addition of Nb does not improve the soft-magnetic characteristics FeSiBAlNi HEA. Also both the amorphous HEAs have similar soft magnetic characteristics after prolong milling.

Xu et al. also investigate the effect of addition of C and Ce on magnetic characteristics of FeSiBAlNi (based-W5) HEAs [30]. Amorphous HEAs has been synthesized through MA. They found that addition of Ce reduced the MA time for the formation of amorphous phase and hence enhanced the glass forming ability (GFA) of the parent HEA. With the addition of C in FeSiBAlNi the formation of amorphous phase and a small amount of Si nanocrystals has been found by the authors. By the addition of both(C and Ce) the thermal stability of the alloy is enhanced. They found that with addition of C the value of Ms increased appreciably. However, with the addition of Ce the value of Ms decreased. This happened because, the addition of Ce promoted the formation of single BCC phase at initial milling time, while for the case of parent alloy BCC and FCC phases was formed. It is well known that BCC phase having lower atomic packing density as compared to FCC solid solution and hence having less ferromagnetic element and a lower total magnetic moment per unit volume as compared to FCC solid solution. Hence yield lower value of Ms with the addition of Ce in base alloy [20]. Moreover the value of Ms decreased as the milling duration increased, because remarkable change may occur in the magnetic moment through the change of the neighbor configuration of the ferromagnetic elements. The decrease in Ms may also be related to the enhanced density of grain boundaries and to the volume fraction of amorphous phase. For the synthesized samples, Hc has been found in the range of 50–378 Oe, indicating that the studied samples having semi-hard magnetic property. Different composition and microstructure together with lattice distortion due to the presence of C and Ce inevitably affect the magnetic domain wall and hence affect the Hc. Moreover, the particle size of FeSiBAlNiCe is less as compared to FeSiBAlNiC also responsible for the higher Hc of FeSiBAlNiC as compared to FeSiBAlNiCe HEA. While constant Hc has been reported after 140 h MA suggested due to the stable particle size and proportion of amorphous and solid solution phase with prolong milling duration.

Xu et al. studied the effects of addition Co, Cu and Ag on the microstructure, thermal property and magnetic properties of mechanically alloyed FeSiBAlNi HEAs [31]. They reported that as milled HEAs showed semi hard magnetic characteristics. Moreover, the value of Ms decreased with the addition of elements in base alloy. They concluded that the coexistence of FCC and BCC phases is beneficial to give rise to the semi hard magnetic characteristics than the fully amorphous or mixture of amorphous plus FCC phase. Further, Zhu et al. investigated the effect of annealing on microstructure thermal stability and magnetic characteristics of MA FeSiBAlNiM (M = Co, Cu, Ag) amorphous high entropy alloys (HEAs) [32]. High phase stability during heating process has been observed with the addition of Co and Ag in FeSiBAlNi. They found that at high annealing temperature HEAs possessed better semi-hard magnetic characteristics. They also reported that the formation of FeSi-rich and FeB-rich phases after annealing is beneficial for the enhanced magnetic characteristics of annealed HEAs. Moreover, they reported that for FeSiBAlNiCo HEAs annealing near re-crystallization temperatures was beneficiatial for the semi-hard magnetic characteristics.

Wei et al. investigated the effect of cooling rate on phase formation and magnetic characteristics of $Fe_{26.7}Co_{28.5}Ni_{28.5}Si_{4.6}B_{8.7}P_3$ HEA [33]. They found amorphous phase was formed with melt spinning at high cooling rate, whereas FCC solid solution phase has been formed at low cooling rate. The better soft magnetic characteristics have been reported for amorphous phase

(saturation magnetization (Bs) of 1.07 T and coercivity (Hc) of 4 A/m) as compared to solid solution phase (Bs of 1.0 T and Hc of 168 A/m). They concluded that Bs is more sensitive towards the composition and atomic level structure and less dependent on the grain size [20]. As compared to amorphous alloy without symmetry, the low Bs has been found for the solid solution phase because high symmetry of FCC phase neutralized the atomic magnetic moment as compared to the amorphous phase. Moreover, Hc is sensitive to grain size, larger grain having high Hc [20, 34, 35].

Zuo et al. prepared equiatomic CoFeMnNi based HEA and investigated the effect of addition of non-magnetic element (Al, Cr, Ga and Sn) on crystal structure and magnetic characteristics [36]. They pointed out that for CoFeMnNi base alloy the value of Ms and Hc are found to be 18.14 emu/g and 119.9 A/m respectively. The addition of Al, Ga and Sn in CoFeMnNi separately increased the saturation magnetization from 18.14 to 147.86, 80.43 and 80.29 emu/g respectively. Furthermore, addition of Cr in base alloy dramatically reduced the value of Ms (1.39 emu/g) and enhanced the Hc up to 10,804 A/m. They reported that the apparent enhancement in Ms of FeCoMnNiX (Al, Ga and Sn) HEAs is associated to the dramatic change in crystal structure, which accordingly influenced the electronic and magnetic structures. They assumed that the antiferromagnetism of Mn atoms in CoFeMnNi base alloy is suppressed to favor the ferromagnetism due to the doping of Al, Ga and Sn. Further, Na et al. substituted the Mn element to Cr and studied the ferromagnetic transition and magnetic behaviour in equiatomic FeCoNiCrX (X = Al, Ga, Mn and Sn) HEAs [37]. They reported that FeCoNiCrMn and FeCoNiCrSn exhibited paramagnetic behaviour. While, addition of Al and Ga in FeCoNiCr base alloy changed the magnetic state from paramagnetic to ferromagnetic. Further, it has been found that with the addition of Al and Ga in base alloy, the value of Ms and Tc increased from 0.5 (Tc = 104 K) to 25 emu/g (Tc = 277 K) and 38 emu/g (Tc = 703 K) respectively. They pointed out that the enhancement in Ms is associated to the partial phase transition (formation of BCC phase).

3. Effects of compositional variation on magnetic characteristics of different HEAs

Apart from the elemental effect on magnetic characteristics of HEAs, the composition of alloying elements also play an important role on magnetic properties of the HEAs [19]. Wang et al. investigated the effect of addition of Ti on microstructure, mechanical property and magnetic characteristics of $CoCrCuFeNiTi_x$ (x = 0, 0.5, 0.8 and 1.0) HEA [38]. Both CoCrCuFeNi and $CoCrCuFeNiTi_{0.5}$ HEAs form a single FCC structure, while as the content of Ti increased in the base alloy, an intermetallic Laves phase of Fe_2Ti type has been evolved along with FCC. They pointed out that both CoCrCuFeNi and $CoCrCuFeNiTi_{0.5}$ HEAs have low value of Ms and exhibits paramagnetic nature. However, $CoCrCuFeNiTi_{0.8}$ and CoCrCuFeNiTi have superparamagnetic nature with the value of Ms of 1.36 and 1.51 emu/g respectively. The superparamagnetic nature of these HEAs is due to the nanoprecipitation.

Zhang et al. substituted Cu from Al and studied the effect of addition of different Al concentration and annealing on mechanical, electrical and magnetic properties of $CoCrFeNiTiAl_x$

(x = 0, 0.5, 1.0, 1.5 and 2.0) HEA [39]. They reported that as the content of Al increased, the value of electrical resistivity of as cast HEAs varied from 107 to 60 μΩ cm. All the as cast and as annealed HEAs exhibit high electrical resistivity as compared to the relative pure elements. It has been found that all annealed HEAs exhibit high electrical resistivity than the as cast HEAs. The enhancement in electrical resistivity after annealing has been associated to the evolution of phase composition and lattice distortion. Zhang et al. also pointed out that the saturation magnetization of the as cast $CoCrFeNiTiAl_x$ HEAs firstly increased as the content of Al increased from x = 0 to 1.0 and then decreased for x = 2.0. The as cast $CoCrFeNiTiAl_{1.0}$ HEA exhibits the best magnetic characteristics having high Ms (14.75 emu/g) with low coercivity (Hc = 22 Oe) than the other as cast HEAs. However, after vacuum annealing at 1000°C for 2 h the value of Ms decreased as compared to their as cast ones. While, the value of Ms for $CoCrFeNiTiAl_{2.0}$ HEA increased from 0.76 (as cast) to 15.74 emu/g and exhibited better magnetic characteristics as compared to the as cast and as annealed $CoCrFeNiTiAl_x$ HEAs. The value of Hc of annealed HEAs lies in the range of 20–285 Oe. They concluded that the as cast and as annealed $CoCrFeNiTiAl_x$ HEAs exhibited semi hard magnetic characteristics and these materials can be used in magnetic relayers, magnetic hysteresis motors and signal memory devices.

Kao et al. investigated the electrical and magnetic properties of Cu and Ti free $CoCrFeNiAl_x$ (x = 0–2.0) HEAs at various temperature range from 4.2 to 300 K [24]. It has been found that as the content of Al increased the structure of the alloy changed from a single FCC to a mixture of FCC and BCC and then it transformed into a single BCC phase. They studied the magnetic properties of these alloys in homogenized condition (denoted as H-x) at three different temperatures. All the homogenized alloys (H-x) exhibit ferromagnetic nature at low temperature (5 and 50 K). In addition to this the value of Ms for H-1.25 and H-2.0 HEAs exceeds at low temperature than that of the H-0 and H-0.25 alloys. This indicated that at low temperature, the BCC phase has a higher value of Ms than the FCC phase. At room temperature (300 K), the homogenized HEAs H-0, H-0.25 and H-0.75 exhibit paramagnetic behaviour, while H-0.5, H-1.25 and H-2.0 remain ferromagnetic. Kao et al. calculated the phase contribution of both FCC and BCC phases for H-0.50 and H-0.75 HEAs at 5 K. It has been found that the value of Ms for FCC phase is higher than the BCC phase. The reason for $Ms_{BCC} < Ms_{FCC}$ is associated to the existence of Al or AlNi-rich phase. The value of Ms decreased in the range of $0 \leq x \leq 0.25$ and $1.25 \leq x \leq 2.00$. The value of Ms for H-0.25 alloy is smaller than that of the H-0 HEA, indicating that the addition of Al reduces the magnetic moment. Besides this, H-2.0 alloy has smaller value of Ms than the H-1.25 HEA. Kao et el. pointed out that this is due to the high content of ordered BCC phase. It has been observed that H-2.00 alloy is mainly composed of AlNi-rich ordered BCC phase, whereas the H-1.25 alloy has less content of AlNi-rich ordered BCC phase. They concluded that the addition of Al reduced the ferromagnetic nature of single FCC and single BCC H-x alloys. In single BCC phase the reduction in the value of Ms is associated to the high content of AlNi-rich ordered BCC phase.

In a similar manner, Vrtink et al. also investigated the magnetic behaviour of $CoCrFeNiZr_x$ (x = 0.40, 0.45 and 0.50) eutectic HEAs at different temperatures (5, 100 and 300 K) [40]. They reported that two magnetic structures, a disordered ferromagnetic (F) and a superparamagnetic-like (S) coexist in the $CoCrFeNiZr_x$ HEAs. The $CoCrFeNiZr_{x\ =\ 0.40,0.45,0.50}$ HEAs exhibit the

paramagnetism at 300 K, whereas at low temperature (5 and 100 K) it shows ferromagnetism. In addition to this, they also reported that at low temperature $CoCrFeNiZr_{0.45}$ and $CoCrFeNiZr_{0.50}$ HEA exhibit negligible coercive field as compared to the $CoCrFeNiZr_{0.40}$. Vrtinke et al. explained that this difference in the coercive field is associated to the vanishing of disordered F phase.

Ma et al. investigated the effect of Nb addition on the microstructure, mechanical property and magnetic behaviour of $AlCoCrFeNiNb_x$ (x = 0, 0.1, 0.25, 0.5 and 0.75) HEAs [41]. They reported that as the content of Nb increased a single BCC phase has been transformed into a mixture of (CoCr)Nb type Laves phase and BCC phase. Additionally, the value of Ms decreased and Hc increased from 64 to 10.31 emu/g and 52 to 94 Oe respectively as content of Nb increased. They reported that the alternation in the value of Ms and Hc may be associated to the magnetic hardening of the CoCrNb alloy and the Laves phase may pin the magnetic domain of BCC phase.

Recently, Zhang et al. reported a new class of CoFeNi based $CoFeNi(AlSi)_x$ ($0 \le x \le 0.8$) HEAs and investigated their structural, mechanical, magnetic and electrical behaviour [20]. They reported that the value of saturation magnetization is primarily determined by the composition and atomic level structures. With increasing the content of Al and Si, the value of Ms monotonically decreased from 1.315 to 0.46 T. Different from saturation magnetization it has been found that the coercivity is highly dependent on the microstructure, grain size and lattice distortion. They reported that addition of Al and Si induced the lattice distortion and changes the microstructure of the HEAs that inevitably affects the magnetic domain wall movement and, thus, the coercivity. It has been found that the optimal balance of magnetic, electrical, and mechanical properties is achieved at x = 0.20, which has the best combination of Ms (1.15 T), Hc (1400 A/m), resistivity (ρ = 69.5 μΩ cm), yield strength (342 MPA) and strain without fracture ($\varepsilon_p > 50\%$) for application as soft magnetic materials.

In a similar manner to Zhang et al. [20], the effects of phase constitution on magnetic and mechanical properties of $FeCoNi(CuAl)_x$ (x = 0–1.2, in molar ratios) HEAs has been investigated by the Zhang et al. [25]. They reported that depending on the content of alloying elements (Cu and Al), the $CoFeNi(CuAl)_x$ HEAs exhibit single FCC for $0 \le x \le 0.6$, BCC combined with minor FCC for $0.9 \le x \le 1.2$ and duplex FCC + BCC phase in the range of $0.7 \le x < 0.9$. The value of Ms decreased as the content of Cu and Al increased from x = 0 to x = 1.2, whereas some deviation in the range of $0.8 \le x \le 0.9$ has been observed. They reposted that the value of Ms is highly sensitive to the composition and phase constitution than their microstructure. Additionally, they annealed these as cast HEAs in three different temperatures (573–673 K) and they found that heat treatment did not impose any impacts on the magnetic characteristics for single FCC phase ($0 \le x \le 0.6$) and nearly single BCC phase ($0.9 \le x \le 1.2$) HEAs. However, the value of Ms increased for FCC + BCC duplex phase ($0.7 \le x < 0.9$ HEAs. For $CoFeNi(CuAl)_{0.8}$ HEA, the value of Ms increased from 78.9 (as cast) to 93.1 emu/g (annealed at 673 K). They pointed that the enhancement in the value of Ms after annealing is associated to the phase transition from FCC to BCC for $CoFeNi(CuAl)_{0.8}$ HEA. In summery they concluded that through the proper alloy composition and annealing one can achieve a superior soft magnetic metallic alloys with high saturation magnetization and high ductility.

Lie et al. also studied the composition dependence of crystal structure, physical and mechanical properties of $FeCoNi(MnAl)_x$ (x = 0, 0.25, 0.5, 0.75, 1) high entropy alloys [42]. They reported that

as the value of x increased from x = 0 to x = 1, the crystal structure changed from single FCC ($0 \leq x \leq 0.25$) to FCC + BCC ($0.5 \leq x \leq 0.75$) and then to a single BCC phase (x = 1). They also reported that with the variation of x values, the value of Ms firstly decreased from FeCoNi (155.7 emu/g) to $FeCoNiMn_{0.5}Al_{0.5}$ (51.9 emu/g) and increased from $FeCoNiMn_{0.75}Al_{0.75}$ 129.6 emu/g) to FeCoNiMnAl (132.2 emu/g). In addition to the saturation magnetization the value of Hc firstly increased from FeCoNi (189 A/m) to $FeCoNiMn_{0.5}Al_{0.5}$ (730 A/m) and decreased from $FeCoNiMn_{0.75}Al0_{0.75}$ (445 A/m) to FeCoNiMnAl (266 A/m) with the variation of x. They reported that the alternation in the value of Ms is associated to the change in lattice parameter and crystal structure. While the alternation in coercivity is associated to the change in microstructure, together with the lattice distortion induced by Al atoms. Moreover, Lie et al. also studied the magnetic characteristics of cold rolled and annealed FeCoNi, $FeCoNiMn_{0.25}Al_{0.25}$ and $FeCoNiMn_{0.5}Al_{0.5}$ alloys. They concluded that annealed FeCoNi and $FeCoNiMn_{0.25}Al_{0.25}$ alloys exhibit the optimal balance of magnetic and mechanical behaviour.

We have also investigated the effect of elemental addition (Mn and Co) on the phase formation and magnetic characteristics of TiFeNiCr base HEAs [15]. HEAs with different elements have been synthesized through the mechanical alloying. XRD analysis of synthesized HEAs confirmed that double FCC and a minor sigma phase have been evolved for TiFeNiCr and TiFeNiCrMn HEAs. However, single FCC phase has been appeared for TiFeNiCrCo HEA. The magnetic characteristic of synthesized and annealed HEA investigated through the VSM at room temperature. The value of Ms for TiFeNiCr HEA was found to be 13.82 emu/g (as shown in **Figure 1(a)**). However, the value of Ms for TiFeNiCrMn and TiFeNiCrCo HEAs was found to be 2.28 and 24.44 emu/g respectively (as shown in **Figure 1(b)** and **(c)**). It is concluded

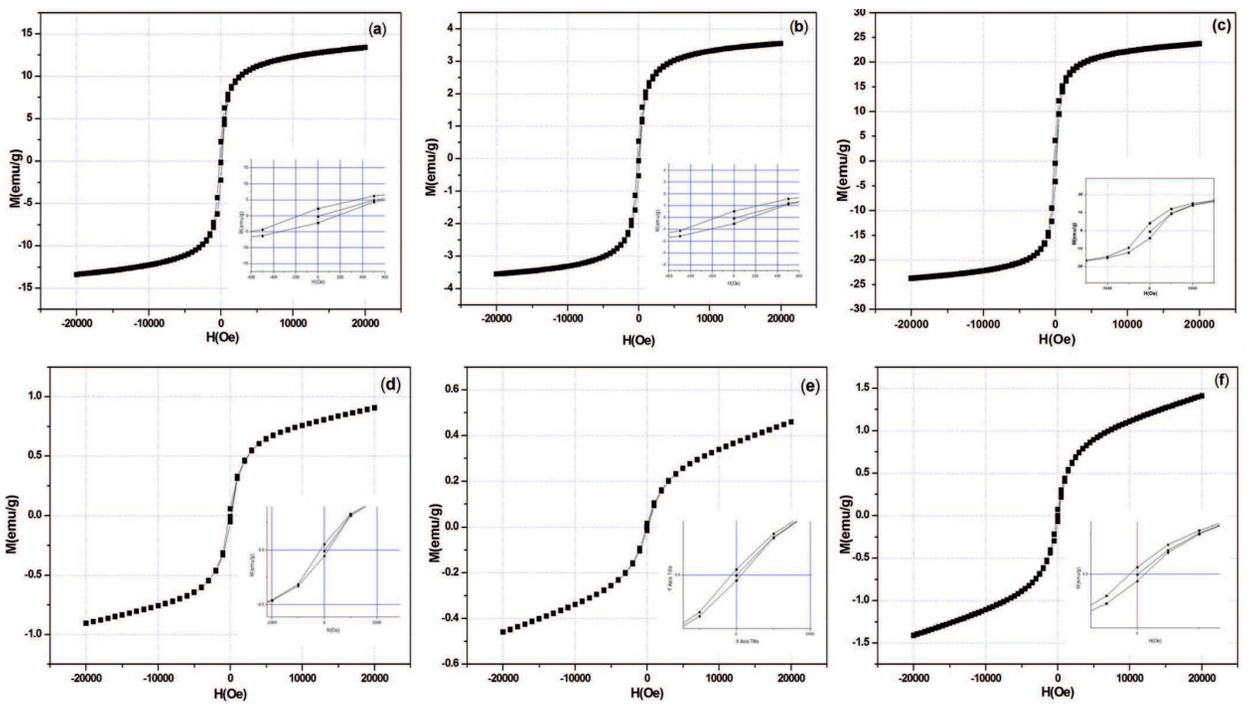


Figure 1. Magnetic hysteresis curve of (a) TiFeNiCr, (b) TiFeNiCrMn, (c) TiFeNiCrCo as synthesized and (d) TiFeNiCr, (e) TiFeNiCrMn, (f) TiFeNiCrCo annealed at 700°C HEAs. The inset represents the magnified view of selected region.

from the M-H curve, with the addition of ferromagnetic element (like Co) the value of Ms increased, while with addition of paramagnetic element (like Mn) the value of Ms decreased appreciably. Thus among TiFeNiCr, TiFeNiCrCo and TiFeNiCrMn HEAs the value of Ms was highest for the case of TiFeNiCrCo HEA because this alloy contained three ferromagnetic elements, i.e., 60 at.% (Fe, Ni and Co) of the alloy is ferromagnetic in nature. Thus, the value of Ms depends on the presence of magnetic elements and as the content of ferromagnetic elements increased the value of Ms increased appreciably. The value of Hc for TiFeNiCr, TiFeNiCrMn and TiFeNiCrCo HEAs was found to be 166.93, 225.83 and 149.54 Oe. We have also been investigated the effect of annealing on magnetic characteristics of HEAs. From figure it can say that the value of Ms, M_R/M_s and Hc decreased dramatically after annealing of the synthesized HEAs at 700°C (shown in **Figure 1**). The reduction in Ms after annealing may be attributed to the increase in lattice parameter after annealing. It has been found that the lattice parameter after annealing increased from 3.592 to 3.595 Å, 3.575 to 3.583 Å and 3.561 to 3.582 Å for TiFeNiCr, TiFeNiCrMn and TiFeNiCrCo, respectively. Hence the separation between the ferromagnetic elements of HEAs increased after annealing due to which the magnetic exchange coupling is altered and the value of Ms decreased for annealed TiFeNiCr, TiFeNiCrMn and TiFeNiCrCo HEAs.

4. Conclusions

High entropy alloys having multi-principal elements and has growing interest of Scientist Engineers and Metallurgists. The applications of HEAs are based on their four core effects. Among these effects the cocktail effect is the most effective for the functional properties of these alloys. HEAs may have wide range of applications along with better functional and structural properties. They have excellent mechanical properties. A soft magnetic material should have good mechanical property, structural stability at high temperature and low coercivity with high magnetization. Recently, reported $FeCoNiMn_{0.25}Al_{0.25}$ and CoCrFeNiM (M = Cu, Mn) HEAs got attention as a better soft magnetic material because these HEAs having good soft magnetic characteristics along with good mechanical and excellent structural stability at high-temperature. We have summarized the key results of magnetic characteristics of some recently investigated promising high entropy alloys. Further the mechanical as well as the magnetic characteristics of HEAs can be tuned through the selection of proper alloying elements and synthesis route. The magnetic characteristics of these alloys basically depend on the alloying element and compositional variation of the magnetic element present in particular HEAs. Thus the magnetic as well as mechanical properties of these alloys can be tuned based on our requirement/applications. As can be seen from the summarized results by the variation of single element the magnetic nature of the material can be changed to ferromagnetic to paramagnetic or super paramagnetic. Similarly, hard, semi-hard and soft magnetic characteristics of the materials have been changed by the change in the processing route of the HEAs. Thus we can conclude that alloying elements, composition and processing route has significant effect on phase evolution and microstructure, which inevitably affects the magnetic characteristics of HEAs. Among them, some HEAs (e.g $FeCoNiAl_{0.2}Si_{0.2}$, $FeCoNiMn_{0.25}Al_{0.25}$) have been

proven to have better soft magnetic characteristics with high Curie temperature (Tc) and excellent mechanical behavior as compared to conventional alloys. Therefore, more researches are needed in future for design and development of new HEAs and to explore their properties for application-oriented viewpoints.

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Conflict of interest

Authors declare that this chapter has no conflict of interest.

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References

[1] Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, Tsau CH, Chang SY. Nanostructured high entropy alloys with multiple elements: Novel alloy design concept and outcomes. Advanced Engineering Materials. 2004;**6**:299-303

[2] Tsai MH, Yeh JW. High-entropy alloy: A critical review. Materials Research Letters. 2014; **2**(3):107-123

[3] Zhang Y, Zuo TT, Tang Z, Gao MC, Dahmen KA, Liaw PK, Lu ZP. Microstructures and properties of high entropy alloys. Progress in Materials Science. 2014;**61**:1-93

[4] Miracle DB, Senkov ON. A critical review of high entropy alloys and related concepts. Acta Materialia. 2017;**122**:448-511

[5] Liu ZY, Guo S, Liu XJ, Ye JC, Yang Y, Wang XL, Yang L, An K, Liu CT. Micromechanical characterization of casting-induced inhomogeneity in an $Al_{0.8}$CoCrCuFeNi high-entropy alloy. Scripta Materialia. 2011;**64**:868-871

[6] Fu ZQ, Chen WP, Wen HM, Zhang DL, Chen Z, Zheng BL, Zhou YZ, Lavernia EJ. Microstructure and strengthening mechanisms in an FCC structured single-phase nanocrystalline $Co_{25}Ni_{25}Fe_{25}Al_{7.5}Cu_{17.5}$ high entropy alloy. Acta Materialia. 2016;**107**:59-71

[7] Otto F, Yang Y, Bei H, George EP. Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys. Acta Materialia. 2013;**106**:2628-2638

[8] Guo S, Liu CT. Phase stability in high entropy alloys: Formation of solid solution or amorphous phase. Progress in Natural Science: Materials International. 2011;**21**:433-446

[9] Guo S, Ng C, Lu J, Li CT. Effect of valence electron concentration on stability of FCC or BCC phase in high entropy alloys. Journal of Applied Physics. 2011;**109**:103505

[10] Alaneme KK, Bodunrin MO, Oke SR. Processing, alloy composition and phase transition effect on the mechanical and corrosion properties of high entropy alloys: A review. Journal of Materials Research and Technology. 2016;**5**:384-393

[11] Murti BS, Yeh JW, Ranganathan S. High Entropy Alloys. 3rd ed. London: Elsevier; 2014

[12] Gao MC, Yeh JW, Liaw PK, Zhang Y. High Entropy Alloys: Fundamental and Application. 1st ed. Switzerland: Springer; 2017

[13] Ghazi SS, Ravi KR. Phase-evolution in high entropy alloys: Role of synthesis route. Intermetallics. 2016;**73**:40-42

[14] Zhang K, Fu Z. Effects of annealing treatment on phase composition and microstructure of CoCrFeNiTiAlx high entropy alloys. Intermetallics. 2012;**22**:24-32

[15] Mishra RK, Shahi RR. Phase evolution and magnetic characteristics of TiFeNiCr and TiFeNiCrM(M=Mn, Co) high entropy alloys. Journal of Magnetism and Magnetic Materials. 2017;**442**:218-223

[16] Shun TT, Chang LY, Shiu MH. Microstructures and mechanical properties of multiprincipal component CoCrFeNiTix alloys. Materials Science and Engineering A. 2012;**556**:170-174

[17] Shun TT, Chang LY, Shiu MH. Microstructure and mechanical properties of multiprincipal component CoCrFeNiMox alloys. Materials Characterization. 2012;**70**:63-67

[18] Liu WH, He JY, Huang HL, Wang H, Lu ZP, Liu CT. Effects of Nb additions on the microstructure and mechanical property of CoCrFeNi high-entropy alloys. Intermetallics. 2015;**60**:1-8

[19] Tsai MH. Physical properties of high entropy alloys. Entropy. 2013;**15**:5338-5345

[20] Zhang Y, Zuo TT, Cheng YQ, Liaw PK. High entropy alloys with high saturation magnetization, electrical resistivity and malleability. Scientific Reports. 2013;**3**:1455

[21] Yu PF, Zhang LJ, Chen H, Zhang H, Ma MZ, Li YC, Li G, Liaw PK. The high entropy alloys with high hardness and soft magnetic property prepared by mechanical alloying and high pressure sintering. Intermetallics. 2016;**17**:82-87

[22] Li P, Wang A, Liu CT. A ductile high entropy alloy with attractive magnetic properties. Journal of Alloys and Compounds. 2017;**694**:55-60

[23] Zuo TT, Li RB, Ren XJ, Zhang Y. Effects of Al and Si addition on the structure and properties of CoFeNi equal atomic ratio alloy. Journal of Magnetism and Magnetic Materials. 2014;**371**:60-68

[24] Kao YF, Chen SK, Chen TJ, Chu PC, Yeh JW, Lin SJ. Electrical, magnetic, and Hall properties of AlxCoCrFeNi high-entropy alloys. Journal of Alloys and Compounds. 2011;**509**:1607-1614

[25] Zhang Q, Xu H, Tan XH, Hou XL, Wu SW, Tan GS, Yu LY. The effects of phase constitution on magnetic and mechanical properties of FeCoNi(CuAl)x (x = 0–1.2) high-entropy alloys. Journal of Alloys and Compounds. 2017;**693**:1061-1067

[26] Lucas MS, Mauger L, Munoz JA, Xiao Y, Sheets AO, Semiatin SL, Howath J, Turgut Z. Magnetic and vibrational properties of high entropy alloys. Journal of Applied Physics. 2011;**307**:07E109

[27] Zhang KB, Fu ZY, Zhang JY, Shi J, Wang WM, Wang H, Wang YC, Zhang QJ. Annealing on the structure and properties evolution of the CoCrFeNiCuAl high-entropy alloy. Journal of Alloys and Compounds. 2010;**502**:295-299

[28] Singh S, Wanderka N, Kiefer K, Siemensmeyer K, Banhart J. Effect of decomposition of the Cr–Fe–Co rich phase of AlCoCrCuFeNi high entropy alloy on magnetic properties. Ultramicroscopy. 2011;**111**:619-622

[29] Wang J, Zheng Z, Xu J, Wang Y. Microstructure and magnetic properties of mechanically alloyed FeSiBAlNi (Nb) high entropy alloys. Journal of Magnetism and Magnetic Materials. 2014;**355**:58-64

[30] Xu J, Axinte E, Zhao Z, Wang Y. Effect of C and Ce addition on the microstructure and magnetic property of the mechanically alloyed FeSiBAlNi high entropy alloys. Journal of Magnetism and Magnetic Materials. 2016;**414**:59-68

[31] Xu J, Shang C, Ge W, Jia H, Liaw PK, Wang Y. Effects of elemental addition on the microstructure, thermal stability and magnetic properties of the mechanically alloyed FeSiBAlNi high entropy alloys. Advanced Powder Technology. 2016;**27**:1418-1426

[32] Zhu X, Zhou X, Yu S, Wei C, Xu J, Wang Y. Effects of annealing on the microstructure and magnetic property of the mechanically alloyed FeSiBAlNiM (M = Co, Cu, Ag) amorphous high entropy alloys. Journal of Magnetism and Magnetic Materials. 2017; **430**:59-64

[33] Wei R, Sun H, Chen C, Han Z, Li F. Effect of cooling rate on the phase structure and magnetic properties of $Fe_{26.7}Co_{28.5}Ni_{28.5}Si_{4.6}B_{8.7}P_3$ high entropy alloy. Journal of Magnetism and Magnetic Materials. 2017;**435**:184-186

[34] Anand G, Goodall R, Freeman CL. Role of configurational entropy in body-centred cubic or face-centred cubic phase formation in high entropy alloys. Scripta Materialia. 2016;**124**: 90-94

[35] Herzer G. Modern soft magnets: Amorphous and nanocrystalline materials. Acta Materialia. 2013;**61**:718-734

[36] Zuo TT, Gao MC, Ouyang L, Yang X, Cheng YQ, Feng R, Chen S, Liaw PK, Hawk JA, Zhang Y. Tailoring magnetic behavior of CoFeMnNiX (X = Al, Cr, Ga, and Sn) high entropy alloys by metal doping. Acta Materialia. 2017;**130**:10-18

[37] Na SM, Yoo JH, Lambert PK, Jones NJ. Room-temperature ferromagnetic transitions and the temperature dependence of magnetic behaviors in FeCoNiCr-based high-entropy alloys. AIP Advances. 2018;**8**:056412

[38] Wang XF, Zhang Y, Qiao Y, Chen GL. Novel microstructure and properties of multicomponent CoCrCuFeNiTix alloys. Intermetallics. 2007;**15**:357-362

[39] Zhang K, Fu Z. Effects of annealing treatment on properties of CoCrFeNiTiAlx multi-component alloys. Intermetallics. 2012;**28**:34-39

[40] Vrtnik S, Guo S, Sheikh S, Jelen A, Koželj P, Luzar J, Kocjan A, Jagličić Z, Meden A, Guime H, Kime HJ, Dolinšek J. Magnetism of CoCrFeNiZrx eutectic high entropy alloys. Intermetallics. 2018;**93**:122-133

[41] Ma SG, Zhang Y. Effect of Nb addition on the microstructure and properties of AlCoCrFeNi high-entropy alloy. Materials Science and Engineering A. 2012;**532**:480-486

[42] Li P, Wang A, Liu CT. Composition dependence of structure, physical and mechanical properties of FeCoNi(MnAl)x high entropy alloys. Intermetallics. 2017;**87**:21-26

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