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Thermodynamic design of high-entropy refractory alloys

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ABSTRACT

The method for design of stabile multicomponent solid solutions with use thermodynamic, mechanical and topological parameters of the constituent elements was developed. The alloys based on W, Ta, Mo, Nb, V, Ti, Zr, Hf and Cr elements were investigated using this approach. Optimal compositions for high entropy alloys were obtained and influence of various factors on formation of stable alloys was described. It is shown that the most resistant alloys have non equiatomic element ratios. The agreement between element distributions in experimental alloys and predicted stable compositions were received for alloys of W-Ta-Mo-Nb and W-Ta-Mo-Nb-V systems.

1. Introduction

Currently, multi-component 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. Usually, HEAs are considered as multi-component alloys that have at least 5 principal elements with close-to-equiatomic ratios. 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 [1,9,10]. High mixing entropy of HEAs has pronounced effect on their structures by reducing the number of phases and sometimes facilitating the formation of sole solid solution phase. Some parameters were discussed in attempts to predict alloy compositions favorable for formation of solid solution phases in HEAs, among them mixing enthalpy (ΔH_{mix}), configurational entropy (ΔS_{conf}) that forms a major part of mixing entropy (ΔS_{mix}), $\Omega = T_m\Delta S_{mix}/|\Delta H_{mix}|$, differences of atomic sizes (δr), electronegativities ($\delta\chi$) and valence electron concentrations (VEC) of alloy constituents [9–15]. The regions favorable for formation of solid solution phases were determined in coordinates ΔH_{mix}–δr [11], Ω–δr [9], k^{cr}–$\Delta H_{im}/\Delta H_{mix}$ [15]. We developed a general thermodynamic approach for the quantitative prediction of compositions of solid solution HEAs that simultaneously account for three parameters - mixing enthalpy (ΔH_{mix}), configurational entropy (ΔS_{conf}) and lattice strain energy (ΔH_{el}).

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

$$G = H - TS$$

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

HEAs production we consider 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 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

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$$\Delta S_{mix} = -k\sum_{i=1}^{n} c_i \ln(c_i) \quad (1)$$

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

According to (1), multicomponent alloys with equiatomic composition would have greatest entropy of mixing. HEAs are the substitution solid solutions with distorted lattice as atoms that form them have different sizes. Elastic distortions, arising from size discrepancy, can affect the free energy of the alloy as well. Consideration of various factors that 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}.

$$\Delta H = \Delta H_{mix} + \Delta H_{el} \quad (2)$$

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 stable solid solutions based on W, Ta, Mo, Nb, V, Ti, Zr, Hf and Cr elements, we estimate Gibbs free energies of these alloys.

Many HEAs based on these refractory elements have been in the focus of experimental studies [16–24]. According to literature data, refractory HEAs exhibit high specific yield strength and their plastic strains are in the range 5–50% in compression loading conditions. Prediction of resistant homogeneous high temperature composition is an actual problem.

2. Method

Substitution solid solutions were considered within of the regular solution approximation. The mixing enthalpy of multicomponent alloy consisting of n elements is as follows [25]:

$$\Delta H_{mix} = \sum_{\substack{i,j=1 \\ i\neq j}}^{n} c_i c_j \Omega_{ij} \quad (3)$$

where Ω_{ij}-parameter characterizing the interaction between i and j elements of the regular solution. $\Omega_{ij} = 4\Delta H^{ij}_{mix}$, c_i – atomic fraction of i component. ΔH^{ij}_{mix}-mixing enthalpy for binary liquid equiatomic alloy. The values ΔH^{ij}_{mix} were taken from Ref. [26]. They have been tabulated by semi-empirical Miedema model [27].

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

The condition of mechanical equilibrium for solid solution lattice can be written as

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

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.

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

α_i-linear expansion coefficient for the i component, $T_0 = 293$ K.

The expression for V (T) can be determined from (4)

$$V(T) = \sum_{i=1}^{n} c_i B_i V_i(T) \Big/ \sum_{i=1}^{n} c_i B_i. \quad (5)$$

Then the elastic distortion energy in the solid solution ΔH_{el} is as follows

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

Solid solution is considered at the effective melting temperature T_m that was estimated as:

$$T_m = \sum_{i=1}^{n} c_i T_m^i \quad (7)$$

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:

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

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

3. Calculation

As a first step the parameters ΔG, ΔH_{mix}, ΔH_{el}, δ, ΔS_{mix} and T_m for equimolar alloys were calculated (Table 1). The parameter δ

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

take into account atomic volumes (V_{0i}) and concentrations (c_i) of components by means of $r_i=(V_{0i})^{1/3}$ and $\bar{r} = \sum_{i=1}^{n} c_i r_i$. Parameter δ describes the comprehensive effect of the atomic size difference in n-element alloy [11].

Table 1 data shows that the addition of elements to the equimolar alloy increases the mixing entropy. The other parameters do not behave monotonically with the addition of elements in the alloy. The resulting value ΔG can be decreased or increased with increasing number of components in the alloy. The problem is to find the alloy compositions with minimal Gibbs free energy.

The procedure of ΔG minimization was carried out to find the corresponding alloy compositions

$$\min \Delta G(c_i) \rightarrow c_i (i = 1 - n) \quad (9)$$

The values of the constants α_i, V_{oi}, B_i, T_m^i in expression (8) were taken from tables [28], and the values of mixing enthalpies for the alloy elements ΔH^{ij}_{mix} from Ref. [26].

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

1. The alloy concentrations $c0_i$ (i = 1–n) were taken as current composition.
2. $\Delta G(c0_i)$ was calculated according to (8).
3. Then the concentrations of the alloy were varied randomly $c0_i \rightarrow c1_i$ with steps of 0.001.
4. $\Delta G(c1_i)$ was determined.
5. At $\Delta G(c1_i) < \Delta G(c0_i)$ the current concentration value was taken as $c1_i$, at $\Delta G(c1_i) \geq \Delta G(c0_i)$ the current concentration was stayed as $c0_i$.