

Review

Physical Properties of High Entropy Alloys

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Abstract: The majority of studies on high-entropy alloys are focused on their phase, microstructure, and mechanical properties. However, the physical properties of these materials are also encouraging. This paper provides a brief overview of the physical properties of high-entropy alloys. Emphasis is laid on magnetic, electrical, and thermal properties.

Keywords: high-entropy alloy; magnetic properties; electrical properties; thermal properties

1. Introduction

High entropy alloys (HEAs) are a novel class of metallic material with a distinct design strategy [1,2]. Different from conventional alloys that are typically designed based on one or two principal elements, HEAs are composed of more than five principal elements. It has been reported that HEAs possess many attractive properties, such as high hardness [3–7], outstanding wear resistance [8,9], good fatigue resistance characteristics [10], excellent high-temperature strength [11,12], good thermal stability [13] and, in general, good oxidation [8] and corrosion resistance [14,15]. These properties suggest great potential in a wide variety of applications. Thus, HEAs have received significant attention in recent years. Up till now, more than 300 HEAs have been developed, forming a new frontier of metallic materials. Most studies on HEAs are focused on the relationships between phase, microstructure, and mechanical properties. Although less attention was paid to the physical properties of HEAs, they are actually also quite encouraging. This paper briefly reviews current understanding of the physical properties of HEAs, with emphasis on the magnetic, electrical, and thermal properties.

2. Magnetic Properties

Studies regarding the magnetic properties of HEAs are mainly focused in alloys derived from Al–Co–Cr–Cu–Fe–Ni–Ti [16–24]. These alloys usually contain more than 50 at.% of magnetic elements (Fe, Co, and Ni). They are either paramagnetic [18–19,21] or ferromagnetic with a saturation magnetization (M_s) typically around 10–50 emu/g (if converted by weighted average density, roughly in the range of 70–350 emu/cc). The phase, M_s , and coercivity (H_c) of some representative HEAs are listed in Table 1. M_s of the alloy depends mainly on the composition and crystal structure. In general, more magnetic elements lead to higher magnetization [24]. However, alloying elements can have considerable impact. For example, the addition of Cr significantly reduces the magnetization [24]. Such effect can be seen in Table 1. CoFeNi and CoCrFeNi alloys both have FCC structures. The former has a high M_s of 1,047 emu/cc, but addition of 25% Cr renders the alloy (CoCrFeNi) paramagnetic. Zhang *et al.* have argued that this is because the magnetic moment of Cr is anti-parallel to that of Fe/Co/Ni (*i.e.*, anti-parallel magnetic coupling), leading to the cancellation of magnetization [24]. Tian *et al.* performed *ab initio* investigations on the CoCrFeNi alloy [25]. They employed the exact muffin-tin orbitals method in combination with the coherent potential approximation to calculate the local magnetic moments of each element in paramagnetic FCC CoCrFeNi. Fe was found to be the only element with magnetic moment. Additionally, paramagnetic and nonmagnetic total density of state (DOS) and partial density of state (pDOS) of the alloy were also calculated and compared [25].

Addition of different elements to the CoCrFeNi alloy leads to different structure and phase—and accordingly, different magnetic behaviors. Addition of Cu only leads to the formation of Cu-rich interdendrite phase and does not affect the CoCrFeNi FCC solid solution much. Thus, the CoCrFeNiCu alloy remains paramagnetic [16]. Addition of Al to CoCrFeNi transforms its single FCC structure to BCC+B2 phases [18,26]. The two phases have almost identical lattice parameters, but very different compositions. The BCC phase is (Co, Cr, Fe)-rich, while the B2 phase is (Al, Ni)-rich. The BCC phase further decomposes into Cr-rich and (Fe, Co)-rich nano-clusters through spinodal decomposition [20]. This BCC phase is found to be the source of ferromagnetism in the alloy. Furthermore, the degree of the spinodal decomposition affects the ferromagnetic behavior. A higher degree of decomposition leads to higher saturation magnetisation, coercivity and remanance [20]. The fact that separation of Cr from Fe and Co leads to higher magnetization seems to agree with the conclusion drawn by Zhang *et al.*, *i.e.*, that existence of Cr leads to cancellation of magnetization [24]. Addition of Pd to CoCrFeNi does not change the crystal structure and phase of the alloys, but the alloy becomes ferromagnetic [19]. The addition of Ti appears to reduce the M_s (Table 1), but the reason is unclear. Most of these alloys are soft magnetic materials with coercivities less than 100 Oe, yet some have higher coercivities around 250 Oe [17,23,24]. The higher coercivities are related with finer microstructures, similar to the case in conventional magnetic materials.

Among reported HEAs, FeCoNiAl_{0.2}Si_{0.2} alloy has a good combination of properties including high M_s (1.151 T), high resistivity (69.5 $\mu\Omega$ -cm), and good malleability, making it a potential soft magnetic material [24]. With the increase of Al and Si content, however, the M_s decreases significantly. This trend is shown in Figure 1 [24]. For example, the M_s of FeCoNiAl_{0.8}Si_{0.8} is 0.46 T.

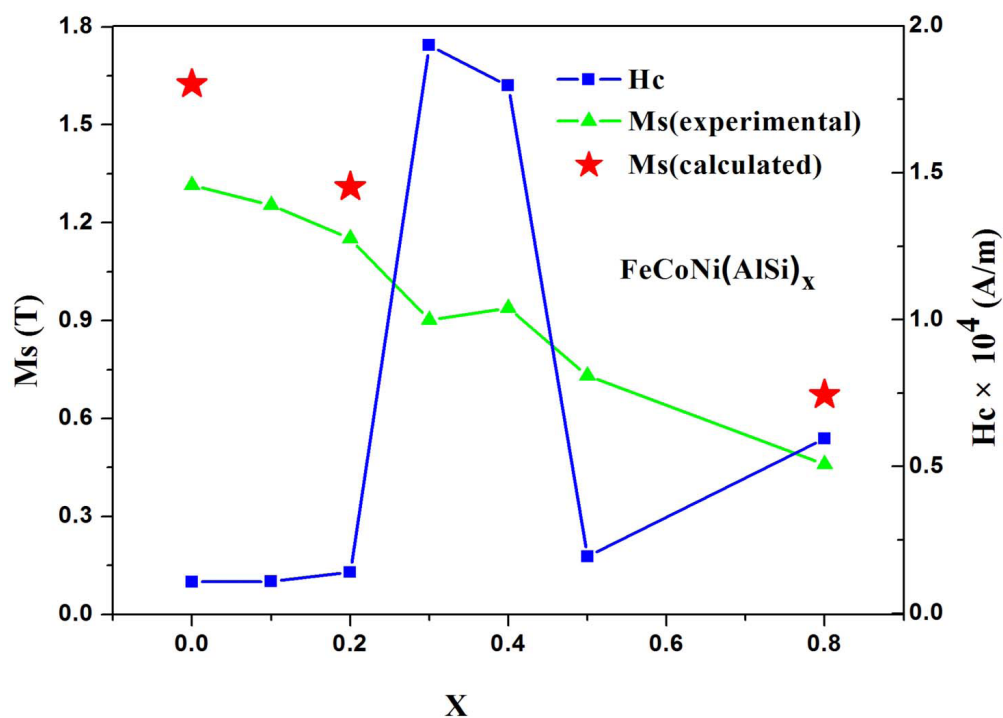
The magnetic properties of another series of alloy, FeNiCuMnTiSn_x, were also studied [21]. When $x = 0$, the alloy is composed of various intermetallic phases such as Fe₂Ti, NiTi, FeTi, and Fe₃Mn₇,

and is paramagnetic. When $x = 1$, the alloy contains two phases which have Cu_3Sn and TiNi_2Sn structure, respectively (both belong to zinc blende structure). Density functional theory technique was used to calculate the atomic magnetic moment of possible zinc blende structures [21]. Among the possible structures, $\text{Ti}_4(\text{Ni}_4\text{Fe}_4)\text{Sn}_4$ is magnetic and the ratio between the elements also agrees with the results of EDS analysis.

Table 1. Phase, saturation magnetization (M_s), and coercivity (H_c) for some representative HEA. M_s provided in emu/g are converted to emu/cc using weight averaged density.

Alloy	Phase	M_s (emu/g)	M_s (emu/cc)	H_c (Oe)
FeCoNi [24]	FCC		1047	13
FeCoNiCr [18–19]	FCC		Paramag.	Paramag.
FeCoNiCrCu [16]	FCC1+FCC(Cu-rich)		Paramag.	Paramag.
FeCoNiCrAl [18,22]	BCC+B2	65	462	52
FeCoNiCrAlCu [17,19–20]	BCC+B2+FCC(Cu-rich)	38–46	281–340	45
FeCoNiCrAlTi [23]	BCC+FCC+FeTi+Co ₂ Ti	15	100	226
FeCoNiCrPd [19]	FCC	33	296	N/A
FeCoNiCrTi [23]	FCC+BCC+Co ₂ Ti	5	37	20
FeCoNiAl _{0.2} Si _{0.2} [24]	BCC+unknown phase		915	18

Figure 1. Magnetic properties of $\text{FeCoNi}(\text{AlSi})_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.8) alloys (H_c and M_s represent the coercivity and saturation magnetization, respectively) [24].



3. Electrical Properties

As-cast high entropy alloy typically have electrical resistivities between 100 and 220 $\mu\Omega\text{-cm}$ [27,28]. These values are 1–2 orders of magnitude higher than that of many conventional metals, and are

similar to that of bulk metallic glasses (BMG). This can be seen in Table 2, in which the electrical resistivities of some representative pure metals, conventional alloys, BMG, and HEA are compared with each other. The higher electrical resistivity of HEA originates from its highly distorted lattice that scatters electron waves [2,28].

Table 2. Electrical resistivity and thermal conductivity of some HEA and representative conventional metals.

Category	Composition/Alloy	Electrical Resistivity ($\mu\Omega\text{-cm}$)	Reference	Thermal conductivity (W/m K)	Reference
High Entropy Alloy	CoCrFeNi	142		12	
	AlCoCrFeNi	221	[18]	11	[28]
	Al ₂ CoCrFeNi	211		16	
Pure Element	Al	3		237	
	Fe	10		80	
	Ni	7	[29,30]	91	[31]
	Ti	42		22	
	Cu	2		398	
Conventional Alloy	7075 Al alloy	6		121	
	Low Carbon Steel	17		52	
	304 Stainless Steel	69	[30]	15	[30,31]
	Inconel 718	125		11	
	Ti-6Al-4V	168		6	
Bulk Metallic Glass	Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5}	171	[32]	N/A	N/A
	Fe ₇₈ Si ₉ B ₁₃	137	[33]	N/A	N/A
	Co ₆₃ Fe ₉ Zr ₈ B ₂₀	188	[33]	N/A	N/A

The change of resistivity as a function of temperature was studied in Al_xCoCrFeNi alloys [18,28]. Like conventional alloys, the resistivity of Al_xCoCrFeNi increases with temperature. However, the slope of the temperature-resistivity curve—the temperature coefficient of resistivity (TCR)—is generally one order of magnitude smaller than that of conventional alloys [18,28]. Kondo-like behavior was also observed in some alloys at low temperatures [18]. Some alloys, such as Al_{2.08}CoCrFeNi, have extremely small TCR. The average TCR of Al_{2.08}CoCrFeNi from 4.2 to 360 K is only 72 ppm/K [27], compared with several thousand ppm/K for most pure metals. The low TCR value spanning such wide temperature range enables it to be used as precision resistors in special applications.

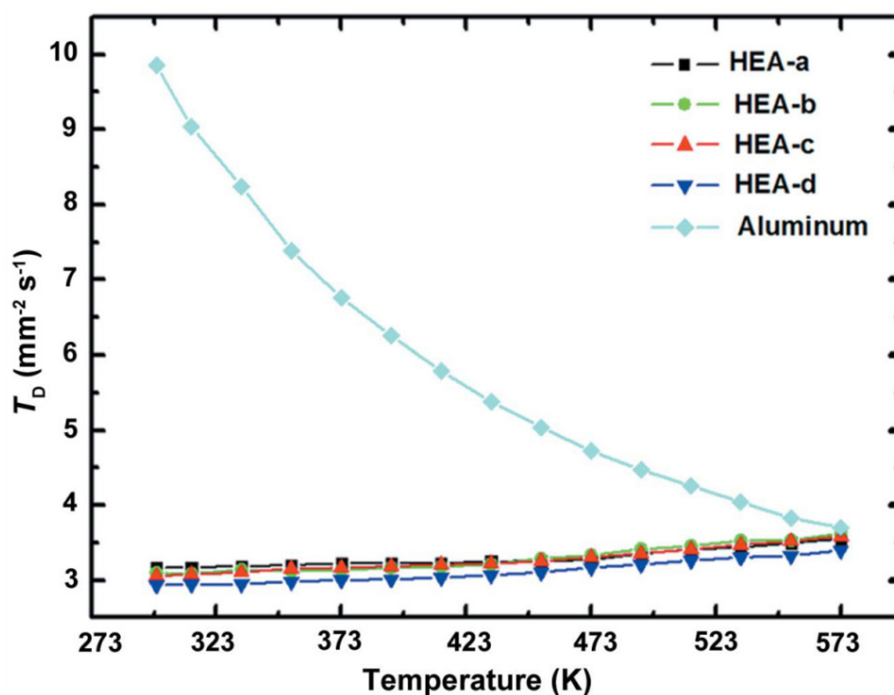
The Hall coefficients in Al_xCoCrFeNi alloys at 5 K and 300 K have been reported [18]. Because these alloys become ferromagnetic at 5 K, anomalous Hall effect is detected in all of them. Similar to conventional alloys, anomalous Hall coefficient is significantly larger than the ordinary Hall coefficient. In all these alloys, the carriers are hole-like. Meanwhile, the carrier density in these HEA (10^{22} – 10^{23} cm²V^{−1}s^{−1}) is similar to that in conventional alloys [18]. In contrast, the carrier mobility is lower than that in conventional ones [18]. The origins of these behaviors are still unknown.

4. Thermal Properties

Thermal conductivity/diffusivity has been measured in $\text{Al}_x\text{CoCrFeNi}$ and $\text{Al}_x\text{CrFe}_{1.5}\text{MnNi}_{0.5}\text{Mo}_y$ alloys [28,34]. Table 2 compares the thermal conductivities of some $\text{Al}_x\text{CoCrFeNi}$ alloys and some representative conventional metals. Thermal conductivity of $\text{Al}_x\text{CoCrFeNi}$ alloys falls in the range of 10–27 W/m·K. These values are lower than those of most pure metals, but are similar to those of heavily alloyed conventional metals such as high-alloy steel or Ni-based superalloys [29,31]. The lower thermal conductivity in HEA should be a result of its distorted lattice, which scatters the phonons more significantly.

Between 27 °C and 300 °C, thermal conductivity/diffusivity of these HEAs increases with increasing temperature [28,34] (see Figure 2). This tendency is opposite to that seen in most pure metals, but is similar to that observed in stainless steel and Inconel alloy [29,31]. The enhanced heat transfer at higher temperatures in the $\text{Al}_x\text{CoCrFeNi}$ alloys was explained by the increased phonon mean free path at higher temperature, owing to thermal expansion of the lattice [34]. Note that the electrical conductivity in the $\text{Al}_x\text{CoCrFeNi}$ alloys decreases with increasing temperature, which means that the electrical and thermal conductivities in the $\text{Al}_x\text{CoCrFeNi}$ alloys show opposite trends with respect to temperature. Therefore, the Wiedemann-Franz law is not obeyed in these HEAs.

Figure 2. Thermal diffusivity as function of temperature for Al and some HEA [33]. Compositions of HEA-a, HEA-b, HEA-c, and HEA-d are $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$, $\text{Al}_{0.5}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$, $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}\text{Mo}_{0.1}$, and $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}\text{Mo}_{0.1}$, respectively.



Thermal expansion coefficients (TEC) of the $\text{Al}_x\text{CoCrFeNi}$ alloys have been reported. The TEC of these alloys ranges from 8.84×10^{-6} to $11.25 \times 10^{-6} \text{ K}^{-1}$, and decreases monotonically with increasing Al content. Because Al promotes the formation of BCC phase, this also means that TEC decreases when the structure of the alloy transits from FCC to BCC.

The magnetocaloric properties of some HEA have been tested for possible magnetic refrigeration applications [35]. The magnetic entropy change (ΔS_m) for cold-rolled CoCrFeNi is $-0.35 \text{ J/kg}\cdot\text{K}$ (the change in applied field is 2T). This value is apparently smaller than that of $\text{Fe}_{0.7}\text{Ni}_{0.3}$ ($-0.6 \text{ J/kg}\cdot\text{K}$). Unfortunately, the cost of Cr and Co is much higher than that of Fe and Ni. Therefore, if the refrigeration capabilities are compared in J/\$, the capability of CoCrFeNi is only 8% that of $\text{Fe}_{0.7}\text{Ni}_{0.3}$.

5. Conclusions and Remarks

Our knowledge about the physical properties of HEAs is still very preliminary. Although some fundamental physical parameters such as saturation magnetization, resistivity, and thermal conductivity have been reported, the data are limited only a few alloy systems. The mechanism behind the composition-property relationship also remains largely unclear, which makes it difficult to control the physical properties. Some important physical characteristics, for example the electronic band structure and phonon behavior, are still completely unknown. Clearly, a lot more work is needed in this regard. Despite our limited knowledge about the physical properties of HEAs, interesting features such as extremely low TCR and favorable soft magnetic properties have been observed. It is expected that further exploration will lead to more excitement about the physical properties of these novel materials.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Yeh, J.W.; Chen, S.K.; Lin, S.J.; Gan, J.Y.; Chin, T.S.; Shun, T.T.; Tsau, C.H.; Chang, S.Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303.
2. Yeh, J.W. Recent progress in high-entropy alloys. *Annales de Chimie Science des Matériaux*. **2006**, *31*, 633–648.
3. Tong, C.J.; Chen, M.R.; Chen, S.K.; Yeh, J.W.; Shun, T.T.; Lin, S.J.; Chang, S.Y. Mechanical performance of the $\text{Al}_x\text{CoCrCuFeNi}$ high-entropy alloy system with multiprincipal elements. *Metall. Mater. Trans. A* **2005**, *36*, 1263–1271.
4. Zhou, Y.J.; Zhang, Y.; Wang, Y.L.; Chen, G.L. Solid solution alloys of AlCoCrFeNiTi_x with excellent room-temperature mechanical properties. *Appl. Phys. Lett.* **2007**, *90*, doi: 10.1063/1.2734517.

5. Wen, L.H.; Kou, H.C.; Li, J.S.; Chang, H.; Xue, X.Y.; Zhou, L. Effect of aging temperature on microstructure and properties of AlCoCrCuFeNi high-entropy alloy. *Intermetallics* **2009**, *17*, 266–269.
6. Zhu, J.M.; Fu, H.M.; Zhang, H.F.; Wang, A.M.; Li, H.; Hu, Z.Q. Synthesis and properties of multiprincipal component AlCoCrFeNiSix alloys. *Mater. Sci. Eng. A* **2010**, *527*, 7210–7214.
7. Chen, S.T.; Tang, W.Y.; Kuo, Y.F.; Chen, S.Y.; Tsau, C.H.; Shun, T.T.; Yeh, J.W. Microstructure and properties of age-hardenable Al_xCrFe1.5MnNi0.5 alloys. *Mater. Sci. Eng. A* **2010**, *527*, 5818–5825.
8. Chuang, M.H.; Tsai, M.H.; Wang, W.R.; Lin, S.J.; Yeh, J.W. Microstructure and wear behavior of Al_xCo1.5CrFeNi1.5Ti_y high-entropy alloys. *Acta Mater.* **2011**, *59*, 6308–6317.
9. Chuang, M.H.; Tsai, M.H.; Tsai, C.W.; Yang, N.H.; Chang, S.Y.; Yeh, J.W.; Chen, S.K.; Lin, S.J. Intrinsic surface hardening and precipitation kinetics of Al_{0.3}CrFe1.5MnNi0.5 multi-component alloy. *J. Alloys Compd.* **2013**, *551*, 12–18.
10. Hemphill, M.A.; Yuan, T.; Wang, G.Y.; Yeh, J.W.; Tsai, C.W.; Chuang, A.; Liaw, P.K. Fatigue behavior of Al_{0.5}CoCrCuFeNi high entropy alloys. *Acta Mater.* **2012**, *60*, 5723–5734.
11. Hsu, C.Y.; Juan, C.C.; Wang, W.R.; Sheu, T.S.; Yeh, J.W.; Chen, S.K. On the superior hot hardness and softening resistance of AlCoCr(x)FeMo(0.5)Ni high-entropy alloys. *Mater. Sci. Eng. A* **2011**, *528*, 3581–3588.
12. Senkov, O.N.; Wilks, G.B.; Scott, J.M.; Miracle, D.B. Mechanical properties of Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys. *Intermetallics* **2011**, *19*, 698–706.
13. Tsai, M.H.; Wang, C.W.; Tsai, C.W.; Shen, W.J.; Yeh, J.W.; Gan, J.Y.; Wu, W.W. Thermal Stability and Performance of NbSiTaTiZr High-Entropy Alloy Barrier for Copper Metallization. *J. Electrochem. Soc.* **2011**, *158*, H1161–H1165.
14. Chou, Y.L.; Wang, Y.C.; Yeh, J.W.; Shih, H.C. Pitting corrosion of the high-entropy alloy Co1.5CrFeNi1.5Ti0.5Mo0.1 in chloride-containing sulphate solutions. *Corros. Sci.* **2010**, *52*, 3481–3491.
15. Kao, Y.F.; Lee, T.D.; Chen, S.K.; Chang, Y.S. Electrochemical passive properties of Al_xCoCrFeNi (x = 0, 0.25, 0.50, 1.00) alloys in sulfuric acids. *Corros. Sci.* **2010**, *52*, 1026–1034.
16. Wang, X.F.; Zhang, Y.; Qiao, Y.; Chen, G.L. Novel microstructure and properties of multicomponent CoCrCuFeNiTi_x alloys. *Intermetallics* **2007**, *15*, 357–362.
17. Zhang, K.B.; Fu, Z.Y.; Zhang, J.Y.; Shi, J.; Wang, W.M.; Wang, H.; Wang, Y.C.; Zhang, Q.J. Annealing on the structure and properties evolution of the CoCrFeNiCuAl high-entropy alloy. *J. Alloys Compd.* **2010**, *502*, 295–299.
18. Kao, Y.F.; Chen, S.K.; Chen, T.J.; Chu, P.C.; Yeh, J.W.; Lin, S.J. Electrical, magnetic, and Hall properties of Al_xCoCrFeNi high-entropy alloys. *J. Alloys Compd.* **2011**, *509*, 1607–1614.
19. Lucas, M.S.; Mauger, L.; Munoz, J.A.; Xiao, Y.M.; Sheets, A.O.; Semiatin, S.L.; Horwath, J.; Turgut, Z. Magnetic and vibrational properties of high-entropy alloys. *J. Appl. Phys.* **2011**, *109*, doi: 10.1063/1.3538936.
20. 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.

21. Liu, L.; Zhu, J.B.; Li, J.C.; Jiang, Q. Microstructure and Magnetic Properties of FeNiCuMnTiSn_x High Entropy Alloys. *Adv. Eng. Mater.* **2012**, *14*, 919–922.
22. Ma, S.G.; Zhang, Y. Effect of Nb addition on the microstructure and properties of AlCoCrFeNi high-entropy alloy. *Mater. Sci. Eng. A* **2012**, *532*, 480–486.
23. Zhang, K.B.; Fu, Z.Y. Effects of annealing treatment on properties of CoCrFeNiTiAl_x multi-component alloys. *Intermetallics* **2012**, *28*, 34–39.
24. Zhang, Y.; Zuo, T.; Cheng, Y.; Liaw, P.K. High-entropy Alloys with High Saturation Magnetization, Electrical Resistivity, and Malleability. *Sci. Rep.* **2013**, *3*, doi: 10.1038/srep01455.
25. Tian, F.Y.; Varga, L.K.; Chen, N.X.; Delczeg, L.; Vitos, L. Ab initio investigation of high-entropy alloys of 3d elements. *Phys. Rev. B* **2013**, *87*, doi: 10.1103/PhysRevB.87.075144.
26. Wang, W.R.; Wang, W.L.; Wang, S.C.; Tsai, Y.C.; Lai, C.H.; Yeh, J.W. Effects of Al addition on the microstructure and mechanical property of Al_xCoCrFeNi high-entropy alloys. *Intermetallics* **2012**, *26*, 44–51.
27. Chen, S.K.; Kao, Y.F. Near-constant resistivity in 4.2–360 K in a B2 Al_{2.08}CoCrFeNi. *AIP Adv.* **2012**, *2*, doi: 10.1063/1.3679072.
28. Chou, H.P.; Chang, Y.S.; Chen, S.K.; Yeh, J.W. Microstructure, thermophysical and electrical properties in Al_xCoCrFeNi (0 ≤ x ≤ 2) high-entropy alloys. *Mater. Sci. Eng. B* **2009**, *163*, 184–189.
29. Lide, D.R., Eds. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, USA, 2003.
30. Gale, W.F.; Totemeier, T.C., Eds. *Smithells Metals Reference Book*, 8th ed.; Butterworth-Heinemann: Oxford, UK, 2004.
31. Shackelford, J.F., Alexander, W., Eds. *CRC Materials Science and Engineering Handbook*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2000.
32. Li, Y.; Bai, H.Y. Superconductivity in a representative Zr-based bulk metallic glass. *J. Non-Cryst. Solids* **2005**, *351*, 2378–2382.
33. Inoue, A. Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Mater.* **2000**, *48*, 279–306.
34. Lu, C.L.; Lu, S.Y.; Yeh, J.W.; Hsu, W.K. Thermal expansion and enhanced heat transfer in high-entropy alloys. *J. Appl. Crystallogr.* **2013**, *46*, 736–739.
35. Lucas, M.S.; Belyea, D.; Bauer, C.; Bryant, N.; Michel, E.; Turgut, Z.; Leontsev, S.O.; Horwath, J.; Semiatin, S.L.; McHenry, M.E.; Miller, C.W. Thermomagnetic analysis of FeCoCr_xNi alloys: Magnetic entropy of high-entropy alloys. *J. Appl. Phys.* **2013**, *113*, doi: 10.1063/1.4798340.