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To cite this article: Arash Tourki Samaei and Ehsan Mohammadi 2015 *Mater. Res. Express* **2** 096501

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Effect of entropy-packing fraction relation on the formation of complex metallic materials

RECEIVED
25 May 2015

REVISED
10 July 2015

ACCEPTED FOR PUBLICATION
21 July 2015

PUBLISHED
1 September 2015

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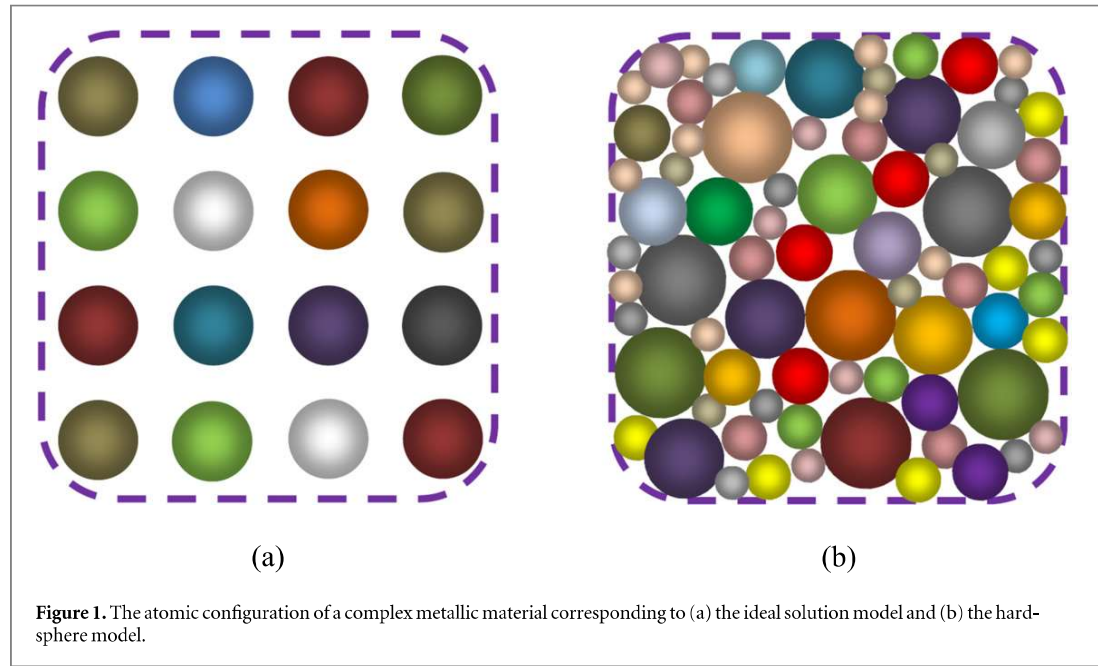
Keywords: entropy, packing fraction, complex metallic materials

Abstract

By combining a number of elements to form complex metallic materials without a base element, it was recently shown that one can obtain rather complex structures, including random solute solutions, multi-phased mixtures and amorphous structures with/without nano-precipitations. Compared to conventional metallic materials, these complex ones could show excellent mechanical and physical properties across a wide range of temperatures, therefore being a promising advanced material for high-temperature applications; however, designing these complex materials, at present, still lacks a unified physical approach but relies on the choice of a few metallurgical parameters, such as atomic size mismatch, heat of mixing and valence electron concentration. Here, we identify a physical mechanism through the optimization of the excess configurational entropy of mixing in the control of phase formation in these metallic materials. The theoretical framework herein established is expected to provide a new paradigm in pursuit of complex metallic materials with superior properties.

Introduction

Pure metals are usually combined with other elements to obtain much better properties for meeting the end of a variety of applications. Since the traditional metallic materials limit the number of useful structural materials because of targeting the fine/coarse tuning of the properties of the base elements, the recent research effort has been directed towards the development of complex metallic materials such as amorphous alloys. To design complex metallic materials, thermodynamic data and phase diagrams of those give us a better understanding of the material properties and phase formation processes [1–4]. While experimental investigation of the thermodynamics of the complex metallic materials is very difficult and expensive, methods based on the physical fundamental to predict the thermodynamic data and phase formation would be very helpful. For example, Miedema *et al* [5–7] proposed an approach to calculate the formation enthalpy of solid and liquid alloys which was simple but very useful to predict the thermodynamic properties of alloys for which no experimental information is available. In addition, Chen [8] reported several physical and thermodynamic factors for the formation of metallic glasses such as atomic size differences, mixing enthalpy, and the number of constituent elements. To further consider the mixing entropy effect, some studies proposed using the atomic size difference parameter to characterize the relative mixing entropy effect against mixing enthalpy [9–12]. A very few theoretical studies of the entropy of mixing have been proposed although there are very few experimental works in this area to compare with them. In this regard, using the entropy of mixing based on the hard sphere theory proposed by Mansoori [13] as a valid method for predicting the thermodynamic properties of metallic material systems, in which the complete experimental data set is not available, is of great importance. The current work is an attempt to open a new insight in this direction. We introduce a physical mechanism through the optimization of the excess configurational entropy of mixing in the control of phase formation in complex metallic materials.



Excess entropy of mixing

The configurational entropy of mixing of metallic materials, which is defined as $S_{\text{conf}} = -R \sum_{i=1}^n c_i \ln c_i$ in which R is the gas constant and c_i is the atomic fraction of the i th element, is affected not only by its chemical composition but also by the general packing fraction and the atomic size mismatch from the theoretical perspective. All constituent atoms are considered equal in size and randomly placed in a 'lattice' in the ideal solution model, as shown in figure 1(a). Therefore, the configurational entropy of mixing, S_{conf} , is nothing but enumerating the possible combinations of atom positions. However, if one considers the coupling effect of atomic packing fraction and atom size, it can be concluded that the real entropy of mixing should be greater than the ideal one. This coupling effect is additive in accord with the Boltzmann formulism, and, therefore, the total entropy of mixing S_T can be given as

$$S_T = S_{\text{conf}} + S_E \quad (1)$$

where S_E represents the excess configurational entropy of mixing due to atomic packing fraction and size mismatch. To calculate S_E for a given metallic material composition, the hard sphere model is adopted in the current study, as shown in figure 1(b).

According to the equilibrium thermodynamic theory [13], S_E can be generally written as follows:

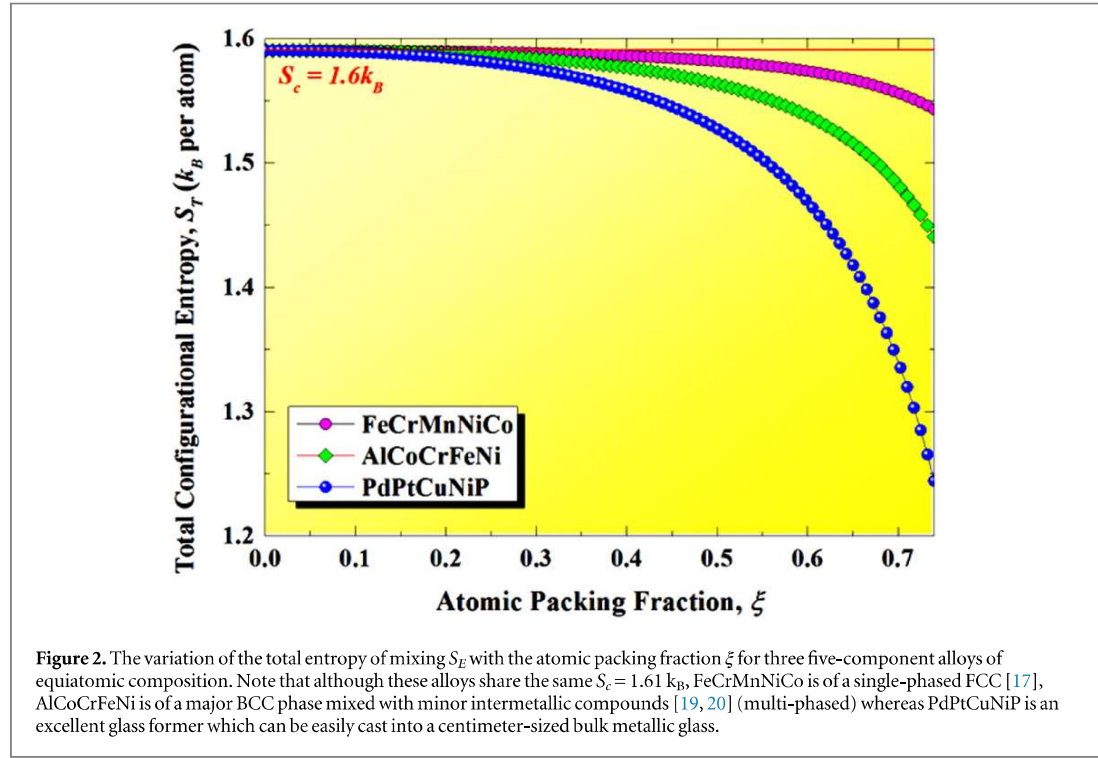
$$S_E = S_E(d_i, c_i, \xi) \quad (2)$$

where ξ is the atomic packing fraction of the n -element metallic material and d_i is the atomic radius of the i th element ($i = 1, 2, 3, \dots, n$). Based on an averaging process over the two results of the solution of the Percus-Yevik integral equation for the mixture of hard spheres, Mansoori [13] presented an equation of state for it to describe the effect of atomic size mismatch in a system. According to the formulism, the mixing entropies entail four terms: ideal gas, packing fraction, concentration, and mismatch terms. Excess entropy S^E for random close packing fraction ξ of hard spheres can be defined as follows [13]

$$\frac{S_E}{k_B} = \frac{(F - F^{id})}{k_B T} - \ln Z - (3-2\xi)(1-\xi)^{-2} + 3 + \ln \left[(1 + \xi + \xi^2 - \xi^3)(1-\xi)^{-3} \right] \quad (3)$$

where

$$\begin{aligned} \frac{(F - F^{id})}{k_B T} = & -\frac{3}{2} (1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)(1-\xi)^{-1} + \frac{3}{2} \left(1 - y_1 - y_2 - \frac{1}{3}y_3 \right) \\ & \times (1-\xi)^{-2} + (y_3 - 1) \ln(1-\xi) \end{aligned} \quad (4)$$



and the compressibility Z for mixtures of hard spheres can be given as follows

$$Z = \left[(1 + \xi + \xi^2) - 3\xi(\gamma_1 + \gamma_2\xi) - \xi^3\gamma_3 \right] (1 - \xi)^{-3} \quad (5)$$

where κ_B is the Boltzmann's constant. The packing fraction ξ and dimensionless parameters γ_1 , γ_2 and γ_3 of n components are given in the appendix. Note that Mansoori [13] validated the above-mentioned relations by extensive molecular dynamics (MD) simulations, and the theory has been widely demonstrated and cited in physics and the materials science area, for example, more recently it was used in the development of bulk metallic glasses [14, 15]. In what follows, we will show that, by considering this additional term S_E , one can rationalize the rather complicated phenomena of phase selection in multi-component alloys in a unified and quantitative manner.

Results and discussion

Figure 2 shows the total entropy of mixing, S_T , determined respectively for the three complex metallic materials, namely, FeCrMnNiCo, AlCoCrFeNi and PdPtCuNiP after taking into account the negative sign of S_E [16]. According to equation (1), they share the same $S_c = 1.6 k_B$ and therefore should be all deemed as a 'high-entropy' metallic material according to the conventional notion [17–20]. However, as found in the previous experiments, the as-cast FeCrMnNiCo exhibited a single-phased FCC structure [17], the as-cast AlCoCrFeNi displayed a mixed BCC and FCC structure [20] while the as-cast PdPtCuNiP turned out to be an excellent bulk-metallic-glass former, possessing an amorphous structure after casting in metal molds. Evidently, this diversity in the phases formed defies the 'high-entropy' concept solely based on the formulation of S_c . Interestingly, it can be seen from figure 2 that the behavior of the total entropy of mixing, S_T , of these complex metallic materials differs from what is expected for an ideal solution. At a very low ξ , their total entropy of mixing S_T approaches S_c , which is sensible since a low packing fraction ξ corresponds more to a gaseous state of random mixing, hence consistent with the ideal-solution model (figure 1(a)). However, as the packing fraction ξ increases, the total entropy of mixing, S_T , reduces significantly from the S_c , which is consistent with the findings obtained previously from binary alloys [16]. This behavior indicates that, as atoms become more densely packed, the total entropy of mixing, S_T , of an alloy is influenced not only by its chemical composition as thought before [21], but also by various geometrical factors such as atom size and atomic packing fraction. As above mentioned, this

confounding effect manifests itself in S_E , the excess entropy of mixing (equation (2)), the magnitude of which quantifies the extent of departure of the real system from the ideal solution model.

Now let us focus on the excess entropy of mixing, S_E , of the aforementioned three alloys, which distinguishes these alloys from one another. As can be inferred from figure 2, for a given atomic packing fraction, FeCrMnNiCo possesses the lowest S_E compared to the others. To be specific, if one fixes ξ at 0.74 which is close to a FCC-like dense packing of atoms, the ratio of the magnitude of S_E to S_c is about 3% for FeCrMnNiCo, 9% for AlCoCrFeNi and 21.5% for PdPtCuNiP. If one takes the $|S_E|/S_c$ ratio as an indicator of how far the final atomic structure of a HEA departs from that of an ideal solution, it follows from these calculations that the structure of FeCrMnNiCo should be closest to that of an ideal solution, which is indeed the case as confirmed by the experiments [17]. However, the real atomic packing fraction varies with the phases formed in the high entropy alloy. Therefore, the values of S_E for AlCoCrFeNi and PdPtCuNiP should be calculated in line with their real phases. Due to the lack of real experimental data, let us assume ξ to be ~ 0.68 for BCC and ~ 0.64 for an amorphous structure for the time being (note that $\xi = 0.64$ corresponds to the random closest packing of hard spheres, while $\xi = 0.7-0.74$ for real amorphous metals and the density difference between crystalline and amorphous states is usually less than $\sim 6\%$). Thus, even for a very conservative estimate after taking into account the effect of atomic packing efficiency, we have $|S_E|/S_c = 5.7\%$ for AlCoCrFeNi and 10% for PdPtCuNiP. Still, the S_E of FeCrMnNiCo remains the lowest, only about one half and one third of that of AlCoCrFeNi and PdPtCuNiP, respectively. This interesting finding implies that S_E is potentially a good indicator for phase selection in HEA: with the increasing magnitude of S_E a HEA tends to transform from a single-phased alloy to a multi-phased alloy and finally to a bulk metallic-glass former.

To confirm the above thinking, we conducted a comprehensive survey of the available experimental data and calculated the magnitude of the excess entropy of mixing, S_E , for a variety of complex metallic material compositions. Here, only the as-cast complex metallic materials, homogenized in order to obtain near-equilibrium phases, are selected for analyses and the results are tabulated in table 1. In doing so, we can rule out the effect of cooling rate, which is not taken into account in the hard-sphere model.

Figure 3 shows the plot of the calculated S_c versus $|S_E|$, which includes the high entropy alloys (HEAs) of equiatomic and nearly equiatomic composition. Here it needs to be emphasized that, as the atomic packing fraction is unknown at present to most HEAs, we take the average of two S_E values computed at $\xi = 0.74$ and 0.68 , which corresponds to two limiting values of ξ , as the one for a given alloy composition. Meanwhile, to simply assess the uncertainty resulting from this treatment, the standard deviation of the calculation is taken as the error bar. As seen in figure 3, it is evident that the phase selection in the HEAs is irrelevant to S_c , which is consistent with the previous findings [40, 41]; however, a correlation is discernable between $|S_E|$ and the phases formed in the as-cast HEAs. This correlation can be better seen using the single parameter $|S_E|$ alone in a log scale. As shown in figure 3, all as-cast HEAs are of a FCC or BCC single phase when their $|S_E|$ is less than $\sim 7 \times 10^{-2} k_B/\text{atom}$, while of an amorphous phase when their $|S_E|$ is greater than $\sim 2 \times 10^{-1} k_B/\text{atom}$; in between, the HEAs are all multi-phased.

Conclusion

To conclude, a generalized entropy rule based on the excess entropy of mixing S_E and its companion S_c is introduced in the current investigation. A unified physical approach that relies on the choice of a few metallurgical parameters, such as atomic size mismatch and packing fraction, is presented to design complex materials. The presented entropy governs the complex phenomena of phase selection in complex metallic materials in which their phase diagrams are unavailable at present due to their complicated chemical composition. This study conceptually provides an analytic framework that strengthens the relation between the atomic packing fraction and atomic size, and phase formation in complex metallic material systems.

Appendix

The packing fraction ξ and dimensionless parameters γ_1 , γ_2 and γ_3 of n components are written as follows:

$$\gamma_1 = \sum_{j>i=1}^m \Delta_{ij} (d_i + d_j) (d_i d_j)^{-1/2} \quad (\text{A1})$$

$$\gamma_2 = \sum_{j>i=1}^m \Delta_{ij} \sum_{k=1}^m \left(\frac{\xi_k}{\xi} \right) \frac{(d_i d_j)^{1/2}}{d_k} \quad (\text{A2})$$

Table 1. The summary of the calculated S_c and S_E 's for the as-cast complex metallic materials with equiatomic or nearly equiatomic composition. Note that the phases of all alloys were identified experimentally and some binary alloys are also included for the sake of comparison.

Material Composition	S_c (k_B per atom)	S_E at $\xi =$ 0.64 (k_B per atom)	S_E at $\xi =$ 0.68 (k_B per atom)	S_E at $\xi =$ 0.74 (k_B per atom)	Phase detected
CoCrCu _{0.5} FeNi[22]	1.5811	0.0014	0.0019	0.003	FCC
FeCoNiCrCu[23]	1.6094	0.0022	0.0029	0.0047	FCC
FeNi ₂ CrCuAl _{0.2} [24]	1.444	0.0184	0.0246	0.0398	FCC
CoCrFeMnNi[17]	1.6094	0.0219	0.0293	0.0474	FCC
FeCoNiCrCuAl _{0.3} [23]	1.789	0.0241	0.0495	0.0296	FCC
FeCoNiCrCuAl _{0.5} [23]	1.7678	0.0367	0.0492	0.0796	FCC
FeNi ₂ CrCuAl _{0.6} [24]	1.5299	0.0425	0.0569	0.092	FCC
CuCoNiCrFe[23]	1.6094	0.00215	0.00288	0.00466	FCC
FeNiCoCr[25]	1.3863	0.000183	0.000244	0.000395	FCC
Al _{0.3} CoCrFeNi[26]	1.5426	0.0302	0.0404	0.0654	FCC
CuCoFeNi[27]	1.3863	0.00262	0.00350	0.00566	FCC
Al _{0.5} CrCuFeNi ₂ [28]	1.5157	0.0373	0.0499	0.0808	FCC
WNbMoTa[29]	1.3863	0.0107	0.0143	0.0231	BCC
WNbMoTaV[29]	1.6094	0.0197	0.0264	0.0426	BCC

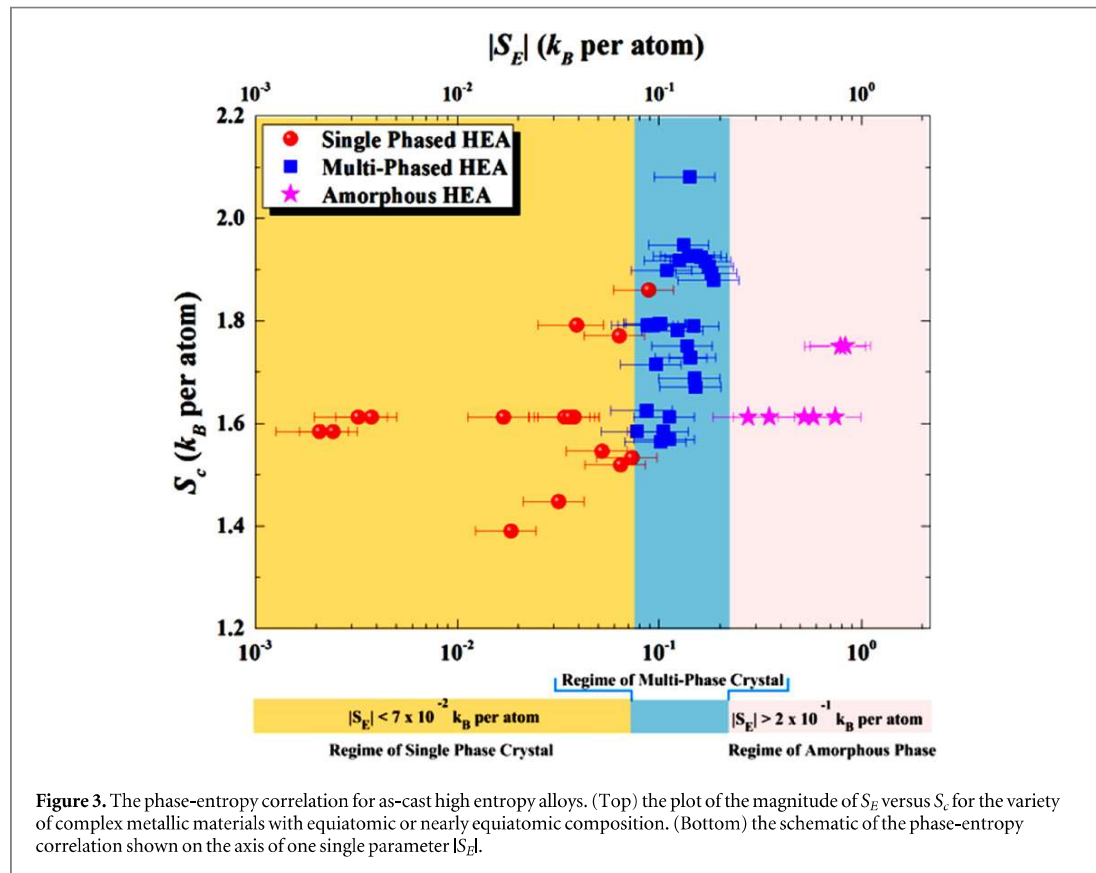
$$\gamma_3 = \left[\sum_{i=1}^m \left(\frac{\xi_i}{\xi} \right)^{2/3} c_i^{1/3} \right]^3 \quad (\text{A3})$$

$$\Delta_{ij} = \left[(\xi_i \xi_j)^{1/2} / \xi \right] \left[(d_i - d_j)^2 / d_i d_j \right] (c_i c_j)^{1/2} \quad (\text{A4})$$

$$\xi = \sum_{i=1}^m \xi_i \quad (\text{A5})$$

$$\xi_i = \frac{1}{6} \pi \rho d_i^3 c_i \quad (\text{A6})$$

in which ρ is the number density and ξ is the overall atomic packing fraction corresponding to a given ρ .



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