# Grain Boundary Segregations in High Entropy CoNiCrFeMn Alloy. Atomistic MD/MC Simulation

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**Abstract.** The formation of grain boundary segregations in the equiatomic high-entropy alloy (HEA) CoNiCrFeMn upon annealing at moderate temperatures was studied using atomistic MD/MC simulation. It has been established that at the early stage of annealing, regardless of the type of grain boundaries (GBs), two types of regions with chemical short-range order Ni–Mn–Cr and Fe–Co are formed in the volume of grains. With increasing annealing time, a pronounced tendency to the formation of unusually wide segregations on the GB is observed. The main element enriching the grain size is Cr, and Fe-Co clusters are displaced to the center of the grain. The influence of GB on the redistribution of alloy components and the phase stability of HEA is discussed.

**Keywords:** *high-entropy alloys, segregation, grain boundaries, atomistic modeling*

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## INTRODUCTION

High Entropy Alloys (HEA) attract considerable attention due to their unique properties and prospects for practical use [1–3]. HEAs are characterized by corrosion resistance, high strength and plastic properties. A well-known example of a single-phase HEA is the equiatomic FCC alloy CoNiCrFeMn, first proposed by B. Cantor [4]. During annealing in the range of moderate temperatures (450< $T$ <900°C), the alloy decomposes with the formation of various phases. The decomposition of the alloy is preceded by the formation of Chemical Short-Range Order (CSRO), which can significantly affect the strength properties of HEA [ 9–12 ]. Therefore, the formation of CSRO during HEA annealing has been actively studied in recent years both experimentally [13, 14] and theoretically [8, 9, 15–17].

The short-range ordering in the CoNiCrFeMn alloy was investigated in [16] using first-principles MC modeling. It was shown that in the ferromagnetic state, the formation of Cr–Cr and Cr–Mn pairs in the second neighbor position is preferred. However, due to limitations of the approach used, the study could not examine the evolution of CSRO during annealing. In [17], using atomistic MD/MC modeling, it was established that in the HEA CoNiCrFeMn during exposure at $T$ = 723 K, two types of chemical short-range order regions form. The first contains predominantly Fe–Co atoms, while the second represents Cr-enriched regions with Ni and Mn atoms at their boundaries. It was shown that the formation of short-range order includes several stages, the sequence of which is determined by the magnitude of Cr–Cr, Fe–Co, and Ni–Mn interactions.

In studies [19, 20], it was shown that grain refinement of single-phase alloys to a size of ~100 nm significantly increases the strength of HEAs, indicating an important contribution of grain boundary strengthening mechanisms. Investigation of the defect structure and hardness in nanocrystalline HEA CoCrFeNiMn showed that reducing the grain size to ~30 nm is accompanied by a significant increase in dislocation density and the probability of twin-like defect formation [20].

Detailed studies of the GB structure in high-entropy alloys have not yet been conducted. In [22], the melting, mechanical properties, and deformation mechanisms of the CoCrFeNiMn alloy in nanocrystalline state were theoretically studied. It was established that when grain size decreases to 2 nm, the most important mechanisms of plastic deformation in HEAs become grain shape change, stacking fault formation, and amorphization.

In the present work, using combined MD/MC modeling, we investigated the redistribution of chemical elements in the grain bulk and near special symmetric tilt GBs Σ5{013}<100> and Σ5{012}<100> during annealing of the equiatomic HEA CoNiCrFeMn. It was shown that pronounced segregations of Cr and Mn form at the GBs during annealing.

## MODELING METHOD

For the study, GBs that have the lowest energy values in pure metals [23] were selected, namely, symmetrical special GBs Σ5{013}<100> and Σ5{012}<100>. Fragments of the initial configurations of the considered GBs are shown in Fig. 1. The modeling block contained two grains separated by one of the considered boundaries located in its center. The number of atoms in the bicrystal varied depending on the GB type and was $(4–8)\times10^4$.

**Fig. 1.** Fragments of initial configurations of bicrystals with GB Σ5{013}<100> (a) and Σ5{012}<100> (b). Green lines show structural units, shaded and non-shaded circles represent atoms in two adjacent {100} planes.

In the initial configuration, atoms of five types Co, Ni, Cr, Fe, Mn, which are part of the HEA, were randomly distributed across the FCC lattice positions; the concentration of each alloy element was 20 at. %. To ensure that the concentration of the five alloy components near the GB in the initial configuration was close to the average in the grain volume, the modeling block dimensions along two directions in the boundary plane were significantly increased compared to those typically used for pure metals; periodic boundary conditions were maintained in these directions. Along the <100> direction in the GB plane ({013} or {012}), the crystallite size was 12 lattice parameters ($a$ =3.59 Å), in the transverse direction (15–16) $a$. The grain size in all cases along the direction perpendicular to the GB plane was ~20 nm (~50 $a$). Periodic boundary conditions were also applied in this direction, which leads to the appearance of a second (fictitious) Σ5 GB with the opposite sign of the Frank vector.

The average concentrations of atoms near the GB in the initial configuration, calculated for a layer with a width corresponding to the transverse dimensions of the structural element, were close to the nominal concentration in the alloy (the deviation did not exceed 5 at.%). For modeling, the LAMMPS package [24] and the multi-particle MEAM (modified embedded-atom method) interatomic interaction potentials proposed in [25] were used . It should be noted that an interatomic potential that more consistently describes many-body interactions was proposed in [26]. Since the question of its applicability for describing decomposition processes in the moderate temperature range currently remains open, the simulation was carried out using the potential from [25].

Annealing was performed at $T$ = 723 K, under isothermal-isobaric ( $NPT$ ) ensemble conditions. The selected annealing temperature corresponds to that used in the experiment [27]. Modeling of structural changes during annealing of HEA CoNiCrFeMn containing GB was carried out using a

hybrid MD/MC approach, in which (as previously in [18]) each MC step was preceded by MD relaxation (50 MD steps for each MC step), and the probability of atomic MC jumps was determined taking into account the energy change during relaxation. Details of the MD/MC procedure for the five-component alloy are given in [18].

## RESULTS AND DISCUSSION

The dependence of potential energy on the number of MD/MC steps at annealing temperature $T$ = 723 K for a bicrystal with GB Σ5{013}<100> is presented in Fig. 2. With increasing number of steps $N$ two stages can be conditionally distinguished: rapid decrease of $E_{pot}$ in the range of short annealing times (I) and stage II, at which the energy $E_{pot}(N)$ changes relatively slowly. The obtained dependence qualitatively coincides with the behavior of $E_{pot}(N)$ for an ideal crystallite without GB [18].

**Fig. 2** . Dependence of potential energy on the number of MD/MC steps for a bicrystal with GB Σ5{013}<100>, $T$ = 723 K.

The presence of GB generally increases the energy of the crystallite, but the overall behavior of $E_{pot}(N)$ is controlled by processes occurring in the grain volume. As shown in [18], the energy of the crystallite decreases due to the formation of short-range order in the grain volume and the formation of various atomic groups; in parallel, changes occur in the distribution of atoms in the region near the GB.

Fig. 3a shows a fragment of a bicrystal near the center of the GB Σ5{013}<100> after completion of MD/MC simulation and formation of the equilibrium structure. It can be seen that the MD/MC relaxation procedure does not lead to a qualitative change in the GB structure. For each pair of atomic layers perpendicular to the tilt axis <100>, structural elements can be identified (marked with a green line in Fig. 3a) containing atoms of different types. In the center of the structural element is a Mn atom, which has the largest ionic radius.

**Fig. 3.** Fragment of the configuration of a crystallite with GB Σ5{013}<100> (a) and the distribution function of atoms along the direction perpendicular to the GB plane, (b) after $25\times10^4$ steps of MD/MC simulation. Vertical lines correspond to the starting configuration, solid curves represent the distribution of atom positions in the crystallite after completion of MD/MC simulation. Black dots correspond to Co, blue to Ni, green to Cr, red to Fe, purple to Mn.

In the GB region, the structural element is deformed and atoms are displaced from their initial positions (marked with crosses in Fig. 3a); such displacements lead to a kind of "blurring" of the GB plane. Fig. 3b shows the distribution function of atoms across the GB width between nodes 2 and 2', which demonstrates the nature of atom displacement. In the starting configuration, the atoms are strictly ordered (vertical lines), occupying one position above another in layers parallel to the GB plane. Solid curves show the spread of atom positions in each position after MD/MC simulation. The width of the spread along the OX axis, perpendicular to the GB plane, is quite large and is ~0.5-1 Å. As a result, the planes containing atoms in positions 2, 3, 5 and 2', 3' 5', cease to be well-defined elements of the GB structure.

**Fig. 4.** Fragment of the bicrystal configuration with GB Σ5{012}<100> (a) and the distribution function of atoms along the OX direction near the GB (b) after $25\times10^4$ steps of MD/MC simulation. Vertical lines correspond to the starting configuration, solid curves represent the distribution function of atom positions in the crystallite after completion of MD/MC simulation.

Figure 4a shows the bicrystal region near the GB Σ5{012}<100> that underwent structural reconstruction due to redistribution of atoms near the GB during MD/MC simulation. It can be seen that the GB Σ5{012}<100> is enriched mainly with Cr atoms. Analysis of structural units (highlighted

in green in Fig. 4a) shows that fragments of the GB related to the original boundary are partially preserved (see Fig. 1b). Additionally, structural elements of modified shape appear, and the position of the GB shifts to the left or right from the dotted line - the starting position of the GB.

Figure 4b shows the distribution function of atoms across the GB width between points 8 and 8' (see Fig. 1b), which demonstrates the change in GB structure during relaxation. First, there is a broadening and decrease in height of peaks related to positions 6, 7', 8. This indicates a reduction in the number and deformation of the original structural elements. Second, new peaks appear between positions 7 and 8, as well as between 7' and 8', with the first being many times higher than the second. This may be due to the fact that the number of distorted structural elements shifted to the left from the original GB position (marked with numbers I, II, III) exceeds the number of other structural elements.

During MD/MC simulation, the distribution of atom types near the GB changes. The dependence of the average concentration of atoms of all five elements forming the HEA near the GB on the number of annealing steps at T=723 K is shown in Fig. 5.

**Fig. 5**. Dependence of the concentration of elements of the alloy in the region near the GB on the number of MD/MC simulation steps for GB Σ5{013}<100> (a) and Σ5{012}<100> (b).

A significant increase in concentration near GB Σ5{013}<100> (Fig. 5a) is obtained for Cr atoms. By the end of the MD/MC relaxation procedure, the concentration of Cr atoms reaches ~35 at. %. Meanwhile, the concentration of Co remains practically constant, and the concentration of Fe atoms significantly decreases (to approximately 8 at. %). The concentration of Ni also decreases to ~13 at. %, while the concentration of Mn increases to ~24 at. %. An even more significant increase in Cr concentration is obtained near GB Σ5{012}<100> (Fig. 5b); by the end of the MD/MC relaxation procedure, the concentration of Cr atoms reaches 45%, and the concentration of Mn increases to ~25 at. %. At the same time, the concentration of Ni and Co atoms decreases to ~12 at. %, and Fe atoms - to ~6 at. %.

Thus, the details in the distribution of atom types near the considered GBs differ, but common patterns of segregation formation are clearly visible. In particular, Cr and Mn demonstrate a tendency to enrich GBs, while other elements remain in the grain bulk.

As seen from Fig. 5, significant changes in the concentration of Mn and Ni atoms near the GB occur after approximately $5\times10^4$ MD/MC modeling steps, which corresponds to stage I of the curve $E_{pot}(N)$, Fig. 2. At the same time, the concentration of Cr and Fe atoms near the GB changes monotonically throughout the entire simulation time. The nature of concentration changes indicates that the enrichment of GB with Cr atoms is accompanied by its depletion of Fe atoms.

Analysis of the distribution of atom types showed that at the end of stage I in the crystallite containing the GB, areas with chemical short-range order (CSRO) with a size of 2-4 lattice parameters are formed, which are uniformly distributed throughout the grain volume. Groups of Ni-Mn-Cr and Fe-Co atoms are distinguished. As shown in [18], their formation is accompanied by rapid changes in the Warren-Cowley short-range order parameters.

**Fig. 6.** Change in concentration of Cr, Mn, Ni in the direction perpendicular to the plane of GB Σ5{013}<100>, (a) and GB Σ5{012}<100> (b). The dashed line shows the starting position of the GB; the horizontal line represents the level of average concentration throughout the bicrystal volume.

The situation changes with increased simulation time and transition to stage II. A significant redistribution of atoms of different types between the grain volume and the area near the GB is observed. Fig. 6 shows the concentration profile of three elements Ni-Mn-Cr involved in the formation of one of the two types of pre-precipitates. Each point is obtained by averaging over a part of the crystallite volume, the size of which in the GB plane coincides with the translation magnitude; along

the OX direction, perpendicular to the GB plane, the length of the selected volume is close to the width of the corresponding boundary. For both studied boundaries, Cr atoms form rather wide (about 20 Å) segregations at the GB. Mn atoms are also predominantly located near the center of the GB, but their concentration is much lower than that of Cr. At the same time, Ni atoms do not participate in the formation of segregations.

It should be noted that at GB Σ5{012}<100>, a much higher segregation of alloying elements is achieved than at GB Σ5{013}<100>. This is apparently due to the structural features of GB Σ5{012}<100> (Fig. 4a), where Cr or Mn atoms are located at the nodes of its structural elements.

**Fig. 7.** Distribution of atoms in two layers of a crystallite of equiatomic CoNiCrFeMn alloy after $25\times 10^{4}$ MD/MC steps. Red atoms – Fe, black – Co. (a) – GB Σ5{013}<100>; (b) – GB Σ5{012}<100>. The dashed line indicates the initial position of the GB center.

Fig. 7 shows the distribution of Fe and Co atoms in two adjacent layers formed after completion of MD/MC modeling. It can be seen that near the GB there is depletion of Fe and Co, while long chains of interconnected fragments of Fe and Co atoms are located away from the GB.

The results presented here for modeling the equiatomic HEA CoNiCrFeMn containing GB show that the structure formed during annealing is quite complex and is determined by two competing processes. First, even in the early stages of annealing, short-range ordering occurs and Ni–Mn–Cr and Fe–Co clusters form [18]. Second, during prolonged annealing, there is a pronounced tendency for segregation at the GB, with Cr being the main segregating element.

The grain boundary segregations formed in HEA CoNiCrFeMn are characterized by unusually high intensity (the increase in Cr concentration reaches 35–45 at. %) and extent (Fig. 6). The latter is due to the fact that the energy of Cr–Cr, Cr–Mn, Cr–Ni interactions in HEA is negative [18], so that the formation of Cr segregation at the GB stimulates decomposition and the formation of Cr and Mn enriched precipitates in the near-boundary region.

The results of MD/MC modeling indicate a significant influence of GB on the development of HEA instability during annealing of fine-grained materials. The formation of grain boundary segregations will lead to depletion of Cr and Mn in the grain volume and deviation of the HEA composition from optimal.

## CONCLUSIONS

In order to clarify the features of grain boundary segregation formation in HEAs, atomistic MD/MC modeling of annealing at moderate temperature ( $T$ = 723 K) was performed for the CoNiCrFeMn alloy containing special tilt GBs © 5. The obtained results allow us to draw the following conclusions.

1. At the early stage of the MD/MC annealing procedure, short-range order regions containing Fe-Co or Ni-Mn-Cr atoms are formed, which are uniformly distributed throughout the volume, regardless of the type of GBs contained in them.

2. With increasing annealing time, the redistribution of atoms of different types between the GB region and the grain volume becomes dominant. There is a pronounced tendency toward the formation of segregations at GBs, with Cr being the main segregating element, whose concentration at GBs reaches 35-45 at.%.

3. Near the GBs, clusters containing predominantly Ni-Mn-Cr are formed, while Fe-Co clusters are displaced to the center of the grains. As a result, unusually wide (about 20 Å) segregations form at the GBs. Thus, GBs can have a significant impact on the phase stability of HEAs due to substantial redistribution of alloy components.

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CONFLICT OF INTERESTS

The authors of this work declare that they have no conflict of interest.

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