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Prediction of Electrophysical and Magnetic Properties of Multicomponent (High-Entropy) Film Alloys

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At the phenomenological level, a theoretical analysis of the concentration dependence of the thermal resistance coefficient (β_T), strain sensitivity coefficient (SC) and Curie temperature (Θ_C) for film high-entropy solid solutions based on Fe, Ni, Co, Cu, Cr was carried out. It was found that β_T of 4- and 5-component film alloys varies within $(1{,}00\text{-}1{,}75)\cdot 10^{-3}$ K^{-1}, and SC – (4.00-5.75) units, which corresponds well to the data for single-component metal films. It was concluded that, from the point of view of β_T and SC, solid solutions of HEA have no advantage over single-component films, but they can be more effective sensitive elements of various sensors due to the thermal stability of the phase composition. The situation is different in the case of Θ_C, when Θ_C can decrease or increase by 350-400 K. Since the information about the HEA domain structure is limited, we assume that the domain structure is realized in magnetic granules based on Cu atoms. But in this case, the size effect can cause a Θ_C decrease, which, unfortunately, we could not take into account within our concept of additivity of the physical quantities of the solid solution of HEA.

Keywords: HEA film, Solid solution, Temperature coefficient of resistance, Strain coefficient, Curie temperature.

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1. INTRODUCTION

The great interest of researchers in the physical properties of high-entropy alloys (HEA) stimulates not only experimental (for example, [1-3], but also computational studies based on the phenomenological approach [4]). The latter is due to the fact that experimental studies of HEA, especially in the film state [1-3], are very complex and financially costly. Despite the approximate nature of the calculations, they can be successfully used to predict various physical properties of HEA depending on the concentration of magnetic and non-magnetic components. For example, in works [1, 2], the electrical and magnetic properties of HEA with a very close elemental composition were studied, which in our notation has the following form: s.s. $(CoFeNiCr)_{1-x}Al_x$ [1] or s.s. $(CoFeNiCr)_{1-x}Cu_x$ [2], where s.s. is a solid solution. We will additionally explain that the notation s.s. (CoFeNiCr) corresponds to the basic (phase-forming) s.s. based on the main group of elements, and s.s. $(Co, Fe, Ni, Cr)_{1-x}Al_x(Cu_x)$ is the designation of s.s. of Al [1] or Cu [2] atoms in s.s. $(CoFeNiCu)_{1-x}$.

In works [1-3], the electronic and magnetoresistive properties of film HEA of the same elemental composition as in works [1, 2] were investigated for the first time.

Note that the authors of the paper [1] used the formulas of classical physics in their calculations: for the density of charge carriers, the wave vector of the electron, the energy and the Fermi speed. As a result, an array of data was obtained, which correspond very well to our own experimental results. The approach of the authors [1] could not be used by the authors [3, 4], because they analyzed the properties of HEA film, in which size effects, which are specific for dimensional objects, play an important role along with concentration effects. The authors [1-3] proposed their research concept, based on the condition of additivity of the resistivity of s.s. HEA

$$\rho_{s.s.} = \sum_{l=1}^{n} c_i \rho_i + \rho_r, \qquad (1)$$

where $\rho_{s.s.}$, ρ_i and $\rho_r \ll \rho_{s.s.}$ are the resistivity of s.s., resistivity of a separate component and the residual resistance, respectively; c_i is the concentration of the i-th component.

From the ration [1], which fully corresponds to the experimental results, it is easy to go [3] to the relation for the thermal coefficient of resistance (TCR):

$$\beta_T = \frac{d\ln\rho}{dT} = \frac{1}{\sum\limits_{i=1}^{n} c_i \rho_i} \frac{\partial}{\partial T}\left(\sum_{i=1}^{n} c_i \rho_i\right) = \frac{\sum\limits_{i=1}^{n} c_i \rho_i \beta_{T_i}}{\sum\limits_{i=1}^{n} c_i \rho_i}. \qquad (2)$$

We proposed a similar ratio for the coefficient of longitudinal strain (SC):

$$\gamma_l = \frac{d\ln R}{d\varepsilon_l} = \frac{d\ln \sum_{i=1}^{n} c_i \rho_i}{d\varepsilon_l} + 1 + 2\cdot\left(\sum_{i=1}^{n} c_i \mu_{fi}\right),$$

where R is the electrical resistance; ε_l is the longitudinal deformation; $\mu_f = \sum\limits_{i=1}^{n} c_i \mu_{fi}$ is the Poisson ratio for s.s. and μ_{fi} – for the i-th component.

Differentiating (1) with respect to ε_l, we obtained the ratio for SC of s.s. HEA (see also [1]):

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$$\gamma_l = \frac{1}{\sum_{i=1}^{n} c_i \rho_i} \frac{\partial}{\partial \varepsilon_l} \left(\sum_{i=1}^{n} c_i \rho_i \right) + 1 + 2 \sum_{i=1}^{n} c_i \mu_i = \\ = \frac{\sum_{i=1}^{n} c_i \rho_i \left(\gamma_{li} - 1 - 2\mu_{fi} \right)}{\sum_{i=1}^{n} c_i \rho_i} + 1 + 2 \sum_{i=1}^{n} c_i \mu_{fi}, \tag{3}$$

where it is taken into account that $\frac{d \ln R_{ss}}{d\varepsilon_l} - \frac{d \ln \rho_{ss}}{d\varepsilon_l} =$

$$= 1 + 2 \cdot \left(\sum_{i=1}^{n} c_i \mu_{fi} \right).$$

We note that when experimental values are used in (2) and (3), the dimensional effects described by us in [1] will be taken into account automatically.

In [5], the concept of additivity of physical quantities for s.s. was extended by us to the case of the mean free path of conduction electrons (λ) and Fermi energy (ε_F).

If in the first case, there is a reason to write the equation:

$$\lambda_{s.s.}^{-1} = \sum_{l=1}^{n} c_i \lambda_i^{-1} ,$$

because $\rho_{s.s.} \sim 1/\lambda_{s.s.}$, then in the second case our hypothetical equation $\varepsilon_F = \sum_{l=1}^{n} c_i \varepsilon_{Fi}$ needs experimental verification. A similar situation is established by us in this work as a result of the proposed equation for the Curie temperature of s.s. HEA:

$$\Theta_c^{s.s.} = \sum_{l=1}^{n} c_i \Theta_{ci} , \tag{4}$$

in which you can limit yourself only to the sum of the indices of the magnetic components.

It is clear that formula (4) contains the idea that magnetic domains are formed by all magnetic components, and therefore it is more convincing compared to the similar one for ε_F. Considerations regarding magnetic domains will be given in subsection 2.2. Taking into account the given information, the purpose of our work can be formulated as follows: calculation of the concentration dependence of TCR, SC and Curie temperature for 4- and 5-component film HEA with a thickness of 50-80 nm, which can act as sensors sensitive elements of non-electric quantities.

2. RESULTS AND DISCUSSION

2.1 Electrophysical Properties

In all three cases of calculations in the initial state, a 4-component film s.s. is supported, respectively, by the fourth or fifth element with x concentration. It is clear that a change in the concentration x will lead to a change in the concentration $(1 - x)$ of basic s.s., which we strictly took into account. It should also be noted that the consideration of s.s. close to equiatomic does not narrow the general conclusions.

The results of calculations of the concentration dependences of β_T are shown in Fig. 1. These data allow us to assert that the electrophysical properties of s.s. HEA, in particular, β_T, have a typical character for metals and do not differ in their uniqueness, as, for example, in the case of magnetic properties [3], which are caused by the degrouping of the crystal lattice.

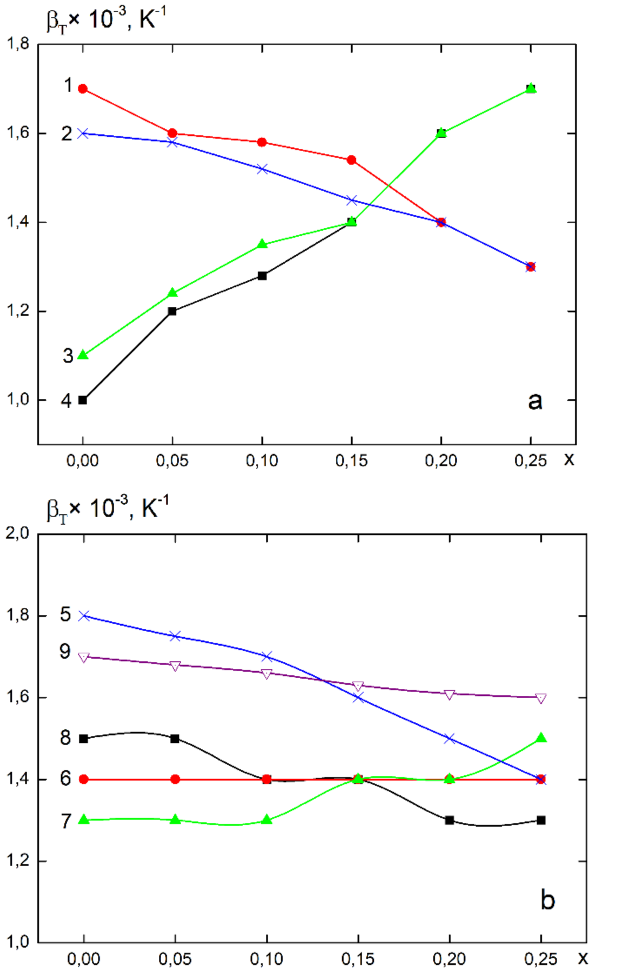

Fig. 1 – Dependence of β_T versus concentration x for 4- (a) and 5-component (b) film systems: s.s. $(FeCoNi)_{1-x}Cu_x$ (1); s.s. $(FeNiCu)_{1-x}Co_x$ (2); s.s. $(FeCoCu)_{1-x}Ni_x$ (3); s.s. $(NiCoCu)_{1-x}Fe_x$ (4); s.s. $(FeNiCoCr)_{1-x}Cu_x$ (5); s.s. $(FeNiCrCu)_{1-x}Co_x$ (6); s.s. $(FeCoCrCu)_{1-x}Ni_x$ (7) and s.s. $(FeNiCoCu)_{1-x}Cr_x$ (9)

A similar conclusion can be drawn in the case of SC γ_l (Fig. 2). A relatively small value of SC is explained by the fact that the HEA can be considered as a single-layer multicomponent sample, in which the deformation dependence of λ and the geometric factor $1 + 2\sum_{i=1}^{n} c_i \mu_i$ (for more details, see [1]) make the main contribution to the SC value.

The main advantage of sensitive elements based on film HEA is the temperature stability of the phase composition.

2.2 Magnetoresistive Properties

In previous works (see, for example, [3]), we observed magnetoresistance with all the signs of giant magnetoresistance (GMR) with a relatively small, no more than 0.3 %, amplitude. Usually, this effect is implemented as a result of spin-dependent scattering of electrons (SDSE) on magnetic granules in a single-layer film or on magnetic interfaces [6]. The first mechanism takes place in our case with the simultaneous condensation of individual components.

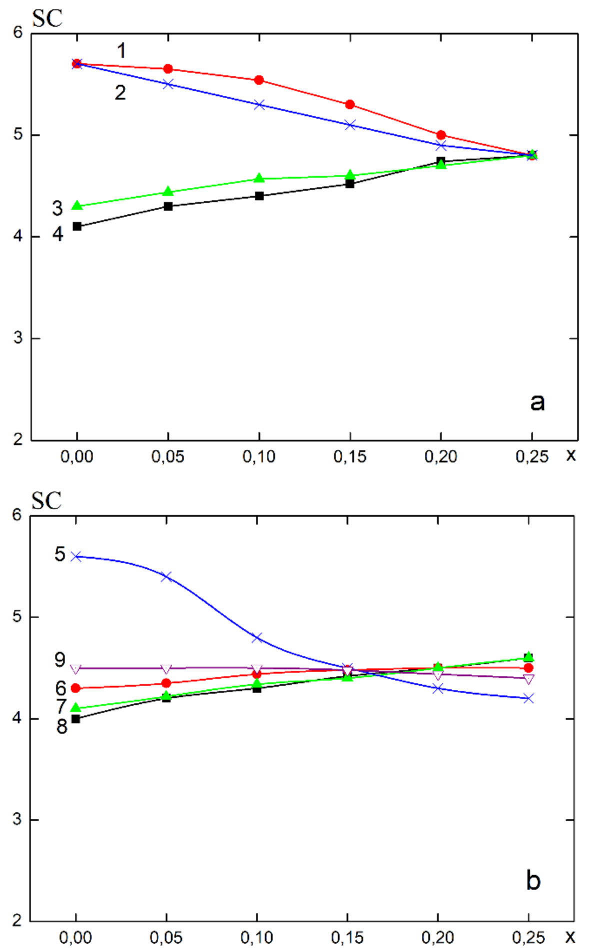

Fig. 2 – Dependence of SC versus concentration x for 4- (a) and 5-component (b) film systems. The designations are as in Fig. 1

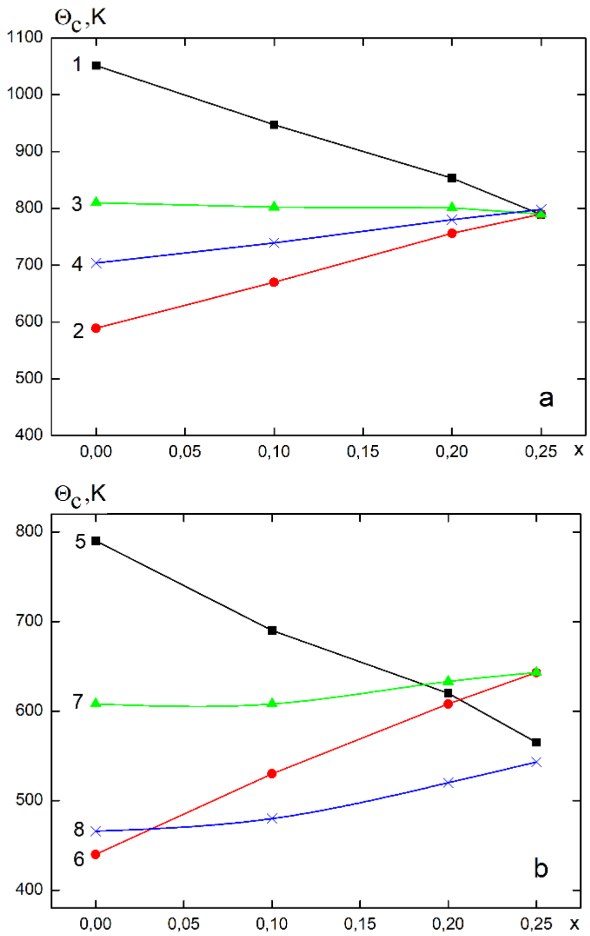

Fig. 3 – Dependence of the Curie temperature Θ_C versus the concentration x for 4- (a) and 5-component (b) film systems. The designations are as in Fig. 1

According to the data of work [2], in a single-layer film of s.s. HEA consists of Cu nanoparticles with a small concentration of Fe, Ni, and Co magnetic atoms. This causes the GMR effect in such films where SDSE will take place during layer-by-layer condensation of individual components, when heat treatment causes incomplete diffusional mixing of atoms. As a result, fragments of magnetic interfaces remain, on which GMR with a small amplitude is realized. At the same time, with effective mixing of components, when granules based on Cu atoms with soluble Fe, Co, and Ni atoms are not formed, classical or anisotropic magneto-resistance is observed [3].

2.3 Curie Temperature

Based on the additivity concept of physical parameters for s.s. HEA, similarly to the analysis of the Fermi energy [5], we considered the concentration dependence of the Curie temperature (Θ_C). Our main idea is the assumption that the domain structure is realized only in Cu nanoparticles with atoms of magnetic components dissolved in them. Although it is hypothetically possible to consider the domain structure over the entire volume of the film s.s. Fig. 3 illustrates the dependence of Θ_C in the case of 4- (a) or 5-component (b) s.s. based on Fe, Ni, Co, Cu and Cr.

These dependences have a typical and understandable character, but it is precisely if the concentration of x atoms of non-magnetic components increases and when this leads to a decrease in the concentration of atoms of magnetic components, which causes a decrease in Θ_C (Fig. 3, dependences 1, 5). Otherwise, an increase in Θ_C by a very significant value is observed (Fig. 3, dependences 2-4, 6 and 7). If we compare the concentration dependences for β_T, SC and Θ_C, we can see that Θ_C is the most sensitive to changes in the concentration of individual components. This feature can be used in the formation of sensitive elements of sensors of magnetic quantities.

3. CONCLUSIONS

A qualitative theoretical analysis of the concentration dependence of the electrophysical (β_T and SC) characteristics indicates that film HEA behave in this respect as single-layer metal films, and it makes no sense to expect an improvement in characteristics. As we have repeatedly emphasized, their essential advantage is the thermal stability of the phase composition, since the isomorphic substitution of atoms of similar sizes does not affect either the phase composition or the electrophysical properties. The situation is somewhat different in the case of Θ_C, which can be changed within 350-400 K by varying the concentration of both magnetic and non-magnetic components, which is largely confirmed by the data of [5].

At the same time, this situation will be realized during the formation of the domain structure, since nanomagnetic granules may not ensure the formation of ferromagnetic domains, and the size effect may significantly reduce Θ_C in comparison with the results of Fig. 3.

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Прогнозування електрофізичних і магнітних властивостей багатокомпонентних (високоентропійних) плівкових сплавів

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На феноменологічному рівні проведений теоретичний аналіз концентраційної залежності термічного коефіцієнта опору (β_T), коефіцієнта тензочутливості (SC) та температури Кюрі (Θ_C) для плівкових високоентропійних твердих розчинів на основі Fe, Ni, Co, Cu, Cr. Отримано, що β_T 4-х та 5-ти компонентних плівкових сплавів змінюється у межах (1,00-1,75)$\cdot 10^{-3}$ К$^{-1}$, а SC – (4.00-5.75) одиниць, що добре відповідає даним для однокомпонентних металевих плівок. Зроблено висновок, що з точки зору величин β_T і SC тверді розчини ВЕС не мають ніякої переваги перед однокомпонентними плівками, але вони можуть бути більш ефективними чутливими елементами різних сенсорів у зв'язку з термічною стабільністю фазового складу. Інша ситуація у випадку Θ_C, коли Θ_C може зменшуватися або збільшуватися на 350-400 К. Оскільки інформація стосовно доменної структури плівок ВЕС обмежена, то ми допускаємо, що доменна структура реалізується в магнітних гранулах на основі атомів Cu. Але у цьому випадку розмірний ефект може спричинити зменшення Θ_C, чого, на жаль, ми не могли врахувати у рамках нашої концепції адитивності фізичних величин твердого розчину ВЕС.

Ключові слова: Плівковий ВЕС, Твердий розчин, Температурний коефіцієнт опору, Коефіцієнт тензочутливості, Температура Кюрі.