Atomic-scale mechanisms of single crystal plasticity in CoCrFeMnNi high-entropy alloys

A V Korchuganov
Institute of Strength Physics and Material Science of the Siberian Branch of the Russian Academy of Sciences, Akademicheskii 2/4, Tomsk 634021, Russia
E-mail: avkor@ispms.ru

Abstract. The behavior of CoCrFeMnNi high-entropy alloys under mechanical loading was studied within the framework of the molecular dynamics method. The mechanisms of local structural transformations of the crystal lattice responsible for the onset of plasticity at the tension of CoCrFeMnNi single crystals were determined. A crystallographic analysis of the structure and identification of the defects formed was carried out. Irrespective of stoichiometric composition of samples the plasticity is realized by the nucleation, growth and intersection of intrinsic stacking faults. Rearrangement of fcc lattice to bcc structure in the regions where the local atom fraction of Fe, Mn and Ni is above average was found to be the mechanism of stacking fault formation. The effect of the stoichiometric composition and crystallographic orientation of single-crystal CoCrFeMnNi samples upon the structural rearrangements at the nucleation and development of plastic deformation under tension was studied.

1. Introduction

Significant attention in recent years has been paid to investigation of high-entropy alloys (HEAs). These materials are composed of 5 or more chemical elements usually present in the alloy in near-equal ratios. Increased interest to them is due to attractive complex of excellent physical-mechanical properties, some of them better than of traditional materials [1].

Despite chemical complexity of HEAs, such alloys are usually stable solid solutions. From thermodynamic principles, their stability is caused by high configurational entropy. It has a maximum value if chemical elements are mixed in equal proportions. That is why most of HEA research is related to equiatomic configurations of alloys. However, configurational entropy was found to be not the only one responsible for HEA stability: deviation from equiatomic compositions also allows to obtain stable configurations of alloys [2]. It should be noted that experimental preparation and mechanical testing of HEA samples with a wide spectrum of chemical compositions is costly and time-consuming process. In this connection, computer simulation is an effective alternative to rapidly generate and screen large amount of data and help to choose the composition with desired properties. For example, based on computer calculations of phase diagrams, Senkov et al recently proposed more than $10^4$ alloy compositions with potentially good properties [3].

At present, research is actively carried out to elucidate the mechanisms governing the behavior of HEAs under mechanical impacts [4]. For example, high strength of HEAs is attempted to be associated with the effects of solid-solution strengthening [5,6]. In [7], on the basis of molecular
dynamics and first-principles calculations, the effects of disordering and segregation of chemical elements in AlCrCoFeNi were observed. It was shown that they play an important role in the mechanisms of plastic deformation of the investigated HEA: specific atomic rearrangements have been observed during the compression of crystallites, leading to chemical disordering and a decrease in the degree of clustering of the elements. In [8] it was found that the dislocation pinning due to the severe lattice-distortion effect is the main mechanism of plastic deformation of the AlCrFeCuNi1.4 alloy.

Notable success has been made in studying of CoCrFeMnNi system which was found to be strong, ductile and crack resistant HEA [9,10]. However, the effect of stoichiometric composition on the properties and mechanical behavior of this HEA remain unexplored. To tackle this problem, molecular dynamics method could be used which is suitable for the investigation of metals and alloys on the atomic level [11]. It accounts for the discrete structure of materials and makes it possible to study the dynamics of structural changes in the atomic system subjected to external impacts [12, 13].

In this connection, the aim of this work is to study the role of stoichiometric composition in the atomic mechanisms of CoCrFeMnNi HEA plasticity on the base of molecular dynamics simulation.

2. Material and methods

The simulations were based on the combination of two methods: molecular-dynamics and Monte-Carlo ones. Within the framework of this approach, randomly selected atoms of different types swap (Monte Carlo steps) in accordance with the probability determined by the local potential barriers, and the relaxation of the atomic structure of the material is carried out within the framework of the molecular dynamics method. Calculations were performed in LAMMPS package [14]. To describe the interatomic interaction in CoCrFeMnNi, modern many-body potentials [15, 16] constructed within the framework of the second nearest neighbor modified embedded atom method (2NN MEAM) were used. These potentials describe the lattice parameters, elastic moduli, structural features and energy parameters of extended defects with a high degree of accuracy, as well as the thermodynamic behavior of various phases of the material, etc, which is important for the correct simulation of HEAs.

The stoichiometric composition of the alloys was varied in such a way that the configurational entropy was always \( \geq 1.5 \), and the fractions of the elements were only 10, 20, and 30%. Fulfillment of these conditions has given 43 alloys with different stoichiometric compositions. The initial distribution of chemical elements in the alloy was set by a random number generator. The samples had the shape of a cube with a side of 10 fcc lattice parameters. The edges of the sample were oriented along the cubic directions, periodic boundary conditions were used along them. The relaxation of the samples was carried out at zero pressure and at a temperature of 300\(^\circ\)K. The integration step for the molecular dynamics simulations was 0.1 fs. Every 80 Monte Carlo steps were followed by 20 000 molecular dynamics steps. The calculations were stopped after the reduction in the energy of the system became less than 0.1%. Then the samples were relaxed at 100 000 molecular dynamics steps with the NVE ensemble retaining initial fcc lattice. The calculation of Young\’s modulus was carried out in uniaxial tension tests along one of the (100) directions. Dimensions of the sample along other two directions were dynamically changed to maintain zero pressure for them.

Based on results of the calculations of the Young\’s modulus of these samples, stoichiometric compositions with a low modulus and a high one were determined: \( \text{Co}_{10}\text{Cr}_{10}\text{Fe}_{30}\text{Mn}_{30}\text{Ni}_{20} \) and \( \text{Co}_{30}\text{Cr}_{30}\text{Fe}_{10}\text{Mn}_{10}\text{Ni}_{20} \). Next, for the convenience, we will refer to the samples with these compositions as FeMn-reach and CoCr-reach sample, respectively. For these two compositions, structural changes during plastic deformation under uniaxial tension were studied for fcc samples with 10 nm cubic edges. Their crystallographic orientation was varied in such a way that the
Figure 1. Stress-strain diagram for CoCr-reach (4 upper curves) and FeMn-reach (3 lower curves) samples tensioned along different directions (in square brackets).

[110] direction was always stationary, and the tension direction had indices [110], [112] or [111]. Strain rate was $10^9$ s$^{-1}$. Zero stress was maintained along directions normal to tension. Periodic boundary conditions were used in all directions.

The identification of the crystal lattice type was carried out on the basis of an algorithm determining the symmetry of the nearest environment of all atoms in the sample—Common Neighbor Analysis (CNA) [17]. Thus, for example, it is possible to identify the intrinsic stacking fault (SF) in an fcc lattice as two layers of atoms in the \{111\} planes, the symmetry of the nearest environment of which corresponds to an hcp lattice. Next, we use the following terminology: if the symmetry of the nearest environment of an atom according to the CNA analysis corresponds to an fcc, hcp, bcc or an undefined lattice, we will simply call it an fcc, hcp, bcc or an undefined atom, respectively.

3. Results and discussion

The mechanical response of crystallites to tension is anisotropic essentially, as can be seen from the calculated stress-strain diagrams in figure 1. The curves for a CoCr-reach sample are always higher than for a FeMn-reach sample. At the same time, the relative arrangement of the elastic limits for the three directions is the same for the considered compositions of the samples: the plasticity is nucleated at lower strains and stresses when the samples are tensioned along the [110] direction, the [112] direction is characterized by the maximum yield stress, and the maximum elongation prior the nucleation of plasticity correspond to the [001] direction. These features are consistent with the Schmid’s law, which gives the maximum Schmid factor 0.5 for the slip system $\langle 112 \rangle \{111\}$ under tension along the [110] direction. In this case, the Burgers vector of the partial dislocations $1/6 \langle 112 \rangle \{111\}$ and the normal to the \{111\} plane lie at an angle of 45° to the tension direction [110]. Calculations showed that for all the samples considered plasticity mechanism is the nucleation of stacking faults, surrounded by partial dislocations $1/6 \langle 112 \rangle \{111\}$.

For more detailed analysis of the structure and the mechanical response, let us consider samples tensioned along the [110] direction. In figure 2, along with the tensile stress (the left
Figure 2. The dependences of the tensile stress (the left axis), fraction of bcc (a, d), hcp (b, e), and undefined atoms (c, f) (right axis) on the tensile strain for FeMn-reach (left column) and CoCr-reach (right column) samples.

The dependences of the number of bcc, hcp, and undefined atoms on the tensile strain (the right axis) are shown. The number of these atoms is normalized to the total number of atoms of each chemical element in the alloy so that the behavior of these dependencies can be qualitatively compared for different stoichiometric compositions and for each chemical element.
Figure 3. Structure of FeMn-reach (left column) and CoCr-reach (right column) samples for different strain values: 0.04 (a), 0.05 (b), 0.055 (c), 0.08 (d), 0.05 (e), 0.07 (f), 0.095 (g), 0.12 (h). For clarity fcc atoms are not shown in all figures and undefined atoms are not shown in figures (f–h).
It should be noted that the stress-strain curves deviate from the linear dependence on the strain values of 0.01–0.02, but the further response of the material can still be considered as elastic, since dislocations and SFs have not yet nucleated before a certain deformation. The decrease in the slope of the stress curves is associated with a change in the symmetry of the nearest environment of atoms in certain regions of the sample. At deformations of 0.02 and 0.04 for FeMn-reach and CoCr-reach samples, respectively, the nearest environment of atoms begins to be distorted and partially rearranged into a bcc structure. As can be seen in figure 2(a, c, d, f) these rearrangements are mostly concerned with Fe, Mn and Ni atoms, and to a lesser extent with Co and Cr atoms. The exception is graphs in figure 2(e), which shows that the surrounding environment is distorted to the same extent for all chemical elements. It should also be noted that, as a rule, structural rearrangements do not occur for separately located atoms in the simulated HEA, as in pure metals, where defect nucleation sites are determined by thermal fluctuations [11, 18], but for those regions where the local atom fraction of Fe, Mn, and Ni is above average, see figure 2(a, e). As analysis of the structure shows, these regions are the nucleation sites for partial dislocations and SFs under further loading.

The time moment of the plasticity nucleation in the samples can be regarded as the beginning of the formation of classical SFs in the samples, which is reflected at the beginning of the intensive growth of the number of hcp atoms in figure 2(b, e), at deformations of 0.045 and 0.060 for FeMn-reach and CoCr-reach samples, respectively, see figure 3(b, f). In a FeMn-reach sample in the range of deformations of 0.045–0.055, the number of bcc atoms reaches a local maximum and then even decreases slightly because at the deformation of 0.055 the initially formed SFs slow down their growth and reach almost maximum dimensions, intersect with each other and the stress decreases significantly. The decrease in the growth rate can be identified from the fact that at the strain 0.055 the slope of the dependence of the number of hcp atoms decreases. Moreover, the analysis of the structure showed that after 0.055, the largest SFs grow more slowly and lots of new small SFs grow more intensively, as can be seen from the comparison of the structures in figure 3(c, d, g, h). But the rate of their growth is less than of the initial SFs, as a dense network of intersecting SFs already formed in the sample, which hinder the further growth of small SFs.

For the CoCr-reach and FeMn-reach samples, the initial stages of nucleation of structural defects are largely similar: in a CoCr-reach sample too, up to the elastic limit at 0.04 deformation there are regions with bcc atoms containing mainly Fe, Mn and Ni atoms, see figure 2(d) and figure 3(e). Then, under deformations of 0.06, SFs are also generated in these regions, see figure 3(f–h). It corresponds to an increase in the number of hcp atoms, which are also, as in the FeMn-reach sample, Fe, Mn and Ni, see figure 2(e). However, the increase in SF area in the course of CoCr-reach sample loading is significantly suppressed compared to a FeMn-reach sample, as can be seen from the comparison of figures 3(b–d) and 3(f–h). A CoCr-reach sample shows 3 times the yield stress as compared to a FeMn-reach sample, and a continuous hardening up to a deformation of 0.16.

The almost linear increase in the number of hcp atoms in the 0.055–0.095 area is not due to the growth of the area of already formed SFs (as in a FeMn-reach sample) but to the constant nucleation of small SFs, which do not increase in size. An analysis of the structure showed that this distinguishing feature is due to the fact that in the vicinity of the stopped partial dislocations surrounding SF, a larger percentage of Co and Cr atoms (64–67%) is contained in a CoCr-reach sample as compared to FeMn-reach sample (20%). For CoCr-reach sample, this number is even greater than the total Co and Cr fraction in them—60%. For FeMn-reach sample, this atom fraction corresponds to a total Co and Cr fraction of 20% in the CoCr-reach sample.

The fact that structural rearrangements mainly affect Fe, Mn and Ni atoms and to a lesser extent Co and Cr even for different stoichiometric compositions is explained by the peculiarities
of the atomic structure of the samples under consideration, which corresponds to the equilibrium configuration obtained in the Monte Carlo calculations. The Monte Carlo relaxation of the structure of the samples showed that there is a strong interaction between the Cr–Cr, Co–Fe, and Ni–Mn pairs. This is reflected in the fact that the first peaks of the radial distribution functions for these pairs are higher than the first peaks for the other pairs of elements. Moreover, the calculation for 43 different stoichiometric compositions showed that an increase in the Co and Ni fraction and a corresponding decrease in the Fe and Cr fraction leads to an increase in Young’s modulus of the alloy. The results of these calculations are confirmed by a similar result obtained in [19]. The effect of the chemical composition of the CoCrFeMnC HEA was detected there, when an increase in the Fe fraction by 8% and a decrease in the fraction of Mn by 6% in certain regions of the sample led to a stress-induced transition from the fcc to the hcp phase.

It should be noted that for the same stoichiometric composition of the alloy, depending on the relative distribution of the chemical elements in the alloy, the plasticity in it develops differently. So, a CoCr-reach sample with a random distribution of chemical elements has a smaller yield stress than a sample with a thermodynamically-equilibrium distribution and does not experiences hardening. In this case, the SFs grow more intensively and in the vicinity of the stopped partial dislocations surrounding SF, the percentage of Co and Cr atoms is equal to the total Co and Cr fraction of 60% in the sample.

4. Conclusions

Based on molecular dynamics simulations, it was shown that for all considered stoichiometric compositions of CoCrFeMnNi HEA plasticity mechanism is the nucleation of stacking faults, surrounded by partial dislocations 1/6 \{112\} \{111\}. It was found that the nucleation of stacking faults is preceded by specific atomic structural rearrangements in the regions where the local atom fraction of Fe, Mn, and Ni is above average for the sample: the nearest environment of atoms begins to be distorted and partially rearranged into a bcc structure. It was shown that the features of nucleation and development of plasticity are to a large extent determined both by the chemical composition of the alloy and by the peculiarities of the of chemical element distribution. So, for FeMn-reach samples, there is intensive growth and intersection of stacking faults, and in CoCr-reach samples the motion of partial dislocations is substantially suppressed. It is connected with the peculiarities of the atomic structure of the samples being studied, which corresponds to the thermodynamically-equilibrium configuration obtained in the Monte Carlo calculations: there is a strong interaction between the Cr–Cr, Co–Fe, and Ni–Mn pairs of atoms. It was found that for the same stoichiometric composition of the alloy, depending on the relative distribution of the chemical elements in the alloy, the plasticity in it develops differently. These results open up new possibilities in the field of material processing: by controlling the formation conditions of the alloy (controlling the mixing of alloy elements), one can obtain the necessary mechanical properties.

Acknowledgments

The work was carried out with the financial support of the Russian Science Foundation (project No. 17-79-10108).

References

[1] Lim X Z 2016 Nature 533 306–7
[2] Tasan C C, Deng Y, Pradeep K G, Yao M J, Springer H and Raabe D 2014 JOM 66 1993–2001
[3] Senkov O N, Miller J D, Miracle D B and Woodward C 2015 Nat. Commun. 6 6529
[4] Pickering E J and Jones N G 2016 Int. Mater. Rev. 61 183–202
[5] Stepanov N D, Shaysultanov D G, Tikhonovsky M A and Salishchev G A 2015 Mater. Des. 87 60–5
[6] Varvenne C, Luque A and Curtin W A 2016 Acta Mater. 118 164–76
[7] Sharma A, Singh P, Johnson D D, Liaw P K and Babasubramanian G 2016 Sci. Rep. 6 31028
[8] Li J, Fang Q H, Liu B, Liu Y W and Liu Y 2016 RSC Adv. 6 76409–19
[9] Gludovatz B, Hohenwarter A, Catoor D, Chang E H, George E P and Ritchie R O 2014 Science 345 1153–8
[10] Skrotzki W, Pukenas A, Joni B, Odor E, Ungar T, Hohenwarter A, Pippan R and George E P 2017 IOP Conf. Ser.: Mater. Sci. Eng. 194 012028
[11] Psakhie S G, Zolnikov K P, Kryzhevich D S and Lipnitskii A G 2006 Phys. Lett. A 349 509–12
[12] Korchuganov A V, Zolnikov K P, Kryzhevich D S and Psakhie S G 2017 Russ. Phys. J. 60 170–4
[13] Psakhie S G, Zolnikov K P, Skorentsev L F, Kryzhevich D S and Abdrashtov A V 2008 Phys. Plasmas 15 053701
[14] Plimpton S 1995 J. Comput. Phys. 117 1–19
[15] Choi W M, Kim Y, Seol D and Lee B J 2017 Comput. Mater. Sci. 130 121–9
[16] Wu C, Lee B J and Su X 2017 Calphad 57 98–106
[17] Honeycutt J D and Andersen H C 1987 J. Phys. Chem. 91 4950–63
[18] Psakhie S G, Zolnikov K P and Kryzhevich D S 2007 Phys. Lett. A 367 250–3
[19] Li Z and Raabe D 2018 Mater. Chem. Phys. 210 29–36