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Concentration Dependence of Thermodynamic and Dynamic Parameters of High-Entropy Alloys

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The concentration dependences of melting temperature $T_s^{s.s.}$, Debye temperature $\Theta_D^{s.s.}$ and lattice parameter $a_{s.s.}$ for massive high-entropy alloys based on Fe, Ni, Co, Cu and Al were analyzed within the concept of additivity of physical values of high-entropy alloys. 4- and 5-component alloys were considered in the form of single-phase solid solutions. It was established that $T_s^{s.s.}$ can vary within 150 K, that is, $T_s^{s.s.}$ is insensitive to changes in the concentration of individual atoms. It is even less sensitive to concentration $\Theta_D^{s.s.}$ since the maximum value is $\Delta\Theta_D^{s.s.} \cong 80$ K. The lattice parameters change in accordance with Vegard's rule.

Keywords: High-entropy alloys, Dynamic parameters, Melting temperature, Debye temperature, Lattice parameter.

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1. INTRODUCTION

The phenomenological concept of additivity of physical quantities in solid solutions (s.s.) of high-entropy alloys (HEA) was developed in previous works [1, 2]. The concentration dependences of specific resistance (ρ) and electron mean free path (λ) [1], thermal coefficient of resistance (β_T) and coefficient of longitudinal strain sensitivity (γ) [2] were analyzed in film s.s. of HEA. To calculate the concentration dependences of ρ and λ, β_T and γ, the authors [1, 2] used a huge amount of experimental data accumulated by them for single-layer films of individual components of 4- or 5-component HEA.

Due to the absence of similar data for the Fermi energy (E_F) and the Curie temperature (Θ_C), the concentration dependences were obtained for massive samples and therefore, unlike previous calculations, they can correspond to the film HEA only qualitatively.

The purpose of this work is to study the concentration dependences of thermodynamic characteristics (melting temperature $T_s^{s.s.}$) and dynamic characteristics (Debye temperature ($\Theta_D^{s.s.}$) and lattice parameter $a_{s.s.}$). 4- and 5-component systems based on Fe, Ni, Co, Cu and Al were analyzed, in which the concentration x of one of the components was set in turn: (s.s. FeNiCoCu)$_{1-x}$Al$_x$; (s.s. FeNiCoAl)$_{1-x}$Cu$_x$, etc., where x = 0, 0.10, 0.15, 0.20, and 0.30. The necessary data of T_s^{Me}, Θ_D^{Me} and a^{Me} were taken from literary sources [3, 4]. The results of the concentration dependence of $T_s^{s.s.}$ are of practical interest from the point of view of the application of HEA.

Obtaining and researching the concentration dependences of the physical parameters of HEA based on metals remains an urgent task of both solid-state physics and functional electronics (see, for example, [1]). In this regard, high technological requirements are placed on HEA: thermal stability of the structural-phase composition and stability or, on the contrary, sensitivity of operating characteristics to the effect of temperature, deformation, magnetic field, etc. This can be achieved first of all by choosing the method (layer-by-layer or simultaneous condensation of components) and conditions of formation (pressure in the vacuum chamber, condensation rate, temperature of the substrate, etc.) of film materials, as well as by changing the thickness or concentration of atoms of individual components of the system. On the basis of the concentration and temperature dependences, it is possible to control the magnetoresistive, magneto-optical, electrophysical and other properties of films within wide limits. The widespread use of the phenomenon of giant magnetoresistance in instrumentation has caused a new wave of both experimental and theoretical research of the HEA properties as functional materials for micro- and nanoelectronics. At the same time, the results of $\Theta_D^{s.s.}$ and $a_{s.s.}$ will be of interest from the point of view of understanding the lattice dynamics, as it has not been considered by anyone yet.

2. RESULTS AND DISCUSSION

2.1 Melting Temperature $T_s^{s.s.}$

We started from the concept of additivity [1, 2] and used the following ratio in the case of a four-component system when calculating $T_s^{s.s.}$:

$$T_s^{s.s.} = \frac{1-x}{n-1}\cdot\left(T_s^{Me_1} + T_s^{Me_2} + T_s^{Me_3}\right) + x\cdot T_s^{Me_4}, \qquad (1)$$

where n is the number of components.

It must be noted that the multiplier $\frac{1-x}{n-1}$ indicates that the basic (phase-forming) combination of atoms is always in an equiatomic ratio both at n = 4 and at n = 5.

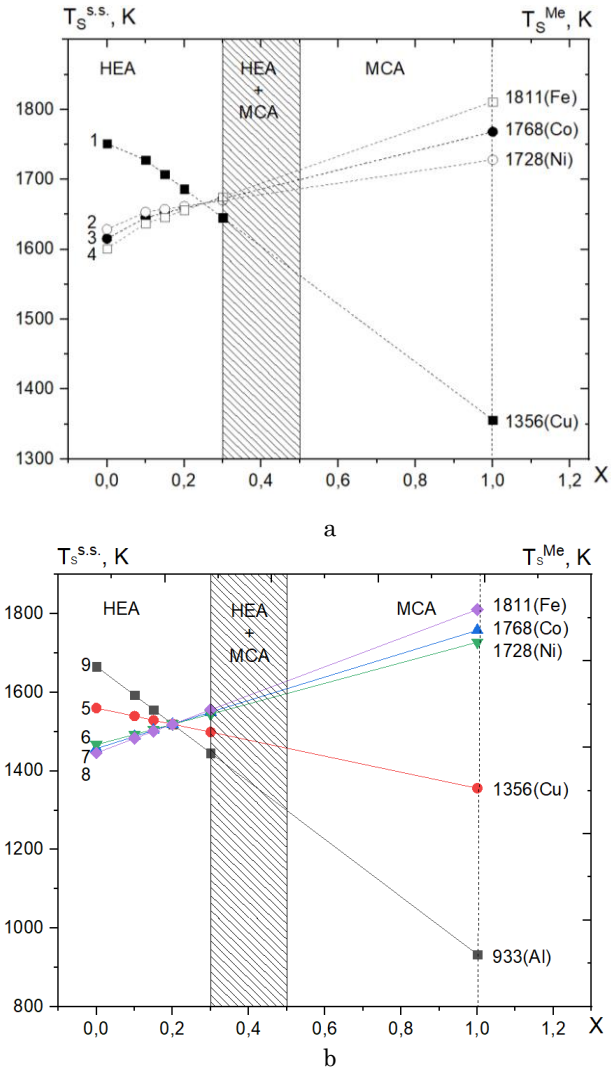


Fig. 1 – Dependence of $T_s^{s.s.}$ on concentration x for 4- (a) and 5- (b) component HEA systems: (s.s. $FeNiCo)_{1-x}Cu_x$ (1); (s.s. $FeNiCu)_{1-x}Co_x$ (2); (s.s. $FeCoCu)_{1-x}Ni_x$ (3); (s.s. $NiCoCu)_{1-x}Fe_x$ (4); (s.s. $FeNiCoAl)_{1-x}Cu_x$ (5); (s.s. $FeNiCoCu)_{1-x}Co_x$ (6); (s.s. $FeCoCuAl)_{1-x}Ni_x$ (7); (s.s. $CoNiCuAl)_{1-x}Fe_x$ (8) and (s.s. $FeCoNiCu)_{1-x}Al_x$ (9)

In addition, it is clear that in the case of a 5-component HEA in relation (1) there will be a term associated with the fifth component.

Fig. 1 presents the results of the calculations of the dependence of $T_s^{s.s.}$ on concentration x, which are extrapolated to T_s^{Me} at $x \to 1$. It is also necessary to give a further explanation for Fig. 1.

In both cases, we assume that HEA with a stable phase composition is limited by the interval $0 < x \le 0.30$, and at $x \approx 0.30$-0.50, a multicomponent alloy (MCA) will form next to HEA.

A single-phase alloy based on Me_4 or Me_5 will eventually form beyond this intermediate interval. At the moment, it is not possible to indicate more precisely the intermediate interval of HEA + MCA.

2.2 Debye Temperature

The calculation of $\Theta_D^{s.s.}$ for a 4-component HEA was carried out according to a relation similar to (1):

$$\Theta_D^{s.s.} = \frac{1-x}{n-1}\cdot\left(\Theta_D^{Me_1} + \Theta_D^{Me_2} + \Theta_D^{Me_3}\right) + x\cdot\Theta_D^{Me_4}. \qquad (2)$$

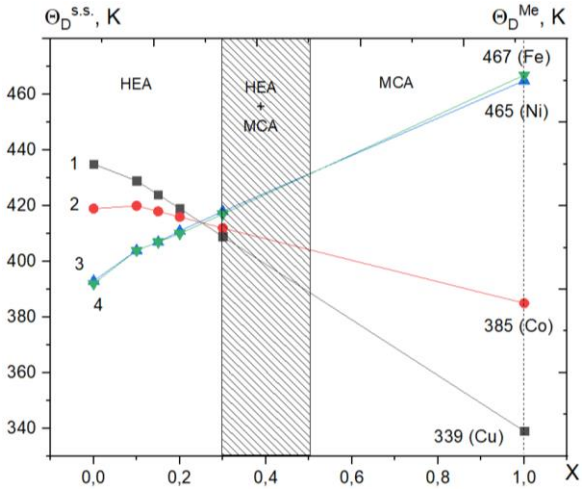
If in the case of the melting temperature (Fig. 1a) there is a significant decrease of $\Delta T_s^{s.s.} = 100$-200 K, then in the case of $\Theta_D^{s.s.}$ (Fig. 2) the effect of $\Delta\Theta_D^{s.s.}$ can be considered insignificant. This means that the HEA phonon spectrum is insensitive to changes in the concentration of atoms. In our case, this can be explained by the closeness of the value of Θ_D^{Me} for four metals Cu, Co, Ni, and Fe, although the value of Θ_D^{Al} differs very significantly. It is also necessary to point out on graphs 7 and 8 in Fig. 2b, according to which the temperature $\Theta_D^{s.s.}$ does not depend on the concentration of Ni and Fe atoms, which is due to the practically identical value of Θ_D^{Ni} and Θ_D^{Fe}.

2.3 The Lattice Parameter

We attribute the change in the lattice parameter to the concentration of atoms and to dynamic effects of the lattice. The lattice parameter was calculated using formulas similar to (1) and (2). In the case of a 4-component system, the relation has the following form:

$$a_{s.s.} = \frac{1-x}{n-1}\cdot\left(a^{Me_1} + a^{Me_2} + a^{Me_3}\right) + x\cdot a^{Me_4}. \qquad (3)$$

Concentration dependences of $a_{s.s.}$ for 4- and 5-component systems are presented in Fig. 3, which in previous cases were extrapolated to the parameter a^{Me_i}. It is possible to establish the fact that slight changes in $a_{s.s.}$ fully correlate with changes in $\Theta_D^{s.s.}$.



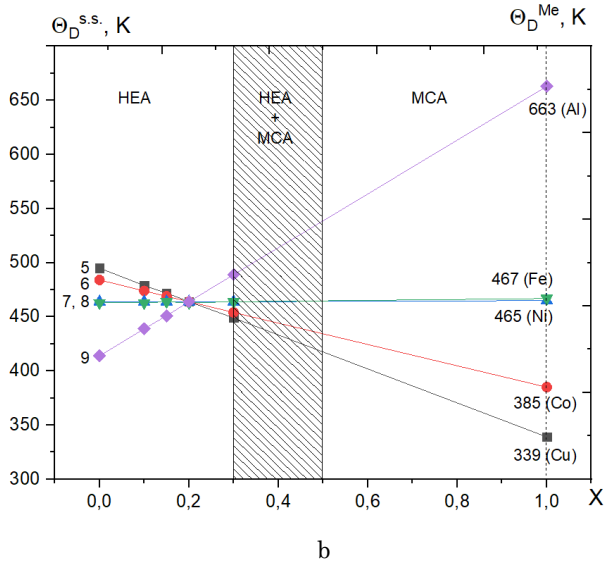
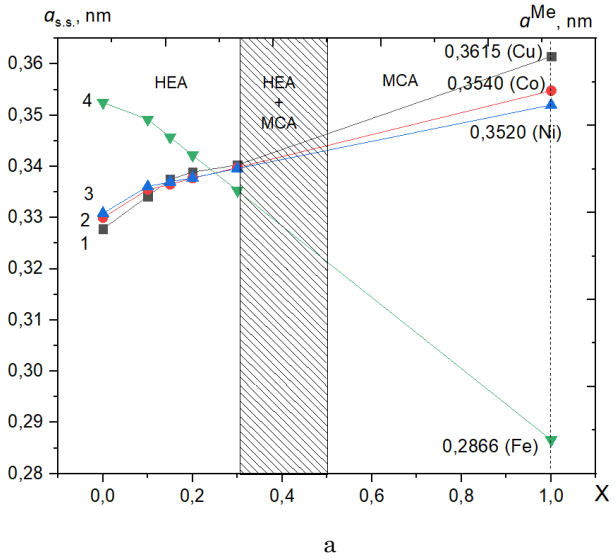


Fig. 2 – Dependence of $\Theta_D^{s.s.}$ on concentration x for 4- (a) and 5- (b) component HEA systems. Designations of systems are the same as in Fig. 1



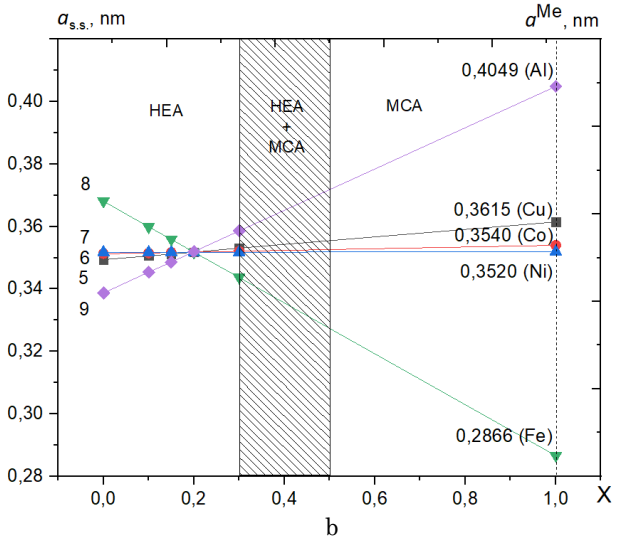


Fig. 3 – Lattice parameter $a_{s.s.}$ for different 4- (a) and 5- (b) component systems. Designations are the same as in Fig. 1

3. CONCLUSIONS

The analysis of the concentration dependences of $T_s^{s.s.}$, $\Theta_D^{s.s.}$ and $a_{s.s.}$ of 4- or 5-component HEA was carried out at the phenomenological level for the first time. Despite the fact that the analysis cannot claim high accuracy, it qualitatively allows us to understand the behavior of the melting temperature, Debye temperature and lattice parameter of the high-entropy s.s. Together with the results of works [1, 2], we have covered a wide range of properties of HEA in both solid and film states. Having no fundamental comments on the concept of additivity of physical quantities in HEA, it is necessary to emphasize that it works only in the case of a single-phase alloy in the form of s.s. The formation of side phases will lead to a decrease in the accuracy of calculations. The next stage of our research will be the experimental verification of the obtained results.

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Концентраційна залежність термодинамічних і динамічних параметрів високоентропійних сплавів

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У рамках концепції адитивності фізичних величин високоентропійних сплавів проаналізовані концентраційні залежності температури плавлення $T_s^{s.s.}$, температури Дебая $\Theta_D^{s.s.}$ і параметра решітки $a_{s.s.}$ для масивних високоентропійних сплавів на основі Fe, Ni, Co, Cu та Al. Розглянуті 4-и та 5-ти компонентні сплави у вигляді твердих розчинів однофазного складу. Установлено, що $T_s^{s.s.}$ може змінюватися у межах 150 К, тобто $T_s^{s.s.}$ не дуже чутлива до зміні концентрації окремих атомів. Ще у меншій мірі чутлива до концентрації $\Theta_D^{s.s.}$, оскільки максимальна величина $\Delta\Theta_D^{s.s.} \cong 80$ К. Зміна параметрів решітки відбувається відповідно до правила Вегарда.

Ключові слова: Високоентропійні сплави, Динамічні параметри, Температура плавлення, Температура Дебая, Параметр ґратки.