



Full length article

Predicting the formation and stability of single phase high-entropy alloys

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ABSTRACT

A method for rapidly predicting the formation and stability of undiscovered single phase high-entropy alloys (SPHEAs) is provided. Our software implementation of the algorithm uses data for 73 metallic elements and rapidly combines them - 4, 5 or 6 elements at a time - using the Miedema semi-empirical methodology to yield estimates of formation enthalpy. Approximately 186,000,000 compositions of 4, 5 and 6 element alloys were screened, and ~1900 new equimolar SPHEAs predicted. Of the 185 experimentally reported HEA systems currently known, the model correctly predicted the stability of the SPHEA structure in 177. The other sixteen are suggested to actually form a partially ordered solid solution – a finding supported by other recent experimental and theoretical work. The stability of each alloy at a specific temperature can also be predicted, allowing precipitation temperatures (and the likely precipitate) to be forecast. This combinatorial algorithm is described in detail, and its software implementation is freely accessible through a web-service allowing rapid advances in the design, development and discovery of new technologically important alloys.

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1. Introduction

Exploratory alloy discovery, design and development is a crucial aspect of materials research for the growth of industries such as aerospace [1], biomedical [2,3] and energy generation and storage [4]. Recently, this aspect of material research has expanded past that of the conventional alloy (consisting of 1 or 2 principle components) into a new class of highly alloyed materials, high-entropy alloys (HEAs). This field has gained attention [5–7] due to findings of high strengths [8,9], ductility [10] and other interesting properties [11]. Efforts to design, characterise and utilise HEAs are currently underway globally. However, the meaning of the term ‘HEA’ is not continuous across the literature. Taken as written, the HEA definition provided by Yeh et al. [7], and re-iterated by others since then [1,12], defines a HEA as any alloy consisting of 5 or more elements between 5 and 35 at %. As such, this type of HEA will

usually possess a microstructure consisting of two or more distinct phases, some of which are likely to be brittle intermetallic compounds. Although, multiphase strengthening is sometimes desirable in alloys, a large amount of any brittle phase will generally make an alloy unusable as a structural material and such HEAs are therefore mundane. However, as will be discussed shortly, in a few special cases, the additional entropy of the multi-element composition will stabilise a microstructure consisting of either (i) a single solid solution having one of the simple close-packed crystal structures (FCC, HCP or BCC) or (ii) a duplex microstructure consisting of two such simple solid solutions. Generally, it is these non-trivial examples of HEA that interest investigators. This is because the resulting random solid solution(s) will exhibit a combination of ductility coupled with significant solid solution hardening. We recommend use of the term single phase high-entropy alloy (SPHEA) as a more restrictive term to differentiate the rare and desirable single phase type of HEA from generic examples of multiphase HEAs.

Combining Yeh's compositional limits [7] with the requirement for a single phase solid solution, we can define a SPHEA as an alloy with ≥ 4 alloying elements, at least 4 of which with a molar ratio

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between 0.33 and 1 to that of the highest contributing element. These alloys must be able to display a single phase of simple, random, close-packed structure below the solidus.

We return now to the factors that might stabilise a SPHEA. The prevailing hypotheses were (i) that the simple crystal structure or structures are thermodynamically stabilised, relative to possible intermetallic compounds, by the increased configurational entropy from large alloying additions, (ii) that the absence of chemical ordering and the presence of the simple crystal structure should provide dislocation mobility and hence ductility similar to the known structural alloys, such as steels, and (iii) higher strengths can be achieved due to the large concentrations of the elements within the solid-solution which contributes to an intrinsic lattice strain, and the so-called “cocktail effect” [13].

Some complications exist that place constraints on the utility of these hypotheses. For example, while configurational entropy of any solid solution would certainly increase as more elements are added to a composition, there is also an increased likelihood that the introduction of an additional alloying element will cause the formation of a stable new intermetallic phase. This concept is hypothesised by Zhang et al. [14] and later confirmed by Senkov et al. [15]. Nevertheless, the number of possible combinations is exceedingly large and it is considered feasible that many useful SPHEAs exist.

The basic assumption underlying the formation of SPHEAs can be explained by considering the equation for Gibbs free energy:

$$\Delta G = \Delta H - T \times \Delta S \quad (1)$$

It follows that ΔG can be rendered negative (i.e. the new phase can be stabilised) by a sufficiently large entropy, ΔS , which is contributed to by the configurational entropy, ΔS_{conf} . Importantly, this stabilisation can occur even if the enthalpy of mixing, ΔH , is positive. ΔS_{conf} is related to the number of ways that the material's atoms can be arranged (ω) as:

$$\Delta S_{conf} = k_B \ln \omega = -nR \sum_i^j x_i \ln(x_i) \quad (2)$$

where k_B is Boltzmann's constant, n is the number of moles, R is the gas constant, x is the atomic fraction of element i in a j element system.

It was first postulated by Yeh et al. [7] that, in alloys consisting of five or more elements in near equimolar concentrations, the formation of intermetallic compounds could be suppressed by the alloys' increased ΔS_{conf} . However, over the last decade or so it has become apparent that this prediction often fails [16–18]. It is evident that the existing predictive framework is incomplete and that the theory must be adjusted to correctly describe these observations. Indeed, many parameters [19] have been proposed as a means of predicting the formation of novel SPHEAs, yet none have been able to reliably separate intermetallic phases from solid solution in the absence of existing experimental or modelled thermodynamic data. Where such data is available, the CALPHAD method has been applied to this problem and, for example, was recently used to screen ~130,000 compositions [15]. However, even in the CALPHAD approach incorrect predictions occur. Furthermore, the sheer number of alloy systems encountered when exploring beyond ternary systems makes the calculation of the Gibbs free energy of unexplored solid solutions both costly experimentally [20] and theoretically [9,21]. In addition, a simplifying scheme to represent the stability of such systems on a 2D diagram (akin to phase diagrams that can represent up to three variables) does not

exist.

Here we apply Miedema's macroscopic atom model [22], for the calculation of *concentrated solid solutions*, to this problem. The existing model is extended to account for multi-component systems and implemented within a new framework to utilise 73 elements of the periodic table. This technique is implemented here in software [23]. The 185 experimentally studied alloys described in past literature are used to benchmark the new algorithm. Furthermore, we present a new way to represent these multi-component systems on a 2D medium that allows for quick analysis of the systems stability. Fifty of the lowest cost, four-element, equimolar systems are reported.

1.1. Current state-of-the-art

In Yeh et al.'s original publication [7] it is stated that the configurational entropy of an equimolar alloy consisting of five elements is of the same magnitude as the *configurational entropy* of a strong intermetallic compound. However, in an ordered system the configurational entropy equates to zero, from Eq. (2). Although other contributions to entropy such as vibrational, electronic and magnetic moment randomness can be present, these entropic contributions are often similar in ordered, segregated and solution phases of the system [24,25], and therefore cancel in comparison. It is mostly the non-zero configurational entropy of a disordered solution system that is thought to stabilise the solid solution phase. Nevertheless, one must consider all aspects of the Gibbs free energy equation in order to draw conclusions about the nature of system stability.

At the heart of current HEA phase prediction models [26], ΔH of a HEA is defined as:

$$\Delta H = \sum_{i=1}^n 4 \Delta H_{ij}^{am} c_i c_j \quad (3)$$

where c is the concentration, in atomic fraction, of element i and j , and ΔH_{ij}^{am} is the enthalpy of mixing per mole between element i and j calculated by the equation for a *liquid binary alloy* in Miedema's model [27]. There are some associated errors with this model [28] and concerns exist that it only represents an ideal solution and assumes a 50/50 mixture will yield the largest magnitude in the enthalpy of mixing [29]. Nevertheless, a ratio of the two contributions to the Gibbs free energy was proposed by Yang et al. [30]:

$$\Omega = \frac{T_m \Delta S_{conf}}{|\Delta H|} \quad (4)$$

A disordered solid solution is expected to form for $\Omega \geq 1.1$. However, this comparison does not include any information of the solid solution phase nor intermetallic compounds. This is because neither the enthalpy of formation of the solid solution (ΔH_{ss}) or of the intermetallic (ΔH_{int}) is included, and instead, it is thought that ΔH_{am} is indicative of ΔH_{ss} and ΔH_{int} . In fact, the maximum absolute difference in Refs. $\Delta H_{am} - \Delta H_{ss}$, and $\Delta H_{am} - \Delta H_{int}$ (for the 185 systems benchmarked in this work) is 19 kJ/mol and 67 kJ/mol, respectively, which would suggest errors of this magnitude should be expected when using this method. In Yang et al.'s original paper [26] it is shown that HEAs which display intermetallic compounds cannot be discerned from those that do not. This model is replicated in Fig. 1.

The well-known Hume-Rothery rules take the size of the alloy's constituent atoms into account. The HEA community generally expresses this factor as a dimensionless representation of the

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