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An understanding of high entropy alloys from phase diagram calculations

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ABSTRACT

The concept of High Entropy Alloy (HEA) is understood from the point of view of phase diagram calculation. The role of entropy of mixing on the phase stability is discussed for both ideal and non-ideal solid solution phases. The relative stability of a solid solution phase and line compounds is illustrated using hypothetical systems. Calculated binary and multicomponent phase diagrams are used to explain the phenomena observed experimentally for HEAs. The potential of using the CALPHAD (CALCulation of PHase Diagrams) approach in aiding the design of alloys with multiple key components is also discussed.

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1. Introduction

High Entropy Alloys (HEAs) have become a very “hot” topic after Cantor et al. [1] and Yeh et al. [2] published their work in 2004, and publications in this area have increased exponentially since then. HEAs have attracted more and more attention due to their potential beneficial mechanical, magnetic, and electrochemical characteristics, such as high strength, high thermal stability and oxidation resistance. These promising properties offer many potential applications in various fields, such as tools, molds, and magnetic films [2–5]. Among the published work, many studies have focused on the CoCrCuFeNi-based alloys with additions of Al, Ti, and Mn to understand the *fcc/bcc* phase transformation [6–13]. In addition to the use of a traditional trial and error approach, effects of enthalpy of mixing, atomic size difference, and valence electron concentration have been discussed [14,15], and rules have been suggested for the selection of the principal components.

Although development of alloys based on multiple key elements with equal/near equal atomic composition indeed broadened the view of materials scientists/engineers on the design of new materials, the role of entropy of mixing in stabilizing solid solution phases should not be over-emphasized. It is well known that the entropy of mixing can be represented by the following

equation when N components are randomly mixed together:

$$S_{mix} = -R \sum_i^N x_i \ln x_i \quad (1)$$

where x_i represents the mole fraction of component i in the system. The entropy of mixing reaches maximum, $R \ln N$, when equal molar amounts of each element are mixed. It should be pointed out that, the definition of Eq. (1) is based on the assumption of random mixing, which does not apply to a phase that forms long-range order or short-range order. Following the paper of Yeh et al. [2], a HEA was defined to contain at least five principal elements with equal/near equal atomic concentration. This paper also indicated that, HEAs tend to form simple solid solution phases instead of multiple intermetallic phases. If entropy of mixing plays a dominant role in the determination of phase stability, it is easy to reach the following conclusions: (1) larger N would lead to higher probability of forming a HEA, (2) different alloys containing equal number of components would have the same probability of forming a HEA, and (3) equal atomic composition is always more advantageous than non-equal atomic composition in forming a HEA. However, experiments have proved that none of these conclusions are valid [1,16].

Cantor et al. first investigated an alloy consisting of 20 components in equal atomic proportions (mole fraction of 0.05 each), and then an alloy consisting of 16 elements again in equal atomic proportions (mole fraction of 0.0625 each). Both alloys were found to be multiphase and brittle, as-cast and after melt spinning. However, they found both alloys consisted predominantly of a

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single-phase *fcc* primary phase enriched with transition metals Cr, Mn, Fe, Co and Ni. They then casted an alloy with the five components Cr, Mn, Fe, Co and Ni (mole fraction of 0.2 each), and developed a single-phase *fcc* alloy exhibiting a dendritic microstructure. However, when one, two, three, or four elements were added to this five-component system, none of the alloys developed a single-phase *fcc* structure. In summary, in Cantor et al.'s [1] experiments only one alloy, CoCrFeMnNi, was found to form a single-phase *fcc* structure so that increasing the number of key components and, therefore, the entropy of mixing did not help at all in this regard.

In Otto et al.'s paper [16], six alloys were investigated with the base alloy of CoCrFeMnNi. The other five alloys were obtained by replacing one element a time of the base alloy using an element with similar properties of the replaced element. The base alloy was found to consist of a single-phase *fcc* phase, while all the other five alloys consisted of more than one phase.

Obviously, the entropy of mixing does not, at least not always, play a dominant role in the determination of phase stability and therefore the microstructure of an alloy. It is well known that a system reaches its equilibrium state when the total energy of the system reaches the global minimum. The stability of each phase is described by its Gibbs energy which consists of contributions from both enthalpy and entropy. The Gibbs energy is a function of temperature for a line compound phase, a function of temperature and composition for a disordered solution phase, and a function of temperature, composition and site fraction for an ordered intermetallic phase with homogeneity range. The most intuitive way of representing the phase stability in a system is by its phase diagram. When a phase diagram is available, it is not difficult to choose the alloy composition so that a desired microstructure, either a single-phase or a multi-phase mixture, can be developed. In this paper, we will use phase diagram calculation based on the CALPHAD (CALculation of PHase Diagrams) approach [17–19] to understand and explain the microstructures obtained for alloys with multiple key elements. The paper will be arranged as follows: first we will use a hypothetical system to illustrate the relative stability of phases in a system, and the role of entropy in this regard; second we will use calculated binary and multi-component phase diagrams to explain the experimental results obtained in the efforts of developing HEAs, and discuss the role of the CALPHAD approach in aiding the design of HEAs; and last we will summarize our findings and conclusions.

2. The role of entropy in the determination of phase stability

In this section, we will discuss the role of entropy in the determination of phase stability using hypothetical systems. Gibbs energy curves (surfaces) will be plotted to demonstrate the phase stability in the composition space. We will first use a hypothetical binary A–B system to show the different roles of entropy of mixing in an ideal and a non-ideal solid solution. We will then extend this binary system to a hypothetical ternary A–B–C system to show the effect of a third component on the relative phase stability of the system. The conclusion obtained in these hypothetical binary and ternary systems can be extended to higher order systems.

2.1. Binary A–B system

Let us first use a hypothetical A–B binary system as an example. In Fig. 1, the blue solid line represents the Gibbs energy curve of a disordered solid solution phase, say an *fcc* phase, at one certain temperature. The green solid square and circle represent the Gibbs energies of two line compounds, $A_{0.75}B_{0.25}$ and $A_{0.1}B_{0.9}$, at the same temperature. In this example, A and B form an ideal *fcc* solid

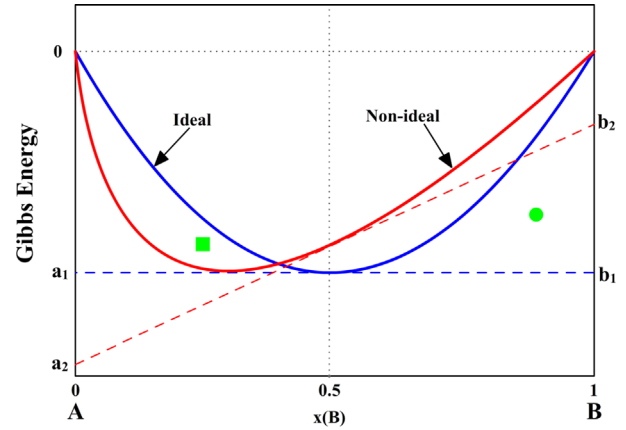


Fig. 1. Gibbs energies of phases in a hypothetical A–B system (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

solution (blue curve), i.e., the enthalpy of mixing is zero and the Gibbs energy of the *fcc* phase is represented by

$$G^{fcc} = x_A G_A^{fcc} + x_B G_B^{fcc} + RT(x_A \ln x_A + x_B \ln x_B) \quad (2)$$

When *fcc*-A and *fcc*-B are chosen as the reference states for the plot, the curve starts at zero at the two ends, and reaches the minimum in the middle ($x_i=0.5$ for each element). Now if we draw a tangent line (a_1b_1) at the composition of equal atomic proportions of A and B, both line compounds are above the line and none of them is stable relative to the ideal solid solution. In this case, the alloy with equal atomic proportions of A and B makes the best choice which favors the formation of single-phase *fcc* phase, and avoids the formation of both line compounds. Slight change of the composition will make the tangent line tilt and one of the two compounds may become stable.

Now, what will happen if A and B do not form an ideal solution? In this case, the Gibbs energy of the *fcc* phase is represented by

$$G^{fcc} = x_A G_A^{fcc} + x_B G_B^{fcc} + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex,fcc} \quad (3)$$

where $G^{ex,fcc}$ is the excess contribution to the Gibbs energy. In the case of a regular or quasi-regular solution the situation is similar to that of the ideal solution as long as the total Gibbs energy of mixing is negative. However, for subregular solutions the Gibbs energy curve is not symmetric. The Gibbs energy curve of such a non-ideal *fcc* phase is plotted as the red solid line in Fig. 1, and the tangent line at the middle ($x_i=0.5$ for each element) is shown by a_2b_2 . In this situation, if equal atomic proportions of A and B are mixed, a mixture of *fcc* and $A_{0.1}B_{0.9}$ will be obtained instead of single-phase *fcc* phase. In this case, the composition of B cannot exceed 0.3 to obtain a single-phase *fcc* structure.

The conclusions we obtained from this simple hypothetical A–B system are: (1) If A and B form an ideal, regular or quasi-regular solid solution, the entropy of mixing plays a dominant role so that the Gibbs energy reaches the minimum at an equal composition of A and B. The high entropy composition is therefore the optimum composition to suppress the formation of line compounds. (2) If A and B form a sub-regular solution, the Gibbs energy does not reach its minimum at the composition of equal amounts of A and B, even though this composition still offers the highest entropy of mixing. (3) Even in the case that A and B do form an ideal solution, the so-called HEA may still not form due to the existence of other more stable phases. For example, if the Gibbs energy of a line compound sits below the a_1b_1 line in Fig. 1, it will be more stable than the solid solution phase even at the composition with highest

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