

Designing high entropy alloys

The complexity of high entropy alloys introduced multiple effects, what makes the use of thermodynamic calculations extremely demanding, due to the amount of data on their subsystems, which has to be collected to make reliable predictions. In fact, in many cases our only aid in projecting high entropy alloys compositions and their properties, are the empirical criteria formulated on the basis of previous studies.

The most basic parameter in HEAs, as their name suggests, is entropy. This extensive thermodynamic property is usually defined by an equation:

$$dS = \left(\frac{dQ}{T} \right)_{rev}, \quad (1.1)$$

where dQ is the heat transferred into a system during the process and T is temperature. Subscript *rev* refers to a reversible process. However, for the purpose of discussion in HEAs, the classic statistical mechanics entropy definition derived in 1877 by Boltzmann is the most appropriate one [1]. Boltzmann suggested that the suitable measure of entropy is the logarithm of the possible distinct microscopic states of the system. The idea was later formulated by Planck in a form of a well-known equation [2]:

$$S = k \ln W, \quad (1.2)$$

where k is the Boltzmann's constant and W is the number of possible microstates corresponding to the macroscopic state of a system.

To determine whether the mixing process at constant temperature and pressure is a spontaneous one, a formulation of Gibbs free energy of mixing is necessary. However, the exact calculation is not possible for the multicomponent system. Takeuchi *et al.* proposed [3] that for a multicomponent system the difference in energy between solid and liquid state (solidification process) is proportional to the free energy of mixing G of the liquid phase. For an alloy system it is given by an equation:

$$G_{mix} = \Delta H_{mix} - T \Delta S_{mix}, \quad (1.3)$$

where G_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. From the equation (1.3) it follows that the higher the entropy of mixing is, the more stable the system (assuming that the enthalpy of mixing remains unchanged). For the random solid solution (so called "Regular solution model"), enthalpy and entropy of mixing can be described by the respective equations:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^r 4\Delta H_{ij}^{mix} n_i n_j = \sum_{i=1, j \neq i}^r \Omega_{ij} n_i n_j \quad (1.4)$$

and

$$\Delta S_{mix} = -R \sum_i^r n_i \ln n_i, \quad (1.5)$$

where R is the gas constant, n_i is the molar fraction of the i -th component, r is the number of components in the system, ΔH_{ij}^{mix} is the enthalpy of mixing for the binary i - j system and Ω_{ij} is the regular solution interaction parameter between i -th and j -th elements, which is assumed to be independent from the composition [4]. The enthalpy of mixing is defined as the difference between the enthalpy of the solution and that of a mechanical mixture of the same components [5]. As for the entropy, Eq. (1.5) is directly connected to the Eq. (1.2), and is considered to be fundamental for high entropy alloys design. It should be noted that to some degree this equation is a simplification, as the total mixing entropy has not only configurational contribution, but also vibrational, magnetic dipole and electronic randomness contributions. For the equimolar composition, the entropy of mixing reaches maximum (as schematically shown in the Fig. 1 on the example of an ideal ternary system) and Eq. (1.5) takes the form:

$$\Delta S_{mix} = R \ln r \quad (1.6)$$

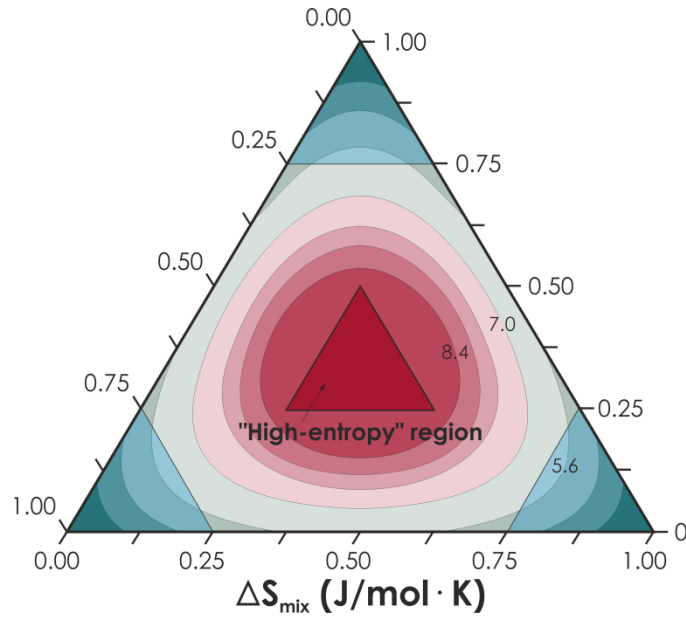


Fig. 1. The contour plot of ΔS_{mix} on a schematic ternary alloy phase diagram. The blue corner regions are showing values typical for the conventional alloys, based on one or two principal elements. The increase of ΔS_{mix} values near the center of phase diagram is clearly visible [6].

There are multiple factors which should be considered during design of the high entropy alloys. Many of them are beyond the scope of the average studies. As a result, from the very beginning of HEAs development, there was a tendency towards seeking for more basic, experimental guidelines, which would help in their synthesis.

Probably the main characteristic of the high entropy alloys is the fact that despite the high number of components, they are believed to possess an increased tendency towards formation of solid solutions of simple structures. For the conventional, binary solid solutions, a number of rules was formulated to describe conditions under which formation of such structures is possible. These are so called Hume-Rothery rules, which for the substitutional solid solutions are as follows [7]:

- If a solute differs in its atomic size by more than 15% from the host, then it is likely to have a low solubility in that metal
- If a solute has a large difference in electronegativity when compared to the host, then it is more likely to form a compound. Its solubility in the host would be therefore limited
- A metal with a lower valency is more likely to dissolve in one which has a higher valency, than vice versa

In the case of high entropy alloys, these rules cannot be applied in a direct way. However, numerous empirical parameters were developed to apply the Hume-Rothery-like rules for the N -component, high entropy systems.

The first one is a Ω parameter. It describes the ratio between the entropy and enthalpy term. Ignoring the solid-state phase transitions, it is natural to use in the entropy term the temperature of melting for a given alloy, as temperature close to the initial formation of solid solution. Basing on the analysis of the HEAs synthesized up to this day, the following conditions should be fulfilled to enable formation of a HEA solid solution [8]:

$$\Omega = \frac{-T_m \Delta S_{mix}}{|\Delta H_{mix}|} \geq 1.1, \quad (1.7)$$

where melting temperature T_m can be estimated from the rule of mixtures:

$$T_m = \sum_{i=1}^r n_i (T_m)_i \quad (1.8)$$

If the value of Ω is lower than the set limit, the chemical interactions between elements may prevail, leading to formation of intermetallic compounds or segregation. Further analysis of the experimental data suggest that additional condition should be put on the value of ΔH_{mix} as formation of solid solution is observed only when $-22\text{kJ/mol} < \Delta H_{mix} < 7\text{kJ/mol}$ [9] (often the range is cited to be even more narrow $-10\text{kJ/mol} < \Delta H_{mix} < 5\text{kJ/mol}$ [10]).

The second parameter - δ , directly corresponds to the Hume-Rothery rule of atomic size difference [11]:

$$\delta = \sqrt{\sum_{i=1}^r n_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \cdot 100\%, \quad (1.9)$$

where r_i is the atomic radius of the i -th element and \bar{r} is the average atomic radius calculated as:

$$\bar{r} = \sum_{i=1}^r n_i r_i \quad (1.10)$$

The analysis of the available experimental data yields the upper limit of δ value at 6.6%, observed for the dual-phase AlCoCrFeNiTi alloy [8]. For higher δ , formation of intermetallics and amorphous phases is observed, as visible in the Fig. 2. It should be noted that the value of 6.6% in quinary system is an equivalent to about 17% difference in atomic radius, assuming the situation where four elements exhibit the same size, while the

fifth element is different. This means that for the case of atomic sizes, presence of multiple elements in the system does not significantly relax the conditions of solid solution formation in comparison to the binary system, where the mentioned 15% limit applies.

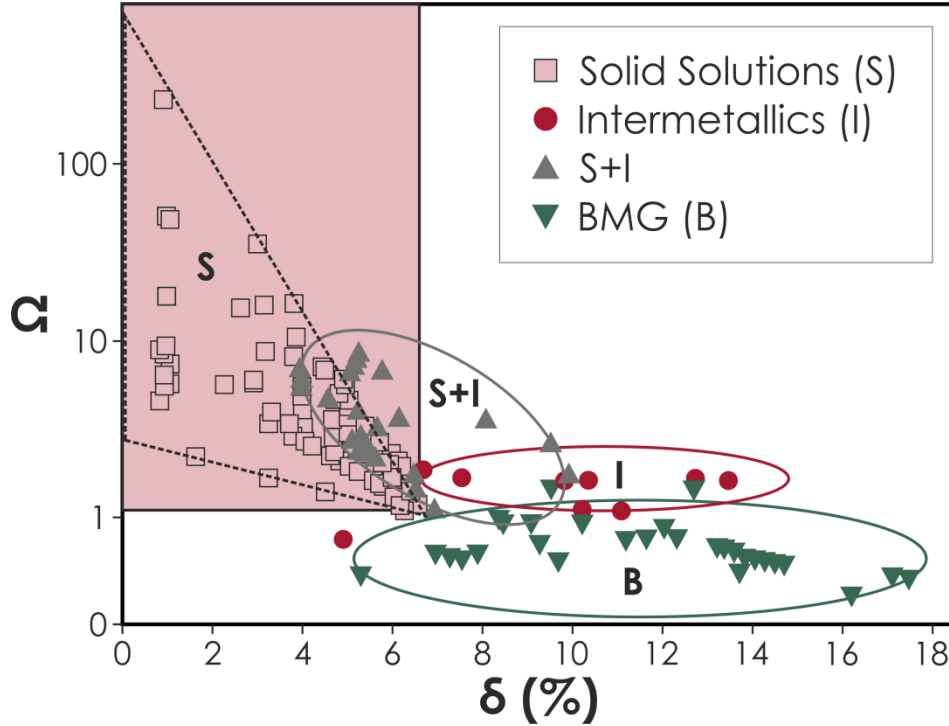


Fig. 2. The relationship between parameters δ , Ω and observed microstructure of the multicomponent alloys. “Solid Solutions” indicates the alloy contains only solid solution; “Intermetallics” indicates the alloy mainly contains intermetallic compound and other ordered phases; “S + I” indicates that not only the solid solution could be formed, but also the ordered compounds could precipitate in multicomponent alloys; and “BMGs” indicates the alloy can form amorphous phase [8].

Basing on the Hume-Rothery rules, it can be expected that the electronegativity of the elements should also play a role in formation of HEA solid solutions. Studies on this subject were conducted by Guo *et al.* [9], basing on the parameter $\Delta\chi$ proposed by Fang *et al.*[12]:

$$\Delta\chi = \sqrt{\sum_{i=1}^r n_i (\chi_i - \bar{\chi})^2}, \quad (1.11)$$

where χ_i is the electronegativity of the i -th element, and $\bar{\chi}$ is the average electronegativity defined as:

$$\bar{\chi} = \sum_{i=1}^r n_i \chi_i \quad (1.12)$$

However, the result at this point do not seem to support the influence of electronegativity on HEAs' formation, therefore $\Delta\chi$ is rarely used to describe their properties.

The next parameter, also to some degree derived from the Hume-Rothery rules, is the valence electron concentration VEC . From the beginning of the development of high entropy alloys, there were questions concerning the relation between composition and crystallographic structure. The first such studies, in which authors examined the microstructure of $Al_xCoCrCuFeNi$ alloys in a function of Al content [13], showed that with the increase of Al content, the alloys' structures started to change from FCC to BCC (when $x \approx 1.0$). This trend was even more surprising in the light of the fact that Al exhibits FCC structure itself. Similar effect was also observed by Chou *et al.* [14] in $Al_xCoCrFeNi$ alloys and Wang *et al.* [15] in $Al_xCoCrCu_{1-x}FeNiTi_{0.5}$ alloys. In the latter case, the authors correlated the occurrence of phase transition with the lattice distortion - the introduction of a relatively large Al atoms leads to increase of the lattice distortion energy, which can be then decreased by transition to the structure characterized by lower atomic packing efficiency, in this case to BCC. However, such approach does not allow to predict the structure of the alloy *a priori*. Further effort was put towards quantitative description of this phenomena, with Ke *et al.* showing that in $Al_xCo_yCr_zCu_{0.5}Fe_vNi_w$ system, Ni and Co act as FCC stabilizers, while Al and Cr are BCC stabilizers [16]. They also introduced equivalent quantities for each stabilizer to describe their relative strength: 2.23 Cr was determined to be equivalent of Al, and 1.11 Co was equal to Ni. Furthermore, if the Co % equivalent was higher than 45% then the alloy had FCC structure, while if the Cr % equivalent was higher than 55% the alloy exhibited BCC structure. This description, while certainly valuable, was still far from being a general one, as the situation varied from one system to another. An alternative approach was presented in 2011 by Guo *et al.* [17], who considered two parameters directly connected with electron concentration: average number of itinerant electrons per atom e/a (often used within Hume-Rothery rules) and number of total electrons, including the d -electrons accommodated in the valence band, known as VEC , used in description of intermetallics and Laves phases [18, 19]. However, due to the controversies surrounding the e/a parameter in transition metals, it was the latter parameter, which was chosen for further investigation. The total VEC value is calculated as:

$$VEC = \sum_{i=1}^r n_i \cdot VEC_i \quad (1.13)$$

where VEC_i is the valence electron concentration of i -th element. The results indicate that while VEC cannot be directly connected with the formation of the solid solutions, there is a strong correlation between its value and the crystallographic structure of the obtained alloy. For alloys with VEC lower than 6.87, the BCC structure is generally observed, while for the VEC higher than 8.0 formation of FCC structure is deemed to be the most probable. In between those values the dual-phase alloys usually occur. It should be noted that multiple exceptions from this criteria can be found. However, the VEC parameter still remains the easiest and quite effective way to predict the structure of the alloy basing on its composition.

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