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Quantitative determination of the lattice constant in high entropy alloys

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ABSTRACT

The variation of the lattice constant with alloying elements is an essential issue in alloy design. In the traditional single-based alloys, there is a tremendous database for predicting the lattice constant. However, the traditional database is not suitable to the emerging multi-principal components alloys referred as high entropy alloys. Here, a framework is proposed to describe the variation of lattice constants in high entropy alloys. Based on the quantitative measurement of the lattice constants of fourteen alloys, we constructed the lattice constant database for concentrated CoCrFeNi alloys. The discrepancy between binary alloys and high entropy alloys revealed the atomic chemical interactions.

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As one of the most important physical parameters in crystalline materials, the lattice constant has been involved everywhere in the material science and engineering [1]. Simply, the thermal expansion can be exactly revealed from the temperature-dependent lattice constants [2]. Another case is the lattice distortion, playing a crucial role in material science [3]. Even in superconductivity, the lattice distortion is thought to be one of the most important factors in determining the transition temperature [4]. Furthermore, the lattice misfit of phase boundaries determines both the functional and mechanical behaviors of multiphase materials [5,6]. Therefore, the regulation of the lattice constant is very important in the material science and engineering.

It is a foundation work to understand and determine the variation of lattice constants from different aspects [1]. The investigations presented all main factors of size, valance, and electrochemical differences, as well as the relative sizes of ions and atoms in determining the lattice spacing of binary solutions. The Vegard's law is commonly used to describe the atomic size effect; while its invalidation has been confirmed with the main effect of valence-electron difference [7,8]. Extensive experiments have been done to determine the variation of lattice spacing in binary and some dilute ternary alloy systems.

Recently, the initiation of high entropy alloys (HEAs) stimulates numerous studies on the multi-principal component alloys [9]. The variation of the lattice constant in HEAs is very important in alloy design,

revealing the unique functional and mechanical behaviors. However, it is improper to simply extend the variation of lattice constants in binary alloys to HEAs. In HEAs, there is no single-element base, where the interactions of different elements in the lattice will make the variation of the lattice constants much more complicated. Up to now, there are only limited high resolution data of HEAs [10]. Most of XRD data in the numerical literatures needs careful calibrations for high precision. On the one hand, the different processes of rolling, quenching, solid solution treatments may cause significant errors. On the other hand, the low-accuracy XRD data cannot quantitatively reveal the lattice constant. A self-consistent high precision measurement is desired to reveal the variation of lattice constants. Usually, (311) peaks in FCC from an extreme low scanning rate could ensure the reproducibility of 0.00001 nm on lattice constant [1].

Besides the high precision measurement, the model for variation of lattice constant also needs to be evaluated. Traditionally, the lattice spacing of binary alloys can be described by

$$a = a_0 + \frac{da}{dc}c, \quad (1)$$

where a_0 is the lattice spacing of the pure metal of a solvent, c is the concentration of solute. In Vegard's law, $da/dc = a_s - a_0$, where a_s is the lattice spacing of the pure solute. Usually, da/dc is a constant in a finite range of small c even with the valence effect. As the development of metallic materials, the problem how to describe the lattice spacing in multicomponent system has emerged. For simplicity, it can be described in

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dilute alloys with different elements as

$$a = a_0 + \sum_{i=1}^{n-1} \frac{da}{dc_i} c_i, \quad (2)$$

where c_i is the concentration of i th solute, da/dc_i is the lattice change coefficient for the corresponding solute. In a dilute solution, da/dc_i is similar to that in the binary alloys. However, in the concentrated alloys of HEAs, the interactions between the solutes will make the da/dc_i deviates from that in the binary alloys. In HEAs, a new model is required to describe the variation of the lattice constants with alloying compositions. A phenomenological model has also been proposed to describe the lattice spacing variation in alloys [11],

$$s = \sum_{i=1}^n \sum_{j=1}^n c_i c_j s_{ij}, \quad (3)$$

where c_i and c_j are the atomic fractions of the components of i and j , s_{ij} is the spacing between the two adjacent atoms of components of i and j . It is obvious that the model has more coefficients than Eq. (2), so they can describe the experimental curves within a wide range of compositions. In binary alloys, Eq. (3) has two unknown parameters of s_{12} and s_{21} . In multicomponent alloys with n elements, there will be $n(n-1)$ parameters in Eq. (3). Even though, this model still does not consider the interaction between the different solutes; for instance, s_{12} is independent of other species.

In order to describe the atomic interactions in HEAs, one choice is to add more terms in Eq. (2), such as

$$a = a_0 + \sum_{i=1}^{n-1} \alpha_i c_i + \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \alpha_{ij} c_i c_j, \quad (4)$$

where α_{ij} is used to describe the interaction of elements of i and j . This method is basically an extension of the single-based alloys, and still has too many parameters for multicomponent alloys. In HEAs, the basic concept is a solid solution of multicomponent elements, not a single element again. Accordingly, we propose a choosing of multicomponent for reference and it can reveal the interactions between the different alloying elements. Based on this, the lattice parameter of HEAs can be described as

$$a = a_0 + \sum_{i=1}^{n-1} \frac{da}{d(c_i - c_0)} (c_i - c_0), \quad (5)$$

where a_0 is the lattice parameter of the reference HEA, $(c_i - c_0)$ is the derivation from the initial composition. Since the HEAs are located in the central region of their phase diagram, the differential $da/d(c_i - c_0)$ can be assumed as a constant in a finite range. The physical meaning of the model is how the lattice spacing changes as the one of the i th element substitute n th elements. Although Eqs. (2) and (5) have the similar form, the different references generate the different physical meanings. Moreover, the interactions between different elements could be revealed in Eq. (5) due to that the other elements will affect the variation of lattice spacing during the change of each element. Accordingly, in the local range of concentrated alloy composition, the $da/d(c_i - c_0)$ will be different from that in binary alloys. Additional advantage of Eq. (5) is the fewer unknown coefficients ($n-1$) compared with Eqs. (3) and (4).

In order to confirm the validity and efficiency of the proposed model, quantitative experiments are designed to find the useful coefficients for future applications. The equiatomic CoCrFeNi alloy is one of the most popular systems among HEAs. Fourteen alloys with different variations of each element are designed to investigate the change of lattice spacing in CoCrFeNi system. The alloys preparation and the detected compositions are listed in Ref. [12]. The as-cast samples were cold-rolled to

60% and recrystallized at 1200 °C for 5 min, and then water quenched to room temperature for lattice parameter measurements. The crystal structures were identified by X-ray diffractometer (XRD, Shimadzu, MAXima XRD-7000), using Cu K α radiation with a scanning rate of 5°/min.

Fig. 1 shows the XRD results. All the alloys are confirmed as FCC single solid solutions. The obvious shift of (311) peaks reveals the variation of lattice spacing in different alloys. The lattice parameters of the alloys can be accurately determined by using (311) peaks. For a higher

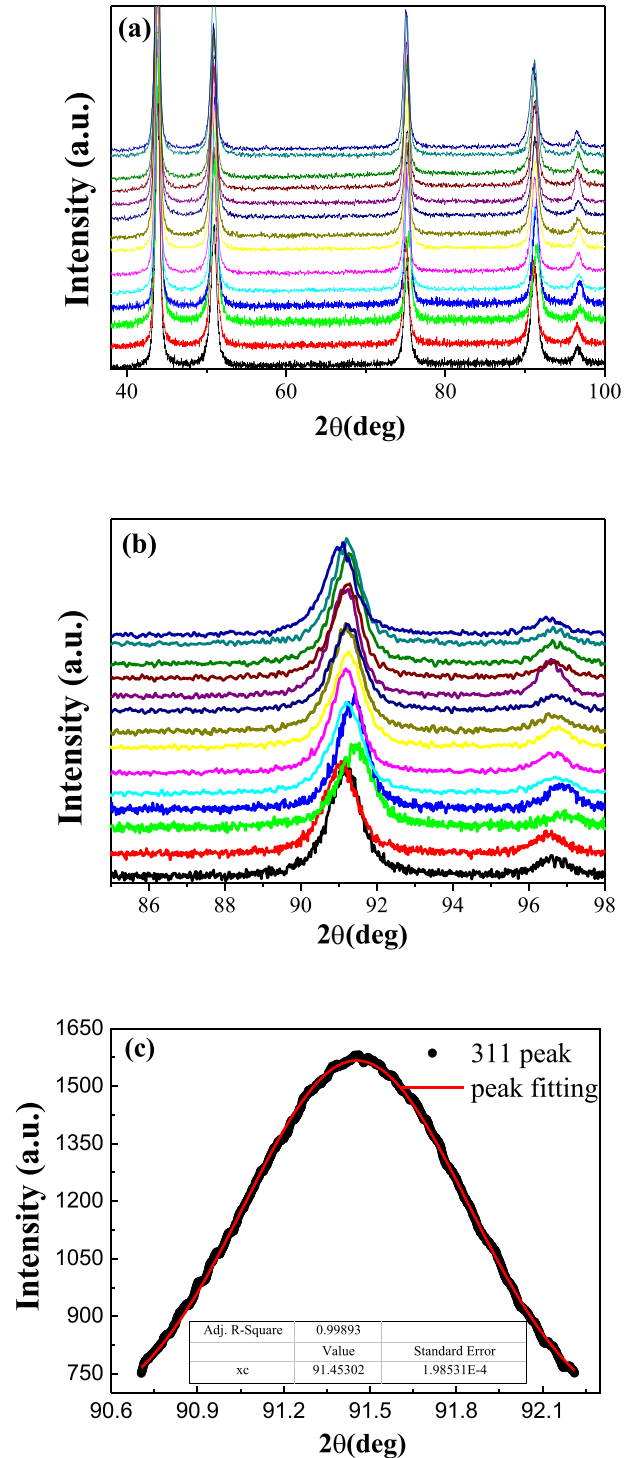


Fig. 1. The XRD results for lattice constant detection. (a) The overall XRD curves of fourteen CoCrFeNi based alloys. (b) The enlarged (311) peaks shows the shift of the peaks. (c) The high precision (311) peak and peak fitting results.

precision measurement, we further scan the sample from 90° to 92.5° with a scan rate of $0.09^\circ/\text{min}$. The increasing step of the angle is 0.001° while the precision of the protractor on the X-ray diffractometer is 0.0001° . In the determination of the (311) peaks, the fitting of the peak shows that the error of 2θ is $\delta 2\theta < 0.0005$, as shown in Fig. 1(c). Combining the errors from the fitting and the increasing step of the angle in the measurement, the error $\delta\theta$ is smaller than 0.001. The lattice constant is calculated by

$$a = \frac{\lambda\sqrt{11}}{2} \frac{1}{\sin\theta}, \quad (6)$$

where λ is 0.104056 nm for the X-radiation wavelengths of Cu $K\alpha_1$, θ is around 45.56° for the Bragg angle of (311) peaks. Then the error estimation of the lattice constant for (311) peaks is

$$\delta a = a\theta - \delta\theta - a\theta + \delta\theta < 0.00002\text{nm}, \quad (7)$$

which is consistent with the high precision lattice spacing measurement [1]. The calculated lattice constants are shown in Fig. 2 (listed in Table 1). The high precision measurement can distinguish the variation of lattice constants caused by a small change of the alloying composition. The error of the lattice constant from the measurement is very small.

In the quaternary alloys, Eq. (5) gives

$$a = a_0 + \alpha_{\text{Co}}(C_{\text{Co}} - C_{\text{Co}0}) + \alpha_{\text{Cr}}(C_{\text{Cr}} - C_{\text{Cr}0}) + \alpha_{\text{Fe}}(C_{\text{Fe}} - C_{\text{Fe}0}), \quad (8)$$

where $\alpha_i = da/d(C_i - C_0)$. By choosing the equiatomic alloy as the reference, the data in Table 1 give the coefficients in Eq. (8) by regression analysis with the linear least square method, where the real alloy compositions detected from EDS in SEM are used. The results show $\alpha_{\text{Co}} = -0.18304 \times 10^{-4} \text{ nm/at.}\%$, $\alpha_{\text{Cr}} = 1.06905 \times 10^{-4} \text{ nm/at.}\%$, $\alpha_{\text{Fe}} = 0.54192 \times 10^{-4} \text{ nm/at.}\%$ with the correlation coefficient of 0.9411. The lattice parameters predicted by Eq. (8) from regression coefficients are also shown in Fig. 2. The predictions are strongly correlated with the experimental measurements. The maximum difference is only 0.0003 nm.

The ab-initio method is further used to calculate the variation of lattice constants with the change of alloying compositions. The first-principles calculations were performed using the Vienna ab initio Simulation (VASP) Package. Projector augmented wave (PAW) potential [13] was used to describe the electron-ion interactions, and the generalized gradient approximation (GGA) [14] was applied to describe the electronic exchange and correlation. For each composition, the supercells with $3 \times 3 \times 5$ fcc unit cells were applied, all of the atoms are randomly distributed across the lattice sites. The energy cutoff for the plane-wave

Table 1

The lattice constants of a series of CoCrFeNi alloys, the subscript in nominal composition represents the atomic ratio of elements.

Alloy number	Alloy nominal composition	2θ deg (311)	Lattice constant (nm)	Error (nm)
1	CoCrFeNi	91.168	0.35767	$3.05828\text{E}-6$
2	CoCrFe ₂ Ni	91.050	0.35803	$3.06768\text{E}-6$
3	Co ₂ CrFeNi	91.453	0.35680	$3.03571\text{E}-6$
4	CoCrFeNi ₂	91.359	0.35708	$3.04313\text{E}-6$
5	Co ₁₇ Cr ₁₃ Fe ₁₇ Ni ₁₃	91.219	0.35751	$3.05423\text{E}-6$
6	Co ₁₃ Cr ₁₃ Fe ₁₇ Ni ₁₇	91.215	0.35752	$3.05454\text{E}-6$
7	Co ₁₇ Cr ₁₃ Fe ₁₃ Ni ₁₇	91.322	0.35720	$3.04606\text{E}-6$
8	Co ₄ Cr ₃ Fe ₄ Ni ₄	91.289	0.35730	$3.04867\text{E}-6$
9	Co ₃ Cr ₂ Fe ₃ Ni ₂	91.253	0.35741	$3.05153\text{E}-6$
10	Co ₂ Cr ₂ Fe ₃ Ni ₃	91.194	0.35759	$3.05621\text{E}-6$
11	Co ₁₃ Cr ₉ Fe ₉ Ni ₉	91.374	0.35704	$3.04195\text{E}-6$
12	Co ₃ Cr ₂ Fe ₂ Ni ₃	91.404	0.35695	$3.03958\text{E}-6$
13	Co ₉ Cr ₉ Fe ₉ Ni ₁₃	91.265	0.35737	$3.05058\text{E}-6$
14	Co ₉ Cr ₉ Fe ₁₃ Ni ₉	91.075	0.35795	$3.06569\text{E}-6$

basis set was set to be 500 eV, and the reciprocal space was sampled by using the Monkhorst-Pack grids [15]. All calculations were performed with spin-polarization. Equilibrium cell volumes and all internal atomic positions of the supercells were fully relaxed until convergence with the total energy tolerance of 10^{-5} eV. The ab initio calculated results are shown in Fig. 3. The calculated lattice parameter is fixed at 0 K, and smaller than the measured data at ambient temperature. However, the change of lattice constant with compositions has the same trend. We further use Eq. (8) to predict the variation of lattice constants with regression coefficients from experiment data. The predictions are very close to the ab initial calculation results. It should be noted that the coefficients in Eq. (8) may be varied with temperatures due to the different thermal expansion coefficients. Here we just use the coefficients at ambient temperature to predict the variation of lattice constants at 0 K for comparison with the ab initial calculation results.

The variation of lattice constants in the experiments and ab initial calculations indicates that the Co has a minor effect on the lattice spacing in the concentrated CoCrFeNi alloys by substituting Ni. The Cr and Fe will significantly increase the lattice spacing by substituting Ni and the Cr is the best one to increase the lattice parameter. Previously, the lattice distortion in HEAs is only discussed by considering the atomic size effects [16,17]. Apparently, the Co has the largest radius in the four elements based on previous reported data [18]. However, the Co has the smallest impact on the lattice constant of the concentrated alloys, and even decreases the lattice constant. The derivation from the hard sphere

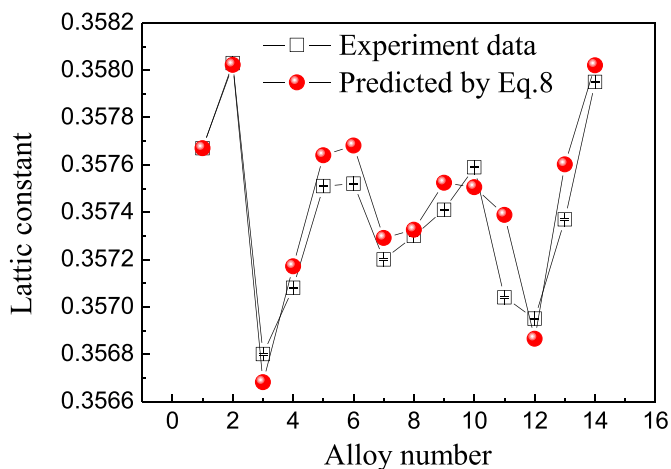


Fig. 2. The comparison of prediction from regression analyses and the experimental results.

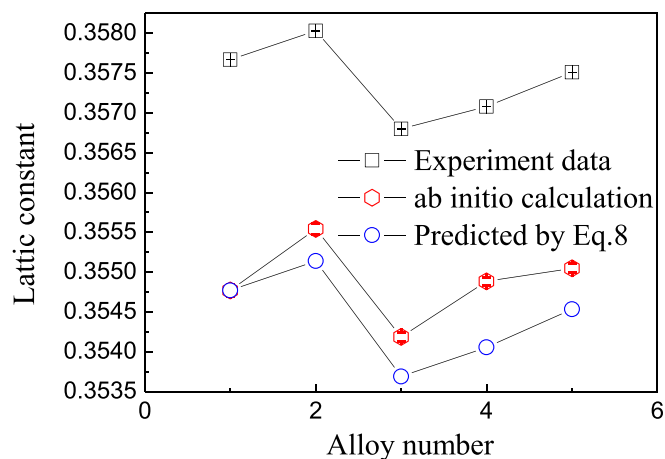


Fig. 3. The change of lattice constant with compositions from ab initio calculation. The experimental results and predictions from regression coefficients are presented for comparison.

packing may come from the chemical interaction of different elements [7].

In HEAs, with interactions between different elements, the variation of lattice constants in HEAs will be different from that in binary alloys. Fig. 4 shows the difference of the coefficients from binary alloys and HEAs. In the Ni–Co, Ni–Cr and Ni–Fe binary alloys, the da/dc are 0.17×10^{-4} , 1.07×10^{-4} and 1.29×10^{-4} nm/at.%, respectively [1,6,10]. In HEAs, $\alpha_{Co} = -0.18304 \times 10^{-4}$, $\alpha_{Cr} = 1.06905 \times 10^{-4}$, $\alpha_{Fe} = 0.54192 \times 10^{-4}$ nm/at.%. These differences are from element interactions in the concentrated alloys. The lattice parameter of CoCrFeNi is larger than that of pure Ni, but smaller than the calculation from the binary effect of Eq. (2). It means that there are extra interactions between these four elements in the concentrated alloys, as compared with the Ni-based binary alloys. By adding Cr as substitution of Ni in the HEAs, some of the Ni–Co, Ni–Fe bonds are substituted by Cr–Co, Cr–Fe bonds. In binary alloys, the increase of Cr–Ni bond contributes to the lattice dilation while in HEAs there are contributions from Cr–Co, Cr–Fe bonds. Therefore, the similar Cr effect in the CoCrFeNi and Ni-based binary alloys indicates that

$$(Cr \leftrightarrow Fe) \approx (Cr \leftrightarrow Co) \approx (Cr \leftrightarrow Ni) \quad (9)$$

$A \leftrightarrow B$ means the atomic bond of A and B elements. As for the Fe and Co elements, the mainly difference in HEAs and Ni-based binary alloys is from

$$(Fe \leftrightarrow Cr) > (Fe \leftrightarrow Ni), \quad (Co \leftrightarrow Cr) > (Co \leftrightarrow Ni) \quad (10)$$

Therefore, the increases of Co and Fe in the CoCrFeNi will cause a smaller effect on the expansion of lattice constants than that of Co and Fe in Ni-based binary alloys. The effects of Co–Co, Fe–Fe and Cr–Cr bonds in HEAs on the lattice constant are hidden in the coefficient of $da/d(c - c_0)$, and reveal that the atomic bonds of $(Cr \leftrightarrow Fe)$, $(Cr \leftrightarrow Co)$ and $(Cr \leftrightarrow Ni)$ are stronger than those of $(Co \leftrightarrow Ni)$ and $(Fe \leftrightarrow Ni)$. These results indicate that the Cr related short chemical range order may exist in the CoCrFeNi alloys at lower temperature. The Cr related short chemical range order has been predicted in CoCrNi by simulations [19].

Moreover, the quantitative information of lattice parameter is a very important factor in alloy design. Firstly, the variation of lattice parameters in solid solutions corresponds to the solid solution hardening determined by the lattice distortion. The results presented here show the Cr has the strongest lattice distortion effect, consistent with previous experiment results [20]. Secondly, the precipitation hardening HEAs are prosperous very recently, where the lattice misfit is a very important factor in strengthening and coarsening [21]. It is one of the core issues to adjust the lattice misfit in the design of advanced high performance

precipitation-hardening HEAs [22]. The prediction of lattice parameters in the solid solution matrix obtained here is helpful in designing high performance HEAs.

In conclusion, we proposed a model to describe the variation of lattice constants with constitution of alloying elements in HEAs. Quantitative measurement of the lattice constant in fourteen CoCrFeNi based alloys confirms the model of lattice variation. The change of lattice constants in the CoCrFeNi alloys deviates from the hard sphere packing model and the lattice change in binary alloys. The comparison shows a chemical effect on the lattice distortion and indicates the existence of a strong Cr-related short range chemical order. The model and the quantitative data of lattice spacing presented here is useful in the alloy design of HEAs.

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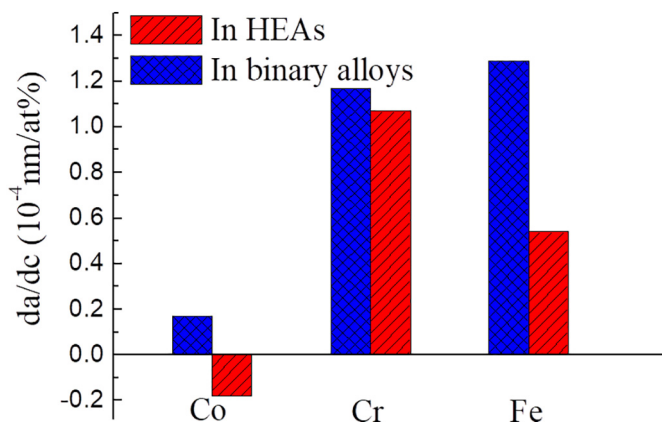


Fig. 4. The comparison of dilation coefficients of Co, Cr, Fe in the Ni-based binary alloys and CoCrFeNi alloys.