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Effects of Different Contents of Each Component on the Structural Stability and Mechanical Properties of Co-Cr-Fe-Ni High-Entropy Alloys

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Abstract: The structural stability of high-entropy alloys (HEAs) is closely related to their mechanical properties. The precise control of the component content is a key step toward understanding their structural stability and further determining their mechanical properties. In this study, first-principle calculations were performed to investigate the effects of different contents of each component on the structural stability and mechanical properties of Co-Cr-Fe-Ni HEAs based on the supercell model. Co-Cr-Fe-Ni HEAs were constructed based on a single face-centered cubic (FCC) solid solution. Elemental components have a clear effect on their structure and performance; the Cr and Fe elements have an obvious effect on the structural stability and equilibrium lattice constant, respectively. The Ni elements have an obvious effect on stiffness. The Pugh ratios indicate that Cr and Ni addition may increase ductility, whereas Co and Fe addition may decrease it. With increasing Co and Fe contents or decreasing Cr and Ni contents, the structural stability and stiffness of Co-Cr-Fe-Ni HEAs are improved. The structural stability and mechanical properties may be related to the strength of the metallic bonding and covalent bonding inside Co-Cr-Fe-Ni HEAs, which, in turn, is determined by the change in element content. Our results provide the underlying insights needed to guide the optimization of Co-Cr-Fe-Ni HEAs with excellent mechanical properties.



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1. Introduction

High-entropy alloys (HEAs) have stimulated widespread interest due to their outstanding properties since they were independently proposed by Yeh and Cantor [1,2]. In general, HEAs are composed of four or more principal elements in equal or similar molar ratios, and the percentage range of each element is 5–35 at.%. HEAs have a high entropy of mixing. Lattice distortion [3], cocktail [4], and sluggish diffusion effects [5] in HEAs have also been reported. HEAs are a single-phase random solid solution. For example, CoCrFeNi HEAs [1] have a FCC structure. MoNbTaV refractory HEAs [6] have a body-centered cubic (BCC) structure. At present, some important works have shown that HEAs have many excellent mechanical properties, such as high strength, wear resistance, high hardness, and high-temperature oxidation resistance and corrosion resistance [6–8].

For Co-Cr-Fe-Ni HEAs, there have been plenty of investigations on phase stability [9–11], local chemical ordering [12,13], mechanical [14–18], tribological [19–21], corrosion [22–27], and magnetic [28,29] and irradiation resistance [30,31]. Most of these works are based on experimental observations. For example, the metastable BCC phase appears in the rapid solidification microstructure along with the primary FCC phase [9]. At a low temperature, the combined effect of deformation twinning and phase transformation led

to an increase in the strength of CoCrFeNi HEAs [15]. At a high temperature, CoCrFeNi HEAs have excellent wear resistance in a vacuum compared with steel and Ni-based intermetallic materials [19]. CoCrFeNi HEAs exhibit high strength and ductility due to stacking faults at a higher strain rate [18]. The addition of Al, Cu, Sn, Nb, and Mo to CoCrFeNi HEAs forms a stable oxide film to improve the corrosion resistance of the alloy in chloride solutions [22,23,26,27]. The magnetic properties of CoCrFeNi indicate that it is a poor candidate for soft magnetic applications at a high temperature, but cold rolling will increase the magnetic entropy change [28]. Decreasing the Cr content in alloys led to an increase in the saturation magnetization or the Curie temperature of alloys [28].

First-principle calculations based on density functional theory (DFT) are also widely used in the study of HEAs' structure and properties. CoCrFeNi alloy undergoes structural phase transition from FCC to hexagonal close-packed (HCP) at 13.5 GPa [32]. Based on the Gibbs free energy, the energy difference between the FCC and HCP structures of CoCrFeNi alloy is very small, but its phase transition pressure can be changed from 1 GPa at room temperature to 6 GPa at 500 K. Studies on CoCrFeNi [33] and CoCrFeNiMn [34] HEAs show that at the short chemical range order of Cr at low temperature, the electronic spin-flip and magnetovolume effects lead to the largest lattice distortion effect of the Cr element. Song et al. [35] demonstrated that the lattice distortion in CoCrFeNi HEAs contributes to the solid solution strengthening of alloys. With increasing Al content, CoCrFeNiAl_x HEAs changed from FCC, FCC+BCC phase to BCC phase [36,37], and their plasticity degraded [14]. The component and crystal structures of paramagnetic CoCrFeNiAl_x alloys [37] have the most significant influence on the single and polycrystal elastic parameters, and the mechanical properties of equimolar CoCrFeNiAl are better than a single-phase structure.

Although Co-Cr-Fe-Ni HEAs are among the most widely studied high-entropy alloys, there is little information on the influence of composition on their structural and mechanical properties. Niu et al. [38] demonstrated that certain components of alloys significantly affected their properties—that is, Co affects the lattice parameter, Cr affects the enthalpy of mixing, Fe affects the bulk modulus, Co affects the shear modulus, and Cr affects the Pugh ratio (B/G). Yang et al. [25] demonstrated that changes in Co, Fe, and Ni content can enhance the corrosion resistance of the Co_aCr₂₀Fe_bNi_{80-a-b} HEAs system. However, the problem is that when one atomic percentage is determined, the other three atomic percentages are not equal, which may lead to the inability to accurately describe the effect of each element on the structure and properties of Co-Cr-Fe-Ni HEAs.

Experimental research on the content of components is greatly restricted by samples. However, first-principle calculations can provide an effective and economical method. In this work, we used the special quasirandom supercell (SQS) [39] model based on empirical parameters and first-principle calculations to study the effect of the different content of each component on the structural and mechanical properties of Co-Cr-Fe-Ni HEAs. When one component percentage is determined, the other three atomic percentages are equally divided. Here, the empirical parameters are calculated to evaluate the structural stability of Co-Cr-Fe-Ni HEAs, and the elastic constants and polycrystal elastic moduli are calculated to evaluate the stiffness and ductility of alloys. Detailed research on the effect of composition on structural and mechanical properties was carried out to obtain a better understanding of Co-Cr-Fe-Ni HEAs.

2. Computational Details

To study mechanical properties, it is necessary to evaluate structural stability. A solid-solution model was used to study the phase structure based on empirical parameters. The valence electron concentration (VEC) was used to determine the phase structure (BCC or FCC) [40,41]. For HEAs, the VEC is expressed as [40]:

$$\text{VEC} = \sum_i^n c_i (\text{VEC})_i \quad (1)$$

where c_i represents the atomic percentage of the i th element, and $(\text{VEC})_i$ is the VEC of the current element. For 3d transition elements, VEC includes all electrons together with d orbitals. The valence electrons of elements are $\text{Cr}3d^54s^1$, $\text{Fe}3d^64s^2$, $\text{Co}3d^74s^2$, and $\text{Ni}3d^84s^2$.

The atomic size difference (δ) is an important parameter related to the solid-solution phase. A larger δ corresponds to severe lattice distortion and sluggish diffusion effects, resulting in a decrease in the stability and transformation rate of the solid-solution phase and precipitate formation in the HEAs [42]. The hardness changes monotonously with δ , which means that the lattice distortion hinders the dislocation motion of plastic deformation, resulting in solid-solution strengthening [40]. Accordingly, δ is defined as [42]:

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}, \bar{r} = \sum_{i=1}^n c_i r_i \quad (2)$$

where r_i represents the atomic radius of the i th element. We use the atomic radius measured by X-ray diffraction in the elemental state [43].

The enthalpy of mixing (ΔH_{mix}) affects the solid-solution phase or compound formation in HEAs [44]. A negative ΔH_{mix} means that different elements form intermetallic compounds, while positive ΔH_{mix} leads to phase separation in alloys. Only when the absolute value of ΔH_{mix} is close to zero is the solid-solution phase stable in the solid phase. ΔH_{mix} is defined as [45]:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n 4\Delta H_{AB}^{mix} c_i c_j \quad (3)$$

where ΔH_{AB}^{mix} is the enthalpy of mixing of the binary liquid alloy. The value of ΔH_{AB}^{mix} can be found from Ref. [46], which is calculated by the Miedema macroscopic model [47].

High-entropy alloys mean higher entropy of mixing (ΔS_{mix}) and the value of ΔS_{mix} is positive in the alloy. A higher ΔS_{mix} corresponds to an increase in the degree of confusion in the multicomponent alloy system, and a decrease in the ordering and separation of different elements in the alloy, resulting in easier and more stable random solid-solution formation. ΔS_{mix} is expressed as [42]:

$$\Delta S_{mix} = -R \sum_{i=1}^n (c_i \ln c_i) \quad (4)$$

where R is the gas constant. HEAs of equal molar ratios have the largest entropy of mixing.

According to thermodynamics, the energy $T\Delta S_{mix}$ increases with increasing temperature, and $T\Delta S_{mix}$ is related to the formation of the solid-solution phase. The phase formation of the alloy usually occurs near the melting point (T_m) if the solid-state phase transformation is not considered. In terms of the Gibbs free energy of multicomponent alloy systems, Yang and Zhang [42] defined a parameter Ω for predicting the solid-solution formation for HEAs as:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (5)$$

where $T_m = \sum_{i=1}^n c_i (T_m)_i$ is the melting point of HEAs following the mixing rules of multicomponent HEAs [42]. The T_m of the atom can be found from Ref. [48].

Equations (1)–(5) or their combination can be used to evaluate the phase stability of HEAs, thereby laying a theoretical foundation for the study of mechanical properties.

The elastic constant calculation of Co-Cr-Fe-Ni HEAs can be implemented in the CASTEP package [49] by the stress-strain method based on Hooke's law. Hooke's law describes the linear relationship between stress component σ_i and strain component ε_j , and it is defined as [50]:

$$\sigma_i = \sum_{j=1}^6 C_{ij} \varepsilon_j \quad (6)$$

where C_{ij} represents the elastic constant and is described by a 6×6 tensor. The elastic constants in all directions can be calculated by the finite displacement method. According to the Voigt–Reuss–Hill approximation method [51], the polycrystal elastic moduli of the alloys was calculated from the elastic constants, including bulk modulus (B), shear modulus (G), Young’s modulus (E), Pugh ratio (B/G), and Poisson’s ratio (ν).

In this work, a series of supercell solid-solution alloy models containing 20 and 32 atoms were established through the SQS method, and they were expanded to $1 \times 1 \times 5$ and $2 \times 2 \times 2$ on the basis of a single cell. The Co-Cr-Fe-Ni HEAs model and the percentage of each element are shown in Table 1 and Figure 1. The first-principles calculation uses the CASTEP package [49] based on plane-wave pseudopotential. This module is a quantum mechanics program developed by the University of Cambridge and has been widely used in the study of properties of complex multicomponent alloys [34,52]. We choose spin polarization and used formal spin as initial conditions because the ferromagnetic state is more stable than the paramagnetic state of room temperature at 0 K [29,53,54]. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [55] was used to describe the exchange–correlation function. The ultrasoft pseudopotential was used to treat the electron–ion interaction. The energy cutoff for the plane-wave basis set was 400 eV. The self-consistent field tolerance is 1×10^{-6} eV/atom, and the Brillouin zone was integrated using a Monkhorst–Pack grid. When x is 0.2 and 0.56, 1 and 1.57, and 2, the k-point set in the reciprocal space is $4 \times 4 \times 3$, $4 \times 3 \times 4$, and $1 \times 7 \times 7$, respectively. The convergence tolerance is that the maximum force is less than 0.03 eV/Å, the energy is less than 1×10^{-5} eV/atom, the maximum stress is less than 0.05 GPa, and the maximum displacement is less than 0.001 Å. Based on the above parameters and alloy models, the structure was first optimized, and then the elastic properties were calculated.

Table 1. Co-Cr-Fe-Ni high-entropy alloys (HEAs) model and the percentage of each element.

Alloy	Alloy Model	x Value	x Elements/at.%	Other Elements/at.%
Co _{x} CrFeNi	Co ₂ Cr ₁₀ Fe ₁₀ Ni ₁₀	0.2	6.25	31.25
	Co ₅ Cr ₉ Fe ₉ Ni ₉	0.56	15.625	28.125
	Co ₈ Cr ₈ Fe ₈ Ni ₈	1	25	25
	Co ₁₁ Cr ₇ Fe ₇ Ni ₇	1.57	34.375	21.875
	Co ₈ Cr ₄ Fe ₄ Ni ₄	2	40	20
CoCr _{x} FeNi	Co ₁₀ Cr ₂ Fe ₁₀ Ni ₁₀	0.2	6.25	31.25
	Co ₉ Cr ₅ Fe ₉ Ni ₉	0.56	15.625	28.125
	Co ₈ Cr ₈ Fe ₈ Ni ₈	1	25	25
	Co ₇ Cr ₁₁ Fe ₇ Ni ₇	1.57	34.375	21.875
	Co ₄ Cr ₈ Fe ₄ Ni ₄	2	40	20
CoCrFe _{x} Ni	Co ₁₀ Cr ₁₀ Fe ₂ Ni ₁₀	0.2	6.25	31.25
	Co ₉ Cr ₉ Fe ₅ Ni ₉	0.56	15.625	28.125
	Co ₈ Cr ₈ Fe ₈ Ni ₈	1	25	25
	Co ₇ Cr ₇ Fe ₁₁ Ni ₇	1.57	34.375	21.875
	Co ₄ Cr ₄ Fe ₈ Ni ₄	2	40	20
CoCrFeNi _{x}	Co ₁₀ Cr ₁₀ Fe ₁₀ Ni ₂	0.2	6.25	31.25
	Co ₉ Cr ₉ Fe ₉ Ni ₅	0.56	15.625	28.125
	Co ₈ Cr ₈ Fe ₈ Ni ₈	1	25	25
	Co ₇ Cr ₇ Fe ₇ Ni ₁₁	1.57	34.375	21.875
	Co ₄ Cr ₄ Fe ₄ Ni ₈	2	40	20

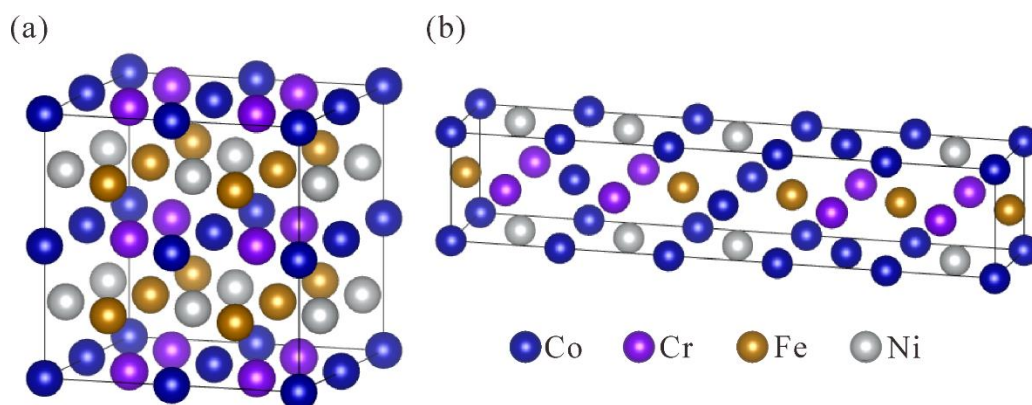


Figure 1. Co-Cr-Fe-Ni HEAs' structures of supercell solid-solution alloy models. (a) The values of x are 0.2, 0.56, 1 and 1.57; (b) the value of x is 2.

3. Results and Discussion

3.1. Structural Stability

To understand the structural properties of Co-Cr-Fe-Ni HEAs with different contents of each component, the VEC, δ , ΔH_{mix} , ΔS_{mix} , Ω , and tetragonal shear modulus (c') were calculated and are shown in Figure 2. The VEC, δ , ΔH_{mix} , ΔS_{mix} and Ω for the equimolar ratio of the CoCrFeNi alloy are consistent with previous works [40,42]. According to previous results [40], HEAs prefer to form a single BCC phase when the VEC is 4.33–7.55, whereas the structure is FCC for VEC between 7.80 and 9.50. As shown in Figure 2a, all calculated VEC values are higher than 7.8, indicating that Co-Cr-Fe-Ni HEAs may maintain a single-phase FCC structure. This result is consistent with previous works [9–11,38]. The VEC of Cr and Fe is lower than the average valence electron concentration of the four elements, which causes the VEC of the alloys to decrease with increasing Cr and Fe contents. On the contrary, the VEC of the alloys increases with Co and Ni contents because the VEC of Co and Ni are higher. The δ is related to the atomic radius. Co has the largest atomic radius, and Fe has the smallest. This indicates that δ increases with Co and Fe contents, and decreases with Cr and Ni contents are shown in Figure 2b. HEAs form solid solutions with $-15 \leq \Delta H_{mix} \leq 5 \text{ kJ mol}^{-1}$ and $11 \leq \Delta S_{mix} \leq 19.5 \text{ J K}^{-1} \text{ mol}^{-1}$ [40]. As shown in Figure 2c,d, the values of ΔH_{mix} and ΔS_{mix} are in the above range, indicating that Co-Cr-Fe-Ni HEAs may be a solid-solution phase. This was confirmed by previous works [25,36–38]. Only when the absolute value of ΔH_{mix} is close to zero can the solid solution be stable in the solid phase. The results show that the solid-solution phase stability of the alloys decreases with increasing Cr and Ni contents and increases with increasing Co and Fe contents. This is consistent with previous work [38]. However, the entropy of mixing result shows that only the alloys with an equal molar ratio have the largest entropy of mixing, which is not affected by the component. For HEAs, $\Omega > 1$ means that the contribution of $T\Delta S_{mix}$ will be higher than ΔH_{mix} , corresponding to the formation of the solid-solution phase in the alloy [42]. As shown in Figure 2e, all alloys are solid solutions and become more stable with decreasing Cr and Ni content and increasing Co and Fe content. According to a previous report [42], a random solid solution is stable when $\delta \leq 6.6\%$ and $\Omega \geq 1.1$. Our results indicate that the Co-Cr-Fe-Ni HEAs studied in this work may be a random solid solution. This result is consistent with previous works [25,36–38]. In addition, the parameter Ω shows a similar trend to that of the δ . The tetragonal shear modulus ($c' = (C_{11} - C_{12})/2$) is related to the energy difference of different crystal structures and also can reflect the structural stability [56]. As shown in Figure 2f, c' decreases with increasing Cr and Ni contents and increases as the contents of Co and Fe increase. For HEAs composed of $3d$ transition elements, c' is determined by the energy difference between the FCC and BCC structures of the multicomponent alloy system, which, in turn, is determined by the d orbital electrons [56]. Therefore, the energy difference of the alloys increases with Co and Fe contents and decreases with Cr and Ni contents. This result is consistent with the

enthalpy of mixing, indicating that the structure is more stable as Co and Fe increase and Cr and Ni decrease. Overall, all parameters indicate that the Co-Cr-Fe-Ni HEAs studied in this work may be a single FCC solid-solution phase, and the structural stability decreases with increasing Cr and Ni contents and increases with increasing Co and Fe contents. It is worth noting that the range of VEC, ΔH_{mix} , Ω , and c' of the Cr element is the largest, which is consistent with previous work [38], indicating that Cr has a significant impact on structural stability. In addition, the Fe element has a significant effect on δ , and the influence on c' is almost the same as that of Cr.

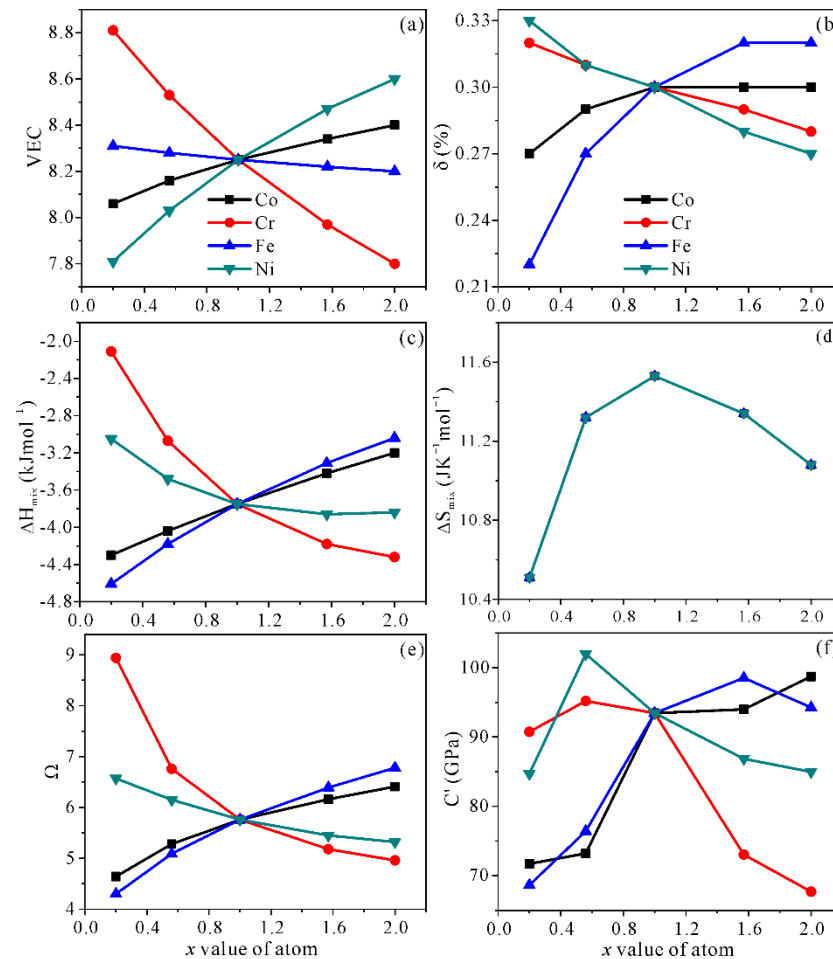


Figure 2. Structural stability parameters of Co-Cr-Fe-Ni HEAs with the x value of elements. (a) Valence electron concentration (VEC), (b) atomic size difference δ , (c) enthalpy of mixing ΔH_{mix} , (d) entropy of mixing ΔS_{mix} , (e) parameter Ω , and (f) tetragonal shear modulus c' .

The equilibrium lattice constants and mass density of the Co-Cr-Fe-Ni HEAs based on the FCC supercell structure are presented in Figure 3. The arithmetic mean cell length of the supercell a_{avg} is used as the lattice constants of the alloy for comparison with experimental data. a_{avg} is calculated as follows [57]:

$$a_{avg} = \frac{1}{n} \sum_{i=1}^n \frac{1}{3} (a_i + b_i + c_i) \quad (7)$$

where n represents the number of unit cells in the supercell, and a_i , b_i , and c_i are lattice constants. The lattice constant for the equimolar ratio is 0.35 nm, consistent with previous works, which found it as 0.3498–0.3587 nm [27–29,32,33,36,58]. In Figure 3a, the lattice constant decreases with increasing Co and Fe content and increases with increasing Cr and Ni content. The lattice constant of the Fe element has the largest variation range, which

is consistent with that of δ , indicating that Fe has the most significant influence on the equilibrium lattice constant. The lattice constants and atomic size difference of Co-Cr-Fe-Ni HEAs vary with the content of each element in the opposite direction. Fe has the smallest atomic radius, which can explain the change in lattice constants and atomic size difference with Fe content. However, the lattice constants decrease with Co contents even though Co has the largest atomic radius. This shows that the atomic radius does not determine the lattice constant of the alloy. This result is consistent with previous work [54], which demonstrated that lattice distortion cannot be accurately described by empirical parameter δ based on the atomic radius, especially for 3d FCC alloys. The variation in VEC can cause charge transfer resulting in distortions even for atoms of FCC Co-Ce-Fe-Ni HEAs with similar atomic sizes [59,60]. Chemical interactions between the elements, electronic spin-flip, and magnetovolume effects in HEAs can maximize the effect of lattice distortion caused by Cr [33,34]. For Co and Fe atoms, the ($Fe \leftrightarrow Cr$) and ($Co \leftrightarrow Cr$) bonds are stronger than ($Fe \leftrightarrow Ni$) and ($Co \leftrightarrow Ni$) bonds ($A \leftrightarrow B$ means the atomic bond of A and B elements), hence ($Fe \leftrightarrow Cr$) and ($Co \leftrightarrow Cr$) bonds will be preferred over ($Fe \leftrightarrow Ni$) and ($Co \leftrightarrow Ni$) bonds [33]. For Co-Cr-Fe-Ni HEAs, the increase in Cr-related bonds will enhance the lattice distortion effect caused by Cr. This may be the reason why the influence of the Cr element on the equilibrium lattice constant is almost the same as that of Ni. Therefore, the lattice distortion caused by the increase in Cr and Ni content or decrease in Co and Fe content may be the cause of the increase in the lattice constant.

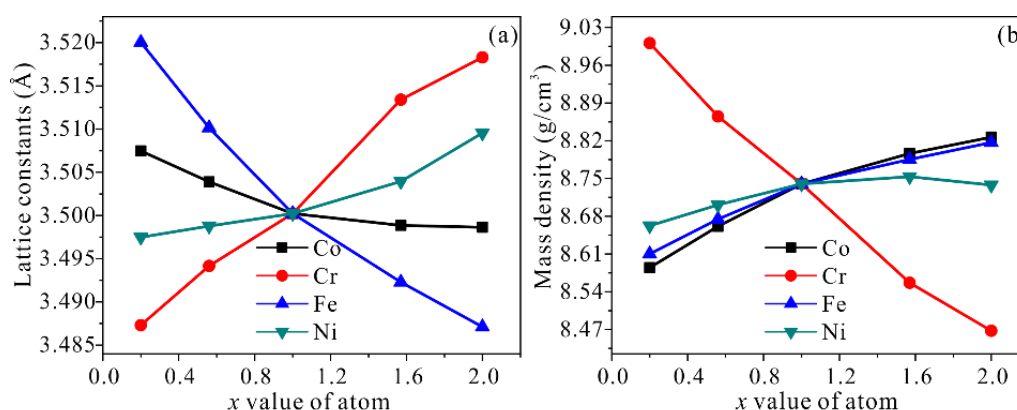


Figure 3. (a) Lattice constants and (b) mass density of Co-Cr-Fe-Ni HEAs with the x value of elements.

As shown in Figure 3b, the mass density of Co-Cr-Fe-Ni HEAs increases with Co, Fe, and Ni contents and decreases with Cr contents. The Cr element has the most significant influence on the density. The decrease in mass density with Cr content is due to the smallest density of Cr and the increase in lattice constant. The densities of Co and Fe are larger and the lattice constants decrease, causing the mass density to increase with the content of Co and Fe. Ni has the highest density, but the lattice constants increase with Ni content, and therefore the density of the alloy increases first ($x \leq 1.57$) and then decreases ($x > 1.57$). That is, the relative effect of Ni content on the mass and volume of the alloy is different with different content. When $x > 1.57$ of Ni, the mass increase of the alloy is less than the volume increase, and the density appears to decrease.

3.2. Mechanical Properties

The mechanical stability of crystal systems is the basis for studying HEAs' hardness and stiffness. FCC crystals usually have three independent elastic constants, but in this work, there are nine independent elastic constants belonging to the orthogonal structure

due to the use of the supercell model. The mechanical stability of the orthogonal structures can be determined from the following equations [52]:

$$C_{ij} > 0 (i = j), [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \\ (C_{11} + C_{22} - 2C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, (C_{22} + C_{33} - 2C_{23}) > 0 \quad (8)$$

The calculated elastic constants of Co-Cr-Fe-Ni HEAs are listed in Table 2, lacking experimental data comparison. Our results show that the elastic constants of Co-Cr-Fe-Ni HEAs satisfy the stability criteria, indicating that the alloys are mechanically stable in the ground state.

Table 2. Elastic constant C_{ij} of Co-Cr-Fe-Ni HEAs. The unit is GPa.

x	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Co-0.2	364.3	397.3	386.4	186.2	193.4	188.7	220.9	207.4	163.0
Co-0.56	358.0	399.9	412.2	189.4	186.9	188.0	211.6	200.1	175.0
Co-1	379.5	400.6	400.3	193.5	188.6	184.4	192.6	216.2	179.3
Co-1.57	382.0	401.0	395.1	193.3	186.4	188.0	194.0	206.8	181.0
Co-2	380.6	402.8	384.9	199.4	188.1	187.8	183.2	209.4	182.9
Cr-0.2	379.7	371.3	384.5	184.7	184.5	194.3	198.3	188.5	196.4
Cr-0.56	386.8	372.1	386.4	185.7	186.3	194.0	196.4	186.6	205.0
Cr-1	379.5	400.6	400.3	193.5	188.6	184.4	192.6	216.2	179.3
Cr-1.57	347.4	387.9	365.0	178.8	189.6	175.7	201.4	228.1	184.6
Cr-2	346.0	372.2	362.5	190.6	200.6	192.8	210.7	222.8	194.2
Fe-0.2	347.8	358.8	374.7	171.3	161.7	182.1	210.5	190.5	177.4
Fe-0.56	366.0	375.0	389.4	181.7	171.6	183.7	213.2	191.8	174.6
Fe-1	379.5	400.6	400.3	193.5	188.6	184.4	192.6	216.2	179.3
Fe-1.57	391.5	418.0	406.8	203.1	194.4	196.5	194.5	213.8	179.3
Fe-2	388.9	412.7	392.9	209.8	205.8	205.5	200.4	222.9	192.2
Ni-0.2	386.4	402.3	401.6	204.6	212.9	215.7	217.0	213.8	201.1
Ni-0.56	391.9	412.7	393.6	193.1	201.0	203.2	188.0	220.7	193.3
Ni-1	379.5	400.6	400.3	193.5	188.6	184.4	192.6	216.2	179.3
Ni-1.57	365.5	382.2	374.7	182.6	177.7	177.9	191.8	202.8	180.4
Ni-2	344.4	370.1	358.3	175.9	166.6	161.7	174.5	199.8	175.9

The elastic constants and polycrystal elastic moduli of CoCrFeNi alloy are shown in Table 3. For the other alloys, only limited data are available. The values for the CoCrFeNi alloy are in agreement with the calculations of Ref. [58]. The error of the B may be affected by the alloy model. B/G and ν of CoCrFeNi alloy also agree well with the values of Refs. [37,50]. However, the calculated C_{ij} , B , G , and E are much higher than the previous results [37,50]. This may be caused by the alloy model, calculation package, and magnetism, which have a great influence on the calculation results [36,48,51]. The comparison of Refs. [50,58] shows that the alloy model may be the main influence factor of the elasticity results.

Table 3. Elastic constants (C_{ij}) and polycrystal elastic moduli (B , G , E , ν , and B/G) for CoCrFeNi alloy. The unit is GPa, except for the dimensionless ν and B/G .

x	C_{11}	C_{12}	C_{44}	B	G	E	ν	B/G	Ref.	Model	Package	Magnetism
CoCrFeNi	379.48	192.62	193.47	261.31	144.75	366.56	0.266	1.81		SQS	CASTEP	FM
	376.63	197.04	184.71	245.3	146.73	367.01	0.251	1.67	[58]	Single	VASP	NM
	271	175	189	207	110	280	0.275	1.88	[37]	EMTO-CPA		PM
				204	118.6	298	0.256	1.71	[50]	USPEX	VASP	NM

SQS—special quasirandom supercell; Single—single FCC cell; EMTO-CPA—exact muffin-tin orbitals and coherent potential approximation; USPEX—Universal Structure Predictor: Evolutionary Xtallography; FM—ferromagnetic; NM—nonmagnetic; PM—paramagnetic.

The brittle–ductile behavior is an important mechanical performance indicator of the energy absorption and plastic deformation ability of materials under external forces. The Pugh ratio is usually used to describe the brittle–ductile behavior of HEAs [61]. Ductile materials typically show $B/G > 1.75$, while brittle materials show $B/G < 1.75$. Poisson's ratio can also reflect the brittle–ductile behavior of HEAs. For isotropic materials, $B/G > 1.75$ implies $\nu > 0.26$ [37], which has been confirmed by Gu et al. [62]. As shown in Figure 4a,b, according to B/G and ν , we find that all Co–Cr–Fe–Ni HEAs are predicted to be ductile, except for Fe-1.57. For CoCrFeNi alloy, this is in line with experiments [15,18]. Unfortunately, no available experimental information on the brittle–ductile behavior was reported for the other HEAs that can be compared with our results. ν has the same changing trend as B/G . Alloys have high values of ν and B/G as the contents of Cr and Ni increase and the contents of Co and Fe decrease, indicating that the ductility of the alloys enhances. Fe element has the largest variation range of B/G and ν , indicating that Fe may have the most significant effect on ductility. However, the effect of the Cr element on ductility is almost the same as Fe. The Cauchy pressure ($C_{12}-C_{44}$) reflects the bonding characteristics of the alloy. A more positive $C_{12}-C_{44}$ means more metallic bonding, and otherwise more covalent bonding [63]. As shown in Figure 4c, alloys have lower negative $C_{12}-C_{44}$ as the content of Cr and Ni decreases and the content of Co and Fe increases, which indicates that the covalent nature of the metallic bond is enhanced. Covalent bonds are more stable than metal bonds, which provides an explanation for the structural stability of the Co–Cr–Fe–Ni HEAs. The stronger the alloy's metallicity, the better the ductility of the materials. The trend of B/G and ν is consistent with that of $C_{12}-C_{44}$. In addition, the severe lattice distortion corresponding to the higher δ hinders the dislocation slip of HEAs in plastic deformation and increases yield strength. Therefore, our results indicate that the structural stability of the Co–Cr–Fe–Ni HEAs decreases but the ductility enhances with increasing Cr and Ni content and decreasing Co and Fe content.

The bulk modulus (B) represents the ability of the alloys to resist volume deformation under external pressure, the shear modulus (G) represents the ability to resist reversible deformation under shear stress, and Young's modulus (E) represents the ability to resist compression or tension within the elastic limit and can describe the stiffness of the materials. As shown in Figure 4d, the bulk modulus increases with increasing Fe content and decreases with increasing Ni content. Ni element has the most significant effect on the bulk modulus. The variation of Co and Cr has a slight effect on the bulk modulus, and the calculated bulk modulus is 255–262 GPa, indicating that the incompressibility of all Co and Cr series alloys is similar. This is consistent with previous work [38]. The variation of the shear modulus with composition is consistent with the variation of Young's modulus, as shown in Figure 4e,f. They increase with increasing Co and Fe contents and decrease with increasing Cr and Ni contents. The G and E variation ranges of Fe and Ni elements are almost the same. With regard to Cr, the shear modulus and Young's modulus increase firstly and then decrease. This change is consistent with the change in the electronic charge gain of the atoms in FCC–Cr material [34]. Among the four elements, only the 4s orbital unsaturation of Cr may change the chemical interactions with other elements [33,34], as well as the unique magnetic characteristics of Cr [53], which affects the structure and elastic properties. Stiffer materials generally have a larger Young's modulus. Hence, increasing Co and Fe contents or decreasing Cr and Ni contents would improve the stiffness of Co–Cr–Fe–Ni HEAs, and the Ni element has the most significant effect on the stiffness. Combining structural stability and brittle–ductile behavior, we find that the variation of stiffness with composition is consistent with that of structural stability but opposite to the brittle–ductile behavior. The relationship between stiffness and ductility is consistent with previous work on $\text{Al}_x\text{FeCuCrNi}$ HEAs [64]. This may be because the covalent nature of the metal bond improves the structural stability, and stiffness, but reduces the ductility. For FCC Co–Cr–Fe–Ni HEAs, the atomic-level pressure variation originating from the charge transfer between neighboring elements in the alloy will also improve the stiffness of the system [59]. Overall, the incompressibility, resistance to shear deformation, and stiffness of Co–Cr–Fe–Ni

HEAs improve with the increasing Co and Fe contents or decreasing Cr and Ni contents, corresponding to a more stable solid-solution structure and weakened ductility.

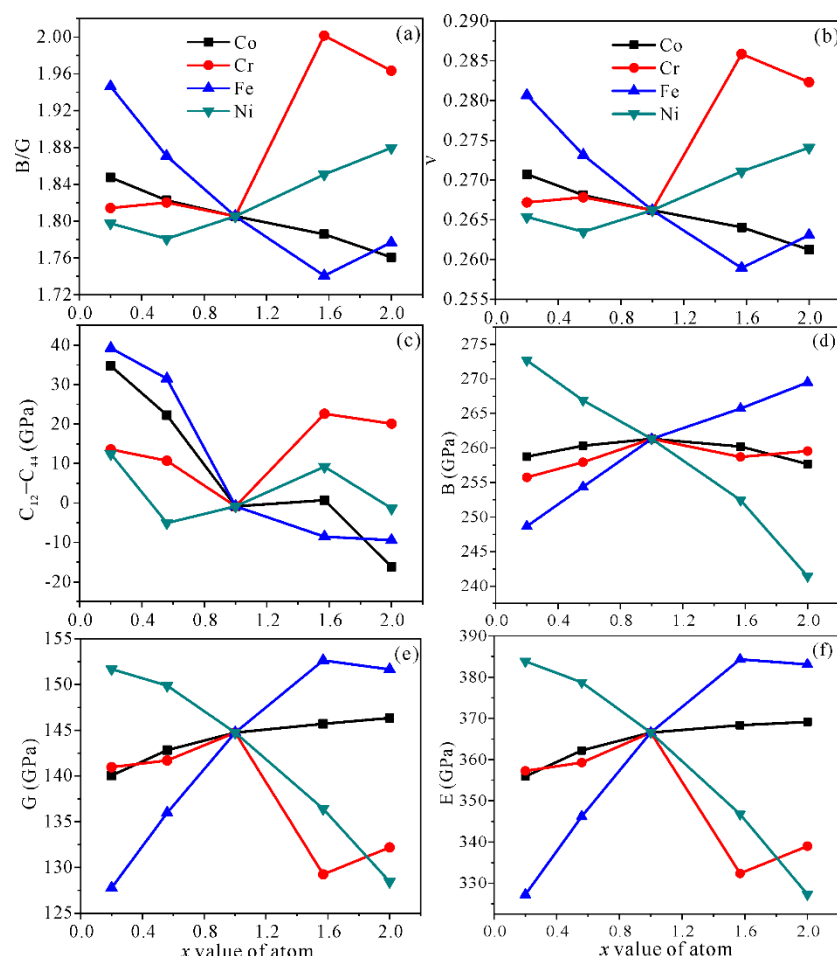


Figure 4. (a) Pugh ratio B/G , (b) Poisson's ratio ν , (c) Cauchy pressure $C_{12}-C_{44}$, (d) Bulk modulus B , (e) shear modulus G , and (f) Young's modulus E of Co-Cr-Fe-Ni HEAs with the x value of elements.

4. Conclusions

In summary, we used a supercell model based on empirical parameters and first-principle calculations to study the effects of different contents of each component on the structural stability and mechanical properties of Co-Cr-Fe-Ni HEAs. The valence electron concentration, enthalpy of mixing, entropy of mixing, atomic size difference, and Ω indicate that the Co-Cr-Fe-Ni HEAs studied in this work may be a single FCC solid-solution phase, and all alloys are mechanically stable at the ground state. The structural stability increases with increasing Co/Fe content and with decreasing Cr/Ni content. The equilibrium lattice constants increase with increasing Cr/Ni content and with decreasing Co/Fe content. The mass density increases with Co, Fe, and Ni content and decreases with Cr content. The ductility may enhance with increasing Cr/Ni content and decreasing Co/Fe content. The stiffness improves with increasing Co/Fe contents or decreasing Cr/Ni contents. Certain components of the alloy significantly affect its performance; specifically, Cr affects the structural stability, Fe impacts the equilibrium lattice constant, Cr affects the mass density, Fe affects the ductility, and Ni impacts the stiffness. The results show that the stiffness and structural stability of Co-Cr-Fe-Ni HEAs are improved, while the ductility may be weakened with increasing Co/Fe content or decreasing Cr/Ni content. The structural stability and mechanical properties may be related to the strength of the metallic bonding and covalent bonding inside the Co-Cr-Fe-Ni HEAs, which, in turn, is determined by the change in element content.

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