On the formation of disordered solid solutions in multi-component alloys

Anil Kumar Singh a, Anandh Subramaniam b,∗

a Department of Physics, Indian Institute of Technology Kanpur, Kanpur 208016, India
b Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

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ABSTRACT

In high entropy alloys (HEA) a disordered solid solution (DSS) is entropically stabilized in competition with possible intermetallic compounds or phase separation. Ranges for many parameters (ΔR max , ΔH mix , ΔS mix , Ω) have been prescribed in literature for the formation of HEA. In the current investigation, we show that not withstanding the centrality of entropy in the stabilization of a DSS, other factors (parameters) like valence electron concentration, atomic size differences between the elements and enthalpy of mixing, play a significant role in the formation of phases. To illustrate the issues involved in the formation of DSS and to understand the phase formation, selected ternary (CoFeNi, CrFeNi), quaternary (CoCrFeNi, CuCoFeNi, AlCrFeNi) and penternary alloys (AlCuCoFeNi) are chosen for the experimental investigations and for the calculation of different parameters. It is shown that the ranges for the relevant parameters prescribed in literature are not satisfactory. It is possible that a (single) DSS can form, even if the entropy of mixing is small, provided all the relevant parameters are within favorable ranges. Contrastingly enough, violation of any of the parameters results in the formation of multiple phases or compounds. Strict and reduced definitions of HEA are invoked to understand the results.

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1. Introduction

Most traditional alloys are based on one or two principle elements, with other elements in much smaller percentages. In 1995, a new concept of ‘high entropy alloys’ (HEA) was proposed, wherein a disordered solid solution (DSS) is stabilized by the addition of five or more elements in equimolar proportions. Notwithstanding the possibility of the formation of multiple inter-metallic compounds, HEA remain solid solutions, typically having simple body centered cubic (BCC) or face centered cubic (FCC) structures [1,2]. This tendency is explained by the high entropy effect, leading to a lowered Gibbs free energy: ΔG mix = ΔH mix − TΔS mix , where, ΔH mix is the enthalpy of mixing and ΔS mix is the entropy of mixing of the solid solution. The enthalpy of mixing of the solid solution can be determined based on the regular solution model as [3]:

$$\Delta H_{\text{mix}} = \sum_{i=1}^{n} \Omega_{i} C_{i} C_{j}$$

(1)

where Ω ij = 4ΔH mix (cal) is the regular melt interaction parameter between the ith and jth elements. C i and C j is the atomic percentage of the ith and jth component and ΔH mix (cal) is the enthalpy of mixing of constituent binary alloys [3]. The configurational entropy of mixing (ΔS mix ) during the formation of n-element regular solution alloy is given by [4,5]:

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

(2)

In the truest sense, in a HEA, the configurational entropy stabilizes a single disordered phase (typically either FCC or BCC). However, often reduced (relaxed) definitions of HEA have been used in literature. This includes the formation of two (or more) disordered phases [5]. Sometimes even intermediate compounds like B2 phases have been included in the ambit of HEA [6]. In our view this is unacceptable since the key aspect of HEA is the formation of DSS (i.e. the formation of compounds should be considered an ‘antonym’ to the formation of DSS).

To understand the formation of DSS many parameters have been proposed in literature and investigators have proposed ranges for these parameters as well. These parameters are briefly described in the following paragraphs.

Atomic size differences in a multi-component alloys have commonly been quantified using two parameters in literature. These are the ΔR max [4] and the δ [7] parameters. The ΔR max parameter can be computed as [4]:

$$\Delta R_{\text{max}} = \frac{\text{Max}(r_{1} - r_{2})}{r_{\text{a}}}$$

(3)
where, \( r_i \) is the radius of a given element and \( r_p \) is the average atomic radius \( (r_p = \sum r_i r_i/C_i) \). It has been stipulated that for the formation of DSS, \( \Delta H_{\text{mix}} \) should have a value less than or equal to 12% \([4]\).

Zhang et al. proposed the \( \delta \) parameter while studying the relationship between the phase stability and the percentage atomic size difference \([7]\):

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

where \( r = r_p \). They found that the solid solution tends to form in the region delineated by \(-15 \text{ kJ/mole} < \Delta H_{\text{mix}} < 5 \text{ kJ/mole} \) and \( 1 < \delta < 6 \) \([7]\) (i.e. a large value of \( \delta \) is clearly expected to oppose the formation of a DSS). However, Guo et al. \([8]\) have cited a smaller range of values for the formation of HEA: \(-5 \text{ kJ/mole} < \Delta H_{\text{mix}} < 5 \text{ kJ/mole} \). Guo and Liu \([9]\) have prescribed the following ranges for the formation of DSS: (i) \(-22 \text{ kJ/mole} < \Delta H_{\text{mix}} < 7 \text{ kJ/mole} \), (ii) \(0 < \delta < 8.5\) and (iii) \(11 \text{ kJ/mole} < \Delta S_{\text{mix}} < 19.5 \text{ kJ/mole} \).

The best value of \( \Delta H_{\text{mix}} \) for the formation of DSS is clearly zero; however, if entropy can offset the effect of non-zero \( \Delta H_{\text{mix}} \), then, we can have the formation of a HEA. This implies that entropy will have to negate the effects of positive \( \Delta H_{\text{mix}} \) to suppress phase separation and similarly suppress compound formation for negative values of \( \Delta H_{\text{mix}} \). Correspondingly, if entropy is unable to suppress phase separation or compound formation, then these alloys cannot be termed as a HEA in the correct sense. This line of thought also implies that ‘high entropy’ should be defined not based on the value (or range) of entropy (as in \([10]\)), but on the ability to form a DSS (for a non-zero \( \Delta H_{\text{mix}} \) and/or \( \delta \)). This is also consistent with the understanding that larger the deviation from ‘ideal’ \( \Delta H_{\text{mix}} \) (or \( \delta \)), more the number of elements required (or for a given number of elements, closer to equimolar composition).

Fang et al. defined the electronegativity difference in a multicomponent alloy system as \([11]\):

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

where \( \chi = \sum_{i=1}^{n} C_i \chi_i \) (\( \chi_i \) is the Pauling electronegativity for the ith component). Even when no range has been prescribed in literature for the DSS to form, it should be noted that a larger value of \( \Delta \chi \) is expected to aid the formation of a compound.

The valence electron concentration (VEC) of a multicomponent alloy system is defined as \([8]\):

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

where, \( (\text{VEC})_i \) are the VEC for individual elements. This quantity indicates the number of all valence electrons in the alloy per number of atoms. Guo et al. \([8]\) have pointed out that a VEC value greater than 8.0 is expected to stabilize a FCC phase and while a value between 6.87 and 8.0 is expected to yield a mixture of FCC and BCC phases. The authors have cited exceptions to this rule (e.g. in the AlCuCoCrFeNi system).

In addition to the above parameters, Yang and Zhang \([12]\) have proposed the \( \Omega \) parameter to understand the formation of DSS and bulk metallic glasses:

\[
\Omega = \frac{T_m \Delta S_{\text{mix}}}{\Delta H_{\text{mix}}}
\]  
(7)

where \( T_m = \sum_{i=1}^{n} C_i (T_m)_i \) is the melting point of the alloy \( (T_m)_i \) is the melting point of the ith component). They have prescribed that \( \Omega \geq 1.1 \) together with \( \delta \leq 6.8\% \) favors the formation of DSS. However, it is to be noted that intermetallics form even within this preferred range \([12]\).

The recent works of Praveen et al. \([13]\), Otto et al. \([14]\) and Pradeep et al. \([15]\) are noteworthy in the context of the current investigations. Praveen et al. \([13]\) have argued that configurational entropy alone cannot justify the formation of a single phase solid solution in HEAs. Otto et al. \([14]\) by replacing one element at a time in a pentenary alloy (CoCrFeMnNi) have shown that configurational entropy is in general unable to dominate over other competing driving forces like enthalpy that also govern phase stability. Pradeep et al. \([15]\) have also pointed out to the limitation of considering entropy alone as an alloy design concept. The reader may additionally consult the works of Ranganathan et al. \([16]\), Zhang et al. \([17]\), Zhang et al. \([18]\) and Wang et al. \([19]\) for detailed analyses regarding phase formation in multicomponent alloys. Recently, Guo et al. \([20]\) have investigated the effect of \( \Delta H_{\text{mix}} \) and \( \delta \) on the formation of not only solid solutions but also amorphous phases and Otto et al. \([21]\) have highlighted the relative effects of enthalpy and entropy with regard to the phase stability in HEA. The readers may additionally consult the following references, which highlight the recent advances in the field of HEA. Dong et al. \([22]\) have studied the effect of microstructure on the mechanical behavior of AlCuFeNiMn alloys. Solidification microstructures in HEA have continued to draw attention of researchers \([23]\). Magnetic properties of HEA have also been investigated \([24]\). Due to their high strength and good corrosion resistance, certain HEA have also been envisaged for technological applications such as surface protection \([25,26]\).

The current investigation is intended to address the following lacunae in literature: (i) inclusion of alloys which contain a compound like the B2 phase, under the ambit of DSS; (ii) prescription of incorrect ranges of \( \Delta H_{\text{mix}} \) and \( \Delta S_{\text{mix}} \) for the formation of DSS (in selected works); (iii) the role of \( \Delta \chi \) has been given due regard in the context of formation of DSS (especially when other parameters are in acceptable ranges). To achieve the stated tasks, an analyses of experimental results are carried out, giving due weightage to the relevant parameters \( (\Delta H_{\text{mix}}, \delta, \Delta \chi, \Delta H_{\text{VEC}}, \text{VEC} \) and \( \Omega \) which play a significant role in the formation DSS vis-à-vis a compound (or a combination of these). Special attention is paid to understand the competition between these parameters with \( \Delta S_{\text{mix}} \) in the formation of HEA. The works of Li and Zhang \([4]\), Zhang et al. \([7]\), Guo et al. \([8]\), Guo and Liu \([9]\) and Yang and Zhang \([12]\) are noteworthy in this context and will be kept in focus in the analyses carried out. Some of the analyses carried out is expected to also throw light on the fundamental question: ‘what constitutes a HEA?’.

Selected ternary, quaternary and pentenary alloys (with \( \Delta S_{\text{mix}} \) less than and above 11 kJ/K/mole – the lower limit set by Guo and Liu \([9]\)) have been synthesized towards this end. The list of alloys is not extended, but is expected to serve as an illustrative set to fortify the points made. These alloys are chosen to provide a range of values of the parameters in focus (e.g. \( \delta \), \( \Delta \chi \), \( \Delta H_{\text{VEC}} \) and \( \Omega \)) which is often in literature nominal ‘intended’ compositions are mentioned, without making available energy dispersive X-ray (EDX) measurement of compositions. Such practice renders computations based on these compositions invalid. In the current work all calculations are performed on the actual EDX compositions.

2. Experimental details

Elements (Al, Cu, Co, Cr, Fe, and Ni) with 99.9 wt.% purity were used in the preparation of the alloys of different compositions, using vacuum induction melting. The as-cast alloys were annealed for 24 h under vacuum at a temperature of 850°C (below the solusids temperature of the alloys \([18]\)). The samples were characterized for phase formation by X-ray diffraction (XRD) using Cu Kα radiation (\( \lambda = 1.54 \AA \), with a scan rate 0.5°/min. Scanning electron microscopy (SEM) in back scattered electron (BSE) mode was used to study the microstructure of the samples.
The composition of the samples (average composition along with the composition of individual phases), was determined by EDX analysis in the scanning electron microscope. EDX data was acquired in three modes: (i) area scan, (ii) point scan and (iii) line scan. Area scan was used for the determination of average composition of the alloy (which might include multiple phases). Additionally, area scan was used to determine the composition of phases present in large volume fraction (i.e. area fraction in SEM image). Point scan was used to determine the composition of phases present in minor quantity. In such cases data was acquired from multiple points (typically five or more points) and averaged (leaving out the outliers) to get the composition of the phase. To characterize the segregation of small amount of phase, line scan was used to determine the variation in composition of various elements. Needless to say, in spite of the care exercised in the acquisition of the EDX data, the accuracy of the composition results is not expected to be better than 1% (the usual limitation of the EDX technique).

XRD data is analyzed in conjunction with the EDX results to understand the formation of phases. Transmission Electron Microscopy (TEM) studies was carried out on one sample to confirm the formation of an ordered phase. Standard TEM specimen preparation techniques (thinning followed by electro-polishing) were used to get an electron transparent region. TEM studies were carried out in Tecnai G² 20 S-TWIN TEM, operated at 120 kV.

3. Results and discussion

3.1. XRD, SEM and TEM (results)

The X-ray diffraction patterns of the CoFeNi (A3), CrFeNi (B3), CoCrFeNi (C4), CuCoFeNi (D4), AlCrFeNi (E4), AlCuCoFeNi (F5) alloys in the annealed state is shown in Fig. 1. These alloys have been designated by the symbols given in the brackets. The number following the alphabet denotes the number of elements in the alloy. The phases detected from the XRD patterns are marked in the figure. Analysis is carried out taking into account SEM results (as discussed next). The exact composition of the phases will be considered in the discussion of the SEM results.

Fig. 2 shows the SEM micrographs (taken using back scattered electrons) of the annealed samples. The average composition of the alloys, along with the composition of the individual phases as determined using EDX, is also shown in the figure. Fig. 2a shows a single phase, with dark curved lines being the grain boundaries (alloy A3). Fig. 2b shows the presence of a Cr rich phase along with an FCC phase (alloy B3). From the ternary phase diagram it is seen that the composition of the second phase Cr$_{59.4}$Fe$_{22.8}$Ni$_{17.8}$ corresponds to a BCC structure [27]. Fig. 2c shows that there is minor Cr rich phase (as seen in the inset showing an EDX line scan), in addition to a major FCC phase having a composition close to the average composition (alloy C4). From Fig. 2d (alloy D4) it can be seen that a minor Cu rich FCC phase forms (labeled (c)), in addition to a major FCC phase (labeled (a), slightly depleted in Cu). In the XRD pattern (Fig. 1d) the peaks for these two phases overlap. The lattice parameter calculated from the XRD data is 3.59 Å. Based on the compositions determined from the EDX results, the lattice parameter of the phases are 3.58 Å ($\alpha_1$) and 3.54 Å ($\alpha_2$) respectively. Lattice parameters are calculated from EDX data as follows: The composition of the alloy is determined from EDX and the radius of an average atom is calculated from the composition. Further, assuming a FCC lattice, the average atom is used as the motif and from this the lattice parameter is calculated. A few important points are noteworthy at this stage, regarding the inherent limitations involved in the analysis of phase formation using XRD and EDX (in SEM). It is difficult to detect minor phase fractions using either of these two techniques. Detection of small amount of phase at the grain boundaries is especially challenging using EDX. Further, the accuracy of measurement of composition by EDX is usually less than 1 atom percent. The results discussed in the foregoing and following paragraphs have to be interpreted keeping in view the inherent limitations of XRD and EDX. However, by using a combined analysis of XRD and EDX results, the overall information gathered and the confidence level on the data acquired is improved (as shown before for the case of lattice parameter calculation).

In Fig. 2e (alloy E4) a nearly uniform microstructure is seen at low magnifications (1kX); however, at higher magnifications (60kX), a two-phase mixture resulting from spinodal decomposition can be identified (as shown in the inset to the figure). This is consistent with the observations of Wang et al. [28]; wherein, they have observed a spinodal microstructure at high magnifications (in SEM). Presence of superlattice peaks corresponding to the B2 phase in the XRD pattern (Fig. 1e) suggests that B2 phase also must be present in the microstructure. To identify the presence of the B2 phase, TEM studies were carried out on this sample. This is discussed after the discussions on the SEM studies on alloy F5. Fig. 2f shows the formation of three phases (alloy F5). The Al rich phase is expected to be the B2 (identified by XRD and labeled as $\beta$ Fig. 1f). This is consistent with the observation that aluminium tends to stabilize the B2 phase with Ni [6]. The other two phases (labeled $\alpha_3$ and $\alpha_4$ in Fig. 1f and marked as $\alpha$ on the peaks) seen in the SEM micrograph have similar lattice parameters and hence give rise to peaks close to each other, which could not be resolved using XRD. The lattice parameter calculated from XRD data is 3.61 Å. Based on EDX data the lattice parameters of the two phases are: 3.58 Å ($\alpha_3$) and 3.60 Å ($\alpha_4$). The methodology for the calculation of the lattice parameter for $\alpha_3$ and $\alpha_4$ from EDX data is similar to that used for alloy D4. A point to be noted is that $\alpha_3$ and $\alpha_2$ phases (in alloy D4) contain Cu, Co, Fe and Ni, while the $\alpha_3$ and $\alpha_4$ phases have an additional element (Al).

Fig. 3 shows TEM results obtained from sample E4 (AlCrFeNi). The Bright Field Image (BFI) in Fig. 3a shows the formation of nanoscale second phase particles (size ~40 nm). Selected Area Diffraction (SAD) pattern from this region (Fig. 3b) shows the formation of an ordered structure (due to the presence of superlattice spots). The inset to Fig. 3a shows the Dark Field Image taken from the 100 superlattice spot. This shows that the nanoscale particles embedded within the spinodal microstructure is the ordered B2 phase. This result is similar to that obtained by Tong et al. [29] for the AlCoCrCuFeNi system.

4. Data and calculations

Using the data for elements listed in Tables 1 and 2, the following quantities are calculated for the different multicomponent alloys (as listed in Table 3): (i) $\Delta R_{\text{max}}$, (ii) $\delta$, (iii) $\Delta G$, (iv) $\nu$, $\Delta H_{\text{mix}}$, (vi) $\Delta S_{\text{mix}}$ and (vii) $\Omega$. Data for Table 2 has been taken from de Boer et al. [3] and Praveen et al. [13]. The alloy compositions are as listed in Table 3 (column 2). Eqs. (1)–(7) are used for the calculations of the above mentioned parameters. The readers may additionally consult Praveen et al. [13], Vura et al. [30] and Singh and Subramaniam [31], regarding alloy systems and phase formation.

The following observations and analyses can be made from the calculations as in Table 3 (the focus is on different parameters and basis for phase formation).

(1) For some of the alloys chosen the entropy of mixing ($\Delta S_{\text{mix}}$) is less than the limit prescribed by Guo and Liu [9] (11.0 J/mole/K), while for the others it is greater than this limit. As expected the entropy increases as we go from ternary to quaternary to penternary alloys. It is to be noted that the entropy calculations are based on the actual composition measured by EDX.

(2) For alloy A3, the parameters $\Delta R_{\text{max}}, \delta, \Delta H_{\text{mix}}$ and $\Omega$ are all within limits for the formation of a DSS (according to [4–7, 9, 12]) and hence, despite the low entropy of mixing (violating the limits set by Guo and Liu [9]), a DSS is obtained. The value of $\Delta G$ is also small aiding the formation of a DSS. The
value of VEC > 8.0, thus favouring the formation of an FCC solid solution. Special attention should be paid to the value of $D_{HH}^{mix}$, which is negative but small in magnitude. Additionally, the lower limit of $d'$ as prescribed by Zhang et al. [7] seems unacceptable, as a low value of $d'$ is preferred for the formation of DSS.

3) The case of alloy B3 is similar to the case of alloy A3 (i.e. the parameters $D_{R}^{max}$, $d'$, $D_{HH}^{mix}$ and $\Omega$ are all within limits for the formation of a DSS), with the important distinction that the value of VEC is < 8.0 (but > 6.87); thus guiding the formation of a two phase mixture of FCC + BCC phases. The value of $D_{S}^{mix}$ is below the limit set by Guo and Liu [9], but the formation of a compound is not evidenced. This is all the more noteworthy, as the value of $D_{V}$ is high for this alloy. This further highlights the importance of a low value of $d'$.

4) C4 is a quaternary alloy based on the B3 ternary (with Co addition). This implies that this alloy is expected to have higher entropy as compared to the B3 ternary alloy. This is reflected in the formation of a nearly homogenous DSS (with a segregation of Cr rich phase labeled ‘S’ in Fig. 2c). That is, the increased $\Delta S_{mix}$ facilitates a higher solubility of Cr in the alloy; but is not sufficient to avoid the segregation of a minor amount of a Cr rich phase. For this alloy all the parameters ($D_{R}^{max}$, $d'$, $D_{HH}^{mix}$, $D_{S}^{mix}$ and $\Omega$) are within limits for the formation of DSS. Thus, except for the minor segregation of Cr rich region, expectations from the study of literature are fulfilled ([4,7–9,12]).

5) In alloy D4, the parameters $D_{R}^{max}$, $d'$, $D_{HH}^{mix}$ and $\Omega$ are all within limits for the formation of a DSS (according to [4,7–9,12]); however, we observe the formation of a two phase mixture of FCC phases. This implies that the upper limit of $D_{HH}^{mix}$ (on the positive side) for the formation of DSS as prescribed in Refs. [7–9] are not valid and this alloy cannot be classified as HEA in the strictest sense (i.e. with a single DSS). It is surprising to note that the tendency of phase separation (with a positive $D_{HH}^{mix}$ value of 4.65 kJ/mole) is not counteracted by a high value of entropy (this being a quaternary alloy) and we observe phase separation. A comparison with alloy A3 emphasizes these points (alloy A3 has lower entropy, but a negative $D_{HH}^{mix}$ and forms a single FCC phase, while D4 even with higher entropy forms two FCC phases due to a positive value of $D_{HH}^{mix}$). The VEC has a value of 9.47 (significantly greater than the limit of 8.0 for the formation of FCC phase), which leads to the formation of FCC phases.

6) In alloy E4, the difference between the two parameters characterizing atomic size difference becomes prominent. While, the value of $D_{R}^{max}$ is within acceptable limits.
for the formation of a DSS [4], the ‘$d$’ falls outside the acceptable limits [7]. Given that this composition does not form only DSS, inference can be drawn that the ‘$d$’ parameter characterizes the strain in the lattice better. The parameters $\Delta H_{\text{mix}}$ and $\Omega$ are all within limits for the formation of a DSS (according to [7,9,12]), but $\Delta H_{\text{mix}}$ value lies outside the
range prescribed by Guo et al. [8] and \(\delta^i\) has a higher value compared to that prescribed for DSS by Zhang et al. [7]. As compound formation is observed (in addition to the BCC phase), it seems that the ranges prescribed in [7] (for \(\Delta H_{\text{mix}}\)), [12,9] are unsatisfactory. \(\Delta H_{\text{mix}}\) has a large negative value, thus favouring the formation of a compound. The value of \(\Delta \gamma\) is also large, which also favors the formation of a compound (as observed). The low value of VEC favors the formation of a BCC phase. These factors put together influence the formation of a mixture of BCC and B2 phases (the ordered version of BCC). Alloy E4 has higher entropy as compared to alloy B3, but this increased entropy fails to offset the decreased enthalpy value (which favors compound formation). Hence, alloy E4 is not a HEA.

(7) For alloy F5 the parameters \(\Delta \rho_{\text{mix}}, \delta^i, \Delta H_{\text{mix}}\), and \(\Omega\) are all within limits for the formation of a DSS (according to [4,7–9,12]). Alloy F5 has a less negative value for \(\Delta H_{\text{mix}}\) as compared to E4 and has a lower value of \(\delta^i\). Despite the large value of \(\Delta H_{\text{mix}}\), which is not too negative (like alloys E4), compound formation is observed. This highlights the importance of a large value of \(\Delta \gamma\) in the formation of a compound. In alloy F5 the volume fraction of B2 phase is not minor (as evident from Fig. 2), thus the increased entropy fails to offset the high value of \(\Delta \gamma\). The value of VEC lies in the range, where a FCC + BCC mixture is favoured, but this is not observed (phases observed: F + F + B2). Thus the 'VEC rule' is approximate (as expected, [8]). This alloy further establishes that the ranges for \(\Delta \rho_{\text{mix}}, \delta^i, \Delta H_{\text{mix}}\), and \(\Omega\) parameters prescribed in Refs. [4,7–9,12] are unsatisfactory.

From the analyses of Table 3 it is seen that a single DSS solid solution can form even if the entropy of mixing is small (as in the case of the ternary A3 alloy). The value of the VEC parameter seems to decide the nature of the phases formed (FCC, BCC or a mixture of the two). A negative enthalpy of mixing beyond ~15 kJ/mol is expected to help the formation of intermediate compounds [7]; however, it is seen that even for lower negative values of \(\Delta H_{\text{mix}}\) compounds can form, especially if other parameters (like the \(\delta^i\) parameter) are beyond acceptable limits (or even close to the limit). Hence, it seems that the limits set by Guo et al. [8] forms a better basis for understanding the role of \(\Delta H_{\text{mix}}\) in the formation of DSS.

In light of the foregoing discussions, it is seen that ranges for the parameters \(\langle \delta^i, \Delta H_{\text{mix}}, \Delta \rho_{\text{mix}}, \Omega \rangle\) prescribed in some literature ([4,7–9,12]) for the formation of DSS are unsatisfactory. Additionally, it becomes clear that analyses have to account for all the parameters (including \(\Delta \gamma\), especially when other parameters fail to address the issue) and their specific values. Extensive investigations are needed to stipulate new ranges of \(\langle \delta^i, \Delta H_{\text{mix}}\rangle\) (with \(\Delta \gamma\) weighted in) for the formation of DSS. Using a reduced definition of HEA, where multiple disordered phases are permitted, the number of ternary and quaternary alloys which can be classified as HEA is increased: e.g. alloy B3, C4 and D4 in addition to A3 are HEA (while E4 and F5 are not).

### 5. Summary and conclusions

(1) Entropy (of mixing) is an important parameter which facilitates the formation of a DSS; however, it is not the sole parameter in this regard. In spite of low \(\Delta \rho_{\text{mix}}\), as in the case of ternary alloys, a DSS can form if all the other relevant parameters \(\langle \Delta \rho_{\text{mix}}, \delta^i, \Delta H_{\text{mix}}\rangle\) are within limits for the formation of a DSS. A low value of \(\Delta \gamma\) helps in this regard. Contrastingly, a high value of entropy (>11 kJ/K/mole), may not be able to stall the formation of a compound. Hence, caution needs to be exercised in employing the term 'HEA' for multicomponent alloys. An alloy should be classified as an HEA, if entropy of mixing is able to offset the effects of positive or negative values of \(\Delta H_{\text{mix}}\), to form a single DSS. It is important to note that B2 phase, being an intermetallic compound, should not be included in the ambit of DSS (as often done in literature). These observations corroborate well with the findings of Praveen et al. [13], Otto et al. [14] and Pradeep et al. [15]; wherein the limitations of interpretation of phase formation, based purely on entropy are pointed out.

### Table 3

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<th>Elements</th>
<th>Atomic radius (Å)</th>
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### Table 2

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</tr>
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<tr>
<td>Ni</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</table>

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* F- FCC, B-BCC. • All calculations are based on actual composition determined by EDX. • Cr rich phase with a composition Cr_{20.2}Fe_{22.8}Ni_{17.4} [BCC based on Cr-Fe-Ni phase diagram]. • S-Cr rich segregation along grain boundaries. Values in ‘bold-italic’ indicate parameters which are not favourable for the formation of HEA. Values in ‘italic’ are close to the limiting value for the formation of HEA. Underlined values indicate VEC values favouring a two phase mixture of F + B.

* Additional value for consultation regarding alloy system and phase formation.
The limits for the various parameters (ΔR_{max}, Δ'h, ΔH_{mix}, ΔS_{mix}, Ω) as listed in some literature seem unsatisfactory for the understanding of the formation of DSS. Even when these parameters lie in the range as prescribed in some literature for the formation of DSS, compound formation is observed in some of the alloys studied.

In case the value of the parameters ΔR_{max}, Δ'h, ΔH_{mix}, ΔS_{mix} and Ω does not conclusively indicate the formation of a compound, a large value of ΔX can be used to predict the formation of a compound. Even if ΔH_{mix} is not too negative, the magnitude of Δv is large – a large volume fraction of compound can be expected.

'd' seems to be a better parameter than ΔR_{max} for characterizing the atomic size difference. An understanding of phase formation can be obtained only by analyses involving all the significant parameters which play a role (i.e. 'd', VEC, ΔX, ΔH_{mix}, ΔS_{mix}). The utility of the Ω parameter (alone or in conjunction with 'd') in this context is not clear. From a broad perspective, 'd' and ΔH_{mix} can be thought of as the most important parameters determining the formation of DSS.

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References