Effects of Mn Content on Mechanical Properties of FeCoCrNiMn_x (0 ≤ x ≤ 0.3) High-Entropy Alloys: A First-Principles Study

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Abstract

Effects of Mn content on mechanical properties of FeCoCrNiMn_x (0 ≤ x ≤ 0.3) high-entropy alloys (HEAs) are investigated via first-principles calculations combining EMTO–CPA method. Related physical parameters, including lattice constant, elastic constants, elastic modulus, Pugh’s ratio, anisotropy factors, Poisson’s ratio, Cauchy pressure, Vickers hardness, yield strength, and energy factor, are calculated as a function of Mn content. The results show that the resistances to bulk, elastic, and shear deformation decrease with increasing Mn content. Pugh’s ratio B/G indicates that the ductility of FeCoCrNiMn_x HEAs has a remarkable reduction between 22 and 24% of Mn content. Meanwhile, Cauchy pressure suggests that the atomic bonding transforms from metallic to directional characteristic from 22 to 24% of Mn content. Vickers hardness and yield strength of FeCoCrNiMn HEA are intrinsically larger than those of FeCoCrNi HEA. Dislocation nucleation easily occurs in FeCoCrNiMn HEA compared to FeCoCrNi HEA, and large dislocation width in FeCoCrNiMn_{0.2} HEA results in low stacking-fault energy, which easily induces twinning deformation. This work provides a valuable insight for further theoretical and experimental study on the mechanical properties of FeCoCrNiMn_x (0 ≤ x ≤ 0.3) HEAs.

Keywords High-entropy alloys · First-principles calculations · Mechanical properties · Elastic constants · Energy factor

1 Introduction

High-entropy alloys (HEAs), also known as multi-component alloys, are a new research frontier in the metallic materials community. Different from traditional alloys with one-principal element, HEAs comprise five or more principal elements in equimolar or near-equimolar ratios [1]. HEAs are featured by high entropy, lattice distortion, sluggish diffusion, and cocktail effect due to multi-element mixtures. In addition, the high mixing entropy in HEAs tends to enhance the phase stability of solid solution and then promotes the formation of simple solid solution phase, instead of complex intermetallic compounds [1, 2]. To date, HEAs have attracted great attention from materials researchers due to their excellent properties, such as high strength [2–4], high hardness [5], good ductility [6, 7], exceptional fracture toughness [8], corrosion resistance [9, 10], and wear resistance [11]. Zhou et al. [6] designed AlCoCrFeNiTi_x (x = 0, 0.5, 1, 1.5) HEAs with body-centered cubic (BCC) solid solution, and the alloy system possessed excellent room-temperature compressive mechanical properties, such as the yield stress of 2.26 GPa, fracture strength of 3.14 GPa, and plastic strain of 23.3%. Gludovatz et al. [8] found that CrMnFeCoNi HEA forming

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a single-phase face-centered cubic (FCC) solid solution, had exceptional damage tolerance with tensile strengths above 1 GPa and fracture toughness exceeding 200 MPa·m^{1/2}. Li et al. [12] presented a metastability-engineering strategy to develop the dual-phase Fe_{80-x}Mn_xCo₁₀Cr₁₀ HEAs induced by phase transformation, and variation of Mn content induced martensite phase transformation from FCC to hexagonal close-packed (HCP) phase during the cooling process. In particular, the dual-phase Fe₅₀Mn₃₀Co₁₀Cr₁₀ HEA with 30% Mn content improved the strength by 100 MPa and ductility by 30%, and work-hardening rate was dramatically enhanced compared with the single-phase HEAs. Meanwhile, Wang et al. [13] used vacuum arc melting and casting method to prepare dual-phase Al_xCoCrFeNi HEAs with BCC and FCC phases, in which BCC phase was a dominant factor resulting in hardening, and Al_{0.9}CoCrFeNi HEA with single BCC structure exhibited a maximum hardness of 527 H_V. In addition, the addition of interstitial atoms in HEAs can also produce excellent mechanical properties. Seol et al. [14] found that minor boron doped in single-phase FeMnCrCoNi and Fe₄₀Mn₄₀Cr₁₀Co₁₀ HEAs dramatically improved their mechanical properties, like increasing their yield strength by more than 100% and ultimate tensile strength by ~40% at comparable or even better ductility. This improvement was attributed to the enhanced interface strengthening and grain size reduction after the segregation of B element to grain boundary. Moreover, other interstitial atoms like C, N, H, and O atoms have strong strengthening effect on HEAs as well [15–19].

Except for extensive experimental studies mentioned above, many theoretical methods were also applied to investigate the mechanical properties of HEAs, including FeCoCrNi-based HEAs. Using density-functional theory (DFT) calculations, Kivy and Zaeem [20] found that Ti or Mo addition in CoCrFeNi-based FCC HEAs increased the tendency of dislocation glide and deformation twinning, while the additions of Mn, Cu, and relatively high amount of Al facilitated dislocation gliding and martensitic transformation. Furthermore, Mn and Cu additions increased the calculated Rice-criterion ductility though other elements decreased it. Combined with the special quasi-random structure (SQS) method, Zhang et al. [21] disclosed the formation mechanism of stacking faults and nano-twins in FCC CrNiCo and FeCrNiCo HEAs by first-principles calculations. It was found that the negative stacking-fault energies (SFEs) originated from the thermodynamic metastability of FCC stacking sequence, local atomic environment and the temperature, and then these factors in turn affected the formation of stacking faults and nano-twins. With the development of HEAs, Vitos [22] developed the exact muffin-tin orbitals (EMTO) method based on coherent-potential approximation (CPA) [23–25]. On the basis of EMTO–CPA method, many works have been conducted in HEAs [26–32]. Sun et al. [26]

applied the EMTO–CPA method to study the lattice stability and magnetic properties of paramagnetic Al_xCrMnFeCoNi (0 ≤ *x* ≤ 5) HEAs with BCC and FCC structures, and the results revealed that Mn reduced the stability field of FCC phase and broadened the width of the duplex region when expressed in terms of Al concentration *x*. Meanwhile, Zhang et al. [27] also utilized the EMTO–CPA method to investigate the elastic properties of paramagnetic Al_xCrMnFeCoNi (0 ≤ *x* ≤ 5) HEAs in BCC and FCC structures. The results showed that the addition of Al content increased lattice constants of BCC and FCC phases, and the brittleness of BCC Al_xCrMnFeCoNi HEAs was raised with increasing Al content. In addition, FCC Al_xCrMnFeCoNi HEAs were predicted to be brittle at low and high Al region and ductile at intermediate Al region. The above-mentioned studies suggest that the EMTO–CPA method is a valid method to investigate and design HEAs. Mn is one of the important alloying elements, which determines the physical and mechanical properties of FeCoCrNiMn_x HEAs. However, the effects of Mn content on physical parameters and mechanical properties of FeCoCrNiMn_x HEAs have not been reported so far.

Thus, this work aims to investigate the effects of Mn content on mechanical properties of FeCoCrNiMn_x (0 ≤ *x* ≤ 0.3) HEAs via first-principles calculations combining EMTO–CPA method. Related physical parameters, including lattice constant, elastic constants, elastic modulus, Pugh's ratio, anisotropy factors, Poisson's ratio, Cauchy pressure, Vickers hardness, yield strength, and energy factor, are calculated as a function of Mn content. The following framework of this paper is arranged as follows: Sect. 2 introduces the theoretical methodology and calculating parameters. Section 3 obtains the calculated results of physical parameters of FeCoCrNiMn_x (0 ≤ *x* ≤ 0.3) HEAs and then discusses the dependencies of these parameters on Mn content. Section 4 presents the detailed conclusion of this work.

2 Theoretical Methodology

The EMTO method [22] in the frame of DFT is used to implement the first-principles energy calculations of paramagnetic FeCoCrNiMn_x (0 ≤ *x* ≤ 0.3) HEAs. Herein, the paramagnetic state of all calculations is described through the disordered-local moment model [33]. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [34] is chosen as the exchange–correlation functional for self-consistent calculations. The total energy is calculated through the full charge-density technique [22, 24]. The single-site CPA method is adopted to address the substitutional and magnetic disorders [22–25]. The atomic short-range order and local lattice relaxation effects are fully neglected on the basis of the CPA method. To solve the Kohn–Sham equations of single electron, the

scalar-relativistic approximation and soft-core scheme are applied. The Green's function of 16 complex energy points is computed to integrate the valence states below the Fermi level. In electronic structure calculations, *s*, *p*, *d*, and *f* orbitals are contained in the basis set. To ensure sufficient accuracy in calculation, we conduct a rigorous *k*-points convergence test by executing Brillouin zone integrations, and the *k*-points of 17 × 17 × 17 are chosen to calculate elastic constants of HEAs, where the change value of elastic constants is less than 0.6 GPa with increasing *k*-points. Via Morse-type function [35, 36], the calculated energy–volume data from eleven different volumes are accurately fitted to the equation of state for obtaining the equilibrium volume, as well as equilibrium lattice constant of HEAs.

3 Results and Discussion

The lattice constant is the most basic physical parameter of crystalline materials. To investigate the dependence of equilibrium lattice constant on the contents of Mn atom in FeCoCrNiMn_x (0 ≤ x ≤ 0.3) HEAs with FCC crystal structures [37], we calculate the equilibrium lattice constant *a*₀ with respect to different Mn contents, as shown in Fig. 1.

Fig. 1 Variation curve of lattice constant *a*₀ versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

The equilibrium lattice constant increases linearly with the increase of Mn content. On the basis of the calculated results, we compare the equilibrium lattice constant *a*₀ with those of other theoretical and experimental results for FeCoCrNi and FeCoCrNiMn HEAs, as listed in Table 1. The equilibrium lattice constants of FeCoCrNi and FeCoCrNiMn HEAs are calculated as 3.568 and 3.578 Å, respectively. The calculated values fit well with the value of theoretical [26, 27, 38, 39] and experimental [39–43] results, suggesting that the calculated results are credible.

Elastic constants play a key role in influencing the mechanical properties of anisotropic materials, which are usually used to estimate the structural stability of materials and reflect the capability to resist external forces. Since FeCoCrNiMn_x (0 ≤ x ≤ 0.3) HEAs have FCC crystal structures [37], the three elastic constants are indicated by *C*₁₁, *C*₁₂, and *C*₄₄ according to high symmetry of cubic structure, where *C*₁₁, *C*₁₂, and *C*₄₄ are used to reflect the capability to resist external forces. On the basis of stability criterion of cubic crystals [44, 45], the three elastic constants must meet the following expression (1); herein, *C*₁₁ − *C*₁₂ can be used to measure the magnitude of shear modulus *G*_{(110)[1̄10]} in the (110)[1̄10] direction, and *C*₁₁ + 2*C*₁₂ can be used to evaluate the one of bulk modulus *B* [44, 45]:

$$(C_{11} - C_{12}) > 0, C_{11} > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0. \quad (1)$$

In the light of the calculated results of elastic constants, we depict the variation curves of elastic constants *C*_{*ij*} as a function of Mn content in FeCoCrNiMn_x (0 ≤ x ≤ 0.3) HEAs, as shown in Fig. 2. The results indicate that the three elastic constants *C*₁₁, *C*₁₂, and *C*₄₄ decrease gradually with the increase in Mn content. Compared with the linear decrease of *C*₄₄, *C*₁₁, and *C*₁₂ present the dramatic decline when the Mn content is in the range of 22% and 24%, which implies that the capability to resist external forces declines with the increase in Mn content. The dramatic decline may be attributed to the structural phase transition induced by severe lattice distortion in HEAs, but it cannot be interpreted via the current EMT0–CPA method for the time being. Additionally, the value of *C*₁₁ − *C*₁₂ is always positive at different Mn contents. Thus, *C*₁₁ − *C*₁₂ meets the stability criterion in Eq. (1), suggesting that FeCoCrNiMn_x (0 ≤ x ≤ 0.3)

Table 1 Comparisons of equilibrium lattice constant *a*₀ with other theoretical and experimental results for FeCoCrNi and FeCoCrNiMn HEAs with FCC crystal structures

<i>a</i> ₀ (Å)	This work	Theoretical results	Experimental results
FeCoCrNi	3.568	3.529 [38], 3.540 [39]	3.575 [39], 3.574 [40], 3.567 [41]
FeCoCrNiMn	3.578	3.528 [26], 3.524 [27] 3.529 [38], 3.540 [39]	3.597 [39], 3.597 [42], 3.598 [43]

Fig. 2 Variation curves of elastic constants C_{ij} versus Mn content for FeCoCrNiMn $_x$ HEAs with FCC crystal structures

HEAs can maintain mechanical stability. Meanwhile, we compare the calculated elastic constants C_{ij} with available theoretical and experimental data for FeCoCrNi and FeCoCrNiMn HEAs, and the calculated results are listed in Table 2, as well as elastic moduli, which agree well with the available theoretical [27, 31, 38, 46] and experimental data [46–51], where the experimental data come from the results of polycrystalline materials [46, 47, 50, 51], as well as monocrystalline materials [48, 49]. In addition, it should be pointed out that since the elastic parameters are sensitive to volume in EMTO–CPA method, this work chooses a larger volume interval (8.1–18.5 Å³/atom) than those of Ref [27]. (9.1–14.4 Å³/atom and 10.4–11.7 Å³/atom) to ensure greater accuracy in calculating elastic parameters.

Material moduli, including bulk modulus B , shear modulus G , and Young's modulus E , are the important physical parameters to evaluate the capability to resist material deformation, such as bulk, shear, and elastic deformation. Thus, the material moduli play a key role in measuring the mechanical properties of materials. Large modulus reflects strong resistance to material deformation, as well as excellent mechanical properties [52, 53]. According to Ref. [54], Eqs. (2)–(4) are used to calculate the material moduli of cubic crystals as a function of elastic constants C_{ij} :

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (2)$$

$$G = \frac{1}{2}(G_V + G_R), \quad (3)$$

$$E = \frac{9BG}{3B + G}, \quad (4)$$

where Voigt shear modulus $G_V = (C_{11} - C_{12} + 3C_{44})/5$ and Reuss shear modulus $G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]$.

According to Eqs. (2)–(4), we calculate bulk modulus B , shear modulus G , and Young's modulus E of FeCoCrNiMn $_x$ ($0 \leq x \leq 0.3$) HEAs at different Mn contents, and the calculated results are depicted in Fig. 3. With the increase in Mn content, the elastic moduli of FeCoCrNiMn $_x$ ($0 \leq x \leq 0.3$) HEAs decrease, suggesting that the mechanical properties of FeCoCrNiMn $_x$ ($0 \leq x \leq 0.3$) HEAs decline; namely, the mechanical property of FeCoCrNi HEA is intrinsically superior to those of other FeCoCrNiMn $_x$ ($0 < x \leq 0.3$) HEAs. Different from shear modulus G and Young's modulus E , bulk modulus B decreases dramatically when the Mn content is in the range of 22% and 24%, which signifies a remarkable

Table 2 Comparisons of current results with available theoretical and experimental results for FeCoCrNi and FeCoCrNiMn HEAs with FCC crystal structures (unit: GPa)

HEAs	This work	Theoretical results	Experiments
<i>FeCoCrNi</i>			
C_{11}	268.9	271.0 [31], 268.2 [38], 252.5 [46]	
C_{12}	187.9	175.0 [31], 175.9 [38], 171.9 [46]	
C_{44}	174.2	189.0 [31], 175.7 [38], 161.6 [46]	
B	215.0	207.0 [31], 206.7 [38], 198.8 [46]	162.9 [46]
G	97.9	110.0 [31], 103.3 [38], 93.2 [46]	84.0 [47]
E	255.0	280.0 [31], 265.7 [38], 241.8 [46]	215.0 [46]
<i>FeCoCrNiMn</i>			
C_{11}	252.1	250.0 [27], 240.0 [38], 245.1 [46]	195.9 [48], 202.6 [49]
C_{12}	175.2	156.0 [27], 146.9 [38], 148.9 [46]	117.7 [48], 116.6 [49]
C_{44}	169.9	180.0 [27], 179.3 [38], 191.5 [46]	129.3 [48], 138.2 [49]
B	200.8	188.0 [27], 177.9 [38], 186.2 [46]	143.8 [48], 140.8 [50], 145.0 [51]
G	94.5	106.0 [27], 105.0 [38], 110.7 [46]	80.2 [48], 79.3 [50], 86.0 [51]
E	245.1	267.0 [27], 263.2 [38], 275.9 [46]	202.2 [48], 200.3 [50], 215.0 [51]

Fig. 3 Variation curves of elastic modulus versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

Fig. 4 Variation curves of Pugh's ratio B/G versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

reduction in the resistance to volume deformation between 22 and 24% of Mn contents. Meanwhile, we compare the calculated elastic moduli with available theoretical [27, 31, 38, 46] and experimental data [46–48, 50, 51] for FeCoCrNi and FeCoCrNiMn HEAs, and the computed results are listed in Table 2, which fit well with the available theoretical and experimental data. Comparing the theoretical elastic constants of FeCoCrNi [31] and FeCoCrNiMn [27] HEAs, we find that large elastic constants decrease the value of mechanical parameters, including elastic moduli, Zener anisotropy ratio, and Pugh's ratio, which are also verified in the theoretical works [38, 46]. Additionally, the experimental results [46–48, 50, 51] in Table 2 also predict the similar changes of elastic moduli, which are in agreement with the main conclusions of this work.

In the phase transition of materials, ductile–brittle transition is an important transition mechanism to affect the mechanical properties of materials. Pugh [52] proposed that the ductile/brittle properties of polycrystalline materials can be evaluated by modulus ratio B/G , and $B/G = 1.75$ was the critical value to distinguish the ductile or brittle properties of materials. $B/G > 1.75$ means ductile materials, and $B/G < 1.75$ signifies brittle materials. In addition, the ductility increases with increasing B/G ratio, but the brittleness increases with decreasing B/G ratio. Figure 4 shows variation curves of Pugh's ratio B/G with respect to different Mn contents in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs. Results in Fig. 4 indicate that the value of Pugh's ratio B/G is greater than 1.75 at different Mn contents, suggesting that FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs show good ductility. However, Pugh's ratio B/G decreases with the increase in Mn content, indicating that the ductility of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs declines with increasing Mn content.

When the Mn content is in the range of 22% and 24%, Pugh's ratio B/G decreases dramatically, which implies a remarkable reduction in the ductility of FeCoCrNiMn_x HEAs between 22 and 24% of Mn contents. By comparing the B/G of FeCoCrNi and FeCoCrNiMn HEAs, the B/G of FeCoCrNi ($B/G = 2.20$) HEA is larger than that of FeCoCrNiMn ($B/G = 2.12$) HEA, thereby indicating that the ductility of FeCoCrNi HEA is intrinsically better than that of FeCoCrNiMn HEA, which agrees well with the experimental results of larger elongation in FeCoCrNi HEA ($\epsilon = 70.3\%$) [55] versus FeCoCrNiMn HEA ($\epsilon = 65\%$) [47].

In general, elastic anisotropy of materials is assessed by anisotropy factor A , which is also used to investigate the mechanical properties of anisotropic materials. Herein, $A = 1$ denotes the isotropy; otherwise, $A \neq 1$ indicates the anisotropy. The magnitude of A decides the degree of anisotropy, and A is larger or smaller than the unit, indicating that the anisotropy of materials is stronger [56, 57]. In the light of elastic constants C_{ij} of cubic crystals, we calculate the Zener anisotropy ratio A_Z and anisotropy factor $A_{(110)[001]}$ by Eqs. (5) and (6) [58, 59], where Zener ratio A_Z indicates the ratio of shear moduli between the (100) and (110) crystal planes, and it can be used to describe the degree of elastic anisotropy in crystalline materials [60, 61]:

$$A_Z = \frac{2C_{44}}{C_{11} - C_{12}}, \quad (5)$$

$$A_{(110)[001]} = \frac{C_{44}(C' + 2C_{12} + C_{11})}{C_{11}C' - C_{12}^2}, \quad (6)$$

Fig. 5 Variation curves of Zener ratio A_Z and anisotropy factor $A_{(110)[001]}$ versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

where $C' = C_{44} + (C_{11} + C_{12})/2$. A_Z denotes the anisotropy factor in the (110)[001] direction. On the basis of Eqs. (5) and (6), we calculate the Zener ratio A_Z and anisotropy factor $A_{(110)[001]}$ as a function of Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, as depicted in Fig. 5. The results show that the Zener ratio A_Z and $A_{(110)[001]}$ are not equal to the unit at any contents of Mn atom, thereby indicating that FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs are the anisotropic materials. With the increase in Mn content, the A_Z and $A_{(110)[001]}$ increase. Thus, the anisotropy of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs is improved between the (100) and (110) crystal planes, as well as (110)[001] direction. By comparing FeCoCrNi and FeCoCrNiMn HEAs, the anisotropy of FeCoCrNiMn HEA is stronger than that of FeCoCrNi HEA between the (100) and (110) crystal planes, as well as (110)[001] direction.

To further study the plastic properties of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, we introduce Poisson's ratio σ to evaluate their plastic properties at different Mn contents. In general, Poisson's ratio σ ranges from 0 to 0.5, and a large σ can induce good plasticity [59]. Through Eqs. (7) and (8) [59], we calculate Poisson's ratios $\sigma_{[001]}$ in the [001] direction and $\sigma_{[111]}$ in the [111] direction for FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, and Fig. 6 exhibits the variation curves of Poisson's ratio $\sigma_{[001]}$ and $\sigma_{[111]}$ as a function of Mn content. Results indicate that Poisson's ratios $\sigma_{[001]}$ and $\sigma_{[111]}$ decrease with the increase in Mn content, suggesting that the plasticity in the [001] and [111] directions declines with increasing Mn content. When the Mn content is in the range of 22% and 24%, Poisson's ratios $\sigma_{[001]}$ and $\sigma_{[111]}$ decrease dramatically, which indicates a remarkable reduction in the plasticity of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs between 22 and 24% of

Fig. 6 Variation curves of Poisson's ratios $\sigma_{[001]}$ and $\sigma_{[111]}$ versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

Mn contents. By comparing Poisson's ratios $\sigma_{[001]}$ and $\sigma_{[111]}$ of FeCoCrNi and FeCoCrNiMn HEAs, the $\sigma_{[001]}$ and $\sigma_{[111]}$ of FeCoCrNi HEA are larger than those of FeCoCrNiMn HEA, thereby suggesting that the plasticity of FeCoCrNi HEA is intrinsically better than that of FeCoCrNiMn HEA; here, Wu et al. [47] also found that the experimental Poisson's ratio of FeCoCrNi HEA ($\sigma = 0.28$) was larger than that of FeCoCrNiMn HEA ($\sigma = 0.26$):

$$\sigma_{[001]} = \frac{C_{12}}{C_{11} + C_{12}}, \quad (7)$$

$$\sigma_{[111]} = \frac{C_{11} + 2C_{12} - 2C_{44}}{2(C_{11} + 2C_{12} + C_{44})}. \quad (8)$$

In order to further investigate the mechanical properties of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, we calculate other material moduli, including $G_{(100)[010]}$, $G_{(110)[\bar{1}\bar{1}0]}$, and $E_{[100]}$, to assess the non-deformability and strength of materials. Moduli $G_{(100)[010]}$ and $G_{(110)[\bar{1}\bar{1}0]}$ denote the resistances to shear deformation in the (100)[010] and (110)[$\bar{1}\bar{1}0$] directions, and they are formulized by $G_{(100)[010]} = C_{44}$ and $G_{(110)[\bar{1}\bar{1}0]} = (C_{11} - C_{12})/2$, respectively. $E_{[100]}$ indicates the resistance to elastic deformation in the [100] direction and is formulized by $E_{[100]} = (C_{11} - C_{12})[1 + C_{12}/(C_{11} + C_{12})]$ [57, 62]. On the basis of the above formulas, we calculate material moduli $G_{(100)[010]}$, $G_{(110)[\bar{1}\bar{1}0]}$, and $E_{[100]}$ of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs. Figure 7a draws the variation curves

Fig. 7 Variation curves of the calculated modulus **a** and Cauchy pressure **b** versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

of the calculated modulus as a function of Mn content. The results show that the values of the calculated moduli $G_{(100)[010]}$, $G_{(110)[1\bar{1}0]}$, and $E_{[100]}$ decrease linearly with the increase in Mn content, indicating that the resistance to material deformation becomes weak with increasing Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, which fits well with the results of Fig. 3. By comparing FeCoCrNi and FeCoCrNiMn HEAs, the non-deformability of FeCoCrNi HEA is intrinsically better than that of FeCoCrNiMn HEA, which agrees well with the experimental results. Experimental results show the resistance to shear deformation of FeCoCrNi HEA ($G = 84$ GPa) is stronger than that of FeCoCrNiMn HEA ($G = 80$ GPa) [47]. Cauchy pressure $C_{12} - C_{44}$ is defined as the difference value of elastic constants C_{12} and C_{44} , which is used to describe the atomic bonding characteristics of materials [63]. According to the works of Johnson [64] and Fu et al. [57], the atomic bonding has metallic characteristics for positive Cauchy pressure, but the atomic bonding has directional characteristics for negative Cauchy pressure. A large Cauchy pressure induces strong directional characteristics. Figure 7b depicts the variation curves of the calculated Cauchy pressure as a function of Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, and Cauchy pressure $C_{12} - C_{44}$ decreases with the increase in Mn content at $0 \leq x \leq 0.22$, indicating that the metallic characteristic weakens. However, the negative Cauchy pressure increases with the increase in Mn content at $0.24 \leq x \leq 0.3$, thereby suggesting that the directional characteristic strengthens. With increasing 22% to 24% in Mn content, Cauchy pressure changes from positive to negative value, which means the

atomic bonding transforms from metallic to directional characteristic.

The hardness and yield strength are two important parameters in terms of evaluating the mechanical properties of materials. The hardness is used to measure the capability to resist material deformation, and yield strength is used to reflect the capability to resist plastic deformation [65]. Based on the existing models [66–69], Chen et al. [70] put forward an improved model to calculate the Vickers hardness of polycrystalline materials, which is formulized by Eq. (9), and $k = G/B$. Due to the common empirical $H_V = 3\sigma_y$ relation [39], yield strength σ_y is roughly obtained by Eq. (10). On the basis of the calculated results, Fig. 8a and b draws the variation curves of Vickers hardness H_V and yield strength σ_y as a function of Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs. Results in Fig. 8a and b indicate that Vickers hardness H_V and yield strength σ_y increase gradually with the increase in Mn content. When the Mn content is in the range of 22% and 24%, Vickers hardness H_V and yield strength σ_y increase dramatically. By comparison, Vickers hardness H_V and yield strength σ_y of FeCoCrNiMn HEA are intrinsically larger than those of FeCoCrNi HEA:

$$H_V = 2(k^2 G)^{0.585} - 3, \quad (9)$$

$$\sigma_y = H_V/3. \quad (10)$$

Energy factor K is used to evaluate the capacity of dislocation nucleation in crystalline materials, which is a vital physical parameter in terms of studying the plastic properties of crystalline materials. In anisotropic materials, energy factor

Fig. 8 Variation curves of Vickers hardness H_V **a** and yield strength σ_y **b** versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

Fig. 9 Variation curves of energy factor K versus Mn content for FeCoCrNiMn_x HEAs with FCC crystal structures

K of dislocation is calculated by elastic constants. For cubic crystals, energy factor K of screw and edge dislocations is formulated by Eqs. (11) and (12) [71, 72]. On the basis of Eqs. (11) and (12), we calculate the energy factor K of screw and edge dislocations as a function of Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs, as depicted in Fig. 9. Results show that the energy factor K of screw and edge dislocations decreases with the increase in Mn content. Thus, the dislocation nucleation is likely to occur at high Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs compared to FeCoCrNi HEA:

$$K_{\text{screw}} = \left[\frac{1}{2} C_{44} (C_{11} - C_{12}) \right]^{\frac{1}{2}}. \quad (11)$$

$$K_{\text{edge}} = (C_{11} + C_{12}) \left[\frac{C_{44} (C_{11} - C_{12})}{C_{11} (C_{11} + C_{12} + 2C_{44})} \right]^{\frac{1}{2}}, \quad (12)$$

In addition, we further investigate the dislocation properties of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs. Based on Eqs. (13) and (14) [71, 73], we calculate the energy factor K_{mixed} of mixed dislocation as a function of direction angle θ ($0 \leq \theta \leq \pi$), where θ is defined as the direction angle between Burgers vector and dislocation line. Meanwhile, dislocation width ζ is also calculated with respect to the energy factor K_{mixed} of mixed dislocation, and the parameter d in Eq. (14) is the spacing between glide planes, and $C = (C_{11} - C_{12})/2$. Figure 10a and b draws the variation curves of energy factor K_{mixed} of mixed dislocation and dislocation width ζ as a function of direction angle θ ($0 \leq \theta \leq \pi$). Results in Fig. 10a indicate that the energy factor decreases with the increase in Mn content ($x = 0, 0.1, 0.2, 0.3$) for screw ($\theta = 0$) and edge dislocations ($\theta = \pi/2$). Moreover, the nucleation of screw dislocation is easier than that of edge dislocation due to small energy factor, which agrees well with the results of Fig. 9. Results in Fig. 10b show that dislocation width of screw dislocation ($\theta = 0$) increases with the increase in Mn content ($x = 0, 0.1, 0.2, 0.3$). For edge dislocation ($\theta = \pi/2$), however, the dislocation width of FeCoCrNiMn_{0.2} HEA is maximum compared with HEAs of other Mn contents ($x = 0, 0.1, 0.3$), which may lead to the minimum stacking-fault energy. Thus, the twinning deformation may occur in FeCoCrNiMn_{0.2} HEA:

$$K_{\text{mixed}} = K_{\text{edge}} \cdot \sin^2 \theta + K_{\text{screw}} \cdot \cos^2 \theta, \quad (13)$$

Fig. 10 Variation curves of energy factor K_{mixed} of mixed dislocation **a** and dislocation width ζ **b** versus direction angle θ ($0 \leq \theta \leq \pi$) between Burgers vector and dislocation line

$$\zeta = \frac{K_{\text{mixed}} \cdot d}{2C}. \quad (14)$$

4 Conclusions

In conclusion, this work is implemented to investigate the effects of Mn content on mechanical properties of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs via first-principles calculations combining EMTO–CPA method. The main conclusions are summarized as follows:

1. Resistances to bulk, elastic, and shear deformation decline with the increase in Mn content in FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs.
2. Pugh's ratio B/G indicates that the ductility of FeCoCrNiMn_x ($0 \leq x \leq 0.3$) HEAs declines with the increase in Mn content. When the Mn content is in the range of 22% and 24%, Pugh's ratio B/G decreases dramatically, implying a remarkable reduction in the ductility of FeCoCrNiMn_x HEAs between 22 and 24% of Mn contents.
3. The anisotropy of FeCoCrNiMn HEA is stronger than that of FeCoCrNi HEA between the (100) and (110) crystal planes, as well as (110)[001] direction.
4. Cauchy pressure reveals that the metallic characteristic of FeCoCrNiMn_x HEAs weakens with increasing Mn content at $0 \leq x \leq 0.22$, but the directional characteristic strengthens with increasing Mn content at $0.24 \leq x \leq 0.3$. The atomic bonding transforms from metallic to directional characteristic with the variation in Mn content from 22 to 24%.
5. Vickers hardness H_V and yield strength σ_y increase gradually with the increase in Mn content. When the Mn content is in the range of 22% and 24%, Vickers hardness and yield strength increase dramatically. Vickers hardness and yield strength of FeCoCrNiMn HEA are intrinsically larger than those of FeCoCrNi HEA.
6. Energy factor K of screw and edge dislocations decreases with the increase in Mn content, and the dislocation nucleation in FeCoCrNiMn HEA is easier than that in FeCoCrNi HEA. Dislocation width of screw dislocation increases with the increase in Mn content, while that of edge dislocation reaches maximum value at $x = 0.2$. Thereby, twinning deformation is easily induced in FeCoCrNiMn_{0.2} HEA due to low stacking-fault energy.

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References

- [1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, *Adv. Eng. Mater.* **6**, 299 (2004)
- [2] J.Y. He, W.H. Liu, H. Wang, Y. Wu, X.J. Liu, T.G. Nieh, Z.P. Lu, *Acta Mater.* **62**, 105 (2014)

- [3] H.W. Yao, J.W. Qiao, M.C. Gao, J.A. Hawk, S.G. Ma, H.F. Zhou, Y. Zhang, *Mater. Sci. Eng. A* **674**, 203 (2016)
- [4] Z.P. Wang, Q.H. Fang, J. Li, B. Liu, Y. Liu, J. Mater. Sci. Technol. **34**, 349 (2018)
- [5] P.F. Yu, L.J. Zhang, H. Cheng, H. Zhang, M.Z. Ma, Y.C. Li, G. Li, P.K. Liaw, R.P. Liu, *Intermetallics* **70**, 82 (2016)
- [6] Y.J. Zhou, Y. Zhang, Y.L. Wang, G.L. Chen, *Appl. Phys. Lett.* **90**, 181904 (2007)
- [7] F. Otto, A. Dlouhý, C. Somsen, H. Bei, G. Eggeler, E.P. George, *Acta Mater.* **61**, 5743 (2013)
- [8] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie, *Science* **345**, 1153 (2014)
- [9] Y.Z. Shi, B. Yang, P.K. Liaw, *Metals* **7**, 1 (2017)
- [10] Y.L. Chou, J.W. Yeh, H.C. Shih, *Corros. Sci.* **52**, 2571 (2010)
- [11] M.H. Chuang, M.H. Tsai, W.R. Wang, S.J. Lin, J.W. Yeh, *Acta Mater.* **59**, 6308 (2011)
- [12] Z.M. Li, K.G. Pradeep, Y. Deng, D. Raabe, C.C. Tasan, *Nature* **534**, 227 (2016)
- [13] W.R. Wang, W.L. Wang, S.C. Wang, Y.C. Tsai, C.H. Lai, J.W. Yeh, *Intermetallics* **26**, 44 (2012)
- [14] J.B. Seol, J.W. Bae, Z.M. Li, J.C. Han, J.G. Kim, D. Raabe, H.S. Kim, *Acta Mater.* **151**, 366 (2018)
- [15] N.D. Stepanov, D.G. Shaysultanov, R.S. Chernichenko, N.Y. Yurchenko, S.V. Zhrebtsov, M.A. Tikhonovsky, G.A. Salishchev, *J. Alloys Compd.* **693**, 394 (2017)
- [16] Z.W. Wang, I. Baker, Z.H. Cai, S. Chen, J.D. Poplawsky, W. Guo, *Acta Mater.* **120**, 228 (2016)
- [17] Y.C. Xie, H. Cheng, Q.H. Tang, W. Chen, W.K. Chen, P.Q. Dai, *Intermetallics* **93**, 228 (2018)
- [18] H. Luo, Z.M. Li, D. Raabe, *Sci. Rep.* **7**, 9892 (2017)
- [19] Z.F. Lei, X.J. Liu, Y. Wu, H. Wang, S.H. Jiang, S.D. Wang, X.D. Hui, Y.D. Wu, B. Gault, P. Kontis, D. Raabe, L. Gu, Q.H. Zhang, H.W. Chen, H.T. Wang, J.B. Liu, K. An, Q.S. Zeng, T.G. Nieh, Z.P. Lu, *Nature* **563**, 546 (2018)
- [20] M.B. Kivy, M.A. Zaeem, *Scr. Mater.* **139**, 83 (2017)
- [21] Y.H. Zhang, Y. Zhuang, A. Hu, J.J. Kai, C.T. Liu, *Scr. Mater.* **130**, 96 (2017)
- [22] L. Vitos, *Computational quantum mechanics for materials engineers: the EMTO method and applications* (Springer, London, 2007)
- [23] P. Soven, *Phys. Rev.* **156**, 809 (1967)
- [24] B.L. Gyorffy, *Phys. Rev. B* **5**, 2382 (1972)
- [25] L. Vitos, I.A. Abrikosov, B. Johansson, *Phys. Rev. Lett.* **87**, 156401 (2001)
- [26] X. Sun, H.L. Zhang, L. Song, X.D. Ding, Y.Z. Wang, L. Vitos, *Acta Mater.* **140**, 366 (2017)
- [27] H.L. Zhang, X. Sun, S. Lu, Z.H. Dong, X.D. Ding, Y.Z. Wang, L. Vitos, *Acta Mater.* **155**, 12 (2018)
- [28] X.Q. Li, *J. Alloys Compd.* **764**, 906 (2018)
- [29] S. Huang, W. Li, S. Lu, F.Y. Tian, J. Shen, E. Holmström, L. Vitos, *Scr. Mater.* **108**, 44 (2015)
- [30] F.Y. Tian, L.K. Varga, N.X. Chen, L. Delczeg, L. Vitos, *Phys. Rev. B* **87**, 075144 (2013)
- [31] F.Y. Tian, L. Delczeg, N.X. Chen, L.K. Varga, J. Shen, L. Vitos, *Phys. Rev. B* **88**, 085128 (2013)
- [32] S. Huang, W. Li, X.Q. Li, S. Schönecker, L. Bergqvist, E. Holmström, L.K. Varga, L. Vitos, *Mater. Des.* **103**, 71 (2016)
- [33] B.L. Gyorffy, A.J. Pindor, J. Staunton, G.M. Stocks, H. Winter, *J. Phys. F: Metal Phys.* **15**, 1337 (1985)
- [34] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
- [35] V.L. Moruzzi, J.F. Janak, K. Schwarz, *Phys. Rev. B* **37**, 790 (1988)
- [36] L.A. Girifalco, V.G. Weizer, *Phys. Rev.* **114**, 687 (1959)
- [37] S.F. Liu, Y. Wu, H.T. Wang, J.Y. He, J.B. Liu, C.X. Chen, X.J. Liu, H. Wang, Z.P. Lu, *Intermetallics* **93**, 269 (2018)
- [38] X.Q. Li, D.L. Irving, L. Vitos, *Sci. Rep.* **8**, 11196 (2018)
- [39] A.J. Zaddach, C. Niu, C.C. Koch, D.L. Irving, *JOM* **65**, 1780 (2013)
- [40] F.X. Zhang, S.J. Zhao, K. Jin, H. Bei, D. Popov, C.Y. Park, J.C. Neuefeind, W.J. Weber, Y.W. Zhang, *Appl. Phys. Lett.* **110**, 011902 (2017)
- [41] A.J. Zhang, J.S. Han, B. Su, P.D. Li, J.H. Meng, *Mater. Des.* **114**, 253 (2017)
- [42] C.L. Tracy, S. Park, D.R. Rittman, S.J. Zinkle, H.B. Bei, M. Lang, R.C. Ewing, W.L. Mao, *Nat. Commun.* **8**, 15634 (2017)
- [43] Z.C. Qiu, C.W. Yao, K. Feng, Z.G. Li, P.K. Chu, *Int. J. Light-weight Mater. Manu.* **1**, 33 (2018)
- [44] J.H. Wang, S. Yip, S.R. Phillpot, D. Wolf, *Phys. Rev. Lett.* **71**, 4182 (1993)
- [45] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, *Phys. Rev. B* **76**, 054115 (2007)
- [46] F.Y. Tian, L.K. Varga, J. Shen, L. Vitos, *Comput. Mater. Sci.* **111**, 350 (2016)
- [47] Z. Wu, H. Bei, G.M. Pharr, E.P. George, *Acta Mater.* **81**, 428 (2014)
- [48] K. Tanaka, T. Teramoto, R. Ito, *MRS Adv.* **2**, 1429 (2017)
- [49] T. Teramoto, K. Yamada, R. Ito, K. Tanaka, *J. Alloys Compd.* **777**, 1313 (2019)
- [50] N.L. Okamoto, S. Fujimoto, Y. Kambara, M. Kawamura, Z.M.T. Chen, H. Matsunoshita, K. Tanaka, H. Inui, E.P. George, *Sci. Rep.* **6**, 35863 (2016)
- [51] A. Haglund, M. Koehler, D. Catoor, E.P. George, V. Keppens, *Intermetallics* **58**, 62 (2015)
- [52] S.F. Pugh, *Philos. Mag.* **45**, 823 (1954)
- [53] Y. Cao, J.C. Zhu, Z.S. Nong, X.W. Yang, Y. Liu, Z.H. Lai, *Comp. Mater. Sci.* **77**, 208 (2013)
- [54] D. Iotova, N. Kioussis, S.P. Lim, *Phys. Rev. B* **54**, 14413 (1996)
- [55] A. Gali, E.P. George, *Intermetallics* **39**, 74 (2013)
- [56] M. Mattesini, R. Ahuja, B. Johansson, *Phys. Rev. B* **68**, 184108 (2003)
- [57] H.Z. Fu, D.H. Li, F. Peng, T. Gao, X.L. Cheng, *Comp. Mater. Sci.* **44**, 774 (2008)
- [58] K. Lau, A.K. Mccurdy, *Phys. Rev. B* **58**, 8980 (1998)
- [59] H.Z. Fu, X.F. Li, W.F. Liu, Y.M. Ma, T. Gao, X.H. Hong, *Intermetallics* **19**, 1959 (2011)
- [60] R.P. Ingel, D.L. Iii, *J. Am. Ceram. Soc.* **71**, 265 (1988)
- [61] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948)
- [62] H.Z. Fu, W.M. Peng, T. Gao, *Mater. Chem. Phys.* **115**, 789 (2009)
- [63] D.G. Pettifor, *Mater. Sci. Technol.* **8**, 345 (1992)
- [64] R.A. Johnson, *Phys. Rev. B* **37**, 3924 (1988)
- [65] J.S. Tse, *J. Superhard Mater.* **32**, 177 (2010)
- [66] F.M. Gao, J.L. He, E.D. Wu, S.M. Liu, D.L. Yu, D.C. Li, S.Y. Zhang, Y.J. Tian, *Phys. Rev. Lett.* **91**, 015502 (2003)
- [67] A. Šimůnek, J. Vackář, *Phys. Rev. Lett.* **96**, 085501 (2006)
- [68] K.Y. Li, X.T. Wang, F.F. Zhang, D.F. Xue, *Phys. Rev. Lett.* **100**, 235504 (2008)
- [69] M.M. Smedskjaer, J.C. Mauro, Y.Z. Yue, *Phys. Rev. Lett.* **105**, 115503 (2010)
- [70] X.Q. Chen, H.Y. Niu, D.Z. Li, Y.Y. Li, *Intermetallics* **19**, 1275 (2011)
- [71] A.J.E. Foreman, *Acta Metall.* **3**, 322 (1955)
- [72] M.M. Savin, V.M. Chernov, A.M. Strokova, *Phys. Status Solidi A* **35**, 747 (1976)
- [73] C.N. Reid, *Acta Metall.* **14**, 13 (1966)