



# The generalized thermodynamic rule for phase selection in multicomponent alloys



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## ABSTRACT

The design of modern multicomponent alloys (MCAs) appears complicated, which usually entails mixing multiple elements that have a variety of sizes and heat of mixing. As a result, different phases, such as single- and multi-phased solid-solution, intermetallic compounds and even metallic glasses, can be formed upon solidification of the corresponding metallic melts. To understand such diversities in the phase selection in MCAs, tremendous research efforts have been dedicated over the past decades, which, however, are empirically or semi-empirically based. In contrast, here we show that a simple thermodynamic rule can be derived from the hard sphere model, which predicts that the phases formed in cast MCAs only depend on two dimensionless thermodynamic parameters: one is related to the entropic departure of the alloy from the ideal solution and the other to the average heat of mixing scaled by the 'ideal' configurational entropy of mixing. Using this simple rule, we are able to unfold a general trend that guides phase selection in MCAs, including super-alloys, bulk metallic-glasses, high entropy alloys and many other engineering materials. The outcome of our current research sheds an important insight into the thermodynamic origin for phase stability and alloy design of MCAs

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## 1. Introduction

Since the Bronze age, alloy design has been one critical task for the civilization of human beings [1]. To obtain good properties for meeting the end of a variety of applications, pure metals are usually alloyed with other elements in a relatively small amount for property enhancement. This traditional alloying strategy, aimed for the fine and/or coarse tuning of the properties of the base elements, has been practiced for thousands of years. Despite that this traditional way is successful in alloy making, it also limits the number of useful alloys that have ever been made. To bypass this limitation, the recent research efforts have been directed towards the design of high entropy alloys [2–5] by mixing a number of elements together in equal or nearly equal molar fraction. Although an increasing degree of complexity in alloy design is foreseen with more elements being mixed together, the basic idea behind this new alloying strategy, however, appears relatively simple [2,3,6]: after combining a number of elements together, the configurational entropy of mixing of the resultant alloy could be maximized with an equiatomic composition; as a result of this 'high-entropy' effect,

the multi-component alloys so-obtained could become very stable at elevated temperatures. As a result, this could impart high flow stress [2,7,8], sluggish diffusion kinetics [9,10], and excellent creep resistance [11] to these multicomponent alloys (MCAs), making them a promising advanced material for high-temperature applications. Despite the simplicity of this 'high-entropy' theory, the structure of these MCAs at low temperatures, however, exhibits an unexpected diversity, comprising random solid solutions, multi-phased mixtures and amorphous phases with/without nano-precipitation.

## 2. Theoretical modeling

### 2.1. Calculation of the excess configurational entropy

In the original proposal [3], the notion of 'high entropy' was derived from the configurational entropy of mixing,  $S_c$ , of an ideal solution. For an alloy with  $n$  elements, this gives:

$$S_c = -k_B \sum_{i=1}^n c_i \ln c_i \quad (1)$$

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where  $k_B$  is the Boltzmann's constant and  $c_i$  is the molar fraction of the  $n$ th element. Thus, the alloy's entropy can be maximized by assigning an equal molar fraction to each element. Along this line of thinking, one can further raise  $S_c$  by increasing the total number of elements in an equiatomic composition. Following this 'high-entropy' theory, a great number of MCAs were synthesized [2,6], some of which indeed show attractive properties, such as low diffusivity, high corrosion resistance and impressive strength [2]. Despite that, this simple notion of high entropy based on  $S_c$  alone was also being questioned [6,12]: if the entropy of an alloy is really so high such that it dominates the thermodynamics during solidification, the alloys so obtained should be of a single phase; otherwise, the definition of the alloy's entropy in Eq. (1) may need further clarification.

In fact, multiple phases appear to be more than often in these MCAs [2,6]. For example, the five-element FeCoNiCrMn alloy is of single-phased FCC; however, after adding a certain amount of Al into this alloy, the new six-element alloy FeCoNiCrMnAl<sub>0.4</sub> becomes multi-phased [7]. As this occurs, one can also notice a general tendency of phase transition which is directed towards reducing the atomic packing fraction, such as a FCC-to-BCC transition [7] or an order-to-disorder transition [13]. In view of all these structural complexities, which cannot be understood from the perspective of the configurational entropy  $S_c$  alone, a great deal of research has also been motivated, in which additional parameters, such as atomic size mismatch, heat of mixing and valence electron concentration [2,6,13–15], were proposed for assisting the design of high-entropy alloys. At present, these prior efforts are all empirically or semi-empirically based, thereby lacking a unified physical approach. Consequently, to design a so-called high-entropy alloy, one has to choose the right combination from a 'pool' of possible parameters, which makes the whole design process sometimes more of a trial-and-error exercise and thus raises the cost in alloy design. In that regard, from the alloy design point of view, an effective design criterion is therefore being called for, which could be as simple as the original  $S_c$  criterion; however, from the scientific point of view, the open question is: whether there is such a simple rule that can rationalize the complicated phenomena of phase selection in MCAs. If there is, what is the physics behind? For materials scientists, this is a puzzling issue not only of a scientific curiosity but also of a high technological impact.

From the theoretical perspective, the configurational entropy of mixing of an alloy is affected not only by its chemical composition but also by atomic size and packing fraction. In the ideal solution

model, all constituent atoms are treated equal in size and randomly placed in space, as illustrated in Fig. 1(a). Therefore, the configurational entropy of mixing,  $S_c$ , is nothing but enumerating the possible combinations of atom positions. However, if one takes into account the coupling effects of atom size, atomic packing fraction and the number of elements, it is evident that the real entropy of mixing should deviate from the ideal one. According to the Boltzmann formalism, this coupling effect is additive and, therefore, the total entropy of mixing  $S_T$  can be written as  $S_T = S_c + S_E$ , where  $S_E$  denotes the excess configurational entropy of mixing that excludes the contribution from an ideal solution. To simplify the computation of  $S_E$  for a given alloy composition, we adopted the hard sphere model as shown in Fig. 1(b). According to the Mannsori et al. [16],  $S_E$  can be generally expressed as  $S_E = S_E(d_i, c_i, \xi)$ , where  $\xi$  is the atomic packing fraction of the  $n$ -element alloy ranging from 0.68 to 0.74 for close atom packing at room temperature, and  $d_i$  is the atomic diameter of the  $i$ th element ( $i = 1, 2, 3 \dots, n$ ). Note that the full set of equations used to calculate  $S_E$  are very tedious and hence omitted here for brevity. Interested readers are herein referred to the Appendix for details.

## 2.2. Generalized thermodynamic phase diagram

Now let us discuss the case where a single-phase solid solution is preferred in phase formation because of the entropic dominance as envisioned in the original proposal of high entropy alloys [2,3]. According to the classic thermodynamics, the Gibbs free energy of mixing,  $G_m$ , can be expressed as  $G_m = H_m - TS_T$ , where  $H_m$  is the enthalpy of mixing and  $T$  the temperature. Should the magnitude of  $G_m$  is dominated by  $S_T$ , we should have  $\left| \frac{H_m}{TS_T} \right| \ll 1$  and thus  $G_m \approx -TS_T$ . Substituting  $S_T = S_c + S_E = S_c - |S_E|$  into the inequality and rearranging the terms (note that  $S_E$  is negative according to the hard sphere model [16,17]), we obtain:

$$\frac{|S_E|}{S_c} < < 1 - \frac{|H_m|}{TS_c} \quad (2)$$

The above inequality involves only two dimensionless thermodynamic parameters, i.e.  $\frac{|S_E|}{S_c}$  and  $\frac{|H_m|}{TS_c}$ , and sets the entropy-based criterion for the formation of a single-phased solid solution.

Aside from the formation of a single-phase solid solution, the formation of an amorphous alloy can be also studied within the framework of the hard sphere mixture model [17] [Fig. 1(b)]. In principle, glass transition takes place when the relaxation time  $\tau_R$  of

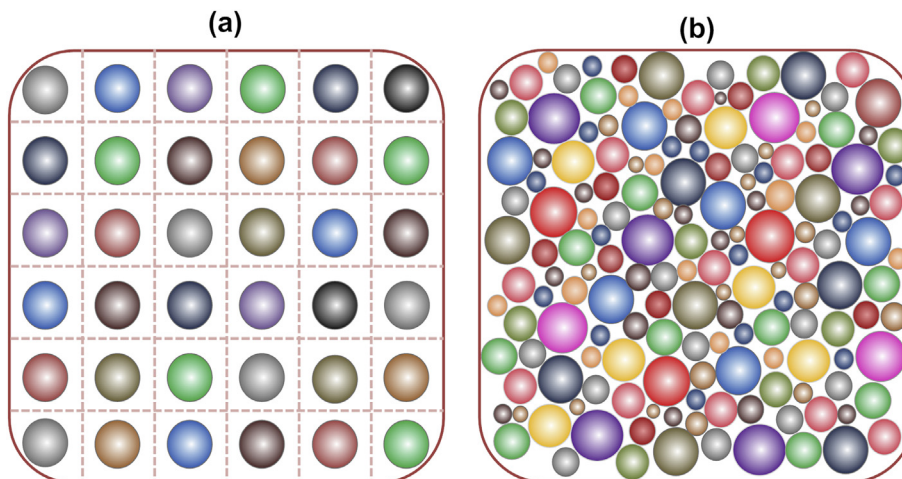


Fig. 1. Schematics of the atomic configuration of a multi-component alloy conforming to (a) the ideal-solution model and (b) the hard-sphere-mixture model.

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