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Prediction and validation of four component High entropy alloys using Principal Component Analysis

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Abstract

Prediction of the crystalline structure formation of High Entropy Alloys is developed while applying Principal Component Analysis to their thermodynamic and electronic parameters. In the simplest form, it shows an excellent discrimination between both face and body centered cubic structures when taking into account the valence electron concentration and enthalpy of mixing. The approach is validated by the successful prediction of a multiphase structure in TiMnFeNi, and the discovery of two novel four components single phase HEAs, MnFeCoNi and NbMnVTi.

Keywords: High entropy alloys, Principal component analysis, thermodynamics, electronic structure

Introduction

The discovery of a new class of metallic materials is a relatively uncommon event which when it does happen is followed by a period of intense research activity. This is certainly true of the multi-principal component metallic materials often referred to as High Entropy Alloys (HEAs). These alloys form solid solutions with simple crystal symmetries and may exhibit remarkable mechanical and functional properties (magnetism, high temperature strength etc.). The formation of such alloys was first observed by Cantor et al. [1] in experiments investigating the confusion principal of glass formation: combinations of 5, 6 or more metals were found to form fcc or bcc solid solutions rather than the intended amorphous alloys or the mixture of intermetallics one might expect. Yeh et al. [2] investigated this discovery and developed the central concept of the high entropy alloy, which was defined as being composed of 5 or more components in roughly equiatomic proportions between 5 and 30 at% and able to form simple bcc and fcc solid solution phases. On first examination it would seem that these alloys break the Gibbs Phase rule but a simple explanation, first expounded by Kubaschewski [3], is that, as the number of constituent phases increases the entropy of mixing and will, at most temperatures of interest, act to stabilise disordered solid solution phase and suppress the appearance of ordered intermetallics. However, this simple and rather appealing concept does not, unfortunately, provide a full explanation for the formation of HEAs and there is a significant body of research related to thermodynamic, atomic size and electronic effects on their formation, stability and crystal structure.

Following on from the work of Yeh et al. [2] it is now accepted that the ability of HEAs to form solid solutions rather than a mixture of intermetallic compounds results, at least in part, from the stabilising contribution of configurational entropy on the system; as the number of

components increases the contribution of entropy to the free energy of the system begins to dominate at solidification temperatures.

In addition to these thermodynamically based analyses, Guo et al. [4] attempted to relate Valence Electron Concentration (VEC) of HEA compositions to their crystal structure in a similar way to that which Hume-Rothery applied to the understanding of the crystal structures of certain copper alloys. Their research yielded the observation that for HEAs with a VEC less than 6.87 the solid solution formed had a bcc crystal structure, those with VEC greater than 8 formed fcc solid solutions and alloys with intermediate VEC formed a mixture of bcc and fcc solid solutions.

These results are remarkable because they were achieved with models developed for ideal pure and dilute systems. This suggests that HEAs are acting as "good" metals and that the bonding in HEA solid solutions is predominantly metallic in nature.

It is therefore evident that many factors could contribute to the formation of single phases in multicomponent systems. Approaches exist to process data where many variables need to be taken into account, reducing dimensionality and allowing the grouping of data and the identification of patterns. One such technique is Principal Component Analysis (PCA), a multivariate analysis method where a statistical tool is employed to reduce the variables of a dataset into principal components consisting of orthogonal linear combinations of the original variables, which retain as much as possible of the original information [5], [6].

Therefore, applying PCA to the analysis of HEA data may help to highlight the most important variables, as well as provide an empirical tool for prediction and discovery of novel materials.

Experimental

A multivariate analysis, based on Principal Component Analysis (PCA), has been performed using Matlab. The data set used is combined of 79 alloy systems collected from those in the literature, and is available in the online supporting information. These alloy systems have been reported as showing single phase bcc, single phase fcc, a mixture of multiple bcc and/or fcc phases and multiple phases including intermetallic compounds. Five thermodynamic and electronic structure variables comprising the enthalpy of mixing of the solid solution, ΔH_{mix}; the entropy of mixing, ΔS_{mix}; the atomic size mismatch, δ; the electronegativity difference, $\Delta \chi$ and the Valence Electron Concentration, VEC, were included in the analysis, being those variables identified and used by Guo et al.[7].

Following the results of this analysis, and examination of the trends observed, three novel alloy systems were selected to test the relationships: TiMnFeNi, MnFeCoNi and NbMnVTi were produced at equiatomic composition, from high purity elemental material (> 99.9%). 5g of each alloy were melted into buttons of around 10mm diameter in an argon backfilled vacuum arc-melter (MAM-1 Edmund Buehler), and remelted 5 times to ensure homogeneity. The samples produced were prepared for X-Ray Diffraction (XRD) scans for crystal structure characterization using a Siemens model D5000 XRD with Cu K-α radiation and also examined under Scanning Electron Microscopy (SEM), using backscattered electrons, and were subjected to Vickers hardness testing using a Struers Durascan 70 system, with a load of 100g and a dwell time of 15s.

Results and Discussion

The PCA output provides the information required for the interpretation of the original dataset, which is visualized through tables and biplots and which are given in the online supporting information.

Firstly, the number of principal components (PCs) required to represent the data is shown in Table 1. It shows the correlation of PCs with the variables (1 means perfect correlation, -1 inverse correlation and 0 no correlation) and the variance represented by each PC. One criterion for selecting the number of PCs needed is based on the cumulative percentage of the total variance which is often considered satisfactory within the range 70% and 90% [8]. Therefore, the first PCs where the cumulative percentage exceeds the cut-off value would preserve most of the information. Looking at Table 1, the cumulative variance exceeds 70% after the second PC, which means that the first two PCs represent the 72% of the information given by the five variables. 3 PCs are enough to describe 86% of the variance.

Secondly, the effect of PC1 and PC2 is visualized through a biplot as shown in figure 1 (a set of biplots of the 3 main PCs is included into the online supporting information). This plot is useful for easy visualization of the data as well as interpretation of the relationship between the alloys structure and the variables.

It includes not only the alloys reported as intermetallics or multiple phases, single phase fcc and single phase bcc, shown by different symbols, but also the positions of the axes corresponding to variations in each of the different input variables as lines. It is clearly observed that alloy systems giving different structures tend to segregate into different regions on the plot. This implies that the crystalline structure of novel HEAs can be predicted in a simple way by identifying the region where the candidate alloy could lie in from its thermodynamic and electronic properties or even by identifying the target properties for an alloy to have a desired structure, (for example, by orthogonal projections of the observations onto the PC axes) [5], [9]. There is a certain region of overlap between regions, but from the alloys plotted the discrimination obtained would be expected to be good.

It should be noted that the enthalpy of mixing used here is a parameter relating to the solid solution, though this could be much larger and negative if the enthalpy of formation of certain intermetallics were considered. This, coupled with the small entropic contribution in (highly ordered) intermetallics, means that the Gibbs free energy of such phases can easily be very low, making them more stable than the solid solution due to effects that are not directly considered in this approach. Here we are effectively assuming that the interactions driving ordering are small, and it is somewhat unexpected that the predictions work in spite of this.

However, even this type of plot this may not be necessary in all cases. For example, it can be noted from Figure 1 that the axes representing the variation in δ and VEC are at a non-zero angle to each other, showing that between the two done a proportion of the variance can be represented.
This is expected as plotting these parameters (or parameters derived from them) against each other has been found by previous authors to go some way to isolating the structures, such as Guo et al.[7] and Polletti et al.[10]. Nevertheless, the angle between the vectors representing VEC and δ is obtuse, indicating some degree of (negative) correlation. The angle between some other variables is closer to 90 degrees, indicating that they express the variability in a

more independent manner (vectors at right angles are fully independent in terms of the plotted components). An example of this would be VEC and ΔH_{mix}.

	PC1	PC2	PC3	PC4	PC5
ΔH_{mix}	-0.660	0.549	0.379	-0.191	0.288
ΔS_{mix}	0.566	-0.501	0.588	-0.281	-0.069
δ	0.911	0.002	-0.112	0.108	0.382
VEC	-0.492	-0.698	0.270	0.429	0.115
$\Delta\chi$	0.407	0.737	0.373	0.357	-0.153
Eigenvalues	2.00	1.57	0.70	0.44	0.27
Percentage of variance(%)	40.02	31.51	14.29	8.76	5.42
Cumulative	40.02	71.53	85.82	94.58	100

Table 1 - The correlation between the first three principal components and the variables, and the representation of the variance by the principal components
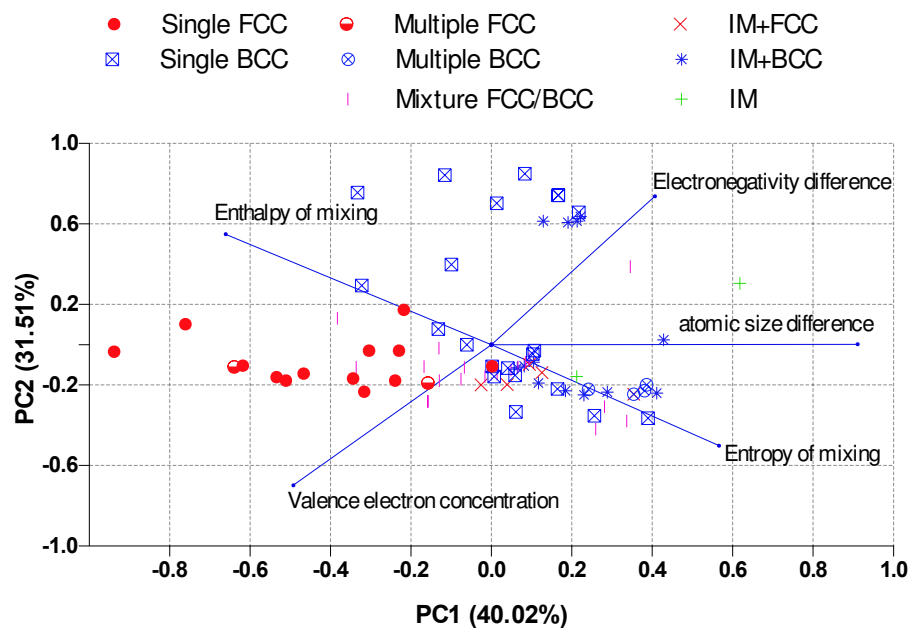

Figure 1 - Biplot of the first two PCs from PCA of the literature data on multicomponent alloy systems (capturing 72% of the variation), showing the strong sensitivity of HEA formation to ΔH_{mix} and VEC.

Examples of the data plotted against only 2 of the five variables are shown in figure 2a and b. These graphs show VEC against δ, representing the type of plot demonstrated in previous work, and VEC against ΔH_{mix}, where trends are found to be particularly clear. The online supporting information also includes a complete series of plots containing the alloys systems reported with respect to parameter pairs.
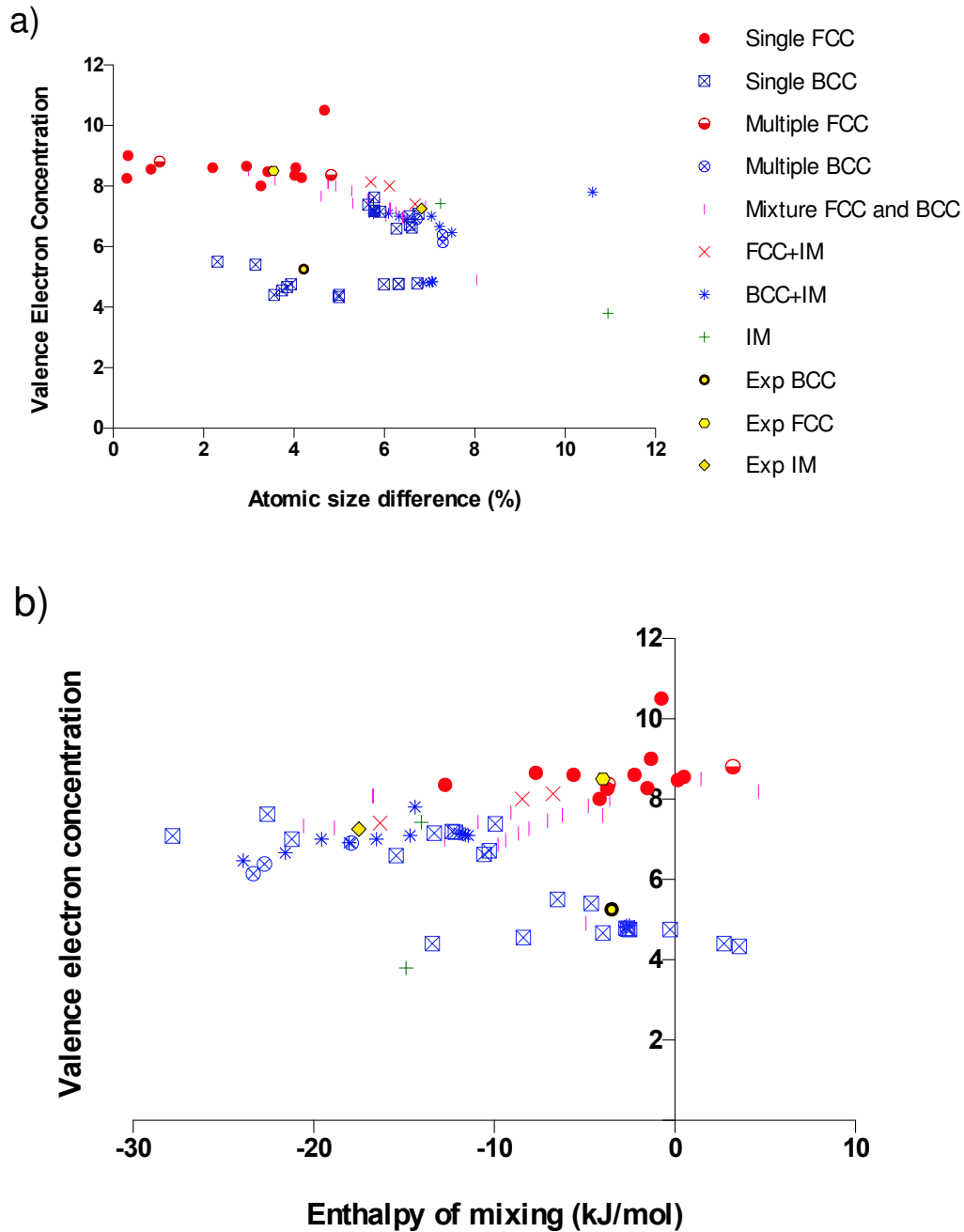
Figure 2 - The correlation between various parameters and the formation of HEAs with different structures. a) VEC against δ and b) VEC against ΔH_{mix}. Note that the plot of VEC versus atomic size difference does not allow discrimination between FCC and BCC.

VEC and δ are plotted against each other for the full dataset in Figure 2a, with different symbols used to indicate the alloys that are reported to form intermetallics or multiple phases, single phase fcc and single phase bcc. These data show clear groupings of the structures in different regions of the plot. However, it is also clear that there are important variables affecting the behaviour that are not fully represented in this plot; the majority of the data points track an apparent curve, hinting at a more complex interrelationship between the parameters.

VEC against ΔH_{mix} is shown in Figure 2b. This way of presenting the data does show almost entirely separated regions for intermetallic or multiphase alloys, and single phase fcc or single phase bcc. The separation between multiple and single phase appears to occur on the ΔH_{mix} axis, while the VEC seems to influence the split between fcc and bcc structure, harking back to the ideas of Hume-Rothery. Importantly, this would appear to permit the design of HEAs, as both the VEC and ΔH_{mix} can be calculated for a candidate alloy, and the location on the graph of the resultant point evaluated to determine the structure.

Taking both of these plots into account, ranges can be defined for each of the 3 parameters where the formation of different structures would be expected, Table 2 (note that these represent the ranges in which these structures are most likely to form without confusion with other structures, not the full extent of their observed envelopes). These ranges can form the basis of design of new alloys.

Table 2 - The required ranges for key variables to produce HEAs of different structures.

Structure	ΔH_{mix} (kJ/mol)		VEC		δ (%)	
	Min	Max	Min	Max	Min	Max
Single phase bcc	-5	0	3	6	2	6
Single phase fcc	-5	0	8	11	2	6
Intermetallic compounds and multiple phases	-20	-15	6	8	6	8

To test these relationships, the novel alloy compositions were selected, designed so that their ΔH_{mix}, δ and VEC values spread them across the plots in Figure 2, with each one falling in a different region. To fully challenge the predictive capabilities, the alloys were further all chosen to have 4 components (at equiatomic composition), as 4 component HEAs are particularly rare. After the predictions were made (values represented as yellow dots in Figure 2), samples of each alloy were produced by arc melting, and were examined using XRD and SEM (Figures 3 and 4). These results show that the structures have formed as expected, TiMnFeNi is a mixture of phases and MnFeCoNi and TiVMnNb are two novel 4 component FCC and BCC alloys respectively.
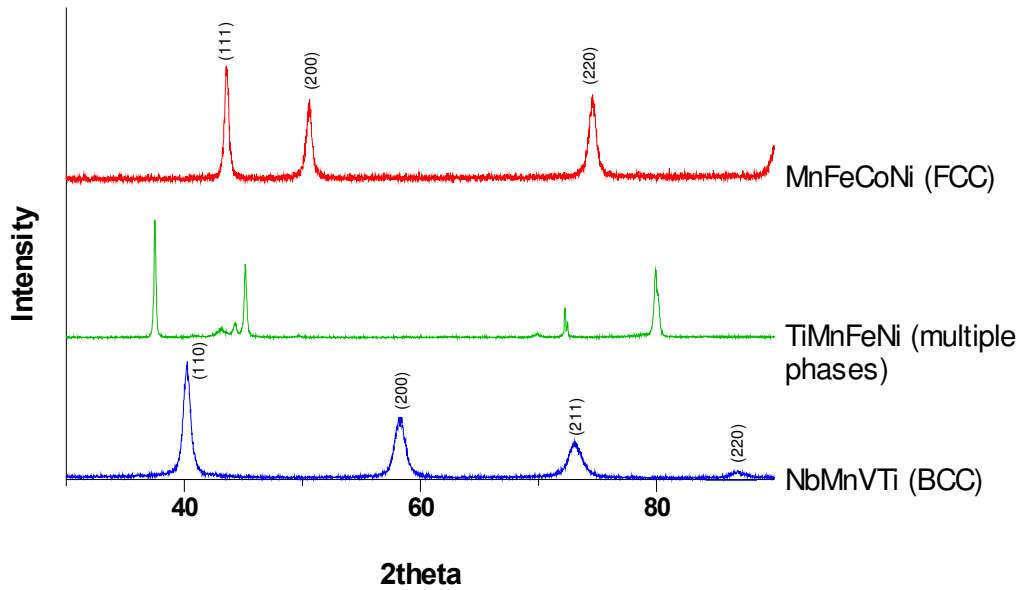
Figure 3 – x-ray patterns θ-2θ scans for samples predicted to be multiphase, fcc and bcc. (a) TiMnFeNi (multiphase), (b) MnFeCoNi (single phase fcc) and (c) TiVMnNb (single phase bcc)
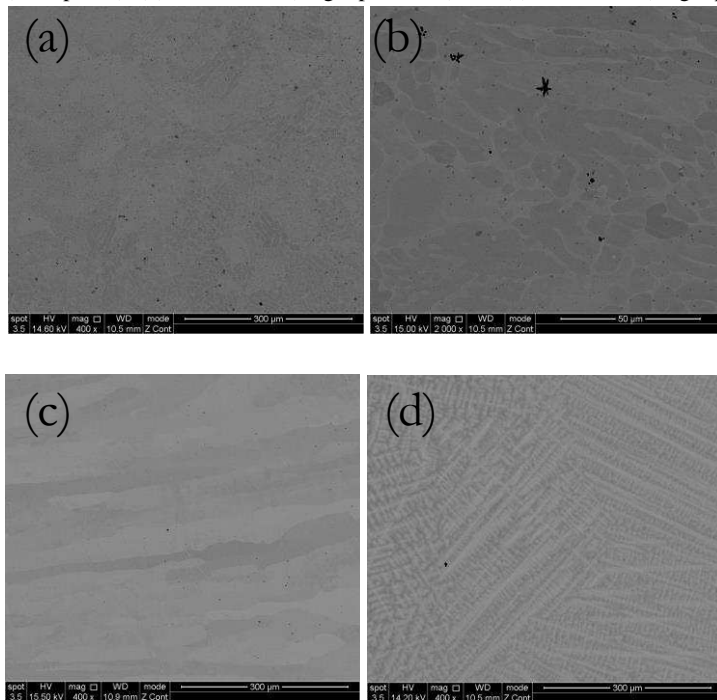

Figure 4 – Backscattered Images of (a) and (b) multiphase TiMnFeNi at low and high magnification respectively, (b) single fcc MnFeCoNi and (c) apparently single bcc TiVMnNb

The x-ray traces of the alloys show peaks consistent with the majority of the material being made up of the predicted phases (fcc for MnFeCoNi, bcc for TiVMnNb and mixed phases/intermetallics for TiMnFeNi). While these traces may not show if there are small amounts of other phases present, results of this type are usually taken as evidence of the formation of HEAs (it should be noted that recent work indicates that many HEAs thought to be single phase actually show segregation on a fine scale [11]). The micrographs shown in Figure 4 are consistent with this view, with a multiphase structure shown by TiMnFeNi (shown in more detail in the high magnification image for clarify), a grain structure present in MnFeCoNi and a dendritic microstructure (with some segregation to the interdendritic

regions) in TiVMnNb. High magnification examination of these last 2 alloys did not reveal any second phases.

The dendritic microstructure observed in TiVMnNb suggests that two phases coexist in the alloy instead of one single phase. This can be confirmed by a more detailed examination of the X-ray diffraction trace. In Figure 3, the X-ray diffraction results of the alloy TiVMnNb is shown for 2θ of 37-45°. This shows broadening at the lowest part of the peak. In general, peak broadening when one single reflection is expected in XRD can be caused by factors such as instrumental broadening and crystallite size among others, but in this particular case, analysis shows the broadening is consistent with the coexistence of two different bcc phases with similar, but different, lattice parameter, 3.14 and 3.15 Å (see Figure 5).
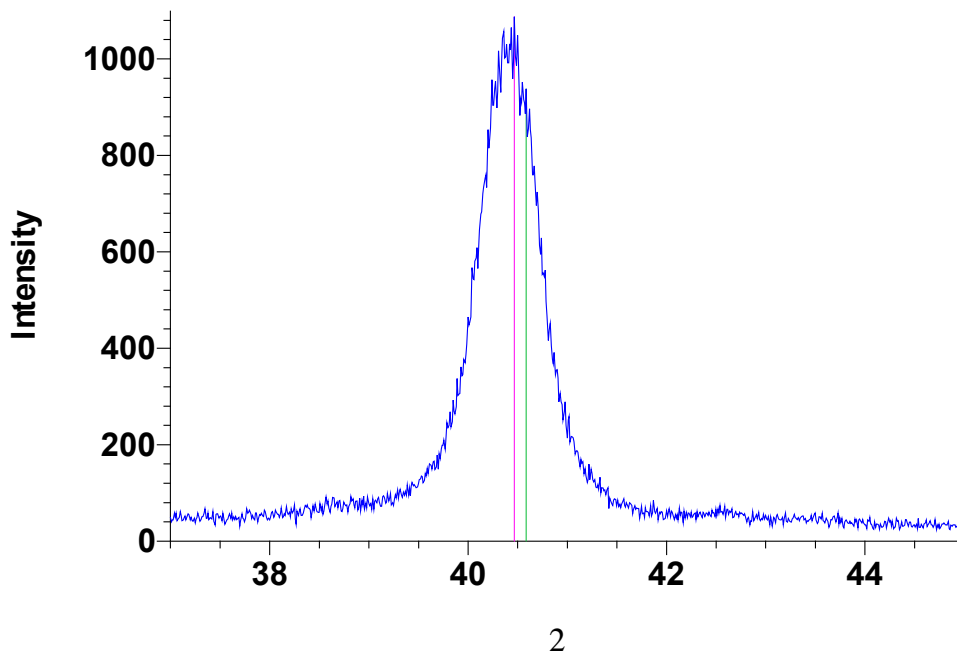

Figure 5: TiVMnNb x-ray trace for 2θ between 37 to 45.

The hardness data for the alloys shows that the fcc structure has the lowest hardness with a value of 164.2±12.4HV, the bcc with a value of 476.3±16.5HV, is the next highest with the highest value occurring for the structure exhibiting multiple phases with a value of 751.5±26.7HV. This would be expected from the nature of dislocation motion in single and multiphase microstructures [12]. We note in passing that TiVMnNb, which shows a high hardness, bcc structure and would be predicted to show a high melting point. It could be an attractive material for applications in high temperature aggressive environments.

Conclusions

This work has performed Principal Component Analysis on a dataset of High Entropy Alloys for the first time. This has shown that while the previously introduced method of exploring the likely phase formation in these materials of plotting electronegativity against atomic size difference captures some of the variability, a greater amount can be expressed in plots of other parameters. In particular, when plotting the wider dataset of multicomponent alloys the

structures formed resolve themselves with an unusually high degree of consistency into largely separate regions on a plot of VEC against ΔH_{mix}. Using this approach, a series of novel four component alloys are predicted with different structures, which on production are found to be consistent. While not giving a conclusive explanation for the reasons behind the formation of these phases, this work provides a simple to use and accurate tool for the prediction of HEA forming compositions of many types.

References

[1]   B. Cantor, I. T. H. Chang, P. Knight, and a. J. B. Vincent, "Microstructural development in equiatomic multicomponent alloys," Mater. Sci. Eng. A, vol. 375–377, pp. 213–218, Jul. 2004.

[2]   J.-W. Yeh, Y. Chen, S. Lin, and S. Chen, "High-Entropy Alloys - a new era of exploitation," Mater. Sci. Forum, vol. 560, p. 1, 2007.

[3]   O. Kubaschewski, "With one auspicious and one dropping eye," Calphad, vol. 8, no. 4, pp. 355–358, Oct. 1984.

[4]   S. Guo, C. Ng, J. Lu, and C. T. Liu, "Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys," J. Appl. Phys., vol. 109, no. 10, p. 103505, 2011.

[5]   I. Toda-Caraballo, E. I. Galindo-Nava, and P. E. J. Rivera-Díaz-del-Castillo, "Unravelling the materials genome: Symmetry relationships in alloy properties," J. Alloys Compd., vol. 566, pp. 217–228, Jul. 2013.

[6]   I. T. Jolliffe, Principal Component Analysis, 2nd ed. New York: Springer-Verlag, 2002.

[7]   S. Guo and C. T. Liu, "Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase," Prog. Nat. Sci. Mater. Int., vol. 21, no. 6, pp. 433–446, 2011.

[8]   I. T. Jolliffe, "Choosing a Subset of Principal Components or Variables," in Principal Component Analysis, 2nd ed., New York: Springer-Verlag, 2002, pp. 111–149.

[9]   I. T. Jolliffe, "Graphical Representation of Data Using Principal Components," in Principal Component Analysis, 2nd ed., New York: Springer-Verlag, 2002, pp. 78–110.

[10]   M. G. Poletti and L. Battezzati, "Electronic and thermodynamic criteria for the occurrence of high entropy alloys in metallic systems," Acta Mater., vol. 75, pp. 297–306, Aug. 2014.

[11] Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. a. Dahmen, P. K. Liaw, and Z. P. Lu, "Microstructures and properties of high-entropy alloys," Prog. Mater. Sci., vol. 61, no. October 2013, pp. 1–93, Apr. 2014.

[12] B. H. Flowers and E. Mendoza, Properties of Matter, 1st ed. London: John Wiley & Sons Ltd., 1970.