

# Design of High-Entropy Alloy: A Perspective from Nonideal Mixing

Q.F. HE,<sup>1</sup> Z.Y. DING,<sup>1</sup> Y.F. YE,<sup>1</sup> and Y. YANG<sup>1,2</sup> 

1.—Centre for Advanced Structural Materials, Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Kowloon Tong, Kowloon, Hong Kong Special Administrative Region (SAR), People's Republic of China. 2.—e-mail: yonyang@cityu.edu.hk

Since the advent in 2004, high-entropy alloys (HEAs) have been attracting a great deal of research interest worldwide. Being deemed as a major paradigmatic shift, the design of HEAs without base elements poses challenges to the existing thermodynamic models and theories that were long established for traditional alloys, one of which is related to the thermodynamic mechanisms for the formation of random solid solution in a concentrated multicomponent alloy. In this article, we discuss the design of HEAs from the perspective of correlated mixing (nonideal mixing of atoms with interatomic correlations). In a quantitative manner, we can show that the formation of a random solid solution in HEAs depends not only on the number of constituent elements but also on the alloy's melting/processing temperature and on various interatomic correlations. Through the correlated mixing rule, we further demonstrate a strategy to screen out equiatomic alloys with the thermodynamic characteristics close to those of random solid solutions from an expanded library of 20 candidate elements.

## INTRODUCTION

Metals and alloys have been playing an essential role during the course of human civilization. Historically, the ancient time of human beings was named after the metals or alloys that were discovered, made, and then widely used. As illustrated in Fig. 1, this includes the Bronze Age that lasted for over 1000 years and the Iron Age that lasted for over 3000 years.<sup>1</sup> In the early efforts for alloy development, one primary metal was usually chosen and alloyed with other elements of a low concentration to improve the properties of the original metal. This paradigm of alloy design prevailed for millennia. Today, the design of many important alloys conformed to this classic alloy design paradigm, including the Fe-based alloys,<sup>2</sup> the Al-based alloys,<sup>3,4</sup> the Mg-based alloys,<sup>5</sup> the Ti-based alloys,<sup>6</sup> and the Ni-based superalloys.<sup>7</sup> Nevertheless, the chemical compositions of modern alloys are much more complex to meet the increasing demand of their functional and structural properties. For example, the typical Ni-based superalloy (Inconel 718)<sup>8</sup> is made up of at least 13 elements and the typical Zr-based bulk amorphous alloy<sup>9</sup> is made up of five elements. In a simple word, it seems that

alloy development in the modern times was still bound by the classic design paradigm; nevertheless, there is a general trend that the chemical complexities in the alloys so designed have been increasing steadily with time, as seen clearly in Fig. 1.

Cantor et al.<sup>10</sup> and Yeh et al.<sup>11</sup> independently reported the discovery of the formation of a random solid solution in multicomponent equiatomic alloys. In sharp contrast to the classic alloy design paradigm, these multicomponent alloys contain no base elements and all constituent elements are mixed in an equi- or nearly equiatomic composition. Going one step further, Yeh et al. proposed that the formation of the random solid solution should be attributed to the high configuration entropy in these multicomponent equiatomic alloys and, thereby, coined the name of “high-entropy alloy” (HEA) for them. Since then, a great deal of research interest has been evoked,<sup>12–20</sup> and HEAs with 5 up to 12 elements have been reported. At the fundamental level, although it is still a matter of debate whether and under what condition a multicomponent equiatomic alloy possesses a high configurational entropy of mixing,<sup>21–31</sup> some HEAs already exhibited the properties unparalleled by conventional alloys. Apparently, this agrees with the general trend that

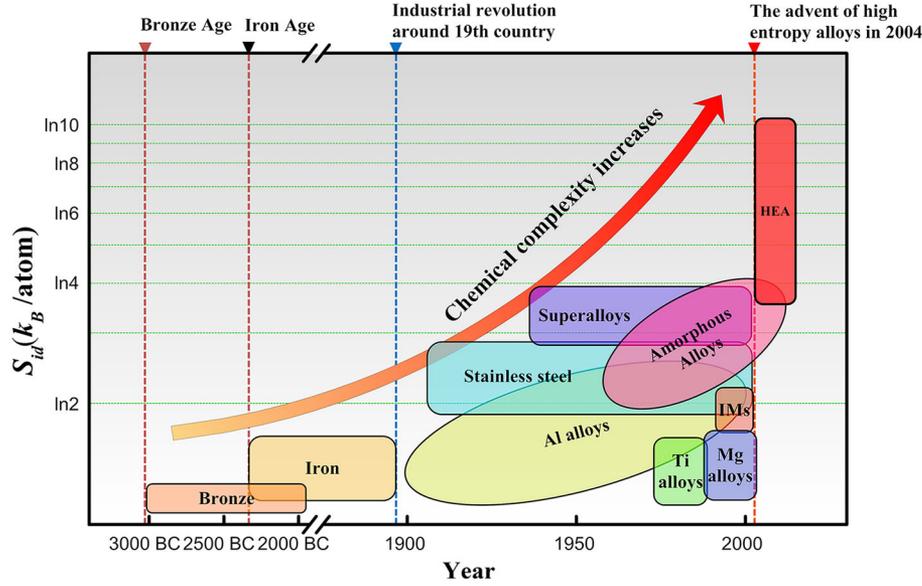


Fig. 1. Rising trend of alloy chemical complexity versus time. Note that “IMs” stands for intermetallics or metallic compounds and “HEA” for high-entropy alloy.

property enhancement in alloys may go hand-in-hand with their chemical complexities (Fig. 1). To set an equal footing for comparison, here we adopt the simple formulas of ideal mixing to quantify the chemical complexity of different alloys, namely,  $S_{id} = -k_B \sum_{i=1}^n c_i \ln c_i$ , where  $k_B$  is the Boltzmann constant,  $n$  is the number of constituent elements, and  $c_i$  is the composition of the  $i$ th element. Please note that  $S_{id}$  should be only taken here as a measure of chemical complexity, which could differ significantly from the real configurational entropy of mixing of a real alloy, particularly at a low temperature.<sup>21,30–35</sup> Evidently, HEAs distinguish themselves from all other alloys by displaying the greatest chemical complexity, as shown in Fig. 1. Conceptually, this enhanced chemical complexity may lead to the improvement of alloy properties, as already witnessed in some of the HEAs, such as a balanced combination of high strength and ductility<sup>36</sup> and ultra-high fracture resistance at low temperature.<sup>37</sup> Today, there are many fundamental issues yet to be fully resolved for HEAs, such as lattice distortion,<sup>38,39</sup> dislocation strengthening mechanisms<sup>40</sup> and thermodynamics for phase selection.<sup>31,41–43</sup> In this article, we would like to focus on the issue of phase selection in HEAs and discuss the underlying thermodynamic mechanisms from the perspective of correlated mixing and potential energy landscape (PEL).

## COMPARISON OF EMPIRICAL RULES FOR RANDOM SOLID SOLUTION

Before we discuss our approach, it is worth revisiting the variety of empirical or semi-empirical rules so far proposed,<sup>11,18,22,29,44–50</sup> which are summarized in Table I.

Indeed, the earliest effort could be dated back to the 1920s when Hume-Rothery established a set of empirical rules for the formation of random solid solution in binary alloys. In general, these include (I) the difference between the atom sizes of solute and solvent elements is less than 15%; (2) the difference between the electronegativities of the constituent elements is small; and (3) the valence electron number of the constituent elements is similar.<sup>44</sup> This contrasts the seminal proposal of Yeh et al.<sup>11</sup> the latter of which suggested that random solid solution is thermodynamically favored if the configurational entropy of mixing outweighs the thermodynamic potential of other competing phases, known as the rule of entropic stabilization. Mathematically, this rule was formulated as  $S_{id} > 1.5k_B$  under the assumption that the configurational entropy of mixing of an equiatomic alloy can be approximated as  $S_{id} = k_B \ln(n)$ .<sup>15</sup> Under such an assumption, one could envision a general trend that the more elements are mixed, the higher is the configurational entropy of mixing of the alloy and, therefore, the more likely it is to form a random solid solution. Unfortunately, the experimental data hitherto reported are seemingly not supportive of this general trend.<sup>13,51,52</sup> To guide the design of HEAs, Zhang et al. proposed a two-parameter empirical rule based on the reported experimental data in 2008,<sup>46,49</sup> which simply suggests that random solid solutions tend to form if the following criteria are met, namely,  $-15 \text{ kJ/mol} < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$  and  $0 < \delta < 5$ , in which the mixing enthalpy  $\Delta H_{\text{mix}} = \sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j$  with  $\Omega_{ij} = 4\Delta H_{ij}$  and  $\Delta H_{ij}$  being the mixing enthalpy for the equiatomic alloy of  $i$ th and  $j$ th elements based on Miedema’s model<sup>53,54</sup> and

Table I. Summary of the empirical rules proposed for the formation of random solid-solution HEAs and BMGs

Empirical rules	Year	Contents	References	Formation of random solid solution
Hume-Rothery rules	1920s	<ol style="list-style-type: none"> <li>1. The atomic size difference &lt; 15%</li> <li>2. Similar electronegativities of the constituent elements</li> <li>3. Similar valence electron number of the constituent elements</li> </ol>	Mizutani <sup>44</sup>	Formation of random solid solution
Yeh's rule	2004	$S_{id} \geq 1.5k_B$ or the number of elements in an equiatomic alloy $n \geq 5$	Yeh et al. <sup>11,45</sup>	
Other empirical rules	2008 2011	$0 < \delta < 5$ , $-15 \text{ kJ/mol} < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$ FCC: VEC = $8.5 \pm 1.0$ ; BCC: VEC = $5.0 \pm 0.7$ ; HCP: VEC = $2.8 \pm 0.2$ $0 < \delta \leq 6.6$ , $\Omega \geq 1.1$ $\phi > 20$	Zhang et al. <sup>46</sup> Ye et al., <sup>14</sup> Guo et al. <sup>47</sup>	
Inoue's rules	2012 2015 2000	<ol style="list-style-type: none"> <li>1. More than three constituent elements</li> <li>2. Atomic size difference of above about 12%</li> <li>3. Negative mixing enthalpy</li> </ol>	Yang and Zhang <sup>49</sup> Ye et al. <sup>22,48</sup> Inoue <sup>50</sup>	Formation of bulk metallic glass

$\delta = 100\% \sqrt{\sum_{i=1}^n c_i \left(1 - r_i / \sum_{j=1}^n c_j r_j\right)^2}$  with  $r_i$  being the atomic radius of the  $i$ th element. Later on, Zhang et al.<sup>49</sup> modified his early criterion by adding in the contribution of the configurational entropy of mixing, which leads to a dimensionless parameter  $\Omega = \frac{T_m S_{id}}{|\Delta H_{\text{mix}}|}$ , where  $T_m$  is the melting point of an alloy. Furthermore, Guo et al.<sup>47</sup> reported that the weighted average of the valence electron concentration (VEC) also plays a role in determining the specific crystal structure of solid solution HEAs,  $\text{VEC} = \sum_{i=1}^n c_i (\text{VEC})_i$ , where  $(\text{VEC})_i$  is the VEC of the  $i$ th element.<sup>47</sup> Alternatively, by taking into the account the excess configurational entropy of mixing, Ye et al. proposed a dimensionless parameter  $\phi = \frac{S_{id} - |\Delta H_{\text{mix}}|/T_m}{|S_E|}$  to guide the design of HEAs further, where  $S_E$  denotes the excess configurational entropy of mixing.<sup>14,22,48</sup> Regardless of the mathematical details, the rules of Zhang et al.<sup>46,49</sup> and Ye et al.<sup>14,22,48</sup> are indeed similar. They all suggest that to obtain a random solid solution, one has to minimize the atomic size difference and the average mixing enthalpy in HEAs. Notably, these are in the same spirit of the Hume-Rothery rules for binary alloys,<sup>44</sup> but they are in sharp contrast to the rules proposed by Inoue in 2000 for the design of bulk metallic glasses (BMGs).<sup>50</sup> According to Inoue,<sup>50</sup> one has to mix more than three types of elements with significant atomic size difference ( $> 12\%$ ) and negative heat of mixing to obtain BMGs. By comparison, it seems that both encourage mixing multiple metallic elements (more than three or even five types) although the former rule aims to form a crystalline random solid solution while the latter aims to form metastable noncrystals. Nevertheless, regarding the specificities associated with constituent elements, such as atomic size, the rules for HEAs suggest minimizing the difference, whereas those for BMGs suggest the opposite.

## CORRELATED MIXING AND CONFIGURATIONAL ENTROPY

Now let us discuss our approach with regard to the design of HEAs. Unlike the previous works,<sup>12–14,41,42,55</sup> the issue we want to address here is NOT that which phase is most thermodynamically or kinetically feasible in a multicomponent alloy but what the specificities of constituent elements would be if the obtained alloy appeared to be a random solid solution. In other words, in theory, we will be discussing the solutions to the issue of a necessary NOT sufficient condition. As such, we do not need to discuss the thermodynamics for phase selection that has to take into account the fact that, like BMGs, most random solid

solution HEAs reported so far are indeed metastable at a low temperature, including the famous Cantor (CoCrFeMnNi) alloy.<sup>51</sup>

Compared with other phases, an ideal random solution possesses the highest configurational entropy of mixing, which can be quantified by the ideal mixing rule  $S_{id} = -k_B \sum_{i=1}^n c_i \ln c_i$ . Yet, as discussed in many previous works,<sup>12,13,21,31</sup> a solid-solution alloy can hardly be an ideal solid solution. Interatomic correlations can result in chemical short-range ordering, thereby reducing the alloy's configurational entropy of mixing. This means that not all configurations being constructed through the permutation of atoms are thermodynamically equivalent. As a result, the solid-solution alloy tends to take on a certain type of configuration or microstates with a higher probability than others. In the case of correlated mixing, the configurational entropy of mixing of the solid solution should be formulated in terms of Gibbs entropy:

$$S_{\text{corr}} = -k_B \sum_{i=1}^n p_i \ln p_i \quad (1)$$

where  $p_i$  is the probability of the  $i$ th configuration or microstate that corresponds to a given macroscopic potential energy. According to Eq. 1, if one wants to compute  $S_{\text{corr}}$ , he has to know how the macroscopic potential energy varies with the microscopic configurations or, in other words, the potential energy landscape (PEL) of the alloy system.

In the language of PEL, the PEL of an ideal random solid solution may be represented by a straight line in its 1D construct, as illustrated in Fig. 2a. This means that all configurations as computed through the permutation of atoms are thermodynamically equivalent, and therefore, it is equally likely for the alloy to be in any one of the configurations. In such a case,  $p_i = 1/\Omega$  with  $\Omega$  the total number of the configurations and, hence,  $S_{\text{corr}} = k_B \ln(\Omega)$ , which produces the same result as the ideal mixing rule. Yet, in the case of correlated mixing, one can envision that the PEL cannot be a straight line anymore. As shown in Fig. 2a, “basins” and “saddle” points appear on the PEL because of the interatomic correlations. As a result, the alloy system prefers to stay more in the “basins” rather than on the “saddle” points, causing the reduction of the configurational entropy of mixing. On the basis of Eq. 1, He et al.<sup>31,56</sup> recently developed a thermodynamic model by assuming that the PEL of the random mixing only undergoes a small fluctuation because of the interatomic correlations, which yields the following formula for  $S_{\text{corr}}$ :

$$S_{\text{corr}} = S_{id} + k_B \cdot \left[ 1 + \frac{x}{2} - \ln(x) + \ln(1 - e^{-x}) - \frac{x}{2} \cdot \frac{1 + e^{-x}}{1 - e^{-x}} \right] \quad (2)$$

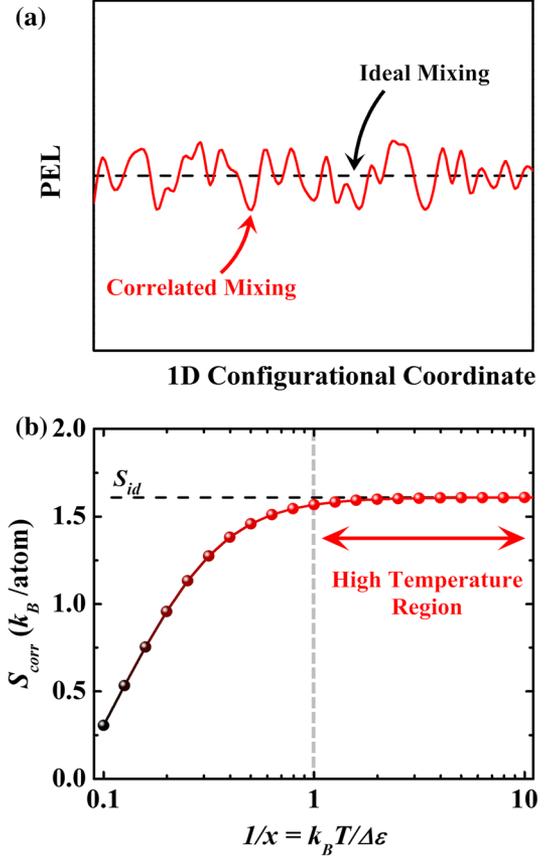


Fig. 2. (a) Potential energy landscape for ideal and correlated mixing. (b) Variation of the correlated configurational entropy of mixing with the reciprocal of the normalized energy fluctuation for a quinary equiatomic alloy.

where  $x = \frac{\Delta\varepsilon}{k_B T}$  is a dimensionless parameter that represents the potential energy fluctuation and  $\Delta\varepsilon$  is the range of the potential energy fluctuation. Furthermore, He et al. analyzed the energy fluctuation caused by the atom size difference  $x_e$  and the chemical bond misfit  $x_c$ ,<sup>31,56,57</sup> which yielded the results of  $x_e = 4.12\delta \cdot \sqrt{\frac{\bar{K}\bar{V}}{k_B T}}$  and

$x_c = 2\sqrt{\frac{\sum_i \sum_{j,i \neq j} c_i c_j (\Delta H_{ij} - \bar{\Delta H})^2}{k_B T}}$ . Here  $\bar{K}$  is the averaged bulk modulus;  $\bar{V}$  is the averaged atomic volume; and  $\bar{\Delta H}$  is the averaged value of  $\Delta H_{ij}$ . Consequently, the total energy fluctuation can be expressed as  $x = x_e + x_c$ . Here it should be noted that other forms of correlations, such as magnetism, can also perturb the PEL and change the configurational entropy of mixing. According to Eq. 2,  $S_{\text{corr}}$  reaches to its maximum value  $S_{id}$  when  $x \leq 1$  (Fig. 2b). This is feasible only for a high-temperature  $T$ , a small atomic size difference, a low chemical bond misfit, or all three. Interestingly, this echoes well some of the empirical rules listed in Table I and many recent experimental and

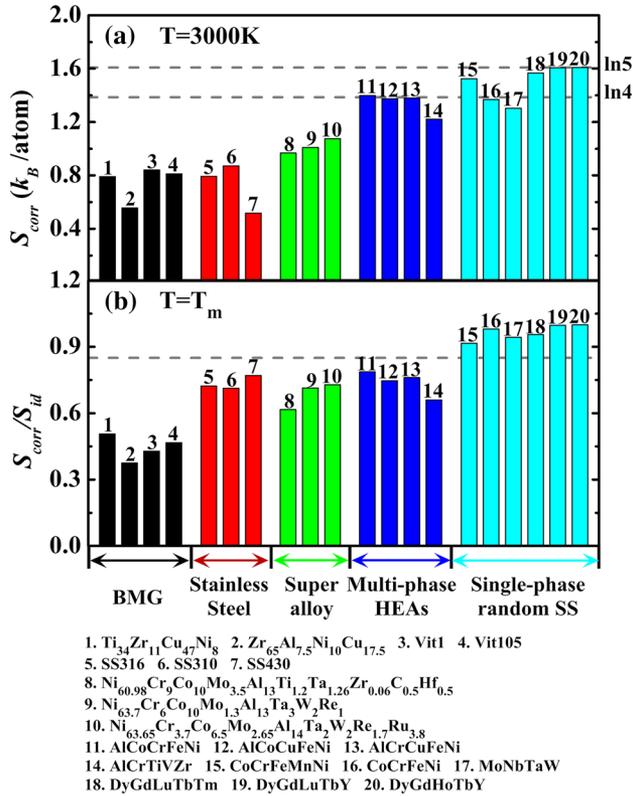


Fig. 3. (a) Correlated configurational entropy of mixing for a variety of alloys at  $T = 3000\text{K}$ . (b) Ratio of  $S_{corr}/S_{id}$  for the variety of alloys at their melting point (the dashed line indicates that  $S_{corr}/S_{id} = 0.85$ , SS indicates a solid solution).

simulation results. For example, Otto et al.<sup>51</sup> observed the precipitation of intermetallic phases in the single-phase CoCrFeMnNi HEA after long annealing at intermediate temperatures. Through CALPHAD simulations, Ma et al.<sup>43</sup> reported a similar behavior in a series of non-equiatom Fe<sub>x</sub>Mn<sub>62-x</sub>Ni<sub>30</sub>Co<sub>6</sub>Cr<sub>2</sub> alloys, which exhibit a single FCC solid solution phase at a high temperature but two phases (FCC + BCC) at an intermediate temperature and three phases (FCC + BCC +  $\sigma$ ) at the room temperature.<sup>43</sup> Theoretically, lowering the temperature reduces not only the Gibbs energy through the term  $-TS_{corr}$  but also the configurational entropy of mixing, which is temperature and atomic size dependent.<sup>21,29,35</sup>

### SEARCH OF A “RANDOM” SOLID SOLUTION THROUGH $S_{corr}$

On the basis of Eq. 2, we can compute the configurational entropy of mixing for different alloys under the assumption that they all form a solid solution with correlated mixing. Furthermore, unlike  $S_{id}$ ,  $S_{corr}$  is temperature dependent according to Eq. 2. Figure 3a compares the values of  $S_{corr}$  for the variety of alloys at the temperature  $T = 3000\text{K}$ . As expected,  $S_{corr}$  reaches  $S_{id}$  at such a high temperature. Meanwhile, we also computed the

$S_{corr}$  values of the alloys at their melting points  $T_m$ .<sup>31</sup> Evidently, as the temperature goes down, the influence of the atomic size and chemical bond emerges and the  $S_{corr}$  values drop for all the alloys. Nevertheless, it can be noted that the values of  $S_{corr}$  drops much less for the alloys that form a random solid solution upon casting than for the others that do not. As one can infer from the empirical rules listed in Table I, this is sensible because there is a lesser degree of atomic size and chemical bond difference in these solid-solution alloys<sup>14,38,46</sup> than in the other alloys, particularly in the glass-forming alloys.<sup>50</sup> Therefore, their  $S_{corr}$  values become less temperature dependent.

As  $S_{corr}$  gauges the combined effect of atomic size and chemical bonding on the configurational entropy of mixing of a multicomponent alloy, one may ask, “Can we use  $S_{corr}$  to distinguish alloys of different phases?” In theory,  $S_{corr}$  could provide a good indicator if one also takes into account  $S_{id}$ , the configurational entropy of mixing for an ideal case. This is because the number of elements also changes the value of  $S_{corr}$  according to Eq. 2. Therefore, it is likely that the configurational entropy of mixing of a solid-solution alloy is smaller than that of a non-solid-solution alloy if the latter contains more elements. For the general case of variant  $S_{id}$ , He et al.<sup>31</sup> proposed that the normalized entropy or the ratio of  $S_{corr}/S_{id}$  could be used for initial alloy screening. As demonstrated in Fig. 3b and in Ref. 31, He et al. found that random solid solutions are likely to form if the ratio of  $S_{corr}/S_{id}$  of an alloy evaluated at  $T_m$  is greater than 0.85. This delivers a strong message that the elemental mixing in the solid-solution HEAs should be close to ideal mixing at their melting points. On the other hand, this also implies that if solid-solution HEAs are annealed at a low temperature, the effect of interatomic correlations will be intensified and the configurational of entropy of mixing will decline. This could lead to chemical short-range ordering, de-mixing, or both and even to the precipitation of second phases.

Following this line of reasoning, we now go one step further to search for the possible equiatomic HEA compositions that could form solid solutions from the expanded library that consists of 20 elements,<sup>12</sup> namely, Li, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Pd, Sn, Hf, and Ta. In theory, this could lead to 616,455 equiatomic alloys, including the ternary, quaternary, quinary, to denary alloys. Figure 4a shows the probability distributions of  $S_{corr}/S_{id}$  for some of these alloy systems. Evidently, with the increase in the number of constituent elements, more alloys are distributed into the region of a mild  $S_{corr}/S_{id}$  ratio ( $\sim 0.5$  to  $0.8$ ). In view of the previous finding that a random solid solution corresponds to  $S_{corr}/S_{id} > 0.85$ ,<sup>31</sup> this behavior implies that forming a random solid-solution HEAs would be hampered by randomly increasing the number of the constituent elements. Based

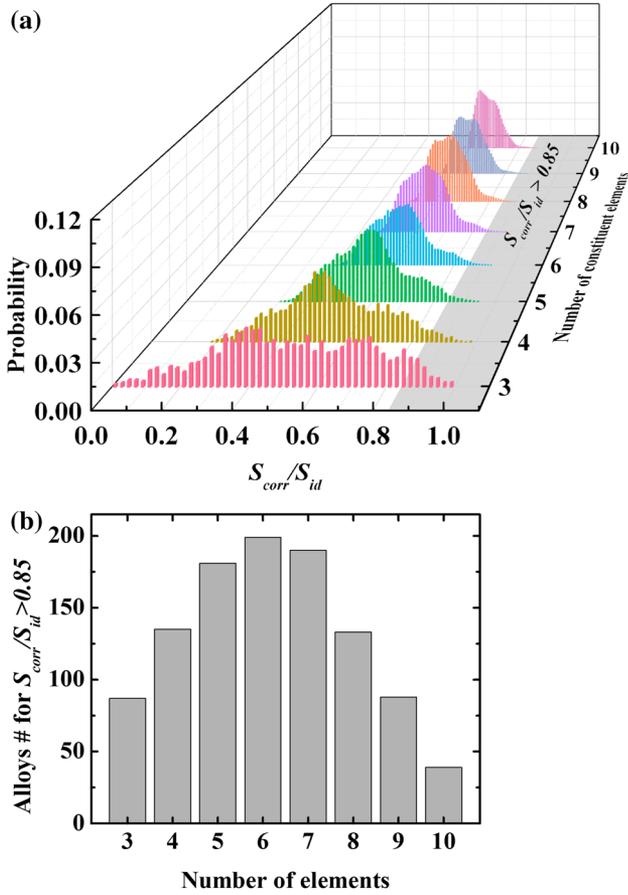


Fig. 4. (a) Probability distribution of  $S_{corr}/S_{id}$  for a variety of equiatomic alloy compositions taken from the library of 20 most frequently used elements in HEAs. (b) Number of alloy compositions with  $S_{corr}/S_{id} > 0.85$  as a function of the number of constituent elements.

on the rule of  $S_{corr}/S_{id} > 0.85$ , we can screen out the possible solid-solution compositions as a function of the number of elements. Interestingly, as shown in Fig. 4b, it can be seen that it is most likely to obtain random solid solutions in quinary, senary, and septenary alloys if one randomly mixes different types of elements within the given library. Notably, using the Calphad calculation as the method of screening, a similar trend was also reported by Senkov et al.<sup>27</sup>

## SUMMARY

To summarize, from the perspective of correlated mixing, we discuss a new approach for the search of solid-solution HEAs in this article. On the fundamental level, our approach is based on the notion that one has to take into account various interatomic correlations to assess the configurational entropy of mixing of a real alloy. Through the thermodynamic model of correlated mixing (Eq. 2), we demonstrate that the configurational entropy of mixing of a multicomponent alloy not only depends on its chemical composition but also on the attributes of the constituent elements as well as

on the alloy's overall melting and processing temperature. These findings rationalize various phenomena associated with phase selection reported in the HEA literature. Finally, based on these discussions, we may argue that the design of HEAs is not just like making a metal "buffet" by randomly mixing a large number of elements. Like the total number of the candidate elements, the properties of the individual elements, the underlying interatomic correlations, the estimated alloy melting temperature and even the processing temperature of the alloy should be also considered in the search of random solid solution HEAs.

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## REFERENCES

1. R.E. Hummel, *Understanding Materials Science: History, Properties, Applications* (New York: Springer Science & Business Media, 2004).
2. J.R. Davis, *Stainless Steels* (Materials Park: ASM International, 1994).
3. I.J. Polmear, *Light Alloys* (Oxford: Butterworth-Heinemann, 2005), p. 97.
4. I.J. Polmear, *Light Alloys* (Oxford: Butterworth-Heinemann, 2005), p. 205.
5. I.J. Polmear, *Light Alloys* (Oxford: Butterworth-Heinemann, 2005), p. 237.
6. I.J. Polmear, *Light Alloys* (Oxford: Butterworth-Heinemann, 2005), p. 299.
7. R.C. Reed, *The Superalloys: Fundamentals and Applications* (New York: Cambridge University Press, 2008).
8. G.A. Khorovskiy, M.J. Cieslak, T.J. Headley, A.D. Romig, and W.F. Hammett, *Metall. Trans. A* 20, 2149 (1989).
9. A. Peker and W.L. Johnson, *Appl. Phys. Lett.* 63, 2342 (1993).
10. B. Cantor, I.T.H. Chang, P. Knight, and A.J.B. Vincent, *Mater. Sci. Eng. A* 375-377, 213 (2004).
11. J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, and S.Y. Chang, *Adv. Eng. Mater.* 6, 299 (2004).
12. D.B. Miracle and O.N. Senkov, *Acta Mater.* 122, 448 (2017).
13. E.J. Pickering and N.G. Jones, *Int. Mater. Rev.* 61, 183 (2016).
14. Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, and Y. Yang, *Mater. Today* 19, 349 (2016).
15. J.-W. Yeh, *JOM* 65, 1759 (2013).
16. Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, and Z.P. Lu, *Prog. Mater. Sci.* 61, 1 (2014).
17. M.C. Gao, *High-Entropy Alloys: Fundamentals and Applications*, ed. M.C. Gao, Y. Jien-Wei, P.K. Liaw, and Z. Yong (New York: Springer International Publishing, 2016), p. 369.
18. Y. Zhang, S. Guo, C.T. Liu, and X. Yang, *High-Entropy Alloys: Fundamentals and Applications*, ed. M.C. Gao, Y. Jien-Wei, P.K. Liaw, and Z. Yong (New York: Springer International Publishing, 2016), p. 21.
19. L.J. Santodonato, Y. Zhang, M. Feynson, C.M. Parish, M.C. Gao, R.J.K. Weber, J.C. Neufeld, Z. Tang, and P.K. Liaw, *Nat. Commun.* 6, 5964 (2015).
20. M.C. Gao, *JOM* 67, 2251 (2015).
21. D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, and D. Raabe, *Acta Mater.* 100, 90 (2015).
22. Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, and Y. Yang, *Scripta Mater.* 104, 53 (2015).
23. S. Praveen, B.S. Murty, and R.S. Kottada, *Mater. Sci. Eng. A* 534, 83 (2012).

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24. F. Otto, Y. Yang, H. Bei, and E.P. George, *Acta Mater.* 61, 2628 (2013).
25. A.K. Singh and A. Subramaniam, *J. Alloys Compd.* 587, 113 (2014).
26. N.G. Jones, J.W. Aveson, A. Bhowmik, B.D. Conduit, and H.J. Stone, *Intermetallics* 54, 148 (2014).
27. O.N. Senkov, J.D. Miller, D.B. Miracle, and C. Woodward, *Nat. Commun.* 6, 6529 (2015).
28. M.C. Tropicovsky, J.R. Morris, P.R.C. Kent, A.R. Lupini, and G.M. Stocks, *Phys. Rev. X* 5, 011041 (2015).
29. Z. Liu, Y. Lei, C. Gray, and G. Wang, *JOM* 67, 2364 (2015).
30. G. Anand, R. Goodall, and C.L. Freeman, *Scripta Mater.* 124, 90 (2016).
31. Q.F. He, Y.F. Ye, and Y. Yang, *J. Appl. Phys.* 120, 154902 (2016).
32. S. Guo and C.T. Liu, *Prog. Nat. Sci.: Mater. Int.* 21, 433 (2011).
33. S. Guo, Q. Hu, C. Ng, and C.T. Liu, *Intermetallics* 41, 96 (2013).
34. A. Takeuchi, K. Amiya, T. Wada, K. Yubuta, W. Zhang, and A. Makino, *Entropy* 15, 3810 (2013).
35. M. Widom, *High-Entropy Alloys: Fundamentals and Applications*, ed. M.C. Gao, Y. Jien-Wei, P.K. Liaw, and Z. Yong (New York: Springer International Publishing, 2016), p. 267.
36. Z. Li, K.G. Pradeep, Y. Deng, D. Raabe, and C.C. Tasan, *Nature* 534, 227 (2016).
37. B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, and R.O. Ritchie, *Science* 345, 1153 (2014).
38. Y.F. Ye, C.T. Liu, and Y. Yang, *Acta Mater.* 94, 152 (2015).
39. J.W. Yeh, S.J. Lin, T.S. Chin, J.Y. Gan, S. Chen, T.T. Shun, C.H. Tsau, and S.Y. Chou, *Metall. Mater. Trans. A* 35, 2533 (2004).
40. C. Varvenne, A. Luque, and W.A. Curtin, *Acta Mater.* 118, 164 (2016).
41. S. Guo, *Mater. Sci. Technol.* 31, 1223 (2015).
42. Z. Wang, S. Guo, and C.T. Liu, *JOM* 66, 1966 (2014).
43. D. Ma, M. Yao, K.G. Pradeep, C.C. Tasan, H. Springer, and D. Raabe, *Acta Mater.* 98, 288 (2015).
44. U. Mizutani, *Hume-Rothery Rules for Structurally Complex Alloy Phases* (Boca Raton: CRC Press, 2016).
45. J.W. Yeh, *JOM* 67, 2254 (2015).
46. Y. Zhang, Y.J. Zhou, J.P. Lin, G.L. Chen, and P.K. Liaw, *Adv. Eng. Mater.* 10, 534 (2008).
47. S. Guo, C. Ng, J. Lu, and C.T. Liu, *J. Appl. Phys.* 109, 103505 (2011).
48. Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, and Y. Yang, *Intermetallics* 59, 75 (2015).
49. X. Yang and Y. Zhang, *Mater. Chem. Phys.* 132, 233 (2012).
50. A. Inoue, *Acta Mater.* 48, 279 (2000).
51. F. Otto, A. Dlouhý, K.G. Pradeep, M. Kuběnová, D. Raabe, G. Eggeler, and E.P. George, *Acta Mater.* 112, 40 (2016).
52. Y.F. Ye, Q. Wang, Y.L. Zhao, Q.F. He, J. Lu, and Y. Yang, *J. Alloys Compd.* 681, 167 (2016).
53. H. Bakker and A. Miedema, *Enthalpies in Alloys: Miedemas Semi-Empirical Model* (Uetikon-Zuerich: Trans Tech Publications, 1998).
54. F.R. Boer, *Cohesion in Metals: Transition Metal Alloys* (Amsterdam: North-Holland, 1988).
55. M. Gao and D. Alman, *Entropy* 15, 4504 (2013).
56. Q.F. He, Y.F. Ye, and Y. Yang, *J. Phase Equilib. Diffus.* (2017). doi:[10.1007/s11669-017-0560-9](https://doi.org/10.1007/s11669-017-0560-9).
57. Y.F. Ye, X.D. Liu, S. Wang, C.T. Liu, and Y. Yang, *Intermetallics* 78, 30 (2016).