



Electronic and thermodynamic criteria for the occurrence of high entropy alloys in metallic systems

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Abstract

The occurrence of multicomponent solid solutions in multinary metallic systems, also called high-entropy alloys (HEAs), is classified and predicted by means of both electronic and thermodynamic criteria. Electronic parameters for alloys, i.e. electronegativity, valence electron concentration (VEC) and itinerant electron concentration (e/a), are derived and employed together with size mismatch in a scheme akin to the Hume-Rothery rules to map HEAs reported in the literature to date. For electronegativity, instead of the usual empirical Pauling scale, the recent Allen scale based on experimental and theoretical data is employed. A thermodynamic approach to the formation of solid solutions in multicomponent systems is then proposed using the regular solution and computing the temperature at which the free energy hyper-surface changes curvature at spinodal points. In all cases the maps which have been obtained (electronegativity vs. size mismatch, VEC vs. e/a , critical temperature vs. size mismatch) rank the composition of HEAs according to their phase constitution (solid solutions, solid solution + σ , intermetallics) and can be used to improve the formulation of HEAs and predict new ones.

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1. Introduction

In the last decade a new family of alloys known as high-entropy alloys (HEAs) has attracted much interest in the field of metallurgy. Traditionally the search for new alloy compositions focused on systems based on one main element. A new way of designing alloy compositions was proposed in 2004 [1,2] by defining for the first time HEAs as those composed of five or more elements in equimolar ratio having a simple crystal structure, i.e. solid solutions where solvent and solutes cannot be distinguished. The topic has seen a steady increase in the number of contributions dealing with various aspects of synthesis, processing and determination of properties, which are promising in various respects, especially mechanical. A comprehensive review

of HEAs [3] as well as general considerations on the metallurgy of HEAs, including the possibility of strengthening them by precipitation hardening [4], have recently been published. The thermodynamic stabilization of a solid solution made of several elements in a HEA is provided by its configurational entropy ΔS^{conf} . This depends on the number of possible ways to arrange N different elements in equimolar ratios in n non-equivalent lattice points of the unit cell, of the solid solution:

$$\Delta S^{conf} = R \cdot \ln N \quad (1)$$

As emphasized in Ref. [5], considering the different number of n non-equivalent lattice points in the unit cell, the solution of a body-centered cubic (bcc) structure presents a higher configurational entropy up to five elements, whereas between 5 and 10 elements the face-centered cubic (fcc) form has greater configuration entropy, while the hexagonal close-packed (hcp) lattice presents ΔS^{conf} greater than

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the *bcc* and *fcc* forms for N higher than 10. It is therefore easy to understand how there is a huge number of possible systems on which to focus. Yeh [2] stresses that, taking equimolar compositions and choosing just 13 metallic elements to form multicomponent systems with 5–13 elements, 7099 HEAs are potentially amenable for synthesis. The high number of possible HEA compositions requires the development of a procedure to predict the formation of a solid solution in such multicomponent equimolar systems. Recently Yang and Zhang [6] proposed a simple parametric model to this purpose employing the enthalpy and entropy of mixing, ΔH_{mix} and ΔS_{mix} , respectively, and the radius mismatch between elements. This will be discussed in detail below. Takeuchi [7] took a statistical approach for possible candidate compositions of HEAs, exploring about 15 million equiatomic combinations in ΔH_{mix} vs. radius mismatch plots where zones for occurrence of either HEAs and bulk metallic glasses (BMGs) were singled out. Otto et al. [8] took the deterministic approach of deriving the thermodynamic properties from phase diagram assessment of the 10 binaries needed to describe a CoCrFeMnNi quinary HEA. Single elements were then substituted for new alloys (e.g. V for Fe) which were synthesized and their phase constitution correlated to the computed differences in free energies between equilibrium states and metastable solid solutions in the respective binaries. Single-phase quinary alloys were found in a limited number of cases. The findings were said to cast doubt on the practice of merely mixing several elements to achieve the formation of HEAs. This term was then limited to true solid solutions. The CALPHAD approach was actually employed earlier to evaluate the properties of multicomponent alloys, such as the primary solidified phases or free energy curves of the equilibrium phases, extrapolating data from binary and ternary systems [9,10]. In this work we report a thermodynamic approach and the application of Hume-Rothery rules (HRRs) in order to rationalize and predict the formation of HEAs in multicomponent alloys. First, two-dimensional maps are developed by considering a modern definition of the electronegativity of the elements vs. the radius mismatch between them. Then, the occurrence of HEAs is discussed in terms of the total number of both valence and itinerant electrons in the alloy. In the second part of the paper, the thermodynamic treatment proposed by Yang and Zhang [6] is discussed and modified to obtain a new parameter for representing HEA formation. The outcome of these approaches is verified by analyzing the microstructure of HEAs which were collected from the existing literature. Note that in a number of papers, the microstructure is reported for the as-cast state. In some cases this may not correspond fully to the equilibrium state of the alloy.

Complex multicomponent systems with more than three elements in high molar fraction have been widely explored in the field of metallic glasses; however, the Inoue rules [11] for the formation of metallic glasses require thermodynamic and physical properties generally

opposite to those needed for the formation of solid solutions: a large negative enthalpy of mixing and a huge radius mismatch. In conventional castings these lead to microstructures composed of mixtures of intermetallic compounds. Rapid solidification is needed to obtain a single glassy phase. For these reasons no glass-forming system will be considered in this work.

2. High-entropy alloys and Hume-Rothery rules

The HRRs have been both invoked and questioned in connection with the occurrence of HEAs. As reported in Ref. [12] Hume-Rothery defined five factors determining the stability of alloy phases:

- an electrochemical effect related to the difference in electronegativity, $\Delta\chi$, of the elements involved;
- a size factor effect related to the difference in the atomic radii of the elements involved;
- atoms of elements near the end of the short periods and those in B subgroups tend to complete their octets of electrons;
- an electron concentration effect stemming from the observation that a definite crystal structure occurs at characteristic numbers of electrons per unit cell, which, if all atomic sites are occupied, is equivalent to saying that similar structures occur at characteristic electrons per atom ratio, e/a , the electron concentration;
- orbital-type restrictions.

For the formation of metallic solid solutions the most important rules to be fulfilled are the first two involving the radius mismatch and the electronegativity while the others are considered when the former are not decisive.

2.1. Hume-Rothery rules and HEAs: electronegativity and radius mismatch

Guo [13] applied the HRRs to HEAs and BMGs together with thermodynamic parameters in order to establish semi-empirically conditions for the formation of either phases. In this work we define two parameters related to the first and second HRR and we verify their ability to predict the formation of a single solid-solution phase in multicomponent systems. The first parameter, δ , concerns the atomic radius mismatch [14]:

$$\delta = \sum_{i=1}^n c_i \cdot \left(1 - \frac{r_i}{r_a} \right) \quad (2)$$

with r_i = radius of i -th element,

r_a = average radius

where r_i is the atomic radius of the i th element and r_a is the average atomic radius in the alloy [14]. The second one expresses the difference in electronegativity between elements, $\Delta\chi$:

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