Computational characterization of the structural and mechanical properties of $\text{Al}_x\text{CoCrFeNiTi}_{1-x}$ high entropy alloys

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Abstract

AlCoCrFeNiTi is one kind of high entropy alloys with potential applications in aerospace, electronics and machinery manufacturing. Its microstructure, thermodynamic and mechanical properties vary with Al and Ti contents. The disordered structures of $\text{Al}_x\text{CoCrFeNiTi}_{1-x} (x = 0–1.0)$ alloys were generated and screened with the special quasi-random method. First-principles calculations with the Perdew–Burke–Ernzerhof functional and projector-augmented wave potential were carried out to further identify the structures and assess their thermodynamic and mechanical properties. The measured lattice constants and observed phase transition from $\text{bcc}$ to $\text{fcc}$ with Ti addition and Al reduction were reproduced in the calculations. The predicted transition point is at the Al content of about 8 at%. The heat capacity of the $\text{bcc}$ and $\text{fcc}$ structures exhibit similar temperature dependence, matching well with the empirical Dulong-Petit Model and the quantum Debye Model. The elastic constants and elastic moduli vary with the phase structures and compositions. The studied $\text{Al}_x\text{CoCrFeNiTi}_{1-x}$ alloys are predicted to possess good comprehensive mechanical performances, especially for $x = 0.8$ and 0.6 for the $\text{bcc}$ structures and $x = 0.5$ for the $\text{fcc}$ structures. The addition/reduction of Al atoms from the systems alters the electron localization/delocalization that has considerable influence on the interatomic interaction strength in the alloy systems.

1. Introduction

High-entropy alloy (HEA), which was first proposed by Yeh et al. [1] and Cantor et al. [2] in 2004, is defined as a solid solution alloy consisting of five or more main elements with equimolar or near-equimolar atomic fractions [3, 4]. HEAs usually have high entropy of mixing that suppresses the formation of intermetallic compounds, and promotes the formation of solid-solution phase in simple crystal structures. Two typical HEA structures, face-centered-cubic ($\text{fcc}$) represented by CoCrCuFeNi [1] and body-centered-cubic ($\text{bcc}$) by AlCoCrFeNi [5] solid solutions have long been identified. In addition, hexagonal close-packed ($\text{hcp}$) FeCoRuRe HEA was reported in recent years [6]. High configurational entropy [3, 4], sluggish diffusion [7, 8], cocktail effect [9] and severe lattice-distortion effect [10] were considered as the key characteristics of HEAs that are responsible for their performances superior to conventional alloys. HEAs usually exhibit high fracture toughness, irradiation resistance, corrosion resistance, great thermal stability, good wear resistance, fatigue resistance and excellent mechanical properties, [11–24] For instance, single-phase CrMnFeCoNi alloy displays tensile strength levels of about 1 GPa, excellent ductility and exceptional fracture toughness [16]. Under ion irradiation, FeNiMnCr HEA possesses superior radiation resistance compared to conventional single phase Fe-Cr-Ni austenitic alloys such as stainless steels [17]. FeCoCrNiMo$_{0.23}$ HEA exhibits excellent combination of strength and ductility (784 MPa ultimate tensile strength and over 50% elongation) and the NbTaTiV refractory HEA exhibits the high yield strength and ductility at both room and high temperatures [18, 19]. Characterization on the
Co1.5CrFeNi1.5Ti0.5Mo, alloys in aqueous solutions of H2SO4 and NaOH reveals that the corrosion resistance of the Mo-free alloy is superior to that of the Mo-containing alloys [20]. The addition Al content of AlxCoCrFeNi high-entropy alloys in a 3.5 wt.% NaCl solution leads to increased volume fraction of Cr-depleted phase, and decreased localized corrosion resistance [21]. The two-phase AlxCoCrCuFeNi HEA has a decent fatigue endurance limit (383 ± 71 MPa) and exhibits a greater and faster-growing plastic zone at 200 °C than that at room temperature [22–24]. Complex magnetic behavior [25] and superconductivity [26] were also found in some HEAs. In a word, HEAs have attracted great interest in the past decade because of their promising properties and potential applications.

Recent advances in HEAs include the preparation of HEA nanoparticles containing eight elements [27], phase transition mechanism from γ′/α to ε phase [28], enhanced performances through surface coating [29], new applications such as hydrogen storage [30], etc. Meanwhile, studies in HEAs were extended to non-equiatomic compositions with a wide design window by rationally changing HEA compositions. For instance, Kupczyk et al [31] investigated the microstructure and magnetic ordering of rapidly quenched amorphous Fe70-xCo10MnxB15 alloys of x = 0, 0.25, 0.5, 1.0 and 2.0. Fazakas et al [32] reported the effect of Fe content on the structures and mechanical properties of Alx2Ti25Ni25Cu25 and (AlTi)60-xNi20Cu25Fe4 (x = 15 and 20) alloys, and found that Al22.5Ti22.5Ni25Cu25Fe15 alloy shows considerably high strength and relatively homogeneous deformation under compression.

Due to their similar atomic attributes, elements Co, Cr, Fe and Ni are usually chosen as the matrix of HEAs. Extensive research has been conducted for CoCrFeNi-based HEAs. Jiang et al [33] studied the effects of Ta content changes on the microstructure and mechanical properties of CoCrFeNiTa100-xMox alloys, (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.75) alloys and found that the alloy of x = 0.4 possesses yield strength up to 1.3 GPa, fracture strength of 2.3 GPa and plastic strain of 22.6%. Chen et al [34] investigated the microstructure, phase transformation and mechanical properties of (CoCrCuFeNi)x100-xMox and (AlCoCrFeNi)y100-xNi10 alloys, and found that the compressive yield strength of the former and the compressive fracture strain of the latter increase with Mo and Ni contents, respectively. Liu et al [35] studied the Al0.8FeCoCrNiTi0.2 HEA with different Al contents in supercritical water and found that it has better corrosion resistance than HR3C heat-resistant steel.

The six-component AlCoCrFeNiTi solid solution has attracted attention [5, 36–41] since 2007. Zhou et al [5] showed that the AlCoCrFeNiTi10 alloys system has good comprehensive mechanical properties, especially for AlCoCrFeNiTi0.5, with a compressive yield strength of 2.26 GPa and a compressive ductility of 23%. Chuang et al [36] designed a series of AlxCo1.5CrFeNi1.5Ti alloys with different Al and Ti contents, and found good wear resistance for Co1.5CrFeNi1.5Ti and Al0.2Co1.5CrFeNi1.5Ti. Jiang et al [37] studied the microstructure, mechanical properties and corrosion resistance of multi-component AlxFeCoCrNiTi1-x-y alloys with different Al and Ti contents, identifying good comprehensive mechanical properties for Al0.4FeCoCrNiTi0.2 and good corrosion resistance for Al0.3FeCoCrNiTi0.2 in sulfuric acid solution. It has been found that the addition of Al and Ti has considerable effect on promoting the hardness and mechanical properties of CoCrFeNi matrix.

Although many studies have been conducted for the six-component AlCoCrFeNiTi alloys, knowledge on their microstructures and their relationship with performances is still scarce. Due to difficulties in preparation, only several separated samples have been characterized for the six-component HEAs. Computational study provides a helpful tool for constructing the microstructures and predicting their properties. In fact, a number of computational studies [42–55] have been successfully performed to investigate the alloy systems. For example, Wang et al [45] investigated the effects of Mn and Al addition on the structural stability and magnetic properties of FeCoNi-based alloys. Li et al [52] studied the equilibrium properties and elastic properties of single bcc solid solution AlxHf1-xNbTaTiZr alloys. Tian et al [53] studied the mechanical and thermal properties of NiCoFeCrAl alloys and Zhang et al [34, 55] studied the elastic properties, lattice stability and magnetic transition temperature of AlxCrMnFeCoNi HEA. In this work we conducted extensive search for the stable structures of AlxCoCrFeNiTi10 alloys and explored the thermodynamic and mechanical properties of the identified structures by means of first-principles calculations. Understanding to the correlation between their structures and properties would be useful for the design and preparation of AlCoCrFeNiTi HEAs with target performances. Our calculations not only reproduced some experimental observations, but also suggested that computations could be helpful in predicting the structural, thermodynamic and mechanical properties of multi-component alloy systems.

2. Computational method

Because of tremendous combinations of elements and atomic locations in the lattice structures, identification of the stable structures of multi-component systems is a challenging job. Two strategies, coherent potential approximation (CPA) [56] and special quasi-random structure (SQS) [57], have so far been proposed to locate the structures for the multi-component alloys. Both strategies have found successful applications in
computational studies for alloy systems [42–55]. To study the chemical environment of atoms in the 
AlCoCrFeNiTi systems, the SQS method combined with first-principles calculations were applied in this work. 
Such approach has been successfully applied for some other HEAs [42–50].

The SQS approach simulates the disordered state of a limited supercell by optimizing the atomic distribution 
and minimizing the correlation function. To generate the initial structures, the named mcsqs algorithm in the 
ATAT package [38, 39] was employed. The supercell size for the SQS screening is usually dependent on three 
conditions: ensuring chemical disorder as good as possible, matching experimental composition, and 
computationally efficient [49, 50]. Screening the best SQS structure from the numerous candidates of a six-
component alloy system is a computationally demanding job. One can hardly figure out the SQS structures for 
these systems with completely random atomic distribution. In our computations, the screening process was 
interrupted when the best SQS structure did not change on the list after a long period of time (>100 h). 
The screening process was repeated at least ten times for each composition. Each run we obtained one structure with 
a reasonably low correlation factor, which was defined in mcsqs for measuring the randomness of atomic 
distribution. Consequently, a family of more than ten candidate structures was generated for a given 
composition. Seven families of candidate structures were then generated for the seven compositions of 
Al1-xCoCrFeNiTi alloy systems, the SQS method combined with 

\[ V_{total} = \sum_{i=1}^{n} E_i c_i \]

where \( c_i \) and \( e_i \) are the concentration and number of valence electrons of atom \( i \) in the cell. Formation energy 
\( (\Delta E_f) \) of the HEA structures is calculated by

\[ \Delta E_f = \left( E_{total} - \sum_i x E_i \right) / N \]

where \( E_{total} \) is the energy of the SQS structure optimized at the first-principles level, \( N \) is atom number of SQS cell and \( x \) is the number of atoms of element \( i \) in the SQS structure. \( E_i \) is the energy of element \( i \), which was obtained from the computations on its most stable phase at the same level. The elastic properties were carried out for 
Al1-xCoCrFeNiTi1 structures which based on the analysis of the total energies of properly strained states of the 
material [56, 64, 65]. Although atoms are on the fcc (or bcc) lattice, the chemical distribution in small SQS cells may lead to an anisotropic environment and scattering elastic constants. To overcome this problem, an 
averaging scheme [30] was proposed to obtain the \( C_{11}, C_{12}, \) and \( C_{44} \) parameters for the small SQS cubic 
structures: \( C_{11} = (c_{11} + c_{22} + c_{33})/3, C_{12} = (c_{12} + c_{23} + c_{13})/3, \) and \( C_{44} = (c_{44} + c_{55} + c_{66})/3 \) in which \( c_{ij} \) \( c_{ij} \) are computed elastic constants. The mechanical properties can be obtained with the elastic constants and the 
Voigt Reuss (V-R) average method [56, 66]. The bulk modulus (B) is evaluated with 

\[ B = (C_{11} + C_{12})/3 \]

The shear modulus (G) is given by the upper and lower (G_{V}) bounds, which are evaluated with

\[ G_V = (C_{11} - C_{12} + 3C_{44})/5 \]

\[ G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \]

G is estimated as \( (G_V + G_R)/2 \), according to Hill averaging method [56, 67]. Young’s modulus (E) is derived from B and G by:

\[ E = \frac{B(3B - 2G)}{2(3G - B)} \]
Finally, first-principles phonon method was applied to predict the phonon density of states (PHDOSs), vibrational entropy ($\Delta S_{vib}$) and heat capacity at constant volume ($C_v$).

### 3. Results and discussion

#### 3.1. Structural stability

Table 1 presents the lattice constants and $VEC$ of the Al$_x$CoCrFeNiTi$_{1-x}$ alloys.

| $x$ | Cal. (bcc) | Exp. | Cal. (fcc) | Exp. | $VEC$ |
|-----|------------|------|------------|------|-------|
| 1.0 | 2.852      | 2.870 [37] | 3.589      | —    | 7.20  |
| 0.8 | 2.861      | 2.880 [37] | 3.592      | 3.600 [37] | 7.24  |
| 0.6 | 2.862      | —      | 3.591      | —    | 7.28  |
| 0.5 | 2.867      | 2.880 [37] | 3.602      | 3.590 [37] | 7.30  |
| 0.4 | 2.869      | —      | 3.593      | —    | 7.32  |
| 0.2 | 2.878      | —      | 3.603      | —    | 7.36  |
| 0.0 | 2.879      | —      | 3.596      | 3.589 [41] | 7.40  |

![Figure 1. Total pair distribution functions of the DFT-relaxed fcc (a) and bcc (b) structures. $x$ represents the Al content in Al$_x$CoCrFeNiTi$_{1-x}$ alloys.](image)

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

(5)

Finally, first-principles phonon method was applied to predict the phonon density of states (PHDOSs), vibrational entropy $(\Delta S_{vib})$ and heat capacity at constant volume ($C_v$).

#### Table 1. Lattice constants (Å) and valence electron concentration (VEC) of the Al$_x$CoCrFeNiTi$_{1-x}$ alloys.

The total pair distribution function (PDF) is often used to analyze atomistic structures of amorphous systems. It measures the number of atoms around a given atom as a function of distance ($r$). The details of $g(r)$ evaluation is given in the supplementary material. Figure 1 shows the total PDF of the fourteen studied Al$_x$CoCrFeNiTi$_{1-x}$ structures. There are several sharp peaks at $r < 7$ Å, which implies ordered structures adopted by the atoms at short distances. The $g(r)$ approaches to 1 when $r > 7$ Å, indicating disordered structures in the systems at long distances. The disordering of solid solutions is well addressed in the structures identified by the SQS-DFT method.
Figures 2(a) and (b) show the dependence of the formation energies $\Delta E_f$ per atom on the fraction of the alloying element Al. One may note that some structures have a tendency to decompose and transform into their neighbors. The $\text{Al}_{x}\text{CoCrFeNiTi}_{1-x}$ alloys may adopt bcc or fcc lattice, or their mixture, depending on the Al and Ti contents. For both the fcc and bcc phases, their $\Delta E_f$ are negative for all the calculated x values. This means that the studied alloys are stable at the studied concentrations. The relative stability of the alloys with a given composition is measured with their energy difference ($\Delta E$) between the bcc and fcc phases, i.e., $\Delta E = (E_{\text{bcc}} - E_{\text{fcc}})/N$, as shown in figure 2(c). A positive $\Delta E$ implies a stable fcc structure, and vice versa. $\Delta E$ changes from negative to positive when the Al content decreases from 1.0 to 0.0. The bcc structure is more stable than the corresponding fcc one for $x = 0.5$–1.0, and the fcc structure becomes more stable for $x = 0.0$–0.4. Our calculations predict a phase transition from bcc to fcc with Ti addition and Al reduction. Several experiments have focused on the microstructures of AlCoCrFeNi systems, confirming that the alloys form bcc solid solutions at high Al concentration, and are fcc dominant at low Al concentration. Liu et al. [35] found the $\text{Al}_{x}\text{CoCrFeNi}$ alloys form fcc solid solutions when $x = 0.15$ and 0.4. Zhou et al. [5] reported that the $\text{AlCoCrFeNiTi}_x$ alloys are composed mainly of bcc solid solution regardless of varying Ti content of $x = 0$, 0.5, 1 and 1.5. A single bcc phase was also identified for NiCoCrFeAl by Li et al. [68]. Butler and Weaver [69] found that the dominant structure of the low Al concentration HEAs is fcc, while the high Al concentration HEAs are bcc dominant, and the structural transition point is at $\sim 15$ at%. Wang et al. [70] found that $\text{Al}_{x}\text{CoCrFeNi}$ alloys form fcc structures for $x = 0.0$–0.3, bcc structures for $x = 0.9$–1.2, and mixed structures of fcc and bcc for $x = 0.5$–0.7. Jiang et al. [37] reported that $\text{Al}_{x}\text{CoCrFeNiTi}_{1-x}$ alloys form bcc solid solution when $x = 1.0$, mixed bcc and fcc when $x = 0.8$ and 0.5. A decrease of bcc volume and an increase of fcc volume were observed when $x$ changes from 0.8 to 0.5. Moreover, the fcc or bcc content varies with temperature, annealing process, etc [70, 71]. Our calculations reproduced the phase transition from bcc to fcc for the $\text{Al}_{x}\text{CoCrFeNiTi}_{1-x}$ alloys when Al content decreases. The predicted transition point is at about $x = 0.4$, corresponding to Al concentration of about 8 at%.

3.2. Thermodynamic properties

The phonon density of states (PHDOSs) of the identified bcc and fcc structures were given in Fig. S1 in the supplementary material. No imaginary frequencies were noted for all the structures, verifying that the studied
structures were local minima on the potential energy surfaces. In addition, the PHDOS was used to calculate heat capacity, $C_v$, as a function of temperature, as presented in figure 3. $C_v$ varies with temperature in a similar way for the fcc and bcc alloys regardless of their compositions and structures. It increases rapidly at low temperature ($<150$ K). The increase slows down between 150 – 400 K, and the $C_v$ approaches to 25 J K$^{-1}$·mol above 400 K. The computed results indicate that the contribution of each atom to $C_v$ is basically the same at the same temperature. At a sufficiently low temperature (near 0 K) under which the total heat capacity is mainly contributed by free electrons for conductors, $C_v$ approaches to 0 and is proportional to $T$. With increasing temperature, the contribution from phonon vibrations increases. For temperature below 400 K, both phonon vibrations and free electrons have considerable contribution to $C_v$. At high temperature, contributions from free electrons becomes neglectable compared to those from phonon vibrations. $C_v$ is then dominated by phonon vibration contribution, which is approximately a constant of 25 J K$^{-1}$·mol at a temperature well above the namely Debye temperature. Our calculations match well with the empirical Dulong-Petit Model [72] and the quantum Debye Model [73].

The calculated vibration entropy $\Delta S_{vib}$ and configurational entropy $\Delta S_{con}$ at 300 K of the studied alloys are listed in table 2. $\Delta S_{con}$ is evaluated from the number of configurations in the systems, as given in the supplementary material. Both $\Delta S_{con}$ and $\Delta S_{vib}$ values are positive, implying that the formation of the alloys is a process of entropy increment. The magnitudes of $\Delta S_{con}$ of Al$_x$CoCrFeNiTi$_{1-x}$ alloys are in line with the quantitative criterion for solid solutions formation, $\Delta S_{con} > 13.38$ J K$^{-1}$·mol [3]. A large entropy change in both

![Figure 3. Heat capacity at constant volume for the fcc (top) and bcc (bottom) structures. $x$ represents the Al content in Al$_x$CoCrFeNiTi$_{1-x}$ alloys.](image)

| $x$ | Bcc | Fcc | $\Delta S_{con}$ (J K$^{-1}$·mol) |
|-----|-----|-----|----------------------------------|
| 1.0 | 1.71| 1.79| 13.38                           |
| 0.8 | 1.93| 2.21| 14.21                           |
| 0.6 | 1.86| 2.15| 14.50                           |
| 0.5 | 3.30| 3.21| 14.53                           |
| 0.4 | 4.56| 4.12| 14.50                           |
| 0.2 | 2.75| 2.42| 14.21                           |
| 0.0 | 2.72| 2.60| 13.38                           |
configuration and vibrational entropy promotes the extent of confusion in alloys and the reduction of Gibbs free energy, favoring the random distribution of different elements in crystal lattice [74]. The $\Delta S_{\text{con}}$ reaches maximum at $x = 0.5$, which provides the largest number of configurations in the systems. $\Delta S_{\text{vib}}$ was computed based on the phonon frequencies at the first-principles level. As shown in figure 4, $\Delta S_{\text{vib}}$ increases with temperature, implying that its contribution to the HEA stability increases at high temperature. Moreover, $\Delta S_{\text{vib}}$ varies with composition. For both phases, the structures of $x = 0.4$ have the largest $\Delta S_{\text{vib}}$ values. The differences in $\Delta S_{\text{vib}}$ for the structures with different compositions are small at low temperature, increase with temperature, and become almost unchanged for temperature over 300–1000 K, reaching at about 3.3 J K$^{-1}$ mol$^{-1}$. At 300 K, the magnitudes of $\Delta S_{\text{vib}}$ are much smaller than those of $\Delta S_{\text{con}}$, as presented in table 2. Although $\Delta S_{\text{vib}}$ becomes greater at high temperature, its contribution to total entropy is still smaller than the $\Delta S_{\text{con}}$ counterpart. Moreover, the $\Delta S_{\text{vib}}$ values in fcc and bcc have similar composition dependence, indicating that $\Delta S_{\text{vib}}$ is sensitive to composition rather than phase structure.

### 3.3. Mechanical properties

Table 3 presents the averaged elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$, which are defined above, of the fcc and bcc structures. The computed elastic constants for all the studied structures satisfy the dynamical stability conditions of the fcc and bcc lattice structures, i.e., $C_{44} > 0, C_{11} > |C_{12}|$ and $C_{11} + 2C_{12} > 0$ [75]. For the structures with the same compositions, their elastic constants are different for the fcc and bcc ones. Some components, for example, $C_{11}$ of $x = 0.6$ and $C_{44}$ of $x = 0.2$, differ remarkably in the two phases. In the same phase, fcc or bcc, the elastic constants are different either for the structures with different compositions. For example, $C_{11}$ of the bcc structures varies between 251 and 336 GPa for $x = 0–1$. Therefore, the elastic constants of Al$_x$CoCrFeNiTi$_{1-x}$ alloys vary with their phase structures and compositions. Their Cauchy pressure ($\Gamma$) and Zener ratio ($A_z$) are also given in table 3. Positive $\Gamma$ is a characteristic of ductile alloys, while negative $\Gamma$ is a definitive signature of brittle alloys [76]. All the studied structures have positive $\Gamma$, indicating that they are ductile regardless of phase structures and Al/Ti contents. $A_z$ is used to predict the elastic anisotropy of materials. $A_z = 1$ represents completely elastic isotropy, and its deviation from 1 measures the degree of elastic anisotropy [52, 77]. The predicted $A_z$ values of all the structures are well above 1, verifying the anisotropic distribution of atoms in the lattice framework, as noted in the SQS structures in table S1.

Using the computed elastic constants, we further evaluated the shear modulus $G$, Young’s modulus $E$, bulk modulus $B$, and Pugh ratio $B/G$ of the Al$_x$CoCrFeNiTi$_{1-x}$ alloys, as shown in figure 5. The computed $B$, $E$ and $G$ values (181, 206 and 79 GPa for the bcc structures, and 189, 223, 85 GPa for the fcc structures) are in agreement with previous computations (78, 204 and 78 for bcc, and 183, 201 and 76 GPa for fcc) [53]. Generally, on one hand, most of the studied alloys possess good mechanical properties. The magnitudes of $G$, $E$ and $B$ vary around 80, 220, 190 GPa, respectively. On the other hand, the $G$, $E$ and $B$ values are dependent on the phase structure and
composition. For most of the structures, the introduction of Al and Ti promotes their mechanical properties. As discussed above, the alloys prefer the \textit{bcc} lattice to the \textit{fcc} one at high Al content. For the \textit{bcc} structures, $B$, $E$ and $G$ increase first and then decrease with the Ti addition and Al reduction. The turnover occurs at about $x = 0.6$ and the alloys of $x = 0.8$ and 0.6 were predicted to possess good mechanical performances. Our predictions basically comply with previous experiments \cite{5, 37}. For example, Zhou \textit{et al} \cite{5} observed that the AlCoCrFeNiTi$_{1-x}$ alloys system have good comprehensive mechanical properties, especially for $x = 0.5$. Jiang \textit{et al} \cite{37} found that among Al$_x$FeCoCrNiTi$_{1-x}$ ($x = 1.0, 0.8$ and 0.5) alloys the composition of $x = 0.8$ exhibits good comprehensive mechanical properties. Room-temperature mechanical properties have been reported for CoCrFeNiTiAl$_x$ ($x = 0, 0.5, 1.0$ and 2.0) alloys among which good performances were found at $x = 1.0$ \cite{40}. Wang \textit{et al} \cite{41} also found that AlCoCrFeNiTi$_{0.5}$ in which Al content is about 18 at\% exhibits the highest Vickers hardness. For the studied \textit{fcc} structures, which are favored at low Al content, their computed $G$, $E$ and $B$ values increase with Al addition and Ti reduction at low Al content, and reach the largest values at about $x = 0.5$. For both the \textit{bcc} and \textit{fcc} structures, their Pugh ratios ($B/G$) is larger than the critical value 1.75, indicating that the
studied Al_{x}CoCrFeNiTi_{1-x} alloys are ductile. This is consistent with the above prediction indicated by Cauchy pressure and with previous observation [52, 76, 77].

Good comprehensive mechanical performances were predicted in our computations for these alloys, especially for $x = 0.6$ for the bcc structures and $x = 0.5$ for the fcc structures. To further correlate their performances with their microstructures, the local electron localization function (ELF) on the (100) facets for the bcc structures of $x = 1.0$ and $0.6$, and for the fcc structures of $x = 0.0$ and 0.5 were given in figure 6. ELF is in general used to analyze interatomic interaction in crystal. ELF = 0 and 1 corresponds to a completely delocalized state and a perfect localized state, respectively [43]. For the studied alloys, their ELF values are less than 0.5, representing a delocalized state of electrons. One notes in figure 6 that Al atom has a great tendency to localize electrons around it. In the bcc structure of $x = 1.0$, the Al atom has the strongest electron localization. The strong localization is weakened in the bcc structure of $x = 0.6$ in which two Al atoms sit together in presence of the neighboring Ti atom. In the fcc structure of $x = 0$, electron delocalization is dominant in absence of Al atoms. The delocalization is also weakened in the fcc structure of $x = 0.5$. The addition/reduction of Al atoms into/from the systems makes the electron localization/delocalization at an appropriate degree that differs from the $x = 0$ or $x = 1$ systems.

Finally, it should be mentioned that the above analysis is based on the SQS structures, which represent a possible distribution of atoms in the bcc or fcc lattice at a given composition. This distribution has the highly disordering atomic arrangement characterized within a reasonable period of computing time. Other distributions of atoms in the lattice may also exist and have to some extent different properties. The characterization of all these possible structures are extremely challenging for multi-component alloys. Although other disordered structures may also have influences on the HEAs, our calculations shed light on the variations of microstructures, thermodynamic and mechanical properties of the Al_{x}CoCrFeNiTi_{1-x} alloys with their compositions, and established the correlation of our computations with other experimental studies.

4. Conclusion

Stimulated by the good comprehensive mechanical performances of six-component AlCoCrFeNiTi alloys, computational characterizations on the microstructures, thermodynamic and mechanical properties of Al_{x}CoCrFeNiTi_{1-x} ($x = 0$–1.0) alloys were carried out by using the combined SQS and DFT approach. The disordered distributions of atoms in bcc and fcc lattices at a given composition were generated with SQS and then sent to further characterization at the DFT level with the PBE functional and PAW potential. First-principles phonon method was applied to predict the phonon density of states, vibrational entropy and heat capacity. All the identified structures were verified to be local minima on the potential energy surfaces and characterized by their disordered atomic distributions that are reflected by their pair distribution functions. The predicted lattice constants are in good agreement with the measurements. By computing their formation energies, the relative
stability of the bcc and fcc structures was compared. The bcc structures are more stable at high Al content, while the fcc structures are more stable at low Al content. The observed phase transition from bcc to fcc with Al reduction was reproduced in our calculations. The predicted transition point is at the Al content of about 8 at%. The heat capacity and its temperature dependence over the range of 0–1000 K were evaluated based on the computed phonon density of states. All the studied structures exhibit similar temperature dependence regardless of their phase structures and compositions. The predicted temperature dependence is in agreement with the prediction from the Dulong–Petit model and the Debye model. The computed vibrational entropy increases with temperature, but is much smaller than its configurational counterpart. The elastic constants and elastic moduli vary with the phase structures and compositions. The Zener ratio and Cauchy pressure indicate that the studied structures are anisotropy and have good ductility. The computed B, E and G values, which are in agreement with previous available computations, imply that these alloys possess good comprehensive mechanical performances. Moreover, these moduli vary with composition and phase structure. Promoted mechanical properties were predicted at x = 0.8 and 0.6 for the bcc structures and x = 0.5 for the fcc structures. Electron localization function analysis revealed that the addition/reduction of Al atoms from the systems alters the degree of electron localization/delocalization and consequently alters the interatomic interaction in the alloy systems. Although only some representatives of AlCoCrFeNiTi1−x alloys were investigated in this work, our calculations shed light on the variations of microstructures, thermodynamic and mechanical properties of the with their compositions, and established the correlation of our computations with other experimental studies, which would be helpful for the design and preparation of AlCoCrFeNiTi1−x alloys with promoted performances.

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