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Electronegativity and enthalpy of mixing biplots for High Entropy Alloy solid solution prediction

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HIGHLIGHTS

- Statistical analyses of four parameters are plotted against the enthalpy of mixing are performed.
- Mulliken electronegativity can be an alternative parameter for prediction of HEA solid-solution stability.
- Electronegativity/VEC- ΔH biplots offer an approximate snapshot of the electronic structure.
- The zones corresponding to HEA and intermetallic phases are listed for reference and approximate alloy-design guidelines.

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ABSTRACT

Analysis of the applicability of different electronegativity scales (X_{Allen}, $X_{Pauling}$, and $X_{Mulliken}$) as a replacement for the empirical valence electron concentration (VEC) parameter to determine High Entropy Alloy (HEA) solid-solution stability is performed, using statistical methods (*via* cluster analysis and probability density function). The analysis is conducted on a dataset consisting of 617 entries. The results show that X_{Allen} is better suited to predict solid-solution stability when utilising only one parameter. However, substituting X_{Allen} for $X_{Mulliken}$ offers better prediction in a biplot with the enthalpy of mixing (ΔH). An analysis of the VEC-ΔH biplot shows that phase separation in the biplots can be attributed to changes in the electronic structure.

1. Introduction

The field of High Entropy Alloys (those which contain multiple ($\geq$4) alloying components with near-equimolar fractions [1]) has spurred research towards alloy compositions that exist in the middle of phase diagrams. Current research suggests that in this region alloy compositions can be found that exhibit simple phases (here defined as phases derived from the FCC, HCP, or BCC structures). On the other hand, compositions can adopt a complex phase (here defined as all non-simple phases, also known as intermetallic structures in other alloy systems) as the compositions deviate further from the ideal solid solution [2–5].

The prediction of the stability of these solid solutions has been made using Hume-Rothery rules and thermodynamic parameters as empirical guidelines, with some success. Dominguez *et al.* [6] studied the contributions of five of these parameters (Enthalpy of Mixing (ΔH), Electronegativity difference, Atomic Size Difference, Entropy of Mixing, and Valence Electron Concentration (VEC)) to HEA phase formation statistically, utilising a Principal Component Analysis (PCA). This research showed that simple and complex phases can be differentiated within a simple 2D plot of VEC and ΔH to a much better extent than previously found [3,7–9].

One critique is that the empirical VEC of a particular alloy composition is obtained from the weighted average of the electrons accommodated in an alloy's constituent elements. Recent work has shown that when the VEC is instead obtained from first-principles (by integrating from the density-of-states), the theoretical VEC parameter is sufficiently accurate to predict the simple-to-complex phase transitions of several HEA compositions [2]. These results highlight the possibility of refining the accuracy of empirical parameters by changing how they are derived.

Of the five parameters studied by Dominguez *et al.*, it is of particular interest that the electronegativity difference parameter,

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defined as the ability of an atom to attract electrons towards itself, has not been shown to successfully discriminate between simple and complex phases in the PCA. One reason for this may be that electronegativity values cannot be directly measured and are only obtained indirectly from other atomic or molecular properties. Several scales exist, and their intended used varies [10] (and is very much dependent on the definition of each scale). Inaccuracies develop when the scales are adapted for use outside of their original purpose (for example, the Pauling electronegativity which is based on bond dissociation energies may not best describe metallic bonding in transition metals) [11]. However, since these scales can describe certain properties of an atom, it may be that the averaged electronegativity value may be used in place of the VEC (which does not differentiate between atomic periodicity) to describe an alloy composition, and that this analysis may be superior to the electronegativity difference parameter.

Electronegativity scales may be broadly divided into either absolute scales, or Pauling-like scales. Absolute scales originate from Parr's 1934 [12] communication discussing an electronegativity scale using the chemical potential as a reference point. In HEAs the electronegativity parameter used for predictions is frequently the Pauling scale. As an exception to this, Poletti *et al.* [9] used a 2-dimensional plot of the Allen scale electronegativity difference, ΔX_{Allen} against the atomic radius mismatch, δ to show separation between the formation of simple and complex phases. For values ranging between: 1) $1\% < \delta < 6\%$, and 2) $3 < \Delta X_{Allen} < 6$, only simple phase formation was observed for all examined compositions. Although the Allen scale offers improved accuracy, since the delocalised electrons in transition metals cannot be exactly determined, a better approach may be to consider the Mulliken electronegativity, which is an exact scale that is related to the chemical potential (and therefore the Fermi energy at 0 K).

It is therefore evident that the failure of the Pauling scale in discriminating between HEA phases may be related to the selection of an appropriate electronegativity scale. One approach to consider the applicability of different electronegativity scales towards phase discrimination is through a cluster analysis, which can determine the centre of zones of simple/complex phase formation in their respective 2D plots. This method is used in this study is to compare the accuracy of the Pauling, Allen, and Mulliken electronegativity parameters and their applicability in alloy design.

2. Method & calculation

The dataset used in this study consists of 617 HEA compositions selected from the literature, largely based on the dataset provided by Miracle and Senkov [13]. The compositions in the dataset consisted of a mix of alloys from both the as-cast state, as well as annealed, and are differentiated by their diffraction patterns (simple structures contain simple diffraction patterns of either FCC, BCC, or HCP type [5], whilst all other structures are termed complex structures, and alloys which possess both structures types are termed mixed structures). The groups are further subdivided depending on the phase present, as well as the average periodicity (or average quantum number) of the alloying components (*e.g.* BCC-4 and BCC-5). The average periodicity was determined by obtaining the weighted average of that of each alloying component in each composition, rounded to the nearest integer and is used to differentiate heavier compositions from one another (as reactivity for metals changes with atomic periodicity). These subdivisions are shown in Table 1. For a full list of the alloy compositions considered please refer to Table S1 in the supporting information.

The partitioning in the *VEC*- *ΔH* biplot [6] may be attributed to the non-conformity of *ΔH* to quantum mechanics as described by Pettifor [14]. There exists a deviation in the ratio between the enthalpy of mixing and the difference in the number of valence electrons squared from Miedema's model, which occurs between $4 < n < 7$, intersecting with what are regarded as zones of complex phase presence in HEAs.

Table 1
Total number of alloy compositions analysed for this study. The dataset has been subdivided into several groups as shown below.

General grouping	Phase	No. of compositions
Complex	C14	21
	B2	21
	Others	23
Mixed	BCC + B2	40
(Non-specific Simple + Complex)	Others	185
Simple	BCC-4	35
	BCC-5	27
	BCC + FCC	89
	FCC-4	136
Total		617

It has been previously reported that the VEC obtained from the integrated density of states could more accurately describe the phase stabilities of HEAs over the empirical VEC [2] calculated from the weighted average of the electrons accommodated in the *s, p*, and *d* orbitals of the alloy's constituent elements [7]. In looking for a better descriptor than the empirical VEC of the atomic energies, the electronegativity parameter may also offer some insights; for example, the Allen electronegativity scale is defined as the average energy of the valence electrons of an atom at the ground state [15].

This leads to our motivation to analyse and investigate the 617 compositions using the empirical parameters *VEC, ΔH* and electronegativity, *X*. Electronegativity values of each alloy's components are combined according to their alloying fraction to obtain the averaged electronegativity value of a particular composition. By comparing three different electronegativity scales (Pauling, Allen, and Mulliken – defined as $X_{Pauling}$, X_{Allen}, and $X_{Mulliken}$ respectively plotted against *ΔH*) against Dominguez *et al.'s VEC-ΔH* biplot, we aim to determine the ability of each parameter to differentiate between the phases present in multicomponent alloys. Although the phases demonstrated by a composition will be affected by its thermomechanical history (and thus affect differentiation at different temperature), it is hoped that such a generalisation will give further insights into the major phases adopted by the compositions.

A general description of each electronegativity scale is shown in Table 2. As can be seen, different electronegativity scales are derived from different parameters, and this may influence their effectiveness as semi-empirical parameters for alloy design. To aid the analysis of the effectiveness of electronegativity parameters vis-à-vis VEC, we employ two different statistical methods. The first method uses a cluster analysis-based approach to determine a point where the total minimum distance between related points is minimised, given in the equation below:

$$distance(x,y) = \sum_i \sqrt{\delta x_i^2 + \delta y_i^2} \qquad (1)$$

This point is defined as the cluster centre, and in the subsequent analysis such cluster centres are represented by points bounded by ellipses whose radii represent the standard deviation of the *x* and *y*-axes, allowing a graphical illustration of the area on the biplot where a composition is most likely to adopt the structure of the cluster. The values of each cluster centre are computed by utilising an evolutionary algorithm to minimise the value of Equation (1). The evolutionary algorithm generates possible solutions from an initial dataset of *x* and *y* coordinates and removes coordinates that