ФАЗОВЫЕ ПРЕВРАЩЕНИЯ

Prediction of Stable Composition for High-Entropy Refractory Alloys

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The common approach for evaluation of stability of multicomponent substitutional solid solutions using thermodynamic, mechanical, and topological parameters of the constituent elements is developed. The high-temperature systems based on refractory elements (W, Ta, Mo, Nb, V, Ti, Zr, Hf, Cr) are investigated using this approach. Optimal compositions for high-entropy alloys are obtained, and influence of various factors in the formation of stable alloys is described. As shown, the most resistant alloys have non-equiatomic element-contents' ratios. The agreement between element distribution in experimental alloys and predicted stable compositions are obtained for the W–Ta–Mo–Nb and W–Ta–Mo–Nb–V systems.

Key words: high-entropy alloys, refractory alloys, solid solution, thermodynamics.

Розроблено загальний підхід для оцінки стабільности багатокомпонентних твердих розчинів заміщення з використанням термодинамічних, механічних і топологічних параметрів елементів, що їх складають. Високотемпературні системи, що містять тяжкотопкі елементи (W, Ta, Mo, Nb, V, Ti, Zr, Hf, Cr), були досліджені за допомогою цього підходу. Одержано оптимальні склади для високоентропійних стопів і описано вплив різних чинників у формуванні стабільних стопів. Показано, що найбільш стійкі стопи мають неекваіатомне співвідношення складів елементів. Для систем W–Ta–Mo–Nb і W–Ta–Mo–Nb–V було одержано узгодженість між розподілами елементів в експериментальних стопах і прогнозованих стабіль-

них композиціях.

Ключові слова: високоентропійні стопи, тяжкотопкі стопи, твердий розчин, термодинаміка.

Разработан общий подход для оценки стабильности многокомпонентных твёрдых растворов замещения с использованием термодинамических, механических и топологических параметров составляющих их элементов. Высокотемпературные системы, состоящие из тугоплавких элементов (W, Ta, Mo, Nb, V, Ti, Zr, Hf, Cr), были исследованы с использованием этого подхода. Получены оптимальные составы для высокоэнтропийных сплавов и описано влияние различных факторов при формировании стабильных сплавов. Показано, что наиболее стабильные сплавы характеризуются неэквиатомным отношением составов элементов. Для систем W−Ta−Mo−Nb и W−Ta−Mo−Nb−V было получено согласие между распределениями элементов в экспериментальных сплавах и предсказанных стабильных композициях.

Ключевые слова: высокоэнтропийные сплавы, тугоплавкие сплавы, твёрдый раствор, термодинамика.

1. INTRODUCTION

Currently, multicomponent high-entropy metallic alloys (HEAs) were given special attention, as materials exhibiting a unique set of physical and chemical properties [1−10]. In particular, they are considered as promising high temperature cast alloys, which have high hardness and strength, high corrosion and wear resistance [1, 4−10]. Usually, as a HEA, multicomponent alloys, which have at least five principal elements with close-to-equiatomic ratios, are considered [2]. Each principal element should have a concentration between 5 and 35 at.% [1].

HEAs are in the forms of solid solutions rather than intermetallic compounds or metallic glasses [1, 3, 4]. Thermodynamic and topological parameters of the constituent elements were used for prediction of high-entropy phase formation and design alloys [1, 3−6]. It should be noted that topological and thermodynamic parameters are not used in one approach. In this paper, we try to develop a general approach for the prediction of compositions of HEA solid solutions.

Multicomponent alloys can have a simple structure of single-phase solid solution with the energy lower than the energies of corresponding multiphase heterogeneous structures. This can be achieved by increasing entropy of mixing of the alloy by involving a large number of elements. This way decreases the Gibbs free energy, which characterizes the thermodynamic stability of the system. Consider the question in detail. Gibbs free energy G is expressed as follows:

$$G = H - TS,$$

where H—enthalpy, T—the absolute temperature, S—entropy.

We consider HEAs production as the transition from liquid state to crystalline. Any transition has to reduce the Gibbs free energy,

$$\Delta G = G_2 - G_1 = \Delta H - T\Delta S < 0,$$

where G_1 and G_2 are free energies of the initial and final states of the system.

According to the Boltzmann hypothesis, the entropy of mixing n elements in a regular solution can be expressed as follows:

$$\Delta S_{\text{mix}} = -k\sum_{i=1}^{n} c_i \ln c_i, \tag{1}$$

where c_i is the atomic fraction of i-th element, k—Boltzmann constant.

According to Eq. (1), multicomponent alloys with equiatomic composition would have greatest entropy of mixing. HEAs are the substitutional solid solutions with distorted lattice as atoms, which form them, have different sizes. Elastic distortions arising from size mismatch can affect the free energy of the alloy as well. Consideration of various factors, which form the Gibbs free energy, is important to determine the elemental composition and concentrations of HEA, including elastic energy ΔH_{el} and enthalpy of mixing in the liquid state ΔH_{mix}:

$$\Delta H = \Delta H_{\text{mix}} + \Delta H_{\text{el}}. \tag{2}$$

The composition of the most stable HEA may be different from the equiatomic one due to the contribution of factors additional to the entropy. To find the compositions of the most stable solid solutions based on the refractory elements (W, Ta, Mo, Nb, V, Ti, Zr, Hf, Cr), we will estimate Gibbs free energies of these alloys. Many HEAs based on these refractory elements have been in the focus of experimental studies [11–19]. According to literature data, refractory HEAs exhibit high specific yield strengths, while their plastic strains are in the range 5–50% in compression loading conditions. Prediction resistant homogeneous high temperature composition is an actual problem.

2. METHOD

Substitutional solid solutions were considered within of the regular solution approximation. The mixing enthalpy of multicomponent alloy consisting of n elements is as follows [20]:

$$\Delta H_{\mathrm{mix}} = \sum_{i,j=1,\,i\neq j}^{n} c_i c_j \Omega_{ij}, \tag{3}$$

where Ω_{ij}—parameter characterizing the interaction between i and j elements of the regular solution, $\Omega_{ij} = 4\Delta H^{ij}_{\mathrm{mix}}$, c_i—atomic fraction of i-th component, $\Delta H^{ij}_{\mathrm{mix}}$—mixing enthalpy for binary liquid equiatomic alloy. The values $\Delta H^{ij}_{\mathrm{mix}}$ were taken from [21]. They have been tabulated by means of the semi-empirical Miedema's model [22].

The local atomic volumes and bulk modules for solid solutions were considered equal to values for one-component systems.

Mechanical equilibrium condition for solid solution lattice can be written as

$$\sum_{i=1}^{n} c_i B_i \frac{V_i(T) - V(T)}{V(T)} = 0, \tag{4}$$

where $V(T)$—the average volume of atom of the alloy, $V_i(T)$—atomic volume, and B_i—bulk modulus of i-th element;

$$V_i(T) = V_{0i}(1 + \alpha_i(T - T_0))^3,$$

where α_i—linear expansion coefficient for the i-th component, $T_0 = 293$ K—room temperature.

The expression for $V(T)$ can be determined from Eq. (4):

$$V(T) = \frac{\sum_{i=1}^{n} c_i B_i V_i(T)}{\sum_{i=1}^{n} c_i B_i}. \tag{5}$$

Then, the elastic distortion energy of the solid solution, ΔH_{el}, is as follows:

$$\Delta H_{\mathrm{el}} = \sum_{i=1}^{n} c_i B_i \frac{(V_i(T) - V(T))^2}{2V_i(T)}. \tag{6}$$

Solid solution is considered at the effective melting temperature T_{m} that was estimated as:

$$T_{\mathrm{m}} = \sum_{i=1}^{n} c_i T_{\mathrm{m}}^i, \tag{7}$$

where T_{m}^i—melting temperature of the i-th element.

We can obtain an expression for the concentration dependence of the Gibbs free energy change for multicomponent alloy upon crystallization from a liquid state to a substitutional solid solution:

$$\Delta G(c_1, \ldots, c_n) = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} c_i c_j \Omega_{ij} + \sum_{i=1}^{n} c_i B_i \frac{(V_i(T) - V(T))^2}{2V_i(T)} - kT_m \sum_{i=1}^{n} c_i \ln c_i. \quad (8)$$

The minimum of expression (8) corresponds to the composition of stable alloy.

3. CALCULATION

As a first attempt, let us calculate the parameters ΔG, ΔH_{mix}, ΔH_{el}, δ, ΔS_{mix}, T_m for the equimolar alloys of these elements. They are given in Table 1. The parameter δ is expressed as follows:

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2},$$

where $r_i = (V_{0i})^{1/3}$, V_{0i}, c_i are the atomic volume and percentage of the i-th component, $\bar{r} = \sum_{i=1}^{n} c_i r_i$. Parameter δ describes the comprehensive effect of the atomic size difference in n-element alloy [2].

The data in Table 1 show that the addition of elements to the equimolar alloy increases the entropy of mixing. Other parameters do not be-

TABLE 1. Calculated parameters (ΔG, ΔH_{mix}, ΔH_{el}, δ, ΔS_{mix}, T_m) for equiatomic alloys.

No.	Alloys	ΔG, kJ/mol	ΔH_{mix}, kJ/mol	ΔH_{el}, kJ/mol	δ, %	ΔS_{mix}, J/(mol·K)	T_m, K
1	WTaMo	−29.822	−5.333	5.596	2.149	9.135	3294
2	WTaNb	−29.845	−6.667	6.463	1.964	9.135	3245
3	TaMoNb	−25.634	−4.888	6.462	2.232	9.135	2979
4	WTaMoNb	−36.217	−6.500	6.681	2.251	11.527	3158
5	WTaMoNbV	−35.800	−4.640	8.487	3.218	13.382	2963
6	WTaMoNbTi	−38.249	−5.280	6.031	2.111	13.382	2914
7	WTaMoNbHf	−30.388	−4.960	15.084	4.349	13.382	3027
8	WTaMoNbZr	−31.313	−5.440	13.627	4.885	13.382	2952
9	WTaMoNbCr	−25.790	−6.240	20.090	4.816	13.382	2962
10	WTaMoNbVTi	−37.704	−4.222	8.120	3.116	14.898	2793
11	WTaMoNbVTiHf	−33.521	−3.673	14.672	4.658	16.180	2751
12	WTaMoNbVTiHfZr	−31.837	−3.563	17.952	5.516	17.290	2674
13	WTaMoNbVTiHfZrCr	−26.3684	−4.938	26.413	6.608	18.269	2619

have monotonically with the addition of elements in the alloy. The resulting value ΔG can decrease or increase with increasing number of components in the system.

Therefore, it is necessary to find the compositions different from equimolar that have the minimal ΔG value.

The minimization procedure was carried out for this goal:

$$\min \Delta G(c_1, ..., c_n) \to c_i \, (i = 1, ..., n). \tag{9}$$

The values of the constants α_i, V_{0i}, B_i, T_m^i in expressions (3)–(8) were taken from tables [23], and the values of mixing enthalpies for the alloy elements ΔH^{ij}_{mix} were taken from Ref. [21].

Minimum (9) was found using the Monte Carlo method. It was performed according to the following cycle algorithm.

1. The alloy concentrations c_{0i} ($i = 1, ..., n$) were taken as current composition.

2. $\Delta G(c_{0i})$ was calculated according to Eq. (8).

3. Then the concentrations of the alloy were varied randomly $c_{0i} \to$ $\to c_{1i}$ with steps of 0.001.

4. $\Delta G(c_{1i})$ was determined.

5. At $\Delta G(c_{1i}) < \Delta G(c_{0i})$, the current concentration value was taken as c_{1i}; at $\Delta G(c_{1i}) \geq \Delta G(c_{0i})$, the current concentration was stayed as c_{0i}.

6. Then transition was performed on second stage and so on.

In this way, the local minimum ΔG on concentrations was determined.

The different concentrations have been chosen as the initials. However, in all cases, the same final concentrations of alloys were obtained that correspond to the minimum Gibbs free energy. This indicates on the absence of local energy minima in the systems studied.

Thus, we have the optimal compositions with minimal ΔG to investigated systems. They are given in Table 2.

4. RESULTS AND DISCUSSION

If we compare the compositions shown in Tables 1 and 2, it can be seen that the alloys of Table 2 have less Gibbs free energy than similar equimolar alloys. The calculated Gibbs free energy of solid solutions for ternary and quasi-ternary alloy systems are presented in the form of energy−composition diagrams in Figs. 1, 2.

It should be noted that the minimum energy compositions on the diagrams do not correspond to equiatomic concentrations. Therefore, it is desirable to analyse all factors that determine their stability.

It can be seen that the free energy of the solution can be reduced by both entropic part and reduction of the lattice deformation. Therefore, an increase of number of components in solid solution opens the possibility to obtain more equilibrium state with less elastic distortions.

TABLE 2. Calculated parameters (ΔG, ΔH_{mix}, ΔH_{el}, δ, ΔS_{mix}, T_{m}) for alloys with optimal compositions.

| No.	Alloys	ΔG, kJ/mol	ΔH_{mix}, kJ/mol	ΔH_{el}, kJ/mol	δ, %	ΔS_{mix}, J/(mol·K)	T_{m}, K
1	$W_{40.6}Ta_{31.4}Mo_{28.0}$	−30.179	−5.328	5.348	2.093	9.031	3344
2	$W_{42.2}Ta_{30.5}Nb_{27.3}$	−30.348	−7.290	6.715	2.066	8.986	3313
3	$Ta_{36.3}Mo_{32.2}Nb_{31.5}$	−25.682	−4.772	6.380	2.212	9.118	2993
4	$W_{34.6}Ta_{23.5}Mo_{21.2}Nb_{20.7}$	−36.879	−6.618	6.383	2.208	11.328	3235
5	$W_{34.1}Ta_{20.6}Mo_{20.0}Nb_{17.7}V_{7.6}$	−38.930	−5.792	6.829	2.623	12.610	3169
6	$W_{32.8}Ta_{20.6}Mo_{18.6}Nb_{17.0}Ti_{10.0}$	−40.076	−6.154	6.096	2.153	12.871	3109
7	$W_{34.2}Ta_{23.0}Mo_{20.4}Nb_{19.9}Hf_{2.5}$	−37.556	−6.499	7.583	2.685	11.996	3221
8	$W_{34.3}Ta_{22.7}Mo_{20.3}Nb_{19.4}Zr_{3.3}$	−37.794	−6.552	7.622	3.000	12.123	3206
9	$W_{34.6}Ta_{23.1}Mo_{21.2}Nb_{20.3}Cr_{0.8}$	−37.093	−6.584	6.983	2.388	11.615	3228
10	$W_{32.7}Ta_{18.5}Mo_{17.9}Nb_{15.1}V_{6.2}Ti_{9.6}$	−41.679	−5.638	6.579	2.539	13.873	3072
11	$W_{32.5}Ta_{18.4}Mo_{17.4}Nb_{14.6}V_{5.9}Ti_{9.5}Hf_{1.7}$	−42.121	−5.621	7.415	2.843	14.316	3067
12	$W_{32.3}Ta_{18.1}Mo_{16.9}Nb_{14.2}V_{5.6}Ti_{8.9}Hf_{1.7}Zr_{2.3}$	−42.712	−5.675	8.304	3.313	14.840	3055
13	$W_{32.5}Ta_{17.7}Mo_{16.9}Nb_{13.9}V_{5.7}Ti_{9.0}Hf_{1.6}Zr_{2.2}Cr_{0.5}$	−42.848	−5.666	8.572	3.365	14.993	3052
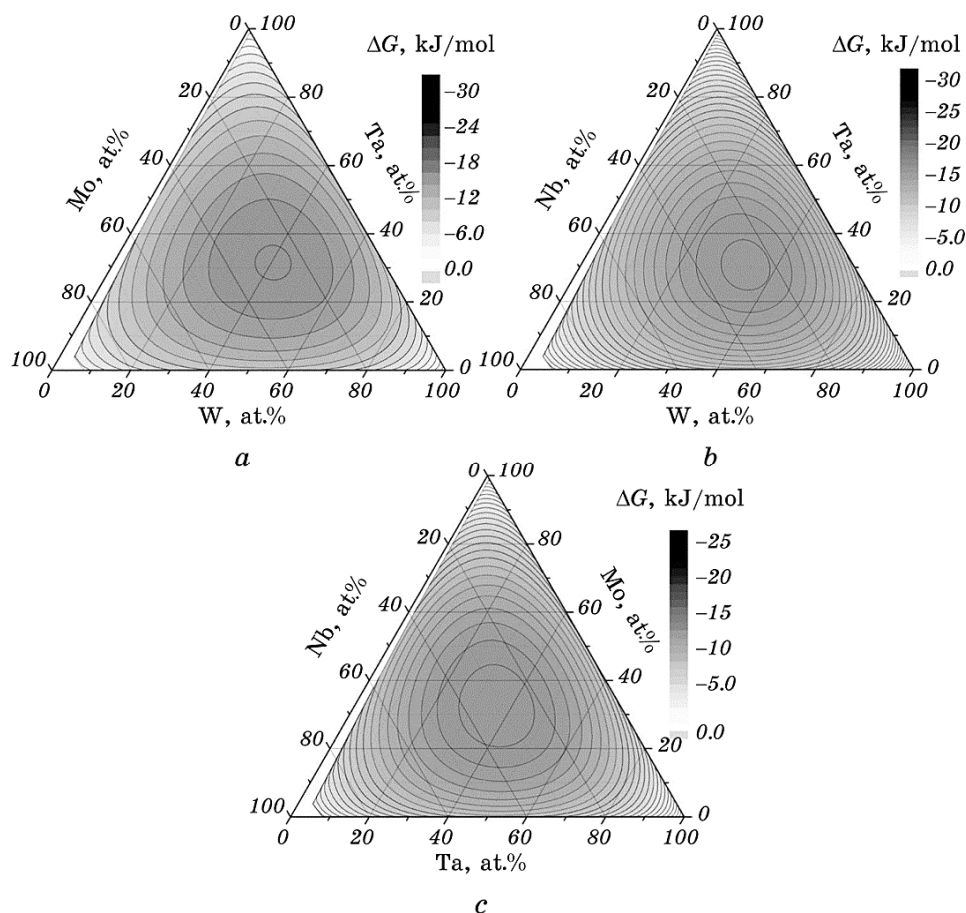
Fig. 1. The calculated Gibbs free energy of solid solutions (ΔG) for ternary alloy systems: W−Ta−Mo (*a*), W−Ta−Nb (*b*), Ta−Mo−Nb (*c*).

The alloys from Table 2 have usually less elastic distortions than similar equiatomic alloys. This is evidenced by the values of ΔH_{el} and δ parameters.

According to [3], ΔH_{mix}, δ parameters play a special role in the formation of solid solutions. A solid solution is crystallized when $\delta < 6\%$ and $\Delta H_{\mathrm{mix}} > -10$ kJ/mol. Therefore, the compositions of Table 2 are formed from substitutional solid solutions.

Alloys of W−Ta−Mo−Nb−V (*1*) and W−Ta−Mo−Nb (*2*) systems with compositions close to equiatomic (see Tables 3, 4) were produced by vacuum arc melting in [11]. All components of these alloys have a b.c.c. lattice, and so formation of b.c.c. substitutional solutions is most probable. This was confirmed by diffraction analysis of these alloys [11]. Moreover, the law of mixture describes density of experimental
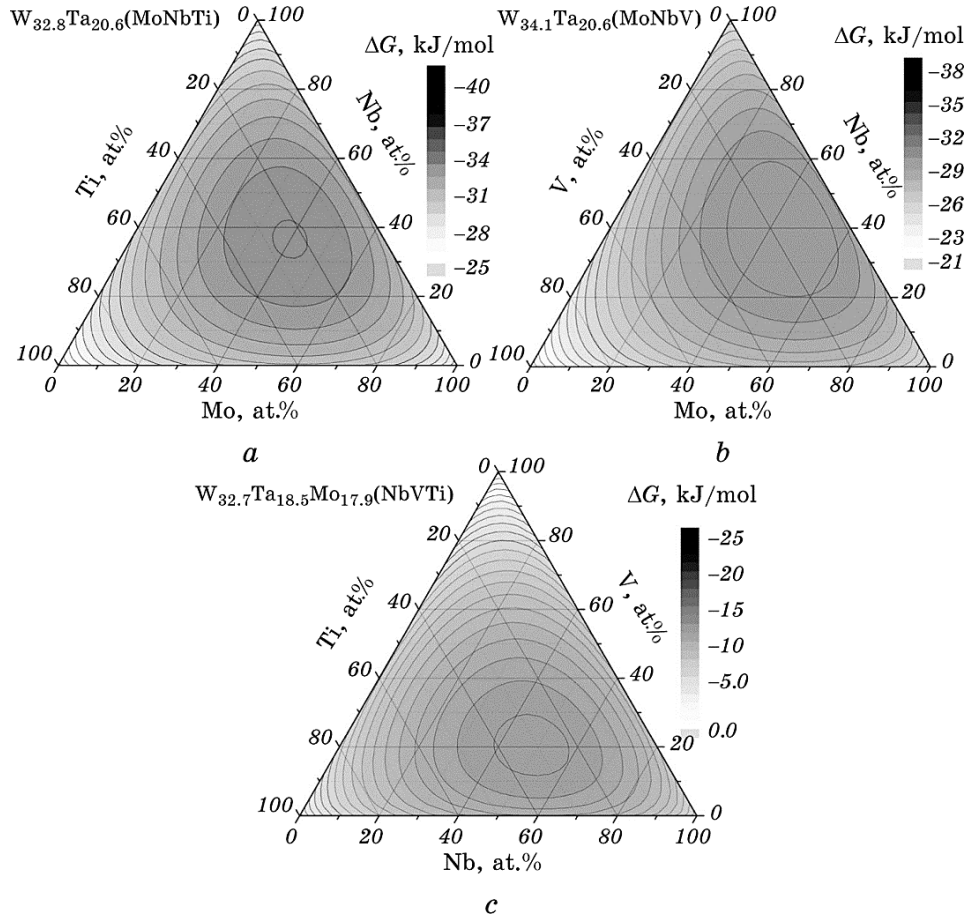
Fig. 2. The calculated Gibbs free energy of solid solutions (ΔG) for quasi-ternary alloy systems: $W_{32.8}Ta_{20.6}(MoNbTi)$ (*a*), $W_{34.1}Ta_{20.6}(MoNbV)$ (*b*), $W_{32.7}Ta_{18.5}Mo_{17.9}(NbVTi)$ (*c*).

alloys and their lattice parameters. Elemental analysis of real alloys shows the heterogeneous distribution of elements [11] (see Tables 3, 4).

We investigated peculiarities of this distribution in alloys (*1* and *2*) and corresponding data are presented in Tables 3 and 4. Here, c_{ea}— average concentrations of the experimental alloys. The distribution of elements in the samples is heterogeneous with the maximal—c_{emax} and minimal—c_{emin} concentrations, according to [11]. Magnitude ($c_{emax} - c_{emin})/2$ describing the amplitude of deviation of element concentrations is given in Tables 3, 4.

Using modelling, we have found that the concentrations of the most energetically favourable solid solutions (c_m) are different from the equiatomic concentrations. It is interesting to analyse the correlation

TABLE 3. c_{m1}—modelled alloy concentration in the W–Ta–Mo–Nb–V system, c_{a1}—average concentration of experiment alloy [11], c_{e1max}—maximal concentration of the element in the experimental alloy [11], c_{e1min}—minimal concentration of the element in the experimental alloy [11].

Concentration	W, at.%	Ta, at.%	Mo, at.%	Nb, at.%	V, at.%
c_{m1}	34,1	20.6	20.0	17.7	7.6
c_{ea1}	22.1	18.0	19.1	20.9	20.0
$(c_{e1max} - c_{e1min})/2$	11.6	4.0	2.2	4.4	12.3
$\left| c_{m1} - c_{ea1} \right|$	12.0	2.6	0.9	3.2	12.4

TABLE 4. c_{m2}—modelled alloy concentration in the W–Ta–Mo–Nb system, c_{a2}—average concentration of experimental alloy [11], c_{e2max}—maximal concentration of the element in the experimental alloy [11], c_{e2min}—minimal concentration of the element in the experimental alloy [11].

Concentration	W, at.%	Ta, at.%	Mo, at.%	Nb, at.%
c_{m2}	34,6	23.5	21.2	20.7
c_{ea2}	26.4	24.8	24.0	24.8
$(c_{e2max} - c_{e2min})/2$	6.8	1.2	3.0	5.0
$\left| c_{m2} - c_{ea2} \right|$	8.2	1.3	2.8	4.1

between values of $\left| c_m - c_{ea} \right|$ and $(c_{emax} - c_{emin})/2$. In the system *1*, the concentrations of W and V have the largest deviation from equiatomic concentration. It was observed for both the model and real alloys (Table 3). For both the model and experimental alloys of system *2*, the largest deviation has W and the smallest deviation has Ta (Table 4).

Deviations from the equiatomic composition predicted by the modelling were observed experimentally [11]. Atomic simulation of the system also showed a low content of vanadium in the solid solution [24, 25].

5. CONCLUSIONS

1. Method was proposed for determining Gibbs free energy of multicomponent substitutional solid solutions in the approximation of regular solution model.
2. It was obtained the most stable compositions for alloys based on the refractory elements (W, Ta, Mo, Nb, V, Ti, Zr, Hf, Cr).
3. It was determined that the thermodynamic optimal compositions do not coincide with equiatomic compositions having the largest mixing entropy.

4. The predicted compositions of the most resistant alloys for the W−Ta−Mo−Nb−V and W−Ta−Mo−Nb systems correlated with element distribution in experimental alloys.

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