# HYBRID MOLECULAR DYNAMICS AND MONTE CARLO MODELING TO STUDY PHYSICAL-MECHANICAL PROPERTIES OF HIGH-ENTROPY ALLOY CoCrFeMnNi

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**Summary.** Structural and physical-mechanical properties of CoCrFeMnNi high-entropy alloys of different stoichiometric composition are investigated on the base of computer modeling. An approach based on the combined use of molecular dynamics and Monte Carlo methods was applied. This made it possible to obtain the thermodynamically equilibrium configurations of CoCrFeMnNi alloys at given fractions of chemical elements, temperature and pressure. Based on the obtained data set, the influence of the stoichiometric composition of CoCrFeMnNi high-entropy alloy on its structural characteristics (lattice parameter, radial distribution functions), phase stability (energy of different phases, configuration entropy) and physical-mechanical properties (Young's modulus and elastic limit) was investigated.

## 1 INTRODUCTION

The study of the structure, physical properties and behavior of high-entropy alloys (HEAs) under thermal and mechanical loading is one of the most actual topics of modern materials science [1]. This is due to the unique complex of HEA properties, which is largely determined by their multicomponent composition. Typically, these alloys consist of five or more elements. According to the thermodynamic considerations, in spite of the complex chemical composition, HEA can be a single-phase solid solution if the alloy elements are in equal ratios. This is also important for the formation of excellent properties of alloy. At the same time, many studies show that HEAs with non-equiatomic composition also remain stable and often have better properties [2]. Therefore, the search for new stoichiometric compositions of HEAs is an actual material science task [3]. The great success in high-throughput combinatorial materials research is achieved for wide variety of applications [4]. For example, making only one sample with compositional gradient allowed to study how the properties of a material change with a chemical composition. However, such approaches allow one to study a limited range of properties, and they are not yet well developed for HEAs. It should be noted that, along with laborious and costly experimental studies, computer modeling is an effective tool that allows one to quickly process large amounts of information and determine the optimal chemical composition of the material that meets the required properties. For example, on the basis of the computer algorithm

developed in [5] automated tuning of chemical composition of $Al_x$CrCoFeNi multicomponent alloys allowed increasing their ultimate tensile strength in molecular dynamics calculations. In the framework of Monte Carlo method and ab-initio modeling, the stability of different phases in the HfNbTaZr HEA was determined [6]. A theoretical approach on the base of phase diagram calculation allowed finding more than 150 single-phase compositions of HEAs with potentially high mechanical properties [7].

To date, CoCrFeMnNi is one of the most promising systems among HEAs, which is characterized by high physical and mechanical properties and has a great potential for their improvement [8, 9]. However, the atomic level insights into its high properties and the influence of stoichiometric composition on them are still not clear. In this connection, for better understanding of CoCrFeMnNi HEA properties, the application of theoretical and computational methods is required. It should be noted, that molecular dynamics method has significant advantages in the study of the atomic structure of metallic materials [10, 11]. It explicitly takes into account the discrete structure of a material and allows to track the evolution of atomic system under various kinds of external loading even in substantially non-equilibrium conditions [12–16]. Therefore, the objective of our work is to investigate the effect of stoichiometric composition on atomic structure, phase stability, physical and mechanical properties of CoCrFeMnNi high-entropy alloys by means of computer modeling.

## 2 COMPUTATIONAL MODEL

In order to investigate the properties of CoCrFeMnNi HEA we first prepared the samples with different stoichiometric compositions. They were the single crystals with fcc and bcc lattice having cubic shape and dimensions of $10 \times 10 \times 10$ lattice parameters. Axes of the samples were the [100], [010] and [001] directions in which periodic boundary conditions were applied. Initially atoms of different chemical elements were placed randomly into lattice sites according to specified fractions $C_i$ which were 0.1, 0.2, or 0.3. Additional requirement, coming from the definition of HEA [17], was that combination of these fractions would give value of configuration entropy $\Delta S_{\text{conf}} = -R \sum_{i=1}^{5} C_i \ln C_i$ higher than $1.5R$, where $R$ is gas constant. As a result, 43 stoichiometric compositions with different fractions of elements were chosen.

Computer calculations were carried out in LAMMPS software [18]. Dynamics was described for $N$ atoms by the system of $2N$ ordinary differential equations of motion:

$$\begin{cases} \dfrac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \mathbf{v}_i, \\ m_i \dfrac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} = -\dfrac{\partial U(\mathbf{r}_i, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_i}, \end{cases} \quad i = 1, \dots, N, \quad i \neq j, \tag{1}$$

where $i$, $\mathbf{r}_i$, $\mathbf{v}_i$, $m_i$ are the number, radius vector, velocity vector, and mass of atom $i$, correspond-

ingly. Function $U(r_i,\ldots,r_N)$ is the interatomic interaction potential. The numerical solution of the equations of motion was carried out using the velocity Verlet scheme with an integration step of $10^{-16}$ s. The interatomic potential was constructed in the works [19, 20] in the approximation of the second nearest neighbor modified embedded atom method [21]. According to this method the total energy of system is:

$$E = \sum_{i=1}^{N} \left[ F_i(\overline{\rho_i}) + \frac{1}{2} \sum_{j=1}^{N} S_{ij} \phi_{ij}(r_{ij}) \right], \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|, \quad i \neq j, \tag{2}$$

where $F_i$ is the embedding function for the atom $i$, $\overline{\rho_i}$ is corresponding background electron density, $\phi_{ij}(r_{ij})$ is the $i$–$j$ pair interaction potential and $S_{ij}$ is the screening function.

To obtain the thermodynamically equilibrium configurations of modelled alloys hybrid molecular dynamics and Monte Carlo calculations were performed. According to this scheme, two random atoms of different chemical elements swap with the probability

$$p = \begin{cases} 1, & \text{if } \Delta E \leqslant 0, \\ \exp\left(\dfrac{-\Delta E}{k_{\mathrm{B}}T}\right), & \text{if } \Delta E > 0, \end{cases} \tag{3}$$

where $k_{\mathrm{B}}$ is Boltzmann constant, $T$ is temperature, $\Delta E$ is the change of sample total energy after swap. After every Monte Carlo swap the system was relaxed for 250 integration steps in molecular dynamics calculations with $NPT$ ensemble (constant number of particles $N$, pressure $P$ and temperature $T$). In our calculations $T = 300$ K and $P = 0$. If $\Delta E < 0.1\%$ of system total energy, that structural configuration of the sample was assumed to be equilibrium. Its further relaxation was done for $10^5$ steps in $NVE$ ensemble (constant number of particles $N$, volume $V$ and total energy $E$). The obtained samples were used to calculate the structural characteristics and physical-mechanical properties of the alloys.

Radial distribution function (RDF) is calculated by binning all distances between atoms of type I and J in a histogram. Count of atoms with type $J$ in spherical bin with radius from $r$ to $r + dr$ is divided to its volume and then normalized to average density of atoms of type J:

$$g_{\mathrm{IJ}}(r, r + dr) = \frac{N_{\mathrm{J}}(r, r + dr)}{4\pi r^2 dr} \frac{V}{N_{\mathrm{J}}}. \tag{4}$$

To calculate mechanical properties of alloys, samples were subjected to uniform tension along the [100] direction with rate $10^8$ s$^{-1}$, while in other two directions samples were allowed to change dimensions to keep zero stress component along them. Periodic boundary conditions were applied in all directions. Young's modulus of alloy was calculated as the slope of the linear region of tensile stress vs. strain curve.

Determination of local type of crystal lattice was performed in the OVITO software [22] which used an algorithm called Common Neighbor Analysis (CNA) [23]. It analyzes topology of bonds between nearest neighbors of a given atom and can identify to which structure it corresponds: fcc, bcc or hcp lattice.

## 3   RESULTS AND DISCUSSION

Calculations of the system total energy have shown that the bcc lattice is less energetically favorable and structurally stable than fcc. After complete relaxation of the samples with an initially ideal bcc lattice, the CNA algorithm in some cases determined that more than half of the atoms have a local environment that does not correspond to any of the crystal lattices. The structure of the alloys with 30% of iron (the maximum atom fraction in chosen compositions) was least disordered, apparently because bulk Fe has bcc lattice. Moreover, undistorted regions with bcc lattice in samples with lower Fe fraction contain more Fe than distorted ones, which points to the fact that iron may be considered as a local bcc stabilizer in a modeled system. For all 43 compositions, samples with an fcc lattice retained a stable crystal structure without significant distortion, which agrees with experimental studies of the phase stability and structure of CoCrFeMnNi alloys with near-equiatomic composition [24]. In addition, our calculations show that alloy retains the fcc structure as being more energetically favorable even with a significant deviation in the fraction of any element from the equiatomic value, which agrees with the experimental results on the stability of non-equiatomic CoCrFeMnNi alloys [25]. The dependence of the system total energy per atom on the lattice parameter of fcc alloys with different compositions is shown in figure 1. It is seen that the alloys with low energy have lower lattice parameters. The computer modeling has shown that for all the compositions considered there is no correlation of the configuration entropy with the calculated properties of the alloys. Based on the analysis of phase stability, we will next consider the properties of alloys with fcc lattice.

As calculations have shown, not all types of atoms are mixed absolutely randomly in the alloy studied. But at the same time, no microscopic segregation has been observed. To illustrate the features of alloy atomic structure let us consider radial distribution functions (RDFs) for two characteristic stoichiometric compositions: all contain 20% Ni, in figure 2(*a*) the alloy contains both 10% of Co and Cr, in figure 2(*b*) the alloy contains both 30% of Co and Cr. For the first composition the first Cr peak is higher and larger in area compared to peaks for other elements. For the second composition, the first Cr peak has the same height with others but it is broader. The second and third Fe peaks are larger in area than others by 50 and 20% correspondingly, but remaining peaks have the same area as others. In both cases, RDFs for Cr are shifted to the right, which means larger interatomic distance for this pair. RDFs for pairs of different elements are shown in figure 3. Their common feature is the higher first peaks for Co–Fe and Ni–Mn pairs,
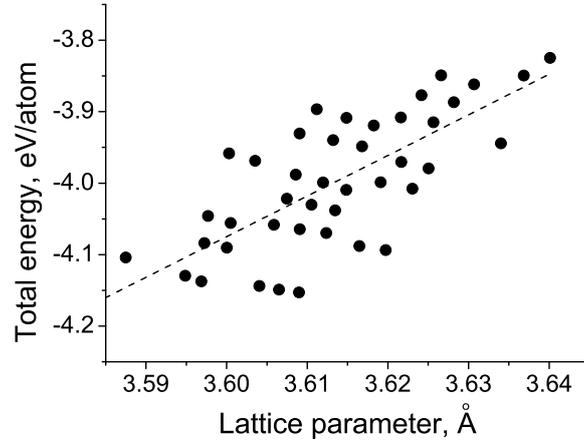
Figure 1. Total energy of fcc alloys per atom as a function of their lattice parameter.
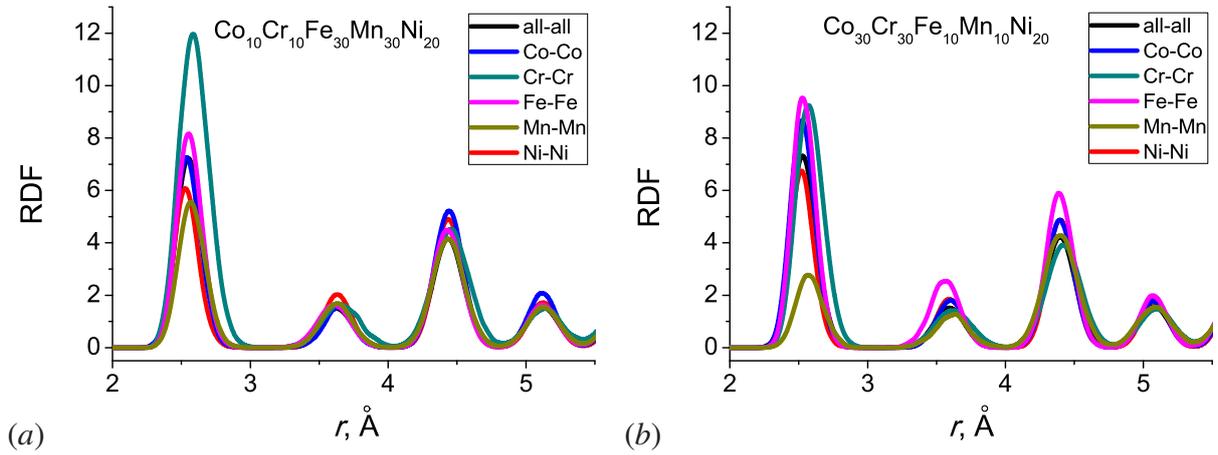


Figure 2. Radial distribution functions for single elements in alloys with different compositions: $Co_{10}Cr_{10}Fe_{30}$–$Mn_{30}Ni_{20}$ (*a*), $Co_{30}Cr_{30}Fe_{10}Mn_{10}Ni_{20}$ (*b*).

which means strong short-range interaction between these elements. First peaks for Cr–Mn and Ni–Fe are also high for the first and second composition, respectively. But this strong interaction is restricted by the first coordination sphere: the second and further peaks are almost the same as peaks for other pairs of elements, which means no segregation—there are no clusters which consist entirely of these atoms and exceed an elementary fcc cell in size. Moreover, if we plot the distribution of the number of atoms along the length of the sample, it will be a straight line.

We have investigated the effect of the stoichiometric composition on the lattice parameter of 43 alloys. For alloys whose lattice parameter lies in a certain range of values, we have calculated the average fraction of each element in them. The results of the calculations are shown in figure 4(*a, b*). It is clearly seen, that increasing of Cr, Fe and Mn or decreasing Ni and Co fraction
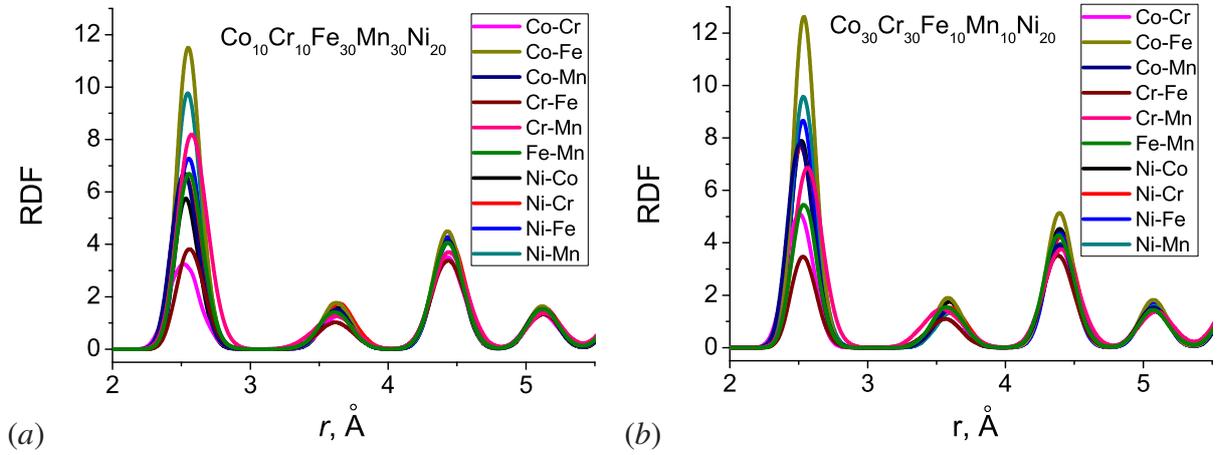
Figure 3. Radial distribution functions for pairs of different elements in alloys with different compositions: $Co_{10}$–$Cr_{10}Fe_{30}Mn_{30}Ni_{20}$ (*a*), $Co_{30}Cr_{30}Fe_{10}Mn_{10}Ni_{20}$ (*b*).

lead to increase of lattice parameter. It is interesting that these simple dependences exist even in spite of the fact that in each range of lattice parameters there are alloys with completely different stoichiometric composition. For example, the equiatomic alloy $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ and such alloys as $Co_{10}Cr_{20}Fe_{30}Mn_{10}Ni_{30}$ and $Co_{30}Cr_{20}Fe_{10}Mn_{30}Ni_{10}$ all correspond to the interval 3.609–3.611 Å. In our opinion, this is due to the stronger long-range interaction of Cr–Cr, Co–Fe and Ni–Mn pairs in comparison with other interactions which is expressed in the high first peaks of corresponding RDFs, as shown in figures 2 and 3. Now if back to figure 1, it will be seen that the lowest total energy is typical for alloys with small lattice parameter, i.e. with a high fraction of Fe, Mn and Cr and low fraction of Co and Ni.

Calculations show that, fraction of Ni, Co, Fe, and Cr have the opposite effect on Young's modulus compared to lattice parameter. Increasing of Ni and Co fraction or decreasing of Fe and Cr fraction lead to increase of Young's modulus, figure 4(*c, d*). Mn has little effect on the modulus value. It should be noted that the elements Co and Fe, which have a different effect on the modulus, are characterized by the strongest interaction between each other. As a consequence, for example, two alloys with 40% total fraction of Co and Fe and the same fractions of other elements, $Co_{30}Cr_{20}Fe_{10}Mn_{10}Ni_{30}$ and $Co_{10}Cr_{20}Fe_{30}Mn_{10}Ni_{30}$, have close moduli 83.5 and 84.2 GPa, correspondingly. This allows one to change the fractions of individual elements, keeping the constant value of the module and changing other properties of the alloy at the same time. Calculations show that the elastic limit of alloys is almost linearly dependent on Young's modulus, and therefore general conclusions on the effect of the stoichiometric composition on the modulus can also be applied to the elastic limit.
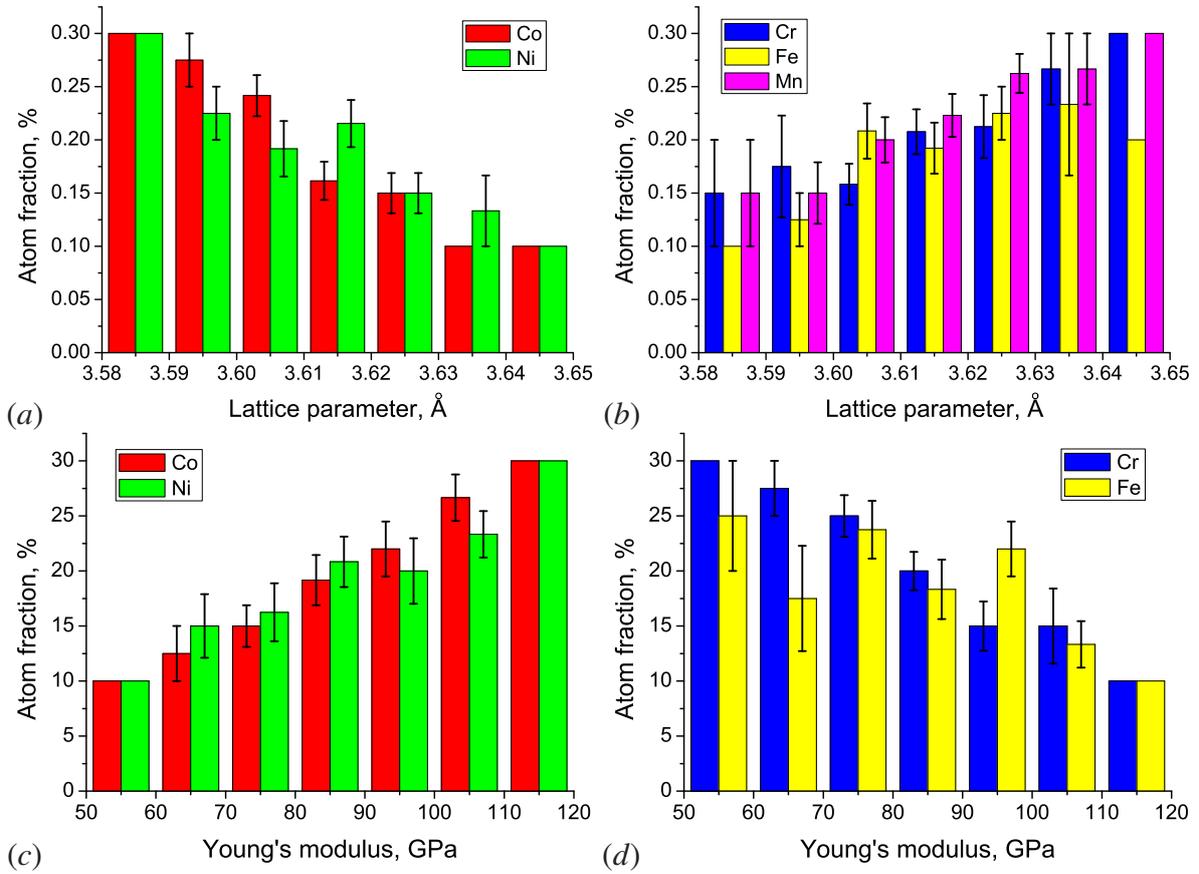
Figure 4. Average fractions of Co and Ni (*a*), Cr, Fe and Mn (*b*) as a function of lattice parameter; the same for Co and Ni (*c*), Cr and Fe (*d*) as a function of Young's modulus of alloys. Error bars show standard deviation.

## 4 CONCLUSIONS

Influence of stoichiometric composition on structure, phase stability, physical and mechanical properties of CoCrFeMnNi high-entropy alloy was studied by computer modeling based on combination of molecular-dynamics and Monte-Carlo methods. It was shown that fcc alloys more stable than bcc for all 43 considered stoichiometric compositions with fractions of each element varying in range 10–30%. RDFs are characterized by high first peaks for Cr–Cr, Co–Fe and Ni–Mn pairs, which mean a high degree of interaction between these elements in the CoCrFeMnNi alloy. It was shown that these structural features cause strong influence of stoichiometric composition on physical and mechanical properties of alloys. Namely, increasing of Cr, Fe and Mn fraction or decreasing Ni and Co fraction lead to increase of lattice parameter and increase of alloy cohesive energy. Opposite to lattice parameter, increasing of Ni and Co fraction or decreasing of Fe and Cr fraction lead to increase of Young's modulus and elastic limit. But in this case fraction of Mn has little effect on the modulus and the limit.

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