



# A geometrical parameter for the formation of disordered solid solutions in multi-component alloys



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## ABSTRACT

One or more disordered solid solutions (DSS) are entropically stabilized in high entropy alloys (HEA) in competition with possible intermetallic compounds or phase segregation. In spite of the supreme role of Gibbs free energy, various parameters have been used to understand the formation of DSS in multi-component alloys. These include, the  $\delta$ -parameter (based on atomic size differences between the elements), the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) the  $\Omega$ -parameter ( $T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$ ). These parameters have had different degrees of success in the context of understanding the formation of DSS in multi-component alloys. In the current work, we develop a purely geometrical parameter ( $\Lambda = \Delta S_{\text{mix}} / \delta^2$ ) to predict the formation of DSS. Ranges are prescribed for this parameter for the formation of: (a) DSS, (b) a mixture involving compounds and (c) (only) compound(s). Results from the literature are used to highlight the utility of the  $\Lambda$ -parameter, in the context of other standard approaches. The role of the value of the  $\Lambda$ -parameter in understanding the nature (complexity) and volume fraction of the compound formed is also highlighted.

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## 1. Introduction

One or more disordered solid solutions (DSS) are entropically stabilized in high entropy alloys (HEA) in competition with possible intermetallic compounds or phase segregation. This is typically achieved by the addition of five or more elements in equimolar proportions in the alloy [1] and the structure of the alloys is usually either (simple) body centered cubic (BCC) or face centered cubic (FCC) [2,3]. The role of enhanced entropy of mixing ( $\Delta S_{\text{mix}}$ ) has been highlighted in this context, although it is noteworthy that ultimately it is the lowered Gibbs free energy ( $\Delta G_{\text{mix}}$ ) that stabilizes the phases [4]:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (1)$$

where,  $\Delta H_{\text{mix}}$  is the enthalpy of mixing. The enthalpy of mixing of the solid solution can be computed using the regular solution model as [5,6]:

$$\Delta H_{\text{mix}} = \sum_{i=1, i \neq j}^n \Omega_{ij} C_i C_j \quad (2)$$

where,  $\Omega_{ij} = 4\Delta H_{\text{AB}}^{\text{mix}(\text{cali})}$  is the regular melt interaction parameter between the  $i$ th and  $j$ th elements,  $C_i$  and  $C_j$  is the atomic percentage of the  $i$ th and  $j$ th component and  $\Delta H_{\text{AB}}^{\text{mix}(\text{cali})}$  is the enthalpy of mixing of constituent binary alloys. Sophisticated methods (e.g. methods based on first principles, subregular model etc.) of computation of  $\Delta H_{\text{mix}}$  also exist [7,8]; which are expected to give a better estimate of the enthalpy of mixing.

The configurational entropy of mixing ( $\Delta S_{\text{mix}}$ ), of an  $n$ -element regular solution alloy is given by Ref. [9]:

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n C_i \ln(C_i) \quad (3)$$

It is proposed that when  $\Delta S_{\text{mix}}$  is greater than  $1.61R$  ( $=13.38$  J/mol/K), DSS will be stabilized [3,10]. This value is achieved in the presence of five (or more) elements in equimolar proportion in the alloy [3].

In spite of the fact that in the strictest sense the configurational entropy stabilizes a single disordered phase in a HEA, often relaxed definitions have been used in literature. Formation of two (or more)

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disordered phases [10] or even intermediate compounds (like the B2 phase), have been included under the umbrella of HEA [11]. It is to be noted that the formation of a compound should be considered as an 'antonym' of a DSS and hence, technically the alloy should not be termed as HEA (ordering will lead to reduced entropy) [12].

The  $\delta$  [13] parameter has been commonly used to quantify the atomic size difference in a multi-component alloy. Zhang et al. [13] used the  $\delta$  parameter to understand the formation of DSS, which is defined as:

$$\delta = 100 \times \left[ \sum_{i=1}^n C_i (1 - r_i/\bar{r})^2 \right]^{1/2} \quad (4)$$

where,  $\bar{r} = \sum_{i=1}^n C_i r_i$  (with  $C_i$  being the mole%). They found that the solid solution tends to form in the region delineated by  $-15$  kJ/mol  $\leq \Delta H_{\text{mix}} \leq 5$  kJ/mol and  $1 \leq \delta \leq 6$  [13]. Guo et al. [14] on the other hand have cited a smaller range of values of  $\Delta H_{\text{mix}}$  for the formation of HEA:  $-5$  kJ/mol  $\leq \Delta H_{\text{mix}} \leq 5$  kJ/mol. In a later work, Guo and Liu [15] cited the following ranges (to be simultaneously satisfied) for the formation of HEA: (i)  $-22$  kJ/mol  $\leq \Delta H_{\text{mix}} \leq 7$  kJ/mol, (ii)  $0 \leq \delta \leq 8.5$  and (iii)  $11$  J/K/mol  $\leq \Delta S_{\text{mix}} \leq 19.5$  J/K/mol. Large positive (favouring phase separation) or large negative values (favouring compound formation) of  $\Delta H_{\text{mix}}$ , will oppose the formation of DSS. A small value of ' $\delta$ ' is expected to favour the formation of DSS.

Electronegativity difference in a multicomponent alloy system can be defined as [16]:

$$\Delta\chi = \left[ \sum_{i=1}^n C_i (\chi_i - \bar{\chi})^2 \right]^{1/2} \quad (5)$$

where,  $\bar{\chi} = \sum_{i=1}^n C_i \chi_i$  ( $\chi_i$  is the Pauling electronegativity for the  $i$ th component). This is an extension of the electronegativity difference as prescribed by Hume-Rothery [17] for binary alloys. A lower value of  $\Delta\chi$  is preferred for the formation of a DSS.

The valence electron concentration (VEC) of a multicomponent alloy system can be determined using the VEC of the individual elements using ((VEC) $_i$ ) [14]:

$$\text{VEC} = \sum_{i=1}^n C_i (\text{VEC})_i \quad (6)$$

According to Guo et al. [14] a high value of VEC ( $>8.0$ ) will stabilize an FCC phase and a low value ( $<6.87$ ) will stabilize the BCC phase. A value between these limits (i.e. between 8.0 and 6.87) will lead to the formation of a mixture of FCC and BCC phases.

Yang and Zhang [18] have used the  $\Omega$ -parameter ( $\Omega = T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$ ) to understand the formation of DSS. They have stated that the formation of DSS is favoured for:  $\Omega \geq 1.1$  and  $\delta \leq 6.6\%$ . The  $\Omega$ -parameter comprises all the terms included in the Gibbs free energy (i.e. H, T, S – except that the temperature is the melting temperature). Hence, in our view, instead of this parameter, ' $G$ ' itself can be used, which is anyhow the final determinant for the formation of phases. In addition to the parameters described above, the reader may consult the recent work of Jinhong and Ye [19] for a new parameter based on enthalpy and radius based entropy.

The parameters discussed above have given considerable insight into the formation of DSS. However, it has been realized that the enthalpy of mixing plays an important role and can often override the role of entropy of mixing [20,21]. Further, a close scrutiny of the ranges for the parameters prescribed ( $\delta$ ,  $\Delta H_{\text{mix}}$ ,  $\Delta S_{\text{mix}}$ ,  $\Omega$ ) reveals that further investigations are required to arrive at more reliable ranges for the parameters [12]. Hence, in spite of the existence of multiple parameters for the prediction of the formation of DSS,

there is an important need to devise a new parameter, which can successfully address the issue. Additionally, it is preferable that a single parameter can perform the requisite task, thus avoiding the need to refer to multiple parameters in conjunction (e.g. in Ref. [15]).

In the current work a purely geometrical parameter is defined to delineate the ranges for the formation of: (a) a DSS(s), (b) phase mixtures involving compound(s) and (c) (only) compound(s). The numerical value of the parameter is further expected to throw light on the nature of the compound formed and its volume fraction (within a given sub-system). Hence, based on the value of the parameter (which can be obtained by pure geometrical calculation, without having to perform calculations of physical parameters like  $\Delta H_{\text{mix}}$ ), it is expected that we will be able to predict alloy compositions which form DSS(s). The utility of the new parameter is highlighted by a comparison with other 'standard' approaches (parameters) in literature (i.e. the well established parameters – maximum of two in conjunction).

## 2. A new geometrical parameter and data from literature

An increased  $\Delta S_{\text{mix}}$  favours the formation of a DSS. It has been observed that a higher value of ' $\delta$ ' opposes this tendency and promotes compound formation [18].  $\Delta S_{\text{mix}}$  scaled by temperature has units of energy per mole. ' $\delta$ ' can be visualized as a measure of strain with respect to a perfect lattice. Further, in a DSS (wherein the atomic positions are disordered with respect to a perfect lattice), many local configurations arise, such that the 'bonds are distorted' (leading to local strains). In binary mixtures the elastic energy ( $E_{\text{strain}}$ ) cost due to size difference between the solvent (matrix) and solute atoms ( $\delta_r$ ) is given by Ref. [22]:  $E_{\text{strain}} = (4\pi E \delta_r^2 r) / (1 + \nu)$ , where,  $E$  is the Young's modulus of the matrix, ' $r$ ' is the radius of the solvent atom and ' $\nu$ ' is the Poisson's ratio. The  $\delta$ -parameter is the dimensionless physical equivalent (in multi-component alloys) to ' $\delta_r$ '. This strain energy cost to the system contributes to the enthalpy of formation of the solid solution, in accordance with the approach of de Boer et al. [5]. Hence,  $\delta^2$  can be conceived to be a measure of the strain energy. Keeping this in view the new parameter is defined to be  $\Delta S_{\text{mix}} / \delta^2$  (given a symbol  $\mathcal{A}$ ). The definition of the parameter has been kept simple and the inclusion of temperature, modulus etc. has been avoided (a considerable portion of the manuscript is devoted to showing that this simple parameter is very useful). The value of the  $\mathcal{A}$ -parameter for a given alloy can be calculated purely from geometrical information like configuration on a lattice (along with the atomic percent of the constituent elements) and the radius of the atoms. A high value of this parameter is expected to favour the formation of a DSS. An important point to be noted is that the temperature at which stability is considered is room temperature, it should be noted that in practical terms it is the temperature below which the system is kinetically frozen.

Seventy six multicomponent alloys from literature are studied in the current work and the value of various parameters from literature ( $\Delta H_{\text{mix}}$ , VEC,  $\Delta\chi$ ,  $\delta$  and  $\Omega$ ), along with the  $\mathcal{A}$ -parameter are computed for these alloys (Table 1). The alloys in the table have been taken from some of the references cited before and additionally from Refs. [23–46]. Data for calculations have been taken from Ref. [47] and Ref. [5]. An attempt has been made to choose alloys, where microscopic and compositional details have been presented in literature, in addition to X-ray diffraction (XRD) results (for the formation of phases). This is required as XRD may not provide conclusive evidence regarding the formation of a minor quantity of a phase (especially an ordered phase) or the formation of two phases with similar lattice parameters [12]. Additionally, EDX results are required as the actual composition of the region being observed could be different from the average composition or

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