



Atomic-size effect and solid solubility of multicomponent alloys

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In physical metallurgy, solid solubility of alloys is known to play a vital role in determining their physical/mechanical properties. Hume–Rothery rules show the great effect of size difference between solvent and solute atoms on the solid solubility of binary alloys. However, modern multicomponent systems, such as high-entropy alloys, defy the classic atomic size effect due to the absence of solvent and/or solute atoms. Here, we propose an effective atomic size parameter by considering atomic packing misfitting in multicomponent systems.

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The solubility of a solute element in an alloy is an important aspect of alloy design. Through the addition of soluble elements, one may obtain a solid solution effect that can significantly improve the alloy's performance. For a substitutional binary alloy, the Hume–Rothery rules provide the key guidance to evaluating whether a solid solution can be formed [1]. These include: (i) the relative atomic size difference between the solute and solvent elements should be less than 15%; (ii) the formation of stable intermediate compounds should be restricted by carefully choosing the combination of metallic elements; and (iii) the electron concentration of the constituent elements should be tuned in favor of the formation of solid solutions, not otherwise.

The Hume–Rothery rules have been used extensively for more than half a century [2–6]. However, the rules are poses a challenge with the recent design of multicomponent alloys [7–10], in some of which the molar fractions of the constituent elements are equal or nearly equal, such as high-entropy alloys (HEAs) [9–13]. As a result, there is no distinct identity of “solvent” or “solute” atoms in such alloys. Therefore, the atomic size factor as defined by the Hume–Rothery rules cannot be applied directly to HEAs. Despite this, some empirical parameters have been suggested as extensions of the Hume–Rothery rules to explain the solid solubility of HEAs [14]; however, they do not do so satisfactorily when compared with experimental data [15].

The atomic size difference is of primary importance in determining the solubility of alloys. The critical value of 15% atomic size difference in binary alloys was confirmed

by the continuum elastic theory [16]. However, it is difficult to define an atomic size parameter in relation to solubility of HEAs. For simplicity, the polydispersity resulting from the atomic size difference has been commonly used for predicting the solid solubility of a given multicomponent alloy [14], which is:

$$\delta = \sqrt{\sum_i^n c_i (1 - r_i/\bar{r})^2}, \quad \bar{r} = \sum_i^n c_i r_i \quad (1)$$

where c_i is the atomic concentration of the i th atom and r_i is the atomic radius of the i th atom. It has been widely applied in the systems of hard-sphere fluids [17], metallic glasses [18] and HEAs [14,15]. In the hard-sphere fluid, $\delta = 0.06$ is the criterion used to predict crystalline structure formation, and this criterion was also claimed in the HEA investigation. However, this parameter does not describe the solubility of HEAs very well; as a result, many intermetallics have been detected around $\delta = 0.06$ [15]. Basically, the δ parameter takes the average effect of the atomic size difference of all elements in the alloy. However, the solid solution instability may essentially be determined by the largest and smallest atoms in multicomponent alloy systems. Moreover, the physical meaning of δ in determining the solubility is also not well understood, and it cannot return to the Hume–Rothery limit. Therefore it is necessary to explore the new and physically acceptable parameter of the atomic size effect on the solubility of multicomponent alloys, especially HEAs, which have received increasing attention recently from the materials community [9,11].

In this letter, we address this issue by considering the atomic size effect based on atomic packing behavior. The proposed parameter not only has a clear physical meaning,

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but is also consistent with the 15% atomic size difference in the Hume–Rothery rules. In particular, this parameter is more effective in describing the solubility of HEAs.

In solid solutions, the atomic size difference influences the topological instability of atomic packing. Egami [19] presented the topological instability of atomic packing in dilute binary alloys to discuss the structural instability involving glasses, and Miracle et al. [20] discussed the atomic packing efficiency in metallic glasses. Random packing in colloidal suspensions has also been studied extensively [21]. To date, however, there has been no report on the random atomic packing in HEAs. The instability of atomic packing is more complicated in multicomponent solid solutions with difference atomic sizes. However, the atoms with the largest and smallest sizes certainly play a dominant role in determining the stability of a lattice. Therefore, the packing state around the atoms with the largest and smallest sizes in HEAs should be the most important factor used to reveal how far away from the ideal case the atomic packings are. Hence, the packing states around the largest and smallest atoms affect the stability of the solid solutions.

The solid angles of atomic packing for the elements with the largest and smallest atomic sizes are chosen to quantitatively describe the atomic packing effect in multicomponent alloys. The solid angles around the largest and smallest atoms in respect to the surrounding atoms are described geometrically by

$$\omega_L = 1 - \sqrt{\frac{(r_s + \bar{r})^2 - \bar{r}^2}{(r_s + \bar{r})^2}}, \quad \omega_S = 1 - \sqrt{\frac{(r_L + \bar{r})^2 - \bar{r}^2}{(r_L + \bar{r})^2}} \quad (2)$$

where r_L and r_s are the radii of the largest and smallest atoms (see Fig. 1). A normalized parameter of the geometric packing state should be a good candidate to reveal the atomic packing instability. Here, we chose the ratio between the solid angles of the smallest and largest atoms

$$\gamma = \omega_S / \omega_L = \left(1 - \sqrt{\frac{(r_s + \bar{r})^2 - \bar{r}^2}{(r_s + \bar{r})^2}} \right) / \left(1 - \sqrt{\frac{(r_L + \bar{r})^2 - \bar{r}^2}{(r_L + \bar{r})^2}} \right) \quad (3)$$

as an indicator to reveal the atomic packing misfitting and topological instability. It is also important to point out that the Hume–Rothery rule of 15% of the atomic size difference in binary alloys corresponds to a critical value of packing misfitting of $\gamma = 1.167$.

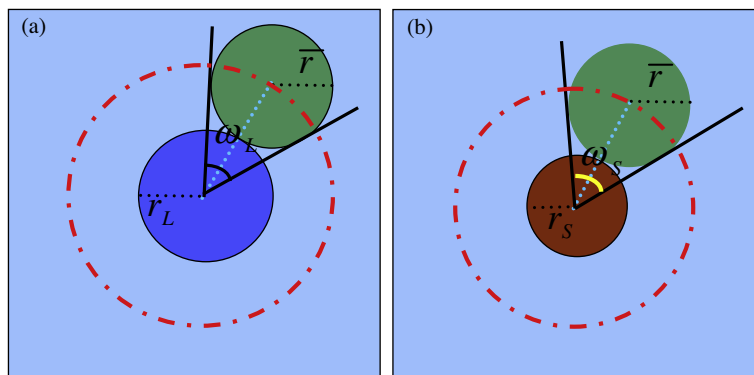


Figure 1. Sketch of the atomic packing around an atom via a solid angle: (a) around a largest atom; (b) around a smallest atom. \bar{r} is the average atomic radius.

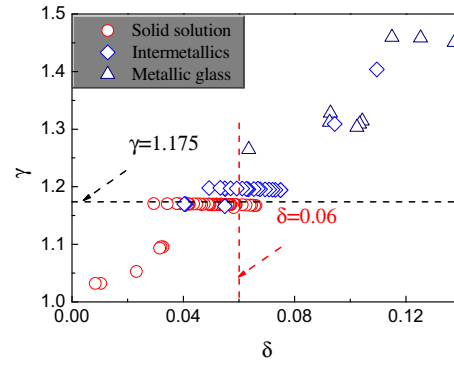


Figure 2. Statistics of the atomic packing parameter γ and the polydispersity parameter δ of atomic size difference from representative experimental results on the phase selection in HEAs. $\gamma = 1.17$ clearly distinguishes the solid solutions from the intermetallics. All the alloys are from Table 1 in Ref. [9].

Figure 2 shows the $\gamma - \delta$ plot from a statistical analysis of representative experimental results regarding the phase selection in HEAs reported recently by Guo et al. [15]. All of the alloys analyzed were prepared by suction and injection casting in metal molds by arc or induction melting. The figure shows that there are many solid solutions and intermetallics coexisting in the region of $0.04 < \delta < 0.08$. Even taking into consideration the mixing enthalpy, it is still impossible to distinguish the two different kinds of phases in the coexistence region [15]. Therefore, δ is clearly not a good parameter for separating the solid solutions and intermetallics. It appears that δ is not competent enough to describe the solubility in HEAs. On the other hand, Figure 2 shows that the atomic packing parameter γ can clearly distinguish solid solutions from multiphase regions with intermetallics. All of the solid solutions are in the region of $\gamma < 1.175$. Most of the multiphase regions with intermetallics together with metallic glasses are all distributed in the region of $\gamma > 1.175$. Note that metallic glasses are in a metastable state, prepared by relatively fast cooling, the glass phases of which mainly change to intermetallic phases during equilibrium treatments.

A total of 95 kinds of HEAs are included in Figure 2. The critical value of $\gamma = 1.175$ can distinguish nearly all the 59 solid solution alloys. The previous parameter, $\delta = 0.06$, misses six solid solutions, with a 10% error for

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