

Features of the Thermomagnetic Behavior of CrMnFeCoNi High Entropy Alloy

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The temperature dependences of magnetic susceptibility $\chi(T)$ in the temperature range of 300-900 K of CrMnFeCoNi high entropy alloy (HEA) with different thermal prehistory (after cutting samples from the bars (as-cast condition) and after annealing at $T_h = 800$ and 950 °C) are studied. It is shown that the investigated alloys are characterized by a positive value of χ , which increases with increasing annealing temperature. The temperature dependences $\chi(T)$ are decreasing with increasing T and characterized by irreversibility in a cycle of heating and cooling. Dependences $\chi(T)$ in the lower temperature range are analyzed in terms of the presence of superparamagnetic particles (complexes) formed by a certain type of atoms placed in the non-magnetic or paramagnetic matrix with low Curie temperature and low effective localized magnetic moment. The model, which couples the formation of these superparamagnetic particles with the structural features of the five-component fcc HEA, is considered.

Keywords: High entropy alloy, Magnetic susceptibility, Localized magnetic moment, Structure, Annealing.

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1. INTRODUCTION

High entropy alloys (HEA), which were discovered very recently [1], are the subject of intense study due to the unique complex of mechanical and physical properties [2-4]. The feature of these alloys is their composition: they consist of five or more metals (in some cases it is considered that HEA are alloys with four metals), the content of which is quite close to the equiatomic one. This is what distinguishes HEA from traditional alloys, in which one or two components are the main ones and all others act as alloying additions. Despite this composition, HEA are characterized by a rather simple crystal structure, which is considered as a simple structure of a solid solution. In most cases, they crystallize in the fcc or bcc lattices, and, as believed, the configuration entropy (mixing entropy) is the main factor which stabilizes the structure of a solid solution, although an important role is assigned to other criteria for stabilization of the single-phase state of HEA [5]. In this case, in addition to the configuration entropy, the mixing enthalpy, atomic radii, and electronegativity are considered [6].

We should note that among a large number of known HEA [6, 7], considerable attention is paid to alloys containing 3d-transition metals. An equiatomic alloy of the CrMnFeCoNi composition belongs to such alloys and has the fcc structure of a disordered solid solution. It shows a nice combination of the mechanical properties, such as hardness [8, 9], tensile strength [9-11], ductility [9, 11], resistance to crack formation at low temperatures [10]. In [12], on an example of this alloy, a rather fine balance between entropy and enthalpy has been exhibited when stabilizing the state of a solid solution in this alloy. The authors of [12] prepared five alloys, in each of which one element replaced an element of CrMnFeCoNi alloy. This substitution was implemented in such a way that the Hume-Rothery criterion was satisfied. It was found that all five alloys are multiphase ones unlike CrMnFeCoNi. A similar result was obtained by replacing Mn with V or

by attempting to form a six-component NiFeCrCoMnV alloy [9]. This result clearly demonstrates that entropy does not always dominate the free energy when the enthalpy contribution becomes more significant.

Until now, it is not finally established which role the short- or long-range ordering plays in HEA. In most papers, the formation of bulk crystal or magnetic structures by atoms in HEA is not considered. At the same time, among them there are Fe, Co, Ni atoms, which by their nature are ferromagnets, and Cr or Mn, which exhibit antiferromagnetic properties in pure form. The relative mixing energy of an antiferromagnet (Cr) during its dissolution in a ferromagnet (Fe) was studied in [13]. It was found that dissolution of Cr has an energy advantage of spatial separation in the ferromagnetic base through the process called magnetic frustration. In [14], when using X-ray spectroscopy and scanning electron microscopy, it was shown that Cr is heterogeneously distributed over the NiFeCrCo alloy, but the resolution of the method did not allow to determine the ordering at the atomic level. The search of the long-range ordering in the same alloy performed in [15] by X-ray and neutron diffraction did not allow to establish its presence. At the same time, the authors of [16] predicted the spin-excited ordering of Cr atoms in the equiatomic fcc NiFeCrCo HEA. Ordering of Cr atoms is induced by a decrease in energy, when the antiferromagnetic Cr is surrounded by ferromagnetic Ni, Fe and Co that causes the L₁₂ structure formation. As predicted, the L₁₂ structure with completely ordered Cr has a smaller magnetic moment than a magnetically disordered solid solution. The calculation results were confirmed based on the study of the magnetic susceptibility of the samples manufactured in different ways; and the presence of ordered nanodomains was established by the results of a special processing of images obtained using scanning electron microscopy.

In general, the magnetic studies make it clear that different magnetic states can be realized in HEA even at a slight change in the composition. Thus, NiCoFeCr,

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NiCoFeTi, CuNiCoFeCr, and CuNiCoFeCrTi_{0.5} are paramagnetic at room T , and the CuNiCoFeCrTi_{1.0} alloy is a superparamagnetic [17-19]. At the same time, it is noted that CuNiCoFeCrTi _{x} ($x \leq 1$) has T_c below 170 K [19]. The thermomagnetic studies of series of the FeCoCr _{x} Ni ($x = 0.5-1.15$) alloys [20] showed the dependence of their magnetic properties not only on the chromium content, but also on the mechanical processing (cold rolling). In [20], this is associated with a change in atomic ordering or the formation of the defect structure.

So, the magnetic properties are rather sensitive not only to the atomic composition, but also to the atomic ordering. Information on the magnetic properties of the CrMnFeCoNi alloy is almost absent; and, therefore, the thermomagnetic studies of the HEA of this composition have been carried out in this work in order to establish the nature of the magnetic ordering in it and the relationship between the atomic and magnetic structures.

2. MATERIALS AND METHODS OF STUDY

HEA of the CrMnFeCoNi composition made of chemically pure elements by melting a charge of the corresponding composition in an electric arc in an atmosphere of pure argon was studied in the work. The obtained ingot was melted 6-7 times to homogenize the composition. After that, the alloy was poured into copper, cooled by water, mold of 10 mm diameter and of 100 mm length. Samples of the required sizes were cut from the ingots obtained. The studies of the temperature dependences of the magnetic susceptibility $\chi(T)$ were carried out in the temperature range of 300-900 K at a field of 550 kA/m in an argon atmosphere using the Faraday-type magnetometer with microbalance. The measurement accuracy of the magnetic susceptibility $\Delta\chi/\chi$ was better than 1.5 %, and the measurement accuracy of the temperature was $\Delta T \leq 0.5$ K. The heating rate in such measurements was equal to 8 K/min. 15-30 mg pieces of material were taken from the ingot to study $\chi(T)$. Thermal treatment of the samples at 800 °C and 950 °C was performed in evacuated quartz ampoules (vacuum is better than 10^{-3} Pa). The material for study was taken after annealing.

3. EXPERIMENTAL RESULTS

The temperature dependences of the magnetic susceptibility $\chi(T)$ of the CrMnFeCoNi HEA are illustrated in Fig. 1. In Fig. 1a we present the dependence $\chi(T)$ of this alloy after smelting and cutting from it a specimen for study (*as-cast* state). In Fig. 1b, c we show the dependences $\chi(T)$ of the samples after annealing during 30 min at temperatures of $T_h = 800$ °C and 950 °C, respectively.

It is possible to distinguish the following features in these dependences:

- the irreversibility of the dependences $\chi(T)$ in heating and cooling for all investigated samples. In this case, the value of χ_{300} at $T = 300$ K after heating to the maximum measurement temperature (900 K) is greater than the value of χ_{300} in the initial state;
- at annealing, χ_{300} increases, and with increasing T_h , an increase in χ_{300} also occurs.
- in the *as-cast* state and after annealing at $T_h = 800$ °C, in the dependence $\chi(T)$ when heated, there is a feature in the vicinity of $T \sim 700$ K, which is absent when cooled.

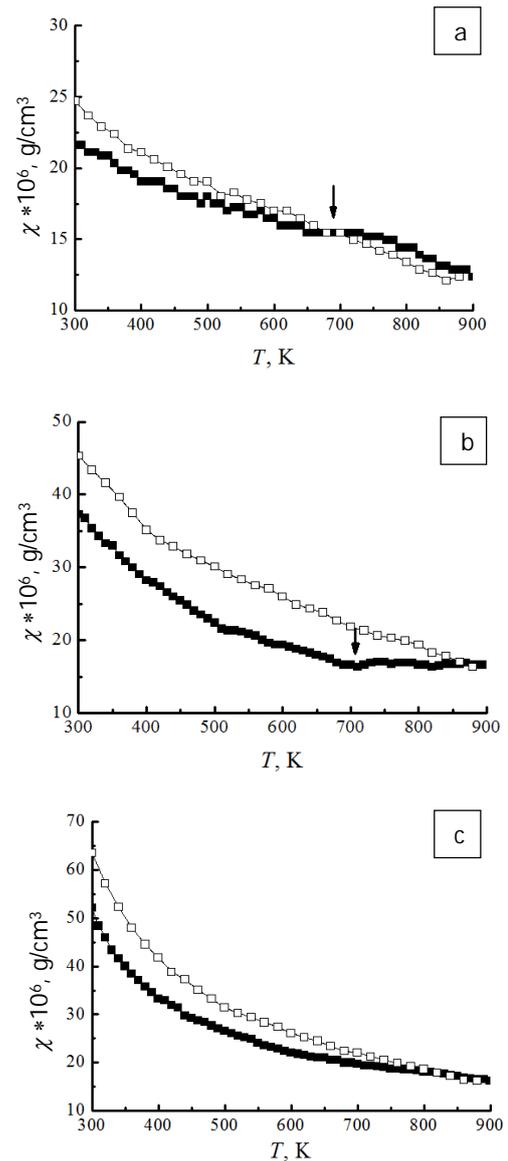


Fig. 1 – The temperature dependences of the magnetic susceptibility in the as-cast state (a), after annealing in vacuum at 800 °C for 30 min (b) and after annealing in vacuum at 950 °C for 30 min (c) (dark icons denote heating, light ones – cooling)

Although $\chi(T)$ of the alloy annealed at $T_h = 950$ °C is irreversible in heating and cooling, but almost monotonic throughout the measurement temperature range.

4. ANALYSIS AND DISCUSSION OF THE RESULTS

Dependences $\chi(T)$ in the temperature range from 300 to 600-700 K in Fig. 1a, b and almost for the whole temperature range in Fig. 1c are reminiscent of the shape of the temperature dependence of the magnetic susceptibility of metals with elements containing localized magnetic moments. In the presence of the exchange interaction between these moments, temperature dependence $\chi(T)$ is described by the generalized Curie-Weiss law [21]

$$\chi = \chi_0 + \frac{Nm^2}{3k(T-\theta)}, \quad (1)$$

where χ_0 is the temperature-independent component of the susceptibility, m is the effective paramagnetic moment per atom of the alloy, θ is the paramagnetic Curie temperature, k and N are the Boltzmann constant and the Avogadro number, respectively.

In the absence of interaction between such localized moments, $\theta = 0$ and equation (1) is nothing other than the Curie dependence for non-interacting magnetic moments, which has the form of

$$\chi = \chi_0 + \frac{M_1}{T}, \quad (2)$$

where

$$M_1 = Nm^2 / (3k). \quad (3)$$

It should be noted that (1) may have an asymptote ($1/T$) in the temperature range where $\theta \ll T$ (low Curie temperature and, consequently, small exchange interaction between atoms).

The analysis showed that none of the dependences can be described satisfactorily by equations (1) or (2) for reasonable values of the parameters included in them.

Further analysis was carried out by plotting the dependences of χ on $1/T$. The result of the plotting is illustrated in Fig. 2a-c (according to the curves of Fig. 1a-c). As seen, in the initial sample and the sample annealed at 800 °C, the dependence $\chi(1/T)$ is linear from room temperature ($T = 300$ K) to a temperature, at which the features are manifested in the dependences $\chi(T)$ (shown by the arrows in Fig. 1a, b). But the linear region for the sample annealed at $T_h = 950$ °C can be distinguished at high T (from 400-450 K and above).

The linear dependence in the coordinates of χ on $1/T$ in the low-temperature range is quite easily interpreted from the standpoint of Curie paramagnetism ($\theta = 0$ in equation (1)) or Curie-Weiss paramagnetism with low θ ($\theta \ll 300$ K).

A deviation from this dependence at high T can be associated with the processes of structural reorganization (relaxation, change in the short-range ordering, etc.) that is entirely consistent with the irreversibility of the dependences $\chi(T)$ in the heating-cooling cycle.

However, the presence of a linear region at high T for HEA annealed at 950 °C cannot be explained from this point of view. Therefore, it was assumed that after such annealing the system is two-phase: one of the phases is paramagnetic, $\chi(T)$ of which is described by the Curie-Weiss dependence, and the second phase is paramagnetic, $\chi(T)$ of which is described by the Curie dependence. In this case, the equation defining the dependence $\chi(T)$ will be written as

$$\chi = \chi_0 + \frac{M_1}{T} + \frac{M_2}{(T - \theta)}. \quad (4)$$

In this equation, the constants M_1 and M_2 depend not only on the effective paramagnetic moments m_1 and m_2 , but also on the concentrations of these phases c_1 and c_2 .

The result of the approximation of the dependences presented in Fig. 1c is shown in Fig. 3 by solid lines. The equation (4) can easily explain the presence of a linear high-temperature region on the dependence of χ on $1/T$. Indeed, at $T \gg \theta$, the second term has an asymptote $1/T$,

i.e. in this case, the transition to the linear dependence of χ on $1/T$ takes place. The approximation parameters of $\chi(1/T)$ in the linear region and the approximation of $\chi(T)$ of the sample annealed at 950 °C by equation (4) are given in Table 1. In this table, the values of the effective magnetic moments per one transition metal atom m_1 calculated by the equation (3) are also presented.

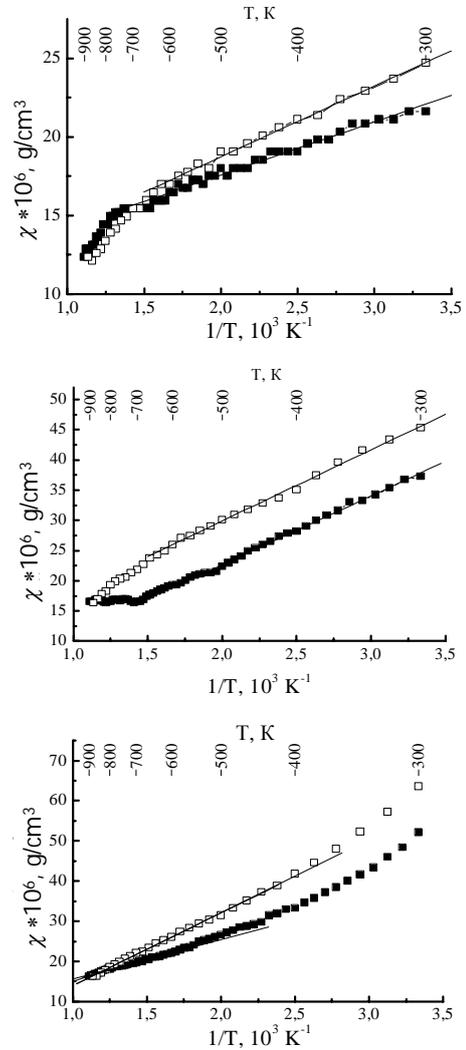


Fig. 2 – Dependence of χ on $1/T$ for the as-cast state (a), after annealing at 800 °C, 30 min (b) and 950 °C, 30 min (c) (as well as in Fig. 1, dark icons denote heating, light ones – cooling)

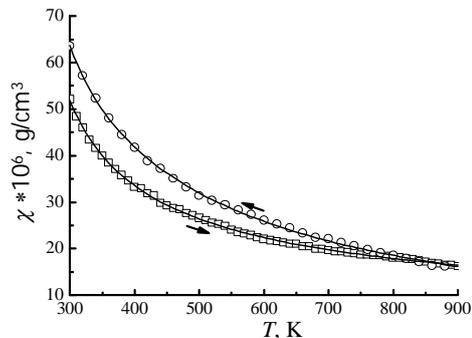


Fig. 3 – Approximation results (solid lines) of the experimental dependences of χ on T (symbols) of HEA annealed at 950 °C, 30 min (arrows indicate the measurement directions)

Table 1 – Approximation parameters of $\chi(1/T)$ in the linear region (*) (“h” is the heating branch and “c” is the cooling branch) and approximation of $\chi(T)$ of the sample annealed at 950 °C by equation (4) (**)

Sample	Branch	$\chi_0 \cdot 10^6, \text{g/cm}^3$	$M_1 \cdot 10^3, (\text{K}\cdot\text{g})/\text{cm}^3$	$M_2 \cdot 10^3, (\text{K}\cdot\text{g})/\text{cm}^3$	θ, K	m_1, μ_B	m_2, μ_B	\bar{S}	S^{Fe}	n_{Fe}	n_{FeCo}
as-cast	h*	10.9	3.37	–	–	6.,5	–	2.8	6.8	29	8
	c*	9.7	4.50	–	–	5.7	–	2.4	5.9	22	6
800 °C	h*	– 0.2	11.42	–	–	3.5	–	1.3	3.4	8	2
	c*	6.4	11.76	–	–	3.5	–	1.3	3.4	8	2
950 °C	h*	5.3	10.12	–	–	3.8	–	1.4	3.8	9	2
	c*	– 4.0	18.03	–	–	2.8	–	0.9	2.7	5	1
	h**	6.3	6.39	2.11	213	4.7	8.3	–	–	–	–
	c**	– 2.4	15.44	0.90	238	3.1	12.6	–	–	–	–

We will not analyze in detail the value of χ_0 and only note that its value in most cases is positive and tends to decrease as the annealing temperature increases. The negative values of χ_0 obtained in approximation of some branches of the dependences $\chi(T)$ of the samples after annealing at 800 °C and 950 °C are insignificant compared with the values of χ in this temperature range. Taking into account the experimental and approximation errors of χ_0 , in this case they can be taken as zero or small positive ones. We will analyze in more detail the temperature-dependent part of the magnetic susceptibility.

In HEA of the CrMnFeCoNi composition, each i -th atom can carry a localized magnetic moment μ_i , i.e. have an uncompensated spin S_i on the outer $3d$ shell. The relationship between the magnitude of this spin and the atomic magnetic moment has the form of

$$\mu_i^2 = g_i^2 \mu_B^2 S_i(S_i + 1), \quad (5)$$

where g_i is the g -factor of the i -th element.

Then, the total magnetic moment m (m_1 or m_2) per one transition metal atom can be written as [22]

$$m^2 = 4 \mu_B^2 \sum_i c_i S_i(S_i + 1). \quad (6)$$

In this equation, c_i is the atomic concentration of the i -th component, and it is assumed that $g_i \approx 2$ for all $3d$ transition metals.

We introduce the average spin value \bar{S} by equation

$$m^2 = 4 \mu_B^2 \bar{S}(\bar{S} + 1). \quad (7)$$

The calculation of \bar{S} by the values of the approximation parameter m_1 is given in Table 1.

Theoretically, in CrMnFeCoNi HEA, the maximum spin value on each i -th atom S_{max} arising from the maximum number of unpaired electrons on the outer $3d$ shell can be equal to: 3 for Cr, 5/2 for Mn, 2 for Fe, 3/2 for Co, and 1 for Ni. The calculation by equations (6) and (7) of the maximum values of the magnetic moment and the average spin gives us the following values: $m_{max} = 2.3 \mu_B$ and $\bar{S}_{max} \approx 0.7$, respectively. As seen, even in this case we obtain the values which are smaller than the values of m_1 and \bar{S} calculated from the experiment. Moreover, various correlation effects usually lead to another (less) value of the uncompensated spin on each atom and even to the disappearance of localized magnetic moments on the atoms [21]. Thus, in Fe, Co, and Ni in the ferromagnetic state, the localized magnetic moment is created by only 2.2, 1.6, and 0.5 unpaired electrons (spins 1.1, 0.8,

and 0.25) [21]. These spin values will correspond to the following magnetic moments: $\mu_{Fe} \approx 3.04 \mu_B$, $\mu_{Co} \approx 2.4 \mu_B$, and $\mu_{Ni} \approx 1.7 \mu_B$, respectively. The magnetic moment of paramagnetic iron, according to the data of [23], has a value of $\mu_{Fe} \approx 3.18 \mu_B$, which is close to the previous one (the spin is 1.2), and of Co – $\mu_{Co} \approx 3.13 \mu_B$ (the spin is 1.1) that is somewhat more than the previous value. That is, the real value of the average spin will be even smaller than that calculated from the maximum spin values of each element and, correspondingly, the values obtained from the experimental results.

In addition to the above, the result of the calculation of the electronic structure done in [24] for CuNiCoFeCr, NiCoFeCr and NiCoFeCrTi HEA showed that the magnetic moment will be absent on Cu, Ti, and Ni atoms irrespective of the Wigner-Seitz cell size. In all alloys, Fe atom in the vicinity of the equilibrium volume may bear a significant localized magnetic moment ($\sim (1.8-2.0) \mu_B$). Co atom remains nonmagnetic in NiCoFeCr, NiCoFeCrTi alloys, but reveals a small ($\sim 0.6 \mu_B$) magnetic moment in composition from the studied one, but, obviously, this also occurs for it, i.e., some atoms in CrMnFeCoNi alloy will not bear a localized magnetic moment.

If, for example, the localized magnetic moment in the alloy will only be present on the Fe atom, then only one term associated with this atom will be present in the equation (6). Taking into account that $c_{Fe} = 0.2$, it is easy to obtain from the experimental values of m_1 the value of spin S^{Fe} , which should be on the Fe atom in this case. These values are given in Table 1. As seen, they exceed the magnitudes of the uncompensated spins which may be present on the iron atom. It is easy to verify that the presence of the localized magnetic moment on some other atoms, for example, Co, will result in the spin values which far exceed those that can be observed in this case. To our opinion, the nature of the emergence of such significant moments is due to the formation in the alloy of complexes (clusters) with a positive exchange interaction that leads to the parallel orientation of the spins. With significant exchange interaction, it should be expected that the parallel orientation in such complexes does not collapse even at high temperatures (at least at study temperatures $\chi(T)$). Such clusters can be identified with superparamagnetic particles. If, for example, these complexes consist of n identical atoms, each of which has the spin S , then the total spin of this complex will be equal to $S_K = nS$. Let us consider how valid this model is.

First of all, we consider will the value of n be reasonable if assume that this complex consists of Fe atoms.

We will try to find the concentration of such complexes, if the concentration of iron atoms in the alloy is known. For this, we will write the HEA composition in the form of $\text{CrMn}(\text{Fe}_n)_{1/n}\text{CoNi}$. Then, the concentration of these complexes can be found using the equation

$$4x + x/n = 1, \quad (8)$$

from which we have $x = n/(4n + 1)$. Thus, the concentration of complexes of n Fe atoms ($c_{n\text{Fe}}$) will be equal to

$$c_{n\text{Fe}} = x(1/n) = 1/(4n + 1). \quad (9)$$

The localized moment per one atom of CrMnFeCoNi alloy under the assumption that the moments are present only on the Fe atoms forming this complex, we obtain

$$\begin{aligned} m^2 &= 4c_{n\text{Fe}}[nS_{\text{Fe}}(nS_{\text{Fe}} + 1)] = \\ &= 4[nS_{\text{Fe}}(nS_{\text{Fe}} + 1)]/(4n + 1). \end{aligned} \quad (10)$$

This equation is a quadratic equation with respect to n . To find it, we will use the experimental values of m_1 and the spin value $S_{\text{Fe}} = 1.2$ obtained in the case when $\mu_{\text{Fe}} \approx 3.18\mu_{\text{B}}$ [23]. The calculated values of n are given in Table 1. As seen, n varies from 29 in the initial, as-cast, state to 5 in the state which is achieved after annealing at 950 °C. The obtained values of n , especially in the initial state, are quite large. Such values should lead to a significant spatial separation of these complexes and the formation of a highly heterogeneous structure, in which the matrix will be strongly depleted with iron.

Now we consider a more complex problem. Let such complexes are formed by Fe and Co atoms, which can bear a localized magnetic moment. For simplicity, we assume that the complex consists of the same number n of Fe and Co atoms (n is the number of atoms of the same type). We estimate n in this case. To this end, we write the composition in the form of $\text{CrMn}(\text{Fe}_n\text{Co}_n)_{1/n}\text{Ni}$. To calculate the necessary concentration, we have the equation $3x + x/n = 1$, from which we obtain $x = n/(3n + 1)$. Thus, $c_{n\text{FeCo}} = x(1/n) = 1/(3n + 1)$.

$$\begin{aligned} m^2 &= 4c_{n\text{FeCo}}[n(S_{\text{Fe}} + S_{\text{Co}})(n(S_{\text{Fe}} + S_{\text{Co}}) + 1)] = \\ &= 4[n(S_{\text{Fe}} + S_{\text{Co}})(n(S_{\text{Fe}} + S_{\text{Co}}) + 1)]/(3n + 1). \end{aligned} \quad (11)$$

To solve this quadratic equation, we use the values $S_{\text{Fe}} = 1.2$ and $S_{\text{Co}} = 1.1$. The corresponding values of n_{FeCo} are entered in Table 1. As seen, the formed complex in the initial state should contain 8 atoms of each element, i.e. only 16 atoms that is less than in the case when such a complex consists of only Fe atoms. And after annealing, this complex contains only 1-2 atoms of each element.

At first sight, it seems that with such a large number of atoms in the complex, strong concentration inhomogeneities can appear in the alloy, and the matrix will be strongly depleted with Fe and Co, i.e. with the elements forming the complex. However, it should be taken into account that such a complex can be not only concentrated around a certain center, which may be considered as the formation of nanoparticles within the matrix structure. Such a complex can have the form of chains of Fe or Fe and Co atoms, between which there is a significant exchange interaction allowing to identify them with superparamagnetic particles. Outside these chains, the exchange interaction between other atoms is either absent or insignificant.

The basis for the probability of existence of such complexes is the simulation of atomic structures of multi-component equiatomic alloys in terms of the maximum entropy [25]. These results showed that the maximum entropy, whose condition is the absence of two identical elements in the immediate environment, can be achieved quite easily in the bcc equiatomic alloys almost starting from four components, but not in the fcc multicomponent alloys. In fcc alloys, the absence of identical atoms in the immediate environment can be achieved only for seven- and even eight-component alloys. According to the results of such simulations, for a five-component CrMnFeCoNi alloy, under the condition of maximum entropy and the condition of homogeneity of element distribution, 47.3 % of atoms in the fcc structure of such an alloy will have identical atoms in the immediate environment (at a distance of $2^{-1/2}\alpha$, α is the fcc lattice constant). Since the probability of identical neighbors is large enough, it is quite logical that there is a probability of forming chains of three and more identical atoms.

We performed our own simulation of the structure of five-component alloy. In this case, the fcc structure was considered as a close packed structure formed by a periodic arrangement of close packed rows in the sequence -A-B-C- (depending on which type of hole is occupied in the layer A). To place five components in a close packed row, a simple program using a random number generator was used. By this program, five components were placed in a close packed plane (for the fcc structure, these are the planes of the family {111}) in such a way that there were no identical components in the immediate environment. In Fig. 4a we illustrate an example of such a structure of a size of 30×30 atoms, in which one of the examples of the arrangement of only one of five elements is shown by dark circles for better perception. In the calculations, the number of components was not normalized on the equiatomic composition, but as demonstrated by testing the algorithm used in the program, the deviation from the equiatomic composition in one layer of a size of 30×30 does not exceed 1 % and almost coincides with the equiatomic one at the number of atoms of about 10^4 . For the analysis, we used three-layer structures obtained by various possible combinations of three different A layers, three different B layers, and three different C layers (total 21 combinations). To facilitate the analysis, an area of a size of 10×10 was selected in the formed structures. An example of such a structure is shown in Fig. 4b. For better perception, the chosen type of atoms in this structure is marked by an asterisk and different layers – by different colors: black – A layer, gray – B layer, and white – C layer. Areas near this type of atoms are marked by circles or oval curves. Areas with isolated atoms of the same type, two and three identical atoms in the immediate environment are formed in such a three-layer structure. It is worth noting that some areas can be visually perceived, for example, as two atoms in the immediate environment (see the upper right corner). But since such areas are formed by black and white asterisks, they belong to the lower (A) and the upper (C) layers and are separated by the B layer, that is, they are the second neighbors. This also applies to areas, in which there is a larger number of atoms of the same type. Thus, it is possible to find in Fig. 4b an area of five asterisks, which are visually located in the immediate environment (an area

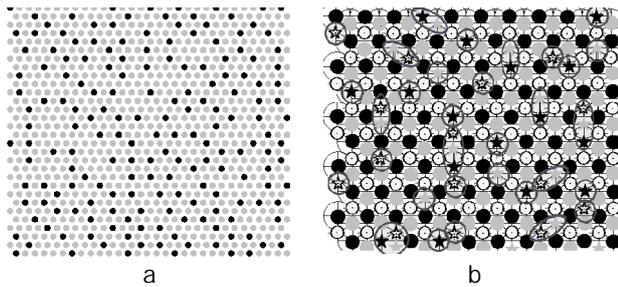


Fig. 4 – An example of the arrangement of one of the elements (black circles) in the simulated close packed row with a size of 30×30 atoms of the five-component HEA (a) and one of the three layer structures with close packing of A-B-C of a size of 10×10 atoms (b). The atomic position in the A layer is marked by black icons, in the B layer – by gray icons, in the C layer – by white icons. Asterisks of the corresponding color denote the location of one of the five atoms. Complexes of one, two, and three adjacent atoms are marked by circles and ovals

near the center). In fact, these are three areas: two areas with isolated atoms of the same type and one area with three atoms. It is quite logical that the nature and number of formed areas will vary if one of the layers is replaced by another, or even when one layer is shifted relative to another into another hole of the same type.

When analyzing 21 combinations of three layer model structures, the following results were obtained: (40 ± 9) % of atoms are isolated, (33 ± 10) % of atoms form complexes of two atoms, and (27 ± 9) % form complexes of three atoms. At first sight, atoms in the isolated (from the same atoms) state prevail in such a structure. In fact, it should be taken into account that only atoms of the B layer may be considered completely isolated in the three layer structure. Atoms forming complexes of two or three atoms with adjacent C and A layers, respectively, can be among isolated atoms of the A and C layers. The analysis shows that only (21 ± 9) % of all atoms of a certain type in the B layer are isolated.

For a similar reason, when forming the structure of more than three layers, double complexes of identical atoms can be expanded to complexes of three, four or even more atoms. This also applies to complexes of three identical atoms.

Such a statistical analysis is far from complete, and formed close packed rows only approximately reflect the real atomic structure, primarily because of the fact that it is possible to separate in the fcc structure as many as eight such close packed rows located in eight planes of the family $\{111\}$.

As already noted, the crystal structures in [25] were constructed taking into account the maximum entropy. As a result, 52.3 % of atoms (atoms with nearest similar neighbors in the second coordination spheres) will be isolated in the five-element fcc alloy, and this is twice as much as in our analysis, where the condition of maximum entropy was achieved only in one close packed row. Moreover, when modeling the structure, the authors of [25] tried to achieve maximum uniformity in the arrangement of atoms. In our analysis, although, in general, the structure is homogeneous with a large number of rows (the content of elements is close to the ideal), but locally, as clearly seen in Fig. 4a, there are certain concentration inhomogeneities in the element distribution. Thus, the obtained structure is in the non-equilibrium state, which

leads to a decrease in the number of separated from each other identical atoms and an increase in the complexes formed by these atoms. It is quite clear that such a non-equilibrium structure at elevated temperatures will try to achieve the energy minimum. The “entropy forces” ($\vec{F}(\mathbf{X}) = T\vec{\nabla}_{\mathbf{X}}S(\mathbf{X})$, where T is the temperature, $S(\mathbf{X})$ is the system entropy for the given configuration \mathbf{X} [26, 27]) and the usual concentration gradient will be the main driving forces in this case.

Despite the negative moments of the estimation, the dependences $\chi(T)$ and the quantitative values of the magnetic moments can be explained quite well by using the simulation results and the presence of “entropy forces” and the concentration gradient in the non-equilibrium state. Indeed, although the alloy underwent homogenizing annealing in the manufacturing, however, for further study, the samples were cut from it, from which then the pieces of material were torn off for studying the magnetic susceptibility. The thermal action when cutting the material and the mechanical effect when tearing off the material for investigations quite logically transfers HEA into the non-equilibrium state that does not correspond to the minimum entropy and uniform distribution of elements (i.e. leads to the formation of a significant amount of superparamagnetic complexes). In the measurements, during and after annealing at temperatures of 800°C and 950°C due to the action of “entropy forces” as well as the concentration gradient, the system tries to achieve the equilibrium state (the maximum entropy and uniform distribution of elements); moreover, the higher the temperature, the greater such an entropy force is and the more complexes of smaller sizes are formed, as follows from the evaluation results.

It is quite reasonable that a decrease in size of these complexes should occur due to the shift of the atoms forming such a complex to other positions. Although HEA are characterized by a slow diffusion [28], and relatively small annealing times even under isothermal conditions (30 min) may cause distrust in the possibility of such a process; however, it should be considered the fact that to destroy the complex, it is enough to move the atom to the nearest adjacent position either in a close packed row, or in the adjacent row. Since the exchange interaction, which is responsible for introducing such a complex, is the short-range one, then the transition of only one atom to the adjacent position is enough to destroy the entirety of the exchange interaction of such a complex. Obviously, this will be facilitated by the defect structure in the non-equilibrium state.

Thus, as seen from the simulation results performed in [25] and the simulation results of the structure we carried out, the assumption that the temperature dependences $\chi(T)$ are determined by superparamagnetic clusters formed by the atoms bearing a localized magnetic moment seems quite reasonable for the alloys with the fcc structure. The evaluations we have reviewed enabled us to determine the number of atoms in such clusters. It is quite clear that these estimates are rather rough, since, as seen from the simulation results we have carried out, the clusters with the same number of atoms are almost not formed in the fcc structure of HEA. Such estimates could be associated with some average number of atoms in these clusters. But for the case of identical (iron) atoms included in such a cluster, we obtained estimates that are

unlikely to occur in the real crystal structure because of a large number of atoms in these complexes. A picture, when such complexes are formed of two types of atoms (Fe and Co), is more realistic. We did not analyze such model structures, but it would be logical that estimates of the number of components in the cluster will also be rather rough, and not only because the particle size dist-

tribution is not taken into account in such a cluster, but also because these estimates are made in approximation of the same number of Fe and Co atoms in the cluster. In this respect, it is hoped that the magnetic moments of these atoms are sufficiently close, and, thus, the estimated values of the number of components in the complex can be close to the average ones.

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