



A geometric model for intrinsic residual strain and phase stability in high entropy alloys

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Abstract—Following the Hume–Rothery rules, it is a longstanding notion that atomic size mismatch induces intrinsic residual strains in a common lattice which may cause lattice instability and thus phase transition in an alloy. For conventional alloys, such an intrinsic residual strain can be derived with the continuum theory of elasticity; however, lack of distinction between solvent and solute atoms in recently developed high entropy alloys simply defies such an approach. Here, we develop a general self-contained geometric model that enables the calculation of intrinsic residual strains around different sized elements in a multi-component alloy, which links the average lattice constant of the alloy to a few critical geometric variables related to the close atomic packing in that lattice, such as atomic size, atomic fraction and packing density. When applied to glass-forming high entropy alloys and bulk metallic glasses, our model unravels that amorphization occurs when the root-mean-square (R.M.S.) residual strain rises above $\sim 10\%$, in good agreement with the Lindemann's lattice instability criterion. By comparison, the transition from a single- to multi-phase solid solution takes place in crystalline high entropy alloys when the R.M.S. residual strain approaches $\sim 5\%$. Our current findings provide a quantitative insight into phase stability in multicomponent alloys, which should be useful in the design of high entropy alloys with desired phases. © 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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1. Introduction

Alloying different types of atoms in a common lattice has been an efficient way to make alloys with improved structural/functional properties. Since the ancient times, human beings have made tremendous efforts in the development of alloys with desired phases, and also in the search of an efficient method that can guide us in finding the compositions of such alloys. Among the early efforts, one important finding is the set of Hume–Rothery rules that were established in the 1920s for the conditions under which an element can dissolve into a metal to form a solid solution [1]. According to the Hume–Rothery rules [1], the stability of a solid solution is controlled by three major factors, i.e. the atomic size, the electronegativity difference and the electron concentration effect. When applied to binary alloys, these rules state that the formation of a primary solute solution is favored if the following conditions are met: (1) the ratio of the Goldschmidt radii of two constituent atoms is between 0.8 and 1.2 or the atomic size difference is less than $\sim 15\%$; (2) the difference in their Pauling electronegativity is small; and (3) the electron concentration

or the total number of valence electrons (VEC) is in a proper range [1].

The physical understanding of the Hume–Rothery rules has been a longstanding research topic in the classic field of metallurgy [1]. While mechanisms proposed for the 2nd and 3rd rules are still debated, the mechanism underlying the 1st rule, i.e. the atomic size rule, was well established, which can be related to the elastic energy of a solid solution [2] or equivalently the atomic level stress occurring in different sized atoms [3–5], which tends to destabilize a crystal structure after being built up to a critical level. By treating solute atoms alloyed with solvent atoms as a sphere-in-hole problem, the elastic theory of the atomic size effect was advanced by Eshelby in the 1950s [2], according to which a tolerable atomic size difference was predicted to be less than 15% for the formation of a binary solid solution. Alternatively, the atomic size effect can be also rationalized with the atomic stress theory proposed by Egami and co-workers [3–5]. According to this atomic stress theory [4], mixing of two sized atoms together brings about atomic stresses, the magnitude of which scales with the atomic size difference. When the volumetric strain resulting from the atomic stresses reaches a critical value [3,5], the crystal structure becomes unstable and therefore shows a tendency to turn into an amorphous structure. In other words, the atomic stress theory suggests that one needs to keep a

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low atomic size ratio for retaining the solid solution crystalline structure in a binary alloy, which is consistent with the Hume–Rothery rule as backed by the elasticity theory of Eshelby [2].

Now let us discuss high entropy alloy (HEA), which offers the motivation of the current work and is loosely defined as the multicomponent alloy with at least five elements mixed in equal or nearly equal molar fractions [6–12]. Despite the relatively large number of constituent elements in HEAs as compared to ordinary alloys, a great number of experiments revealed that, upon solidification, some HEAs tend to form single- or multi-phased solid solutions rather than intermetallics [7,10–15]; while some others tend to form metallic glasses as metastable structures [8,9,11,15]. To understand such phase diversities in HEAs, several empirical rules were put forward, such as the modified VEC rule [14,16] and the variety of atomic size difference rules [11,15,17,18], which are similar to the original Hume–Rothery rules. Although some of these newly proposed empirical rules are seemingly applicable to HEAs, the underlying physical mechanisms however are still debated. Following the similar line of reasoning as for the Hume–Rothery rules, it was once proposed that mixing of different sized elements would cause a high residual strain and thus phase transition in HEAs [6,17]. Nevertheless, as of today, there still lacks a theoretical model to evaluate the residual strain in HEAs, despite its fundamental importance and technologic relevance to the design of these newly developed alloys.

Conceptually, the equiatomic composition of HEAs defies the direct use of the Eshelby’s elasticity approach in calculating the residual strain because one cannot simply define the solvent (“matrix”) atoms versus the solute (“inclusion”) atoms in HEAs. To circumvent this difficulty, here we propose a geometric approach, which is based on the fact that most of the HEAs display well-defined lattice structures, such as fcc and bcc, with very sharp X-ray or neutron diffraction peaks like ordinary alloys [6,7,10,12–14,19]. In such a case, if atoms still remain in close packing in HEAs just like in ordinary alloys, one can then infer that the different sized atoms need to be “squeezed-in” or “stretched-out” in order to retain a common lattice. Otherwise, atomic packing misfit could arise throughout the whole lattice (obviously, a large atom can always be closely packed with more neighbors than a small one), which defies the establishment of a long-range periodic lattice structure with a uniform packing density and contradicts the diffraction spectra of HEAs that indicate well-behaved lattice structures similar to those in conventional alloys [6,7,10,12–14,19]. In other words, to avoid atomic packing misfit, the sizes of the constituent atoms in HEAs must be adjusted and differ from those in pure metals. Indeed, it was noticed decades ago that the apparent atomic size of an element changes with alloying [20], which was then thought to be caused partly by residual strains and partly by the alteration in the electronic structures of elements. For the current work, we focus on the atomic size effect alone while neglecting the other possible effects, such as the Pauling electronegativity and VEC effect. In such a sense, the residual strain as derived from our model provides an upper-bound estimate due to the neglect of these chemical effects. In what follows, we first develop a general self-contained geometric model that can enable us to calculate the residual strain in multi-component alloys; after that, we apply this model to study phase stability in many different types of

alloys, such as bulk metallic glasses and HEAs; finally, based on the comparison of our theoretical model and the experimental data, we would discuss the possible mechanisms of phase transition in HEAs.

2. Theoretical modeling

2.1. A geometric model

To quantify the local atomic packing efficiency, we adopt the concept of the three-dimensional solid angle as illustrated in Fig. 1(a), which can be generally expressed as $\omega = 2\pi(1 - \cos\theta)$ [21], where θ denotes the semi-angle of the cone [Fig. 1(a)]. For the solid angle ω_{ij} subtended by the atom j around the central atom i , we have:

$$\omega_{ij} = 2\pi \left[1 - \frac{\sqrt{r_i(r_i + 2r_j)}}{r_i + r_j} \right] \quad (1)$$

where r denotes the atomic radius. Following the atomic stress theory [4], the atomic packing efficiency η_i of the central atom i can be expressed as:

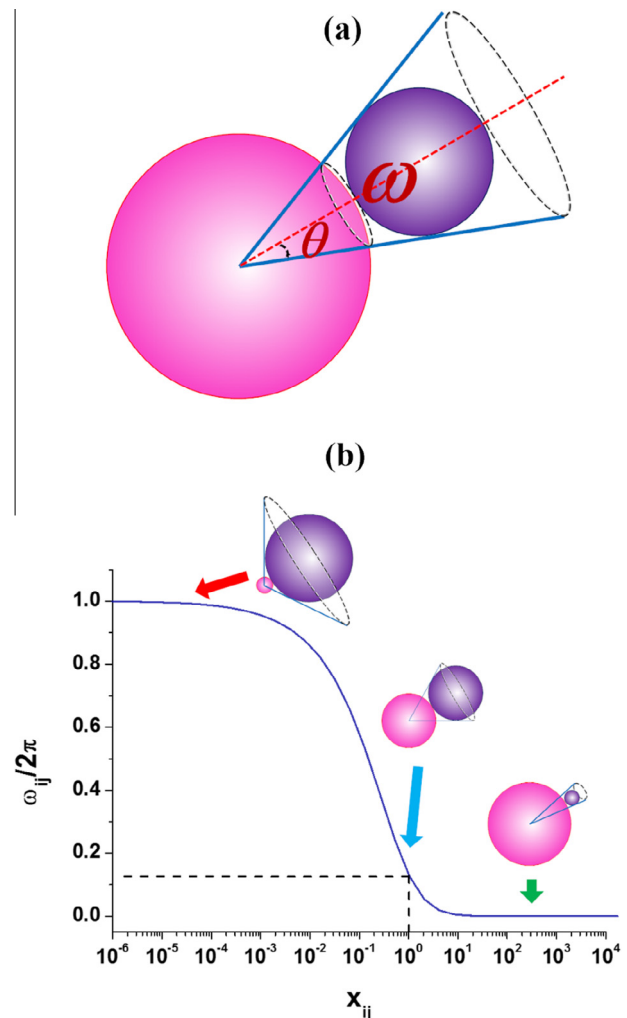


Fig. 1. (a) The schematic of the three-dimensional (3D) solid angle defined for the two spheres in direct contact, and (b) the variation of the solid angle $\omega_{ij}/2\pi$ with the atomic size ratio x_{ij} .

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