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Concentration Effects in the Electronic Properties of High-entropy Film Alloys

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Calculation results regarding the concentration dependence of the electrical transfer parameters of resistivity, mean free path and Fermi energy for high-entropy alloys HEA (number of components from 4 to 6) in the form of film or bulk alloys are presented. Calculations were made assuming the additivity of parameters: $\rho = \sum_{i=1}^{n} c_i \rho_i$, $\lambda^{-1} = \sum_{i=1}^{n} c_i \lambda_i^{-1}$ and $\varepsilon_F = \sum_{i=1}^{n} c_i \varepsilon_{Fi}$ (ρ is the resistivity; λ is the mean free path of electrons; ε_F is the Fermi energy), which in the case of resistivity is confirmed experimentally. Based on the obtained results and analysis of the Fermi surface form for HEA, a qualitative conclusion is made regarding the fact that studied in the work HEA should not be classified as new substances, since they are one of the types of metallic solid solutions with electronic parameters close in magnitude to metals.

Keywords: Film HEA, Resistivity, MFP, Fermi energy, Concentration dependence, Fermi surface.

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1. INTRODUCTION

The unique mechanical properties of bulk high-entropy alloys (HEA) have been a constant stimulus for research of their structural, thermodynamic, mechanical, and functional properties. A fundamental generalization of the main results of these studies is carried out in [1]. Since 2010, intensive studies of the electrophysical, magnetic, and magnetoresistive properties of HEA, both bulk samples and coatings and thin films have begun (see, for example, [2-8]).

In this regard, [2] is largely a software work, since in it, perhaps for the first time, on the example of $(Co\text{-}Cr\text{-}Fe\text{-}Ni)_{1-x}Al_x$ HEA (in the notation of the authors of [2] – $Al_xCoCrFeNi$), where x = 0-2 at. %, the electrophysical, magnetic, magnetoresistive and Hall properties were studied experimentally and by calculation. Three types of samples were investigated: after condensation, homogenization and deformation. In all three cases, the temperature dependence of the resistivity has a typical character for metallic magnetic materials: $\rho = \rho_r + A\ln T + BT^2 + CT^3$ (interval 4.2-66 K) or $\rho = \rho_r + BT^2 + DT$ (interval 100-300 K), where ρ_r is the residual resistivity, and the terms proportional to $\ln T$, T^2, T^3 i T are responsible for the Kondo electron scattering mechanism, for electron-magnon and low- or high-temperature electron-phonon interaction, respectively. The resistivity and the corresponding thermal coefficient of resistance vary within the limits $(100\text{-}280)\cdot10^{-8}$ Ohm·m or from $3\cdot10^{-4}$ to $4\cdot10^{-3}$ K^{-1} respectively, which is in good agreement with the data for metallic materials.

The authors of [2] also calculated the average mean free path (MFP) of electrons λ depending on the Al atoms concentration at T = 5 K and 300 K. In the first case, the indicated dependence has a different character: at 5 K, the value of λ monotonically decreases from 94 nm (x = 0.25 at. %) to 33 nm (x = 1.25 at. %), and at T = 300 K, λ in the same concentration interval increases non-monotonically from 72 nm to 128 nm.

Such a non-standard dependence of λ versus T can be explained only by the fact that, according to the conclusions of the authors [2], the conductivity of the samples has a hole character.

A large number of original results of the authors [2] allows to follow the concentration dependence of the resistivity and Fermi energy for $(Co\text{-}Cr\text{-}Fe\text{-}Ni)_{1-x}Al_x$ HEA. Although the samples had different processing history, almost monotonic dependences $\rho(x_{Al})$ and $\varepsilon_F(x_{Al})$ are observed: $\rho(x_{Al})$ at 250 K increases in the interval $(110\text{-}190)\cdot10^{-7}$ Ohm·m and ε_F (x_{Al}) at 300 K decreases from 6.94 eV (x_{Al} = 0.50 at. %) to 2.15 eV (x_{Al} = 1.25 at. %). Note that the results of [2] in relation to ρ, λ, and ε_F will be used by us in the analysis of our own results.

Works [3-5] are devoted to virtually the same problem – the influence of non-magnetic components on the magnetic properties of HEA: (Co-Cr-Fe-Ni-W) [3], $(Fe\text{-}Co\text{-}Ni\text{-}Cr)_{1-x}Cu_x$ [4] and $(Co\text{-}Fe\text{-}Ni)_{1-x-y}Cr_y\text{-}Cu_x$ [5].

Data on the magnetization, magnetic moments, stabilization of paramagnetic and magnetic phases are given in these works. From our point of view, the authors obtained a very important results [4]. They made maps of the element distribution, on which the areas of individual elements localization (in other words – granules) are recorded. This observation will greatly clarify the stabilization of granules, the existence of which is considered as a hypothesis rather than a fact.

In our works [6-8], we described the observations of film HEA in the form of Co(20 nm)/Ni(14 nm)/Cu(20 nm)/Fe(30 nm)/Al(15 nm)/S multilayer (S is the substrate) of the giant magnetoresistance with an amplitude of 0.30 %. We associated the realization of this effect with the spin-dependent scattering of conduction electrons on hypothetical AlNi particles [2].

The aim of our work can be formulated as follows: the study of the electronic properties of film HEA, namely, the calculation of the concentration dependences of resistivity, MFP and Fermi energy based on a partially tested hypothesis about the

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additivity of these electronic parameters for s.s. In particular, we are talking about the correctness of the application when calculating the following ratios:

$$\rho = \sum_{l=1}^{n} c_l \rho_l + x_i \rho_i + \rho_r,$$

$$\lambda^{-1} = \sum_{l=1}^{n} c_l \lambda_l^{-1} + x_i \lambda_i^{-1},$$

$$\varepsilon_F = \sum_{l=1}^{n} c_l \varepsilon_{Fl} + x_i \lambda_i,$$

where index "l" is the numbers of the basic elements that form the main phase of the HEA, index "i" is the doping element; ρ_r is the residual resisttivity.

The ratio for λ^{-1} is approximate, since we wrote the value ρ as follows:

$$\rho = \frac{\overline{A}}{\lambda} = \frac{c_1 \overline{A}}{\lambda_1} + \frac{c_2 \overline{A}}{\lambda_2} + \ldots + \frac{c_n \overline{A}}{\lambda_n},$$

where $\overline{A} = \frac{A_1 + A_2 + \ldots + A_n}{n}$ is the average coefficient of proportionality in the ratio $\rho = \frac{\overline{A}}{\lambda}$. We use parameter $\overline{A}$, since the values of A_i for each component are unknown. This causes some error in the calculation.

It should be noted that when calculating $\rho(x_i)$ and $\lambda(x_i)$ we used an array of our own data accumulated during the study of the dimensional effects in the parameters of electrical transfer of single-layer films. When calculating $\varepsilon_F(x_i)$, literature data for bulk metals were used. The properties of four-, five-, and six-component film HEA based on Fe, Co, Ni, and Cr were studied (Fe, Co, Ni, Cu and Cr and Fe, Co, Ni, Cu, Cr and Al). The value of x_i was 0, 0.05, 0.10, 0.15 and 0.20 at 300 K.

In the future, we will use more convenient notations, namely (s.s. FeCoNi)$_{1-x}$– Cr$_x$; (s.s. FeCoCr)$_{1-x}$ – Ni$_x$; (s.s.(FeNiCr)$_{1-x}$ – Co$_x$; (s.s. (CoNiCr)$_{1-x}$ – Fe$_x$, etc., where s.s. denotes a solid solution.

2. RESISTIVITY AND MFP

Fig. 1 shows the calculated data for four- and five-component film alloys, which at all values x are three- or four-component equiatomic systems. Note that the resistivity values agree well with similar data for five-component film alloys [6, 7]. To some extent, this can satisfy the correctness of our hypothesis about the additivity of the resistivity of single-component films, on the basis of which HEA is formed. Since this issue is of a methodological nature for us, a comparison was made [7] of the calculated values and experimental data for the thermal coefficient of resistance and the so-called magnetic coefficient of giant magneto-resistance. In these cases, there was very good correspondence of these coefficients [6].

The given facts served as a basis for us to perform similar calculations for MFP (Fig. 2) in order to establish the correlation between ρ and λ using the method of calculations for resistivity (see also [9-11]).

In general, the indicated correlation takes place, i.e., with a decrease in λ, the value of ρ increases and vice versa. Only in the case of the dependences 2 (Fig. 1a and Fig. 2a) and 3 (Fig. 1b and Fig. 2b), no correlation is observed. The reason for this may be related to the inaccuracy of the data regarding the dependence of ρ and λ on the thickness of single-layer films. The error of the value of ρ can be related to the inaccuracy of the thickness determination, while the accuracy of the calculations of λ is primarily determined by the theoretical model. We used the theoretical models of Tellier, Tosse, and Pichard (for more details, see [12]) in the form of a linearized relationship and an isotropic scattering model. Their effectiveness depends entirely on the accuracy of measuring film thickness, average crystallite size, and resistivity. The combination of these factors does not always guarantee the necessary accuracy of the MFP determining.

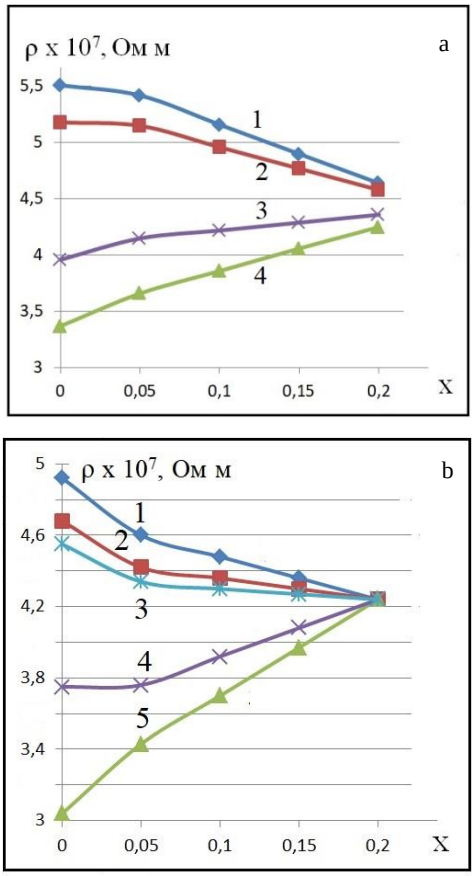

Fig. 1 – Dependence of resistivity ρ versus concentration x for four-component (a) HEA (s.s. FeCoNi)$_{1-x}$ – Cr$_x$ (1); (s.s. FeCoCr)$_{1-x}$ – Ni$_x$ (2); (s.s. FeNiCr)$_{1-x}$ – Co$_x$ (3); (s.s. CoNiCr)$_{1-x}$ – Fe$_x$ (4) and for five-component (b) BEC (s.s. FeCoNiCu)$_{1-x}$ – Cr$_x$ (1); (s.s. FeCoCrCu)$_{1-x}$ –Ni$_x$ (2); (s.s. FeCoNiCr)$_{1-x}$ – Cu$_x$ (3); (s.s. CoNiCrCu)$_{1-x}$ – Fe$_x$ (4) and (s.s. FeCoNiCr)$_{1-x}$ – Co$_x$ (5)

3. FERMI ENERGY AND SURFACE

The problems of this subsection are of a fundamental nature from the point of view of classifying HEA as a class of new substances or only as a variety of metal alloys. Despite the fact that we cannot give an unequivocal answer to this question, we will conduct qualitative considerations and present our vision.

From the point of view of the data shown in Fig. 1 and Fig. 2, the samples of film HEA do not differ from bulk single- or multi-component materials. Along with ρ and λ, the Fermi energy (ε_F) is also a very important kinetic parameter.

Fig. 3 presents the dependences of ε_F on concentration x for bulk five- and six-component HEA, since we used the values of ε_F for bulk one-component materials in our calculations. It should be noted that the minimum on curves 1 and 2 (Fig. 3b) may be related to the fact that the concentration effect is not implemented in its pure form, but under conditions of change not only in the concentration x, but also in the s.s. elemental composition with concentration $(1 - x)$.

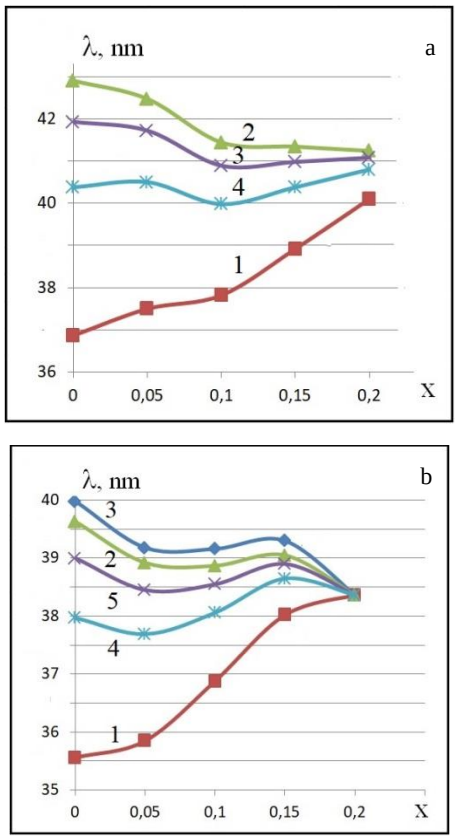

Fig. 2 – Dependence of MFP versus concentration x for four-component (a) and five-component (b) film HEA. Designations are the same as in Fig. 1

In order to get an answer to the question, it is necessary to have information not only about ρ, λ and ε_F, but also about the shape of the Fermi surface, which is the most important. This problem has been well studied on the example of binary intermetallics (see, for example, [13]). For us, [14] is a software work, which presents the Fermi surface for NiFeCoCr FCC HEA, the appearance of which fully corresponds to the Fermi surface FCC-Cu, given in [15]. We conclude that the HEA Fermi surface will correspond to the lattice type on the basis of which the s.s. HEA is formed. From this point of view, it can be argued that studying the electronic properties of various materials allows to conclude whether they belong to a new class of substances.

4. CONCLUSIONS

The electronic properties of four-, five- or six-component HEA films have been studied. In particular, the concentration dependences of ρ, λ and ε_F were calculated under the condition that the doped element concentration x varied in the range 0.05-0.20, and HEA represents a diluted solid solution with a variable concentration $(1 - x)$.

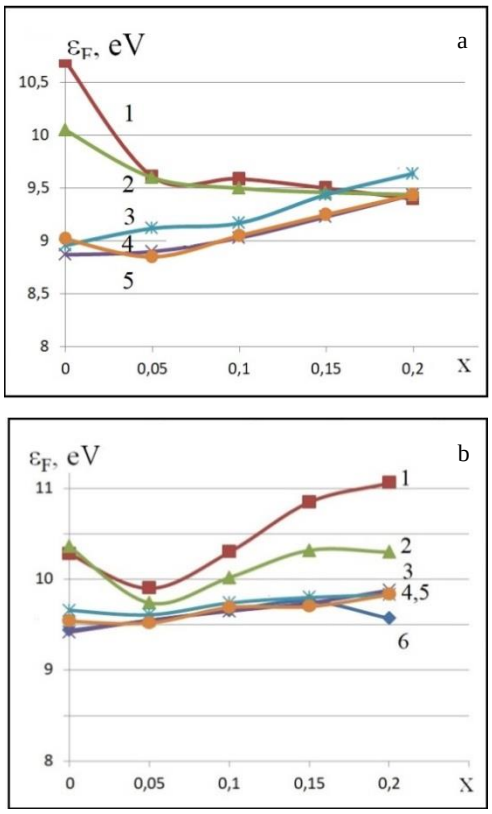

Fig. 3 – Dependences of ε_F versus concentration x for bulk five-component samples (s.s. $FeCoNiCu)_{1-x} - Cr_x$ (1); (s.s. $FeCoNiCr)_{1-x} - Cu_x$ (2); (s.s. $FeCoCrCu)_{1-x} - Ni_x$ (3); (s.s. $FeNiCrCu)_{1-x} - Co_x$ (4) and (s.s. $CoNiCrCu)_{1-x} - Fe_x$ (5) (a) and (s.s. $FeCoNiCuCr)_{1-x} - Al_x$ (1); (s.s. $FeCoNiCuAl)_{1-x} - Cr_x$ (2); (s.s. $FeCoNiCrAl)_{1-x} - Cu_x$ (3); (s.s. $FeCoCuCrAl)_{1-x} - Ni_x$ (4); (s.s. $FeNiCuCrAl)_{1-x} - Co_x$ (5) and (s.s. $CoNiCuCrAl)_{1-x} - Fe_x$ (6) (b)

Based on the assumption of additivity of ρ, λ^{-1} and ε_F, the concentration dependences of these parameters were calculated for four-, five- and six component HEA. The generalized analysis of the obtained results using the data of [14, 15] made it possible to draw a qualitative conclusion that HEA in the film or bulk state should be attributed to a new type of solid solutions, and not to a new type of substances (materials), since different substances should be characterized by their Fermi surface.

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Концентраційні ефекти в електронних властивостях високоентропійних плівкових сплавів

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Представлені розрахункові результати стосовно концентраційної залежності параметрів електроперенесення питомого опору, середньої довжини вільного пробігу та енергії Фермі для високоентропійних сплавів ВЕС (число компонент від 4 до 6) у вигляді плівкових чи масивних сплавів. Розрахунки велись у припущенні адитивності цих параметрів: $\rho = \sum_{i=1}^{n} c_i \rho_i$, $\lambda^{-1} = \sum_{i=1}^{n} c_i \lambda_i^{-1}$ та $\varepsilon_F = \sum_{i=1}^{n} c_i \varepsilon_{Fi}$ (ρ – питомий опір, λ – середня довжина вільного пробігу електронів, ε_F – енергія Фермі), що у випадку питомого опору підтверджується експериментально. На основі отриманих результатів і аналізу форми поверхні Фермі для ВЕС зроблений якісний висновок стосовно того, що вивчені у роботі ВЕС не слід відносити до класу нових речовин, оскільки вони є одним із різновидів металевих твердих розчинів із електронними параметрами, близькими за величиною до металів.

Ключові слова: Плівкові ВЕС, Питомий опір, MFP, Енергія Фермі, Концентраційна залежність, Поверхня Фермі.