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Incorrect predictions of simple solid solution high entropy alloys: Cause and possible solution

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ABSTRACT

One of the key issues in high-entropy alloys (HEAs) is the development of alloys that contains only simple solid solution (SSS) phases. Researchers have proposed various parametric models to predict SSS formation. However, incorrect predictions are not uncommon. Here, we investigate the main cause of these mispredictions. It is found that the premises of most existing models do not apply to some intermetallic phases. Hence, the models cannot distinguish alloys containing these intermetallics from alloys containing only SSSs. A possible solution to this issue is proposed. With this strategy, the accuracy of existing models can be evidently improved.

High-entropy alloys (HEAs) have received significant attention in the past decade [1–4]. These alloys can form multi-principal-element simple solid solutions (SSS) which possess unique properties [5–8]. Thus, the development of these simple-structured (i.e., FCC, BCC, and HCP) HEAs is of great interest and their design principle becomes an important issue in the community [1,9]. Researchers design different physical parameters (which can be calculated based on composition), and attempt to relate the formation of SSS HEAs with the values of these parameters [10–20]. For example, parameters such as ΔH_{mix} [10,11,13,14,17], ΔS_{mix} [11], δ [10–14,17,18,20], Ω [12], $\Delta\chi_{Allen}$ [18], Λ [19], γ [20], and φ [21] have been proposed. Very often two or more parameters are combined to form a parametric model to better describe the stability of SSS phases [10–14,17,18,20].

The majority of physical parameters proposed are based on two core concepts: enthalpy of mixing and atomic size difference. Basically, if an alloy has large negative enthalpy of mixing or large atomic size difference among its composing elements, it typically forms intermetallic compounds. Therefore, the two conditions can be used to screen out IM-forming HEAs and the inverse of them suggests formation of SSSs. Enthalpy of mixing and atomic size difference can be described in different ways. The earliest and most notable parameters to describe them are ΔH_{mix} and δ, which relate to the former and the latter, respectively [10,11,13]. For example, Zhang et al. analyzed numerous HEAs from the literature and suggested that SSSs will form when $-15 \le \Delta H_{mix} \le 5$ kJ/mol and $\delta \le 6.5\%$ [12]. Based on the same parameters but a different set of alloy database, Guo et al. suggested different SSS-forming ranges of ΔH_{mix} and δ [11,13]. For example, one of their models is $-11.6 \le \Delta H_{mix} \le 3.2$ kJ/mol and $\delta \le 6.6\%$ [13].

Many more physical parameters and parametric models were proposed later on [12,18–21]. Most of them, however, are still based on or closely related to the two concepts. For example, Zhang suggested a new parameter $\Omega = T_m\Delta S_{mix} / |\Delta H_{mix}|$ to replace ΔH_{mix} [12]. Singh et al. proposed a different geometrical parameter $\Lambda = \Delta S_{mix} / \delta^2$ [19]. Wang et al. used γ instead of δ to describe atomic size difference [20]. Yang proposed another parameter $\varphi = (S_c - S_H) / |S_E|$, which combines both concepts in a single parameter [21]. Although these parameters/models offer useful guidelines to the design of simple-structured HEAs, mispredictions are not uncommon. In other words, even though an alloy satisfies the proposed conditions for SSS formation, it can still contain intermetallic (IM) phases. A good example is the ΔH_{mix}–δ plot in Ref. [13], where IM-containing HEAs are still found in the SSS-forming region delineated by the authors. Thus, current models are still not truly predictive.

In this paper, a series of systematically alloyed CoCrFeNiX alloys is used as model systems to assess the efficacy of existing parameters/models. Our focus is on parameters based on the two concepts mentioned above, i.e., enthalpy of mixing and atomic size difference. Failed predictions are analyzed carefully, and their cause is identified. Finally, a possible solution is provided.

The CoCrFeNiX alloys used here are designed by alloying one element (X) to the single phase FCC alloy CoCrFeNi. The alloying element is systematically changed (X = Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W), leading to a total of ten alloys. Details on the fabrication and analysis of the alloys can be found in Ref. [22]. Table 1 lists the indentified phases and the values of various parameters of each alloy. Due to limited space, the readers are referred to the respective references for the definition of these parameters. From Table 1, nine of the ten alloys contain IM phases. Table 2 lists the SSS-forming conditions proposed in some representative publications. These conditions are used to predict SSS

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Table 1
Indentified phases in the CoCrFeNiX alloys. The values of various physical parameters are also calculated based on the compositions of the alloys. The units for ΔH_{mix}, δ, and Λ are kJ/(mole of atoms), %, and J/K·(mole of atoms), respectively.

X	Phase	ΔH_{mix}	Ω	δ	γ	φ[a]	Λ
Y	$Y(Fe,Co,Ni)_3$ + BCC + YNi + $Y_2(Fe,Co,Ni)_{17}$	−9.3	2.7	16.4	1.518	0.8	0.05
Ti	χ + C14 + η	−16.3	1.6	6.7	1.197	2.8	0.30
Zr	C15 + BCC	−22.7	1.1	10.8	1.328	0.4	0.11
Hf	C36 + BCC	−19.5	1.4	10.1	1.304	0.9	0.13
V	σ + FCC	−9.0	2.9	2.2	1.066	48.8	2.74
Nb	C14 + FCC	−14.9	1.8	5.7	1.167	5.1	0.41
Ta	C14 + FCC	−14.4	2.0	5.7	1.168	5.5	0.41
Cr	FCC + BCC	−4.3	6.0	0.3	1.009	3967.2	170.66
Mo	σ + FCC	−4.6	6.0	3.7	1.107	22.4	0.99
W	μ + FCC	−2.9	10.4	3.8	1.111	22.7	0.93

[a] φ was calculated using ζ = 0.74.

formation in the CoCrFeNiX alloys, and incorrect predictions made by each model are also listed in Table 2. The models can screen out three to seven of the nine IM-forming alloys, but none of them is 100% successful. It is worth noting that the incorrect predictions made by the five models overlap significantly – three of the nine IM-forming alloys (X = V, Mo, and W) are consistently mispredicted to be SSSs.

The inability to screen out the three alloys (X = V, Mo, and W) with the models listed in Table 2 is because these models are all based the idea that near-zero enthalpy of mixing and small atomic size difference favor the formation of SSSs. The three alloys do satisfy these conditions. For example, the values of ΔH_{mix} and δ of the CoCrFeNiW alloy are only −2.9 kJ/(mole of atoms) and 4.3%, respectively. Although these values seem pleasing, the phases actually formed in the alloy is suprising – >50 vol.% of the alloy is IM phase. Hence, perhaps the rationale for the use of these conditions should be re-examined.

The reason for the use of near-zero mixing enthalpy as a condition of SSS formation is that in binary systems, a large negative Δ^{AB}_{mix} (mixing enthalpy of binary liquid $A_{50}B_{50}$ alloys [23]) value between two elements leads to the formation of stable IM phases (ΔH_{mix} is merely a multi-component version of Δ^{AB}_{mix}). However, the inverse of the above statement is not necessarily true. Namely, small negative (near-zero) enthalpy of mixing values do not guarantee that IM phases will not form. This is demonstrated in Table S1 (see Supplementary information) and Fig. 1, where the ΔH_{mix} and δ values for four representative types of IM phases are shown. It is seen that the ΔH_{mix} values for most Laves C14 and C15 intermetallics are indeed negatively large, with most of them being negatively larger than −10 kJ/(mole of atoms). Therefore, most of them can be filtered by large negative ΔH_{mix}. However, the ΔH_{mix} values of σ and μ phases are very small – most of them are negatively smaller than −5 kJ/(mole of atoms). Thus, most of the σ and μ IMs cannot be filtered by conditions based on large negative ΔH_{mix}. In fact, the same applies to any other IMs that has near-zero ΔH_{mix} values. For example, some Laves IMs in Fig. 1 also have near-zero ΔH_{mix} values.

The case for the use of atomic size difference is very similar. The Hume Rothery rules state that binary solid solutions will be frustrated if the atomic size difference between the two elements is larger than 15%. Again, however, the inverse is not necessarily true - small atomic size differences do not guarantee the absence of IM phases. Tsai et al. analyzed the atomic size differences of several hundred compounds in eight common topologically close-packed (TCP) IM phase types [22]. They found that each TCP phase type has its own allowable atomic size difference. Large atomic size differences do favor the formation of some TCP phase types, such as Laves C14, C15, C36, and $PuNi_3$, but there are also IM phase types that form between elements with small atomic size differences. These include σ, μ, χ, and A15 phases [22]. This is reflected in Fig. 1, where σ and μ phases indeed locate in the lower half of the figure. Thus, screening these IM phases with large atomic size differences is simply ineffective. In short, near-zero enthalpy of mixing and small atomic size differences are necessary but not sufficient for SSS formation.

If, unfortunately, the IM phase formed in an alloy have *both* near-zero mixing enthalpy and small atomic size difference, then models based on these two concepts will fail to screen it out (i.e., will predict it to be SSS). Based on the above discussions, most σ and μ phases belong to this type. This can be clearly demonstrated by Fig. 1, in which the critical values of ΔH_{mix} and δ proposed in Ref. [13] are marked with dashed lines. Regions corresponding to IM and SSS formation can therefore be delineated and colored. Although these conditions successfully screen out most of the Laves C14 and C15 IMs, the majority of σ and μ phases, having near-zero mixing enthalpy and small atomic size difference simultaneously, are predicted to be SSSs. This is exactly what happened in the three mispredicted CoCrFeNiX alloys – the IM phases in them are indeed σ and μ phases! This agreement indicates that the above argument is indeed the cause for the mispredictions. It should be noted that σ and μ phases are not the only compounds found in the SSS-forming region, some Laves C14 and C15 phases also fall in the lower-right corner of Fig. 1.

It should be emphasized that the data points shown in Fig. 1 are pure IM compounds. HEAs can comprise both IM and SSS phases. This means that the values of ΔH_{mix} and δ of the whole alloy can be less negative (for ΔH_{mix}) and smaller (for δ) than that of the IM it contains (the SSS phase dilutes them). Therefore, the position of the alloy is likely located to the lower right of the IM phase it contains. This means that even if the IM phase in an alloy can be screened by the above conditions, the alloy itself may actually satisfy the conditions – which further increases the chances of misprediction.

To further validate our theory, the alloy databases listed in Refs. [11–13] are collected and assessed with the above ΔH_{mix}–δ conditions. Alloys that are predicted to be SSS but are in fact not are listed in Table 3 [14,24–33]. Indeed, the IM phases found in 17 of the 21 mispredicted alloys belong to the σ phase, which strongly supports our theory.

The above analysis indicates that incorrect predictions of SSS HEAs originate largely from IM phases that have both near-zero mixing enthalpy and small atomic size difference. Therefore, these phase types, most notably σ and μ phases, need to be addressed with other strategies. There is very little information regarding the stability of the μ phase in HEAs. However, the stability of the σ phase has been systematically investigated. Tsai et al. proposed two criteria to predict σ phase formation in HEAs. The first is based on valence electron concentration (VEC) [26] and the second on the content of paired sigma-forming element (PSFE) [34]. An alloy is prone to σ phase formation if its VEC is between 6.88 and 7.84 and its PSFE content is higher than 40 at.%. If the PSFE content is between 25 and 40 at.%, σ phase may or may not form, but the likelihood of its formation increases with PSFE content. These criteria are used to predict σ phase formation in the σ-phase-containing alloys listed in Table 3. The results are also shown in the same table. Among the 17 σ-containing alloys, 15 of them are indeed predicted to contain σ phase. In the rest two alloys, σ phase formation is predicted to be possible but uncertain. Therefore, these criteria can effectively address alloys that previous models fail to screen out. In other words, with the help of criteria specifically targeted at these IM types, the number of mispredictions can be significantly reduced.

In conclusion, the majority of parametric models to predict SSS HEAs are based on two core concepts: near-zero mixing enthalpy

Table 2
The SSS-forming conditions in some representative publications. These conditions are used to predict SSS formation in the CoCrFeNiX alloys, and incorrect predictions made by each model are also listed.

Ref.	SSS-forming conditions	Incorrect predictions
[13]	$-11.6 \le \Delta H_{mix} \le 3.2$ kJ/mol, δ < 6.6%	X = V, Mo, W
[20]	$-11.6 \le \Delta H_{mix} \le 3.2$ kJ/mol, γ < 1.175	X = V, Mo, W
[12]	Ω ≥ 1.1, δ ≤ 6.6%	X = V, Nb, Ta, Mo,W
[19]	Λ > 0.96 J/K·mol	X = V, Mo
[21]	φ > 20	X = V, Mo, W