Influence of chemical composition of the surface layer on the nucleation of plasticity in CoCrFeMnNi high-entropy alloys

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Abstract. The role of segregation of chemical elements upon free surfaces in the peculiarities of the plastic deformation mechanisms of thin films of the high-entropy CoCrFeMnNi alloy was clarified using a combined simulation of the Metropolis Monte Carlo and molecular dynamics. Irrespective of surface orientation and stoichiometric composition of alloy Mn escapes to free surface and Fe goes to the bulk of the films. Ni also enriches the (111) surface while Co content is reduced. It is shown that for different compositions segregation reduces or decreases the elastic limit of the samples. In $\text{Co}_{10}\text{Cr}_{10}\text{Fe}_{30}\text{Mn}_{30}\text{Ni}_{20}$ for all considered free surfaces, segregation equally influences the type and volume fraction of the formed defects. In $\text{Co}_{30}\text{Cr}_{30}\text{Fe}_{10}\text{Mn}_{10}\text{Ni}_{20}$, they may remain the same or the mechanism of plastic deformation may change drastically in samples with segregation depending on the orientation of the free surface. Despite the redistribution of the volume fractions of various type defects, in general, the main mechanism for the development of plasticity in samples both before and after segregation is the growth of the hcp-bands. Change of defect structure in samples with surface segregation compared to samples with random distribution of elements is not necessary related to change of elastic limit.

1. Introduction

As is known, many processes in metals and alloys, including the nucleation and development of lattice defects, are determined by the structure, orientation, and chemical composition of free surfaces [1, 2]. For example, in experiments and molecular dynamics simulations it was shown that the orientation of free surfaces determines the type of nucleated structural defects and the features of deformation-induced phase transitions in metallic nanowires, pillars and thin films [3–6]. In nanosized samples, surface tension can lead to a change in the stress state of the bulk, and the influence of the surface increases with decreasing system size [7]. The authors of [1] using in-situ atomic-scale resolution electron microscopy and computer simulations showed that the segregation of chemical elements on the surface of the Cu–Au solid solution leads to a redistribution of stresses and the heterogeneous nucleation of misfit dislocations.

It can be expected that in multi-element alloys, the segregation of chemical elements on the free surface will have an even greater effect on the mechanical behavior of the material due to their much more complex chemical and stoichiometric composition. Recently, the great attention in materials science has focused on high-entropy alloys (HEAs), which are solid solutions with 5 or more chemical elements, the fraction of each can vary from 5 to 35% [8]. Experimental
studies show that HEA films and coatings have excellent mechanical and physical properties [9]. Therefore, it is crucial to understand the surface effects during the loading of HEA films and coatings. Since segregation of chemical elements occurs at the atomic level, one of the most effective methods for studying it and its influence on the mechanisms of plasticity is computer simulation using the molecular dynamics method. It directly accounts for the discreetness of a material and allows studying its response under various types of external loading at the atomic level [10–12]. This paper is devoted to the molecular dynamics study of the effect of chemical element segregation near free surfaces on the peculiarities of plasticity nucleation under tension of CoCrFeMnNi thin films. The choice of this HEA is due to the fact that it has a single-phase fcc structure and outstanding mechanical and physical properties compared with traditional structural materials [13].

2. Simulation details
Simulated samples were films with three different orientations of free surfaces: (001), (110) or (111). The simulation box was of $10 \times 10 \times 10$ nm$^3$ in volume. Periodic boundary conditions were set along directions perpendicular to free surfaces. Samples were stretched till 20% of strain at room temperature by uniform change of distance between all atoms along the [110] direction parallel to (001) and (111) free surfaces and the [110] direction parallel to the (110) surface. Size of simulation box along another periodic dimension (the [110] direction for (001), (111) surfaces and the [001] direction for the (110) surface, respectively) was allowed to change in order to keep zero value of corresponding stress component. A strain rate was equal to $10^9$ s$^{-1}$. LAMMPS computational package was used for simulations [14]. Atomic interactions in CoCrFeMnNi HEA were described by the second-nearest neighbor modified embedded atom method potentials developed in [15,16]. To investigate mechanical response of HEAs with low and high mechanical properties, Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$ and Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$ compositions were simulated, respectively. Thermodinamically-equilibrium redistribution of atomic species in simulated HEAs was obtained using approach utilizing the Metropolis Monte Carlo and molecular dynamics simulations [17,18]. According to this approach atoms of different chemical elements are swapped with the probability, which depends on potential energy change after swap and temperature of the system. After swapping of 2% of sample atoms the system is equilibrated during 100 molecular dynamics steps. Integration step is equal to 5 fs. This procedure is repeated till the change of potential energy of the sample become smaller than 0.1%. To extract the influence of surface segregation on plasticity of HEAs response of these equilibrated samples (further—after segregation) was compared with response of initial films (further—before segregation) with absolutely random distribution of chemical elements. For each free surface and stoichiometric composition at least 8 samples with different initial distribution of chemical elements were simulated to obtain statistically meaningful results. Common Neighbor Analysis [19] was used to reveal the type of nucleated defects and calculate their density in the loaded samples. This algorithm identifies the symmetry of the nearest neighbors of each atom in the sample and allows us to determine the corresponding local type of the crystal lattice. Using this results we are able to identify the type of nucleated defects. For example, intrinsic stacking faults correspond to two adjacent layers of atoms with hcp symmetry of local environment in {111} fcc planes. One and more than one atomic layers of fcc lattice lie between these hcp layers in extrinsic stacking faults and twins, respectively.

3. Results and discussion
To assess the redistribution of chemical elements near the surface after segregation, we calculated their content in a layer containing surface atoms and their nearest neighbors. The results are presented in figure 1 in comparison with the initial values before the redistribution. It can be seen that segregation of Mn takes place on all three free surfaces for both stoichiometric compositions.
Figure 1. Fraction of alloy elements in surface layer for different free surfaces and stoichiometric compositions: (a) Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$; (b) Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$.

On the contrary, Fe leaves the surface region and its content decreases in proportionally to the increase in the fraction of Mn. In turn, the Co content near the (111) surface slightly decreases, while Ni fraction increases by about the same value. The fraction of Cr after segregation of elements practically does not change as compared with a random distribution.

Important mechanical characteristics of the material are the stress $\sigma_y$ and the deformation $\varepsilon_y$ at the elastic limit. Figure 2 illustrates how these quantities change after the redistribution of chemical elements near the surface. For Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$, segregation leads to an increase in $\sigma_y$, most significantly for the (001) surface. In addition, $\varepsilon_y$ increases only for this surface. For Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$, on the contrary, segregation leads to lowering of mechanical properties. On average, $\sigma_y$ drops by 1–3 GPa, which is almost an order of magnitude greater than the change in $\sigma_y$ for the previous composition—0.1–0.3 GPa. The greatest difference between stresses and strains before and after segregation is observed for samples with the (111) surface. This may be due to the fact that Ni and Co were also significantly redistributed on this free surface in addition to Mn and Fe.

Summarizing the results of structural analysis for samples stretched by 20%, we found the most common types of defects formed for a given stoichiometric composition and orientation of the free surface. These are the bands in the \{111\} fcc planes with a hcp lattice structure more than 2 atomic layers thick (hcp-bands), twins, intrinsic and extrinsic stacking faults (ISFs, ESFs). To identify the effect of surface segregation of chemical elements on the structural response of HEAs, we estimated the average volume fractions of defects of various types in samples with segregation and random distribution of elements. The results of calculations are given in the form of column bar plots in figure 3. In Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$ samples for all free surfaces hcp-bands dominate, twins are less numerous, and ISFs are in the third place by population. Compared to the samples with a random distribution, more hcp-bands and ISFs and less twins are nucleated in the samples with the segregation. In Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$ with random distribution and the (001) surface, twins and hcp-bands dominate, their fraction is the same in the sample with segregation, however, the fraction of ISFs becomes almost comparable to the fraction of these defects. Segregation on the (110) surface leads to the fact that ESFs begin to play a leading role in the development of plasticity instead of hcp-bands and ISFs. Twinning remains as a secondary mechanism of plastic deformation. In spite of a significant change in the elastic limit values, no observable difference in defect structure of specimens with the (111) surface before and after segregation was found.
Figure 2. Stress components and deformations along tension direction at the elastic limit for different stoichiometric compositions of samples loaded before and after element segregation: (a) Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$; (b) Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$. Each point corresponds to a different distribution of elements in the sample.

Figure 3. Volume fraction of most common structural defects in (a) Co$_{10}$Cr$_{10}$Fe$_{30}$Mn$_{30}$Ni$_{20}$ and (b) Co$_{30}$Cr$_{30}$Fe$_{10}$Mn$_{10}$Ni$_{20}$ samples loaded before and after element segregation.

The found defect structures are in good agreement with the results of experimental studies and simulations of other authors. The stability of thick hcp-bands in deformed fcc matrix is caused by the fact that hcp lattice is energetically more favorable than fcc structure according to the used interatomic potential [20] and ab-initio simulations [21]. However, full transition to hcp structure does not take place due to finite potential barrier for fcc-hcp transformation according to our simulations. Negative stacking fault energies which favor twinning were found for fcc HEAs in [22, 23]. In [13], it was shown that twinning is one of the main mechanisms of plastic deformation responsible for high crack resistance of CoCrFeMnNi HEA. In the work [24], it is shown that the deformation-induced phase transformation in the CoCrFeMnNi HEA alloy starts at 7.1 GPa under compression. In [25], the mechanism for hcp phase formation in FeCoCrNi was proposed based on successive glide of partial dislocations in $\{111\}$ fcc planes. ISFs in Fe$_{40.5}$Mn$_{30}$Co$_{10}$Cr$_{10}$C$_{0.5}$ were suggested to be the nucleation sites of hcp phase [26].
4. Conclusions
The influence of surface segregation on the mechanical and structural response of high-entropy CoCrFeMnNi alloy thin films subjected to uniaxial tension was studied by molecular dynamics and Monte Carlo simulations. It was shown that Mn escapes to the surface while Fe goes to the bulk after Monte Carlo relaxation of samples.

For all considered free surfaces and HEA compositions in samples with a random distribution of elements, the majority of defects are the bands in fcc \{111\} planes with a hcp lattice structure, which have thickness from a few to tens of atomic layers in the ⟨111⟩ direction. Twins are the second in terms of the volume fraction, followed by ISFs. Segregation does not significantly change the type and number of structural defects in Co\textsubscript{10}Cr\textsubscript{10}Fe\textsubscript{30}Mn\textsubscript{30}Ni\textsubscript{20}. The most remarkable influence of segregation on defect type is found for Co\textsubscript{30}Cr\textsubscript{30}Fe\textsubscript{10}Mn\textsubscript{10}Ni\textsubscript{20} samples with (110) surface: ESFs almost completely replace the hcp-bands and ISFs.

In general, the main mechanism for the development of plasticity in samples both before and after segregation is the growth of hcp bands, which is associated with low energies of stacking faults for the considered stoichiometric compositions of HEA. The change in the defect structure in samples loaded before and after segregation is not necessary related to the change in elastic limit value and vice versa. The different degree of influence of segregation on the elastic limit and structure is associated with different relative change in the surface composition of the Co\textsubscript{30}Cr\textsubscript{30}Fe\textsubscript{10}Mn\textsubscript{10}Ni\textsubscript{20} and Co\textsubscript{10}Cr\textsubscript{10}Fe\textsubscript{30}Mn\textsubscript{30}Ni\textsubscript{20} samples: in the sample that contains more Fe and Mn, the fraction of these elements changes greater than in the sample with their low content.

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