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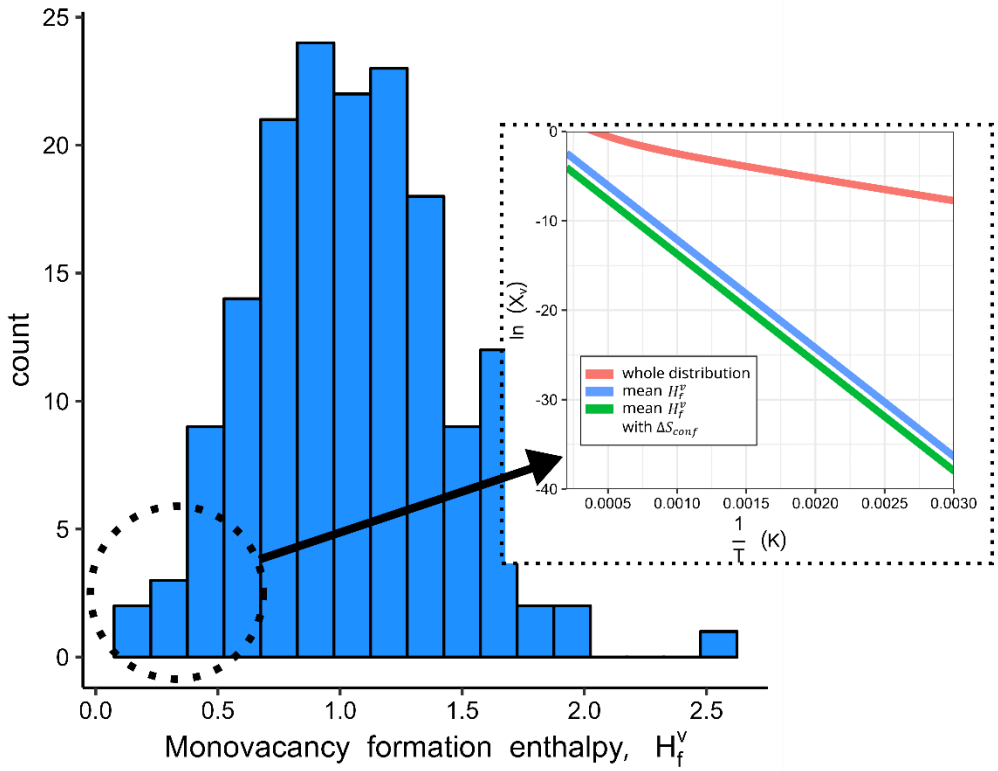
Graphical abstract



Abstract

Accurate determination of monovacancy formation enthalpy is vital for work on diffusion, melting point determination of high temperature materials, radiation damage, and thermophysical stability of alloys. These enthalpies take on a single value in pure metals but is made more complex in concentrated solid solutions due to the local chemical environments possible around each vacancy. Herein, using first-principles density functional theory, we report the distributions of vacancy formation enthalpies in 21 equiatomic 5-component solid-solution alloys from the Hf-Mo-Nb-Ta-Ti-W-Zr system. Chemical disorder is treated using the special quasi-random structure method, and the chemical potential of vacant element is treated by approximating it to its total energy in its standard state. We find that the highest vacancy formation enthalpies belong to the MoNbTaTiW alloy (which incidentally is the most reported in literature) and the lowest belongs to HfNbTaTiZr, with other alloys in-between. We use the whole distribution of formation enthalpies to estimate the equilibrium concentration of vacancies as a function of temperature.

1. Introduction

High entropy alloys (HEAs), sometimes referred to as compositionally complex alloys, multicomponent element alloys, or concentrated solid solutions, pioneered by Cantor *et al.* [1] and Yeh *et al.* [2], offer innovative multi-component alloy compositions for extreme environment materials such as in the nuclear [3,4] or aerospace [5] industries. Originally defined as having 5 or more elements in high concentrations (5 – 35 at%) [2], high entropy alloys could offer superior properties, including strength and hardness [6,7], oxidation resistance [8–11], and high thermal stability [12]. Vacancies, their formation energies, and their equilibrium concentration have been studied for their role in diffusion kinetics [13], precipitation [14], radiation resistance [13,15,16], and material properties such as strength [17,18]. HEAs are observed to have higher concentrations of vacancy defects compared to conventional alloys [18,19]. The exact mechanism behind this higher concentration is not yet fully understood.

Wang *et al.* presented a thermodynamic analysis which concludes that configurational entropy causes a substantial increase in equilibrium vacancy concentrations in high entropy alloys compared to pure metals and binary alloys [19]. Contrary to this, Daigle *et al.* propose that configurational entropy reduces the equilibrium vacancy concentration in high entropy materials [20]. This viewpoint is supported by Jodi *et al.*, who demonstrated that alloys with higher configurational entropy in the $Fe_x(CoCrMnNi)_{100-x}$ system had lower equilibrium concentrations of monovacancies, although the authors attributed this to the compositional effect of Fe on the vacancy formation enthalpy [21]. Daigle *et al.* suggests that most equilibrium vacancies in high entropy materials are produced from the lower tails of the vacancy formation enthalpy distribution, which tend to be significantly lower than the mean. This results in an enhanced vacancy concentration in complex materials such as HEAs, compared to conventional alloys and pure metals [20].

Experimental research on vacancy formation in HEAs predominantly relies on positron annihilation lifetime spectroscopy [21,22] and tracer diffusion experiments [23], but presently, few of these studies have been performed. To support experimental efforts, recent advances in density functional theory [24,25], molecular dynamics [26], and machine learning models [27] have enabled the study of vacancy formation in compositionally complex alloys such as HEAs. Many previous studies on vacancy formation enthalpies of compositionally complex alloys have focussed on the Cantor alloy [28] and

derivative alloys thereof [22,25,29–34], although studies on some refractory alloys do exist [24,35–38]. For example, Cunliffe *et al.* proposed a method to calculate the vacancy formation enthalpy in multi-component amorphous alloys, including refractory alloys, which involves averaging the vacancy formation enthalpy of the respective pure metals [37]. Roy *et al.* determined the vacancy formation energy of $(Mo_{0.95}W_{0.05})_{0.85}Ta_{0.10}(TiZr)_{0.05}$ via density functional theory to be between 2.87 – 3.84 eV [35]. Zhang *et al.* investigated vacancy energetics in the Al-Hf-Sc-Ti-Zr system, including the binary to quaternary alloys. From this, they calculated the temperature dependence of the Gibbs energy of vacancy formation [24]. Zhao *et al.* determined the vacancy formation enthalpy of CrTaVW to be between 2.45 – 3.94 eV, with a mean value of 3.18 eV [39]. The literature however remains sparse on thorough interrogations of vacancy formation enthalpies in refractory HEAs.

Using density functional theory, we examine the vacancy formation enthalpies of all quinary alloys in the seven-element Hf-Mo-Nb-Ta-Ti-W-Zr system. The formation enthalpies of vacancies and their trends are presented. We show that refractory solid solutions have higher equilibrium vacancy concentrations than pure elements, which is not attributed to their increased configurational entropy. Rather, vacancy formation energies at the lower-end tail of the distribution are responsible for the higher equilibrium vacancy concentrations observed in high entropy alloys. These findings suggest important phenomena that may occur in the migration of species (e.g., oxygen and hydrogen), bubble formation and phase segregation and other equilibrium processes in high entropy alloys, compositionally complex alloys, and alloys in general.

2. Methodology

2.1. Special quasi-random structure supercells.

Density functional theory [40,41] is computationally intensive (generally limited to hundreds of atoms at a time). The conventional way to capture bulk material properties is to use periodic boundary conditions, but this imposes non-random periodicity on simulations, which poses challenges for modelling infinitely random lattices in density functional theory computations. Special quasi-random structures (SQS) attempt to replicate random materials by matching correlation functions between pairs of atoms within a defined cut-off radius (short-range interactions are more dominant than long-range interactions) to capture bulk random lattice features. In this study, special quasi-random structures were constructed using the mcsqs code in the Alloy Theoretic Automated Toolkit [42] similar to previous work [38]. We set cut-off distances to include up to third nearest neighbour pair interactions. We did not consider triplet and higher order interactions.

2.2. Total energy Relaxations

Density function theory [40,41] structural relaxation calculations at constant pressure were based on the plane wave pseudopotential approach as implemented in the Vienna *ab initio* simulation package VASP [43,44] version 5.4.4. Projector augmented-wave (PAW) pseudopotentials are used [45,46]. Electrons treated as valence are: Hf: 10, Mo: 14, Nb: 13, Ta: 11, Ti: 12, W: 12, and Zr: 12. The Perdew, Burke, and Ernzerhof version of the generalised gradient approximation exchange-correlation functional was applied [47]. Cut-off energy for plane waves were set to 500 eV for all calculations. A Methfessel-Paxton smearing width of 2 eV was used [48]. A K-point mesh was selected based on convergence of the total energy to 0.01 eV/atom which resulted in a $4 \times 4 \times 4$ Γ-centred mesh for all cells. Convergence testing for plane wave cut off energies and K-points can be found in **Supplementary Figures S1-2**.

2.3. Calculating local Bias

We adopt a measure for how the immediate environment of a vacancy is biased towards particular elements using nomenclature from Li *et al.* [33]. For example, for a vacancy in a body-centred cubic lattice surrounded by 8 atoms of elements A, B, C, D and E, a measure of (2,2,2,1,1), respectively would indicate a relatively unbiased vacancy without predilection for any particular element. A measure of (5,3,0,0,0) indicates a biased local arrangement, and a measure of (8,0,0,0,0) indicates that all local atoms within an appropriate cut off distance are of a single element, A. From this notation, we calculate an overall measure of local element bias per vacancy via

$$local\ element\ bias = \sqrt{\frac{1}{N}\sum_{i=element\ A}^{E}(j_i - nx_i)^2} \quad (1)$$

Where N is the total number of elements in the alloy, n is the coordination number (8 for body-centred cubic, 12 for face-centred cubic and hexagonal close-packed), x_j is the atomic fraction of element j, j is the number atoms of each element, A to E, surrounding a vacancy, and $\bar{j}$ is the mean number of atoms of each elements surrounding vacancies in an infinitely random solid solution (calculated to be 1.6 for an equiatomic quinary body-centred cubic alloy). and **equation 1** resembles that of the root-mean-square deviation. For the previous examples, (2,2,2,1,1), (5,3,0,0,0), and (8,0,0,0,0), we respectively obtain local element biases of 1.04, 3.46, and 4.29, with more examples listed in **Supplementary Table S1**. Each alloy is assumed to be completely equiatomic among constituent elements in **equation 1** and has negligible effect on the biases calculated (**Supplementary Figure S3**).

2.4. Calculating vacancy volumes

Vacancy volume is calculated by calculating the volume of the convex hull constructed between coordinates of the nearest neighbour atoms to the vacancy chosen with a cut off distance of 2.75 Å to include first nearest neighbours but exclude second and further nearest neighbours. **Figure 1a** illustrates a body-centred cubic 53-atom cell with a vacancy. **Figure 1b** indicates the cut off radius around the vacancy used to calculate the vacancy volume. However, in some alloys with large lattice strain some 9 or so neighbours can exist within the cut off distance. Due to the small number of these occurrences, we therefore treat all these atoms as 1st nearest neighbours similar to previous work [27] for calculations involving local bias or vacancy volume.

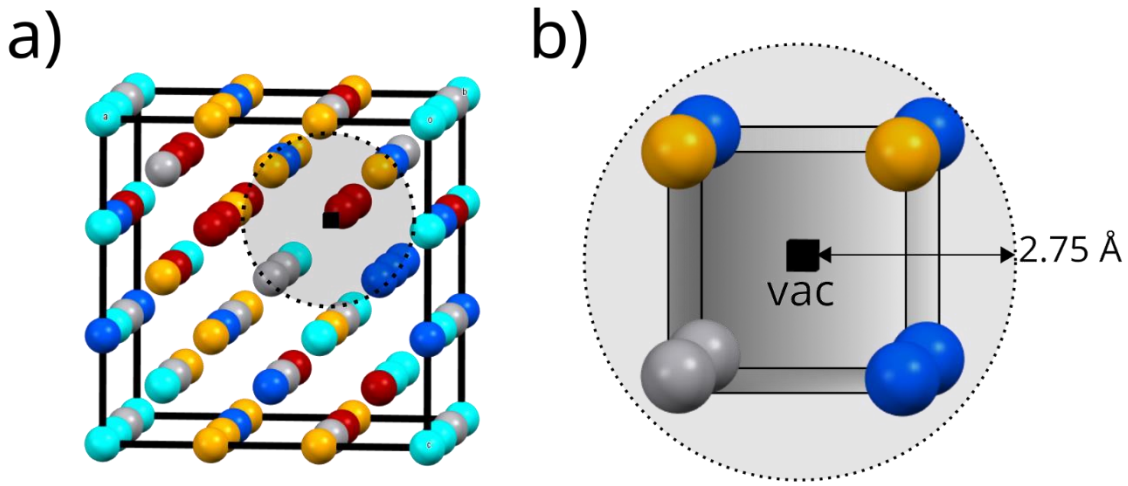


Figure 1. **Vacancy volume of body-centred cubic supercells.** a) vacancy within a body-centred cubic supercell, and b) atoms within the cut off radius used to calculate vacancy volume.

2.5. Vacancy formation energy calculations

Vacancy formation enthalpies were calculated by structurally relaxing each 54-atom supercell at constant pressure. Each atom was then removed in turn, and the supercell allowed to relax around the vacancy, again, at constant pressure. The vacancy formation enthalpy, $\mathrm{H_f^v}$, is calculated via

$$\mathrm{H_f^v} = \mathrm{E_v} - \mathrm{E_0} + \mu_\mathrm{v} \tag{2}$$

where $\mathrm{E_v}$ is the total energy of the supercell containing a vacancy, $\mathrm{E_0}$ is the total energy of the supercell without a vacancy, and μ_v is the chemical potential of the removed species. The sign of μ_v corresponds to either a vacancy (+ sign) or an interstitial (- sign). In the literature, variation of μ_v in bulk metals versus in complex alloys were found to be insignificant [25,35,39]. For example, Roy et al. investigated the relationship between μ_v in the refractory Mo-Ta-Ti-W-Zr system and their constituent pure metals and found that the chemical potential differed by less than 1.1% [35]. Herein, we approximate the chemical potential of the defect species as that in its bulk metal form via the equation

$$\mathrm{H_f^v} = \mathrm{E_v} - \mathrm{E_0} + \mathrm{E_{defect}} \tag{3}$$

where $\mathrm{E_{defect}}$ is the total energy, normalised to energy-per-atom, of the pure metal in its bulk form at 0 K (hexagonal close packed Hf, Ti, and Zr, and body-centred cubic Mo, Nb, Ta, and W). The accuracy of these pure bulk metal lattice energy calculations was similar to that of the alloy supercells.

2.6. General calculation information

Each supercell afforded 54 unique vacancy formation enthalpies. These were calculated at least in duplicate for each quinary alloy in the Hf-Mo-Nb-Ta-Ti-W-Zr system (using a different special quasi-random structure supercell each time), yielding a total of at least 108 vacancy formation enthalpies per alloy. The element whose number of atoms is slightly deficient in each supercell, was allowed to vary at random, and no significant effect of this was observed in the resulting distributions of vacancy

formation enthalpies (via a two-tailed Kolmogorov-Smirnov test). Datasets and calculation outputs will be made available on request to the author.

To interrogate any correlations between vacancy formation enthalpy and bulk properties, such that $\mathrm{H_f^v}$ might be predicted using easily obtained properties, the Pearson product-moment correlation coefficient between $\mathrm{H_f^v}$ and several properties were calculated including electron valence concentration, atomic size mismatch factor, and lattice parameter. These properties are easily obtained via the parametric approach to phase stability of concentrated solid solution alloys [49–51].

3. Results and discussion

3.1. Phase stability and structure

Before assessment of vacancies, the stability and properties of the perfect solid solutions are investigated. The various properties will be subsequently used to assess the impact on vacancy formation enthalpies. The solid solution formability of high entropy alloys has been estimated via various parametric approaches in the past [52–54]. We calculate the solid solution mixing enthalpy, $\Delta\mathrm{H_{mix}}$, for equiatomic alloys via the regular solid solution model given by Yang *et al.* [54], ideal configurational entropy, $\Delta\mathrm{S_{conf}}$, valence electron concentration [53], (VEC), atomic size mismatch parameter, δ, solid solution formability parameter at the theoretical melting point [54], Ω, and the atomic packing parameter, γ [55].

$$\Delta\mathrm{H_{mix}} = \sum_{i=1,\mathrm{i}\neq j}^{\mathrm{n}} 4\Delta\mathrm{H}_{ij}^{\mathrm{mix}}\mathrm{c}_i\mathrm{c}_j \tag{4}$$

$$\Delta\mathrm{S_{conf}} = -\mathrm{R}\sum_{i=1}^{\mathrm{n}}(\mathrm{c}_i \ln(\mathrm{C}_i)) \tag{5}$$

$$\mathrm{VEC} = \sum\nolimits_{i=1}^{n} c_i(\mathrm{VEC})_i \tag{6}$$

$$\delta = 100 \times \sqrt{\sum_{i=1}^{\mathrm{n}} \mathrm{c}_i\left(1-\frac{\mathrm{r}_i}{\bar{\mathrm{r}}}\right)^2} \tag{7}$$

$$\Omega = \frac{\mathrm{T_m}\Delta\mathrm{S_{mix}}}{|\Delta\mathrm{H_{mix}}|};\ \mathrm{T_m} = \sum\nolimits_{i=1}^{\mathrm{n}} \mathrm{c}_i(\mathrm{T_m})_i \tag{8}$$

$$\omega_s = 1-\sqrt{\frac{(r_L+\bar{r})^2-\bar{r}^2}{(r_L+\bar{r})^2}};\ \omega_L = 1-\sqrt{\frac{(r_s+\bar{r})^2-\bar{r}^2}{(r_s+\bar{r})^2}};\ \gamma = \frac{\omega_s}{\omega_L} \tag{9}$$

Where c_i and c_j are the atomic fractions of elements i and j, respectively. $\Delta\mathrm{H}_{ij}^{\mathrm{mix}}$ is the enthalpy of mixing of binary liquid alloys, based on the Miedema macroscopic model for liquid binary alloys obtained from Takeuchi *et al.* [56]. R is the ideal gas constant in $\mathrm{JK^{-1}mol^{-1}}$, $(\mathrm{VEC})_i$ is the valence electron concentration of the ith element, $\bar{r} = \Sigma_{i=1}^{n} c_i r_i$ is the average atomic radius and r_i is the atomic radius of element i, $(\mathrm{T_m})_i$ is the melting point of the ith element.

The putative boundaries for each parameter for solid-solution formation are: $-15\ \mathrm{kJmol^{-1}} < \Delta\mathrm{H_{mix}} < 5\ \mathrm{kJmol^{-1}}$ [52]; $12\ \mathrm{JK^{-1}mol^{-1}} < \Delta\mathrm{S_{mix}} < 17.5\ \mathrm{JK^{-1}mol^{-1}}$ [52,54]; $\mathrm{VEC} \leq 6.87$ for body-centred cubic structures, $\mathrm{VEC} \geq 8$ for face-centred cubic structures [53]; $\delta \leq 6.6\%$ [52]; $\Omega \geq 1.1$ [54]; and $\gamma \leq 1.175$ [55]. The calculated values for the thermophysical parameters in the present alloys are in **Table 1.**

Table 1. Thermophysical parameters for equiatomic alloys. ΔH_{mix}, δ, VEC, γ, and Ω.

composition	$\Delta\mathrm{H_{mix}}$ ($\mathrm{kJmol^{-1}}$)	δ (%)	VEC	γ	Ω
HfMoNbTaTi	-1.44	6.23	4.8	1.0526	24.87
HfMoNbTaW	-4.64	3.51	5.2	1.0717	8.73
HfMoNbTaZr	-1.12	3.56	4.8	1.0341	32.42
HfMoNbTiW	-4.48	6.06	5	1.0719	8.24
HfMoNbTiZr	-1.6	6.68	4.6	1.0523	20.44
HfMoNbWZr	-4.96	3.94	5	1.0712	7.54
HfMoTaTiW	-4.48	6.18	5	1.0719	8.56
HfMoTaTiZr	-1.92	6.73	4.6	1.0523	17.79
HfMoTaWZr	-4.96	3.94	5	1.0712	7.83
HfMoTiWZr	-5.6	6.7	4.8	1.0714	6.29
HfNbTaTiW	-2.72	6.11	4.8	1.0719	13.95
HfNbTaTiZr	2.72	6.46	4.4	1.0523	12.41
HfNbTaWZr	-2.56	3.03	4.8	1.0712	15.02
HfNbTiWZr	-3.04	3.03	4.8	1.0714	11.46
HfTaTiWZr	-3.36	3.03	4.8	1.0714	10.8
MoNbTaTiW	-5.28	4.95	5.2	1.0362	7.39
MoNbTaTiZr	-1.76	5.97	4.8	1.0526	19.77
MoNbTaWZr	-5.44	3.16	5.2	1.0717	7.26
MoNbTiWZr	-5.28	5.75	5	1.0719	6.8
MoTaTiWZr	-5.28	5.88	5	1.0719	7.07
NbTaTiWZr	-3.2	5.85	4.8	1.0719	11.54

All present alloys satisfy the boundaries for solid solution phase formation for $\Delta\mathrm{H_{mix}}$, $\Delta\mathrm{S_{conf}}$, Ω, and γ. VEC of the alloys are below 6.87 which suggests a body-centred cubic is preferred [53]. The alloys HfMoNbTiZr, HfMoTaTiZr, and HfMoTiWZr have δ values of 6.68, 6.73, and 6.7, respectively, which suggest these alloys may not form solid solutions. HfNbTaTiZr has a positive mixing enthalpy of $\Delta\mathrm{H_{mix}} = +2.72\ \mathrm{kJmol^{-1}}$ which suggests a miscibility gap at $0\ \mathrm{K}$.

The parametric method suggests that the alloys investigated in this paper produce stable body-centred cubic solutions. However, there is a lack of information regarding the thermal stability of the alloys that were investigated in this work. It is possible for local ordering, precipitation, segregation, and clustering of elements to occur, which will influence the vacancy energetics within the alloy. HfNbTaTiZr, for instance, has a positive $\Delta\mathrm{H_{mix}}$, indicating a thermodynamic tendency to decompose at low temperatures. MoNbTaTiW is known to undergo B2-like ordering at intermediate temperatures, which may influence the vacancy formation enthalpies of this alloy. Vacancy sinks, such as grain boundaries, are another factor that has an impact on the vacancy concentrations in

concentrated solid solutions. Additionally, vacancy migration contributes to the observed vacancy concentrations in real materials. Migration is affected by dislocation density [57], clustering of vacancies, and the presence of defect sinks like grain boundaries.

3.2. Calculating lattice constants

There is no generally agreed upon method in literature for calculating lattice constants for HEAs or alloys in general. Experimentally, this is normally determined via a technique such as X-ray diffraction where the maximum peak intensity points are used to assess the general structure of the material. Lattice constants for the alloys in this study were predicted via three methods:

1. The cube root of the total supercell volume is taken and divided by the unit cell width (3 for a $3 \times 3 \times 3$ cubic supercell) and this is taken as an estimate for the lattice constant across the cell.
2. All neighbour distances across the cell are measured and the mean of those expected around the 2nd nearest neighbour (similar treatment to Wang *et al.* [27]) are taken to be representative of the alloy.
3. The rule of mixtures (Vegard's law [58]) is applied to lattice constants of fully relaxed body-centred cubic supercells of pure elements in the Hf-Mo-Nb-Ta-Ti-W-Zr system. This third method is known to neglect the influence of lattice distortion on the crystal and is therefore likely to overpredict lattice parameter of concentrated solid solution alloys.

A discussion of methods to calculate the lattice constant in high entropy alloy supercells is found in **Supplementary Figure S4**. It was found that by cube rooting the volume and dividing by the unit cell width (Method 1), was able to provide an average lattice constant whilst taking into account the distortion of the lattice. The lattice constant of the present alloys is in **Table 2**. The volume averaging scheme was used for subsequent correlation studies.

Table 2. Lattice constant of refractory alloys calculated via the volume averaging scheme.

composition	lattice constant (Å)
HfMoNbTaTi	3.31 $\pm$ 0.01
HfMoNbTaW	3.29$\pm$ 0.01
HfMoNbTaZr	3.38$\pm$ 0.01
HfMoNbTiW	3.28$\pm$ 0.01
HfMoNbTiZr	3.36$\pm$ 0.01
HfMoNbWZr	3.34$\pm$ 0.01
HfMoTaTiW	3.28$\pm$ 0.01
HfMoTaTiZr	3.37$\pm$ 0.01
HfMoTaWZr	3.35$\pm$ 0.01
HfMoTiWZr	3.34$\pm$ 0.01
HfNbTaTiW	3.32$\pm$ 0.01
HfNbTaTiZr	3.41$\pm$ 0.01
HfNbTaWZr	3.38$\pm$ 0.01
HfNbTiWZr	3.38$\pm$ 0.01

HfTaTiWZr	3.37± 0.01
MoNbTaTiW	3.23± 0.01
MoNbTaTiZr	3.32± 0.01
MoNbTaWZr	3.30± 0.01
MoNbTiWZr	3.28± 0.01
MoTaTiWZr	3.29± 0.01
NbTaTiWZr	3.32± 0.01

3.3. Vacancy formation enthalpies

At least 2 unique special quasi-random cells were generated for each of the 21 alloys in the study. To determine if each special quasi-random cell produced enthalpies likely from the same population distribution, we performed a two-tailed Kolmogorov-Smirnov test between each sample distribution (**Supplementary Table S2**). After confirming we likely adequately sampled the same probability distribution for each alloy, we combined each sample distribution to produce a single distribution of energies for each alloy. For completeness, the vacancy formation enthalpies for the pure hexagonal close packed (Hf: 2.20; Ti: 2.04; and Zr: 1.98 eV) and body-centred cubic (Mo: 2.80; Nb: 2.62; Ta: 2.83; and W: 3.33 eV) elements were calculated.

The vacancy formation enthalpy adopts a single value in pure elements. However, the local chemical variations in concentrated solid solutions produce a distribution of vacancy formation enthalpies. The calculated enthalpies of the quinary Hf-Mo-Nb-Ta-Ti-W-Zr alloys are in **Figure 2** (ordered from highest to lowest mean values for $\mathrm{H_f^v}$) The largest mean $\mathrm{H_f^v}$ belongs to MoNbTaTiW, which, incidentally, is the most reported quinary refractory alloy in literature [59–62]. The mean $\mathrm{H_f^v}$ for MoNbTaTiW is 3.14 eV and is similar to body-centred cubic W (3.11 [63] – 3.19 [64] via density functional theory, and 3.1 - 3.4 eV experimentally [65]). HfNbTaTiZr exhibited the lowest mean enthalpy of vacancy formation of 1.04 eV which is similar to low melting face-centred cubic elements like Cu (1.33 eV) and Ag (0.96 eV) [66]. This indicates the possible low thermal stability of these solid solutions, and the high probability that these alloys either have a low relative melting point compared to alloys in this study, or that they decompose into more stable, multiphase systems The rest of the solid solutions considered in this study exhibited intermediate $\mathrm{H_f^v}$, with mean values from 1.46 – 2.93 eV. Mean values of $\mathrm{H_f^v}$ for all alloys in this study are in **Table 3**.

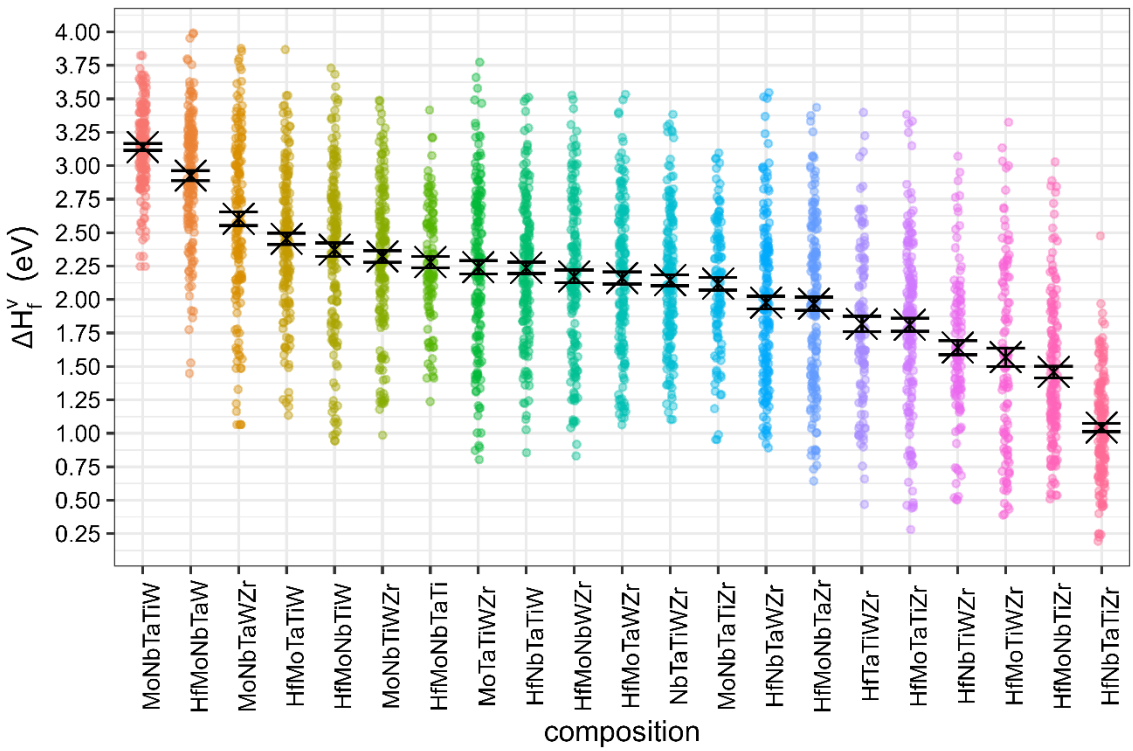


Figure 2. **Vacancy formation enthalpy for equiatomic alloys in the Hf-Mo-Nb-Ta-Ti-W-Zr system.** H_f^v values are ordered from highest to lowest. A cross indicates mean H_f^v values for each alloy. Error bars indicate standard error of the mean.

Table 3. Mean H_f^v values for concentrated solid solutions. Where σ is the standard deviation of the mean H_f^v.

composition	$mean\ H_f^v\ (eV)$	$\sigma(eV)$
MoNbTaTiW	3.14	0.32
HfMoNbTaW	2.93	0.48
MoNbTaWZr	2.6	0.65
HfMoTaTiW	2.45	0.54
HfMoNbTiW	2.37	0.64
MoNbTiWZr	2.32	0.56
HfMoNbTaTi	2.28	0.44
HfNbTaTiW	2.24	0.54
MoTaTiWZr	2.24	0.63
HfMoNbWZr	2.17	0.6
HfMoTaWZr	2.16	0.57
NbTaTiWZr	2.14	0.52
MoNbTaTiZr	2.12	0.5
HfNbTaWZr	1.98	0.6
HfMoNbTaZr	1.97	0.63

HfTaTiWZr	1.82	0.61
HfMoTaTiZr	1.81	0.62
HfNbTiWZr	1.64	0.55
HfMoTiWZr	1.57	0.72
HfMoNbTiZr	1.46	0.55
HfNbTaTiZr	1.04	0.39

There is little correlation between $\mathrm{H_f^v}$ and the element being removed [27]. However, $\mathrm{H_f^v}$ does depend on the elements which make up the nearest neighbour environment. For example, Hf, Ti, and Zr have vacancy formation enthalpies of 2.20, 1.98, and 2.04 eV, respectively. When these elements form the nearest neighbour environment, $\mathrm{H_f^v}$ is likely to decrease. In contrast, the presence of Mo and W as neighbouring elements (with $\mathrm{H_f^v}$ values of 2.80 and 3.33 eV, respectively), is likely to increase $\mathrm{H_f^v}$. Therefore, the resulting vacancy formation energy appears to be the result of an averaging scheme based on the local environment. **Supplementary Figure S5** shows the product-moment correlation coefficients of nearest neighbour elements versus the calculated $\mathrm{H_f^v}$ for each environment. Local element bias was found to have no direct correlation with $\mathrm{H_f^v}$, as a strong bias toward a particular element shifts the enthalpy of vacancy formation towards that of the biased element.

Local properties surrounding each vacancy were collected (vacancy volume, immediate neighbour atoms) as well as bulk properties of the alloys (valence electron concentration, lattice constant, average electron shell number, atomic size mismatch factor, δ, among others). The thermophysical parameters are found in **Table 1**. **Figure 3** shows that the mean $\mathrm{H_f^v}$ of the studied alloys strongly correlates with valence electron concentration (**Figure 3a**: $r = 0.88$), number of hexagonal close packed alloying elements (**Figure 3b**: $r = -0.91$), and lattice constant (**Figure 3c**: $r = -0.87$). Vacancy volume, calculated from the convex hull between atomic coordinates of atoms within 2.75 Å around the removed atom, was found to weakly correlate with $\mathrm{H_f^v}$ (r = +0.28; **Supplementary Figure S6).**

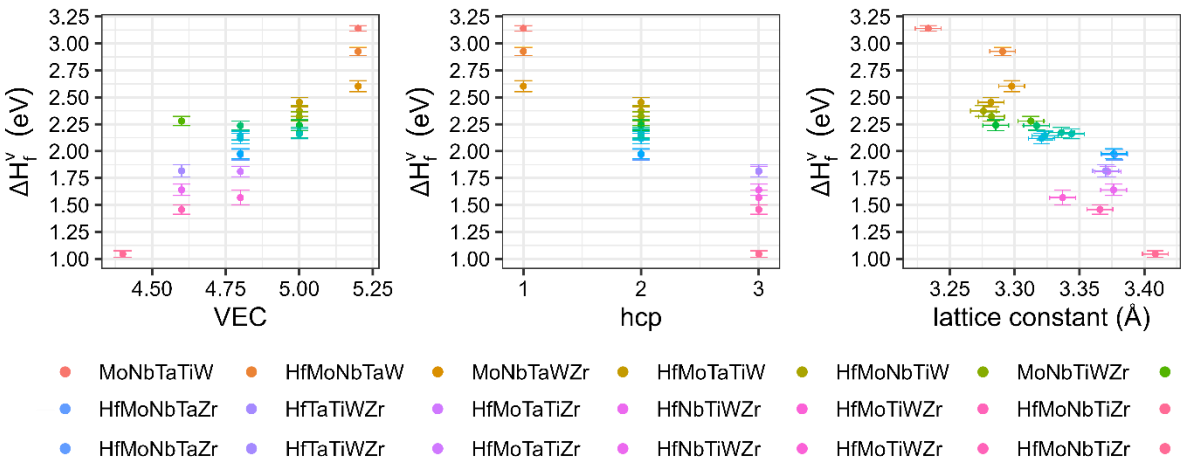


Figure 3. Mean $\mathrm{H_f^v}$ values for alloys in the Hf-Mo-Nb-Ta-Ti-W-Zr system plotted versus a) valence electron concentration; b) number of constituent hexagonal close packed elements; and c) calculated lattice constant. Vertical error bars indicate the standard error of the mean of $\mathrm{H_f^v}$; horizontal error bars indicate maximum deviation observed in lattice parameter across all the alloys.

$\mathrm{H_f^v}$ is largely dependent on the first nearest neighbours [67]. This suggests that element clustering and segregation have a significant role in defining the vacancy energies of real materials. In addition, the enthalpies at the lower end of the distribution have a greater impact on the equilibrium vacancy concentration. Future research should make a concerted effort to sample these smaller enthalpies. The enthalpy of vacancy formation has been found to correspond with bulk parameters such as lattice constant, valence electron concentration, and several Hume-Rothery factors including the preferred crystal structure of the constituent elements at 0 K. These parameters may be used as a simple empirical relation to estimate $\mathrm{H_f^v}$ as a first approximation.

3.4. Population of vacancies in Hf-Mo-Nb-Ta-Ti-W-Zr quinary alloys

The value of $\mathrm{H_f^v}$ can be used to estimate probability of vacancy formation and therefore the vacancy concentration, X_i, in a material [68]. Similar to Daigle *et al.*, we calculate the vacancy concentration in equiatomic concentrated solid solutions with the configurational entropy of the added monovacancy (**equation 10**) [20]. Furthermore, we compute the vacancy concentration using the entire enthalpy distribution, which takes into account the preferential formation of vacancies with enthalpies at the lower tail of the $\mathrm{H_f^v}$ distribution (**equation 11**).

$$X_i = \frac{n}{N} = \frac{1}{m} e^{\frac{-\Delta \mathrm{H_f^v}}{\mathrm{k_B T}}} \tag{10}$$

$$X_i = \frac{n}{N} = \frac{\sum_{i=1}^{n} \frac{1}{m} e^{\frac{-\Delta \mathrm{H_f^v}(i)}{\mathrm{k_B T}}}}{n} \tag{11}$$

where $\frac{n}{N}$ is the fraction of vacancies in the system, m is the alloying number, $\Delta \mathrm{H_f^v}$ is the mean enthalpy of monovacancy formation (eV), $\mathrm{k_B}$ is the Boltzmann constant (eVK^{-1}), T is temperature (K), $\Delta \mathrm{H_f^v}(i)$ is the enthalpy of vacancy formation for the ith observation, and n is the number of observations. **Equation 10** considers the configurational entropy of adding a vacancy to an m number of elements at the dilute limit and is with accordance to the $m + 1$ species scheme [69]. Adding a vacancy to concentrated solid solutions results in a lower additional configurational entropy with increasing m (**Supplementary Figure S7**). The derivation for **equation 10** is given in **Supplementary Appendix 1**.

We calculate the equilibrium vacancy concentration here for two alloys, MoNbTaTiW, and HfNbTaTiZr, using a) the mean $\mathrm{H_f^v}$ only; b) with the additional configurational entropy of the vacancy; and c) by using the entire distribution of $\mathrm{H_f^v}$. From **Figure 4a**, the configurational entropy associated with monovacancies in complex materials reduces their concentration in the MoNbTaTiW alloy compared with pure metals and dilute alloys. However, when the entire distribution of energies is considered, there is a significantly higher concentration of vacancies throughout the entire temperature range. This is because vacancies with lower formation enthalpies preferentially form within the alloy crystal, and therefore contribute most to the equilibrium vacancy concentration. Likewise, the same effect can be seen in **Figure 4b** for HfNbTaTiZr. In both cases, the equilibrium vacancy concentration significantly deviates from typical Arrhenius behaviour especially at temperatures > 2000 K. This non-Arrhenius dependence of vacancy concentration is found to be characteristic for all HEAs in the present study (**Supplementary Figure S8**) and may be a general property of all high entropy systems such as high entropy alloys and high entropy ceramics.

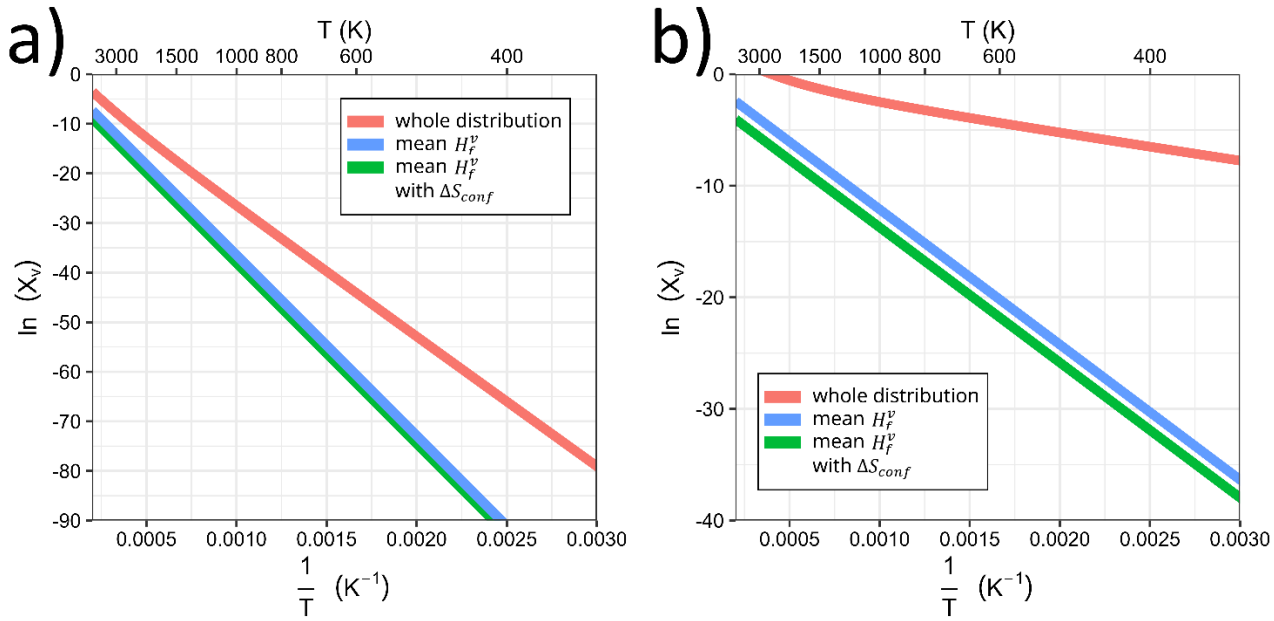


Figure 4. Equilibrium vacancy concentration versus temperature. For a) MoNbTaTiW; and b) HfNbTaTiZr. $\mathrm{X_v}$ is the equilibrium vacancy concentration, $\mathrm{X_v} = \frac{n}{N}$.

By considering the entire distribution of monovacancy formation in HEAs, it is possible to compute an effective $\mathrm{H_f^v}$ as if the solid solution were a pure element. For the alloys in this study, this result is significantly lower than the mean $\mathrm{H_f^v}$ that is typically used previously to predict vacancies in pure elements and dilute alloys:

$$\mathrm{H_f^v(effective)} = -\mathrm{k_B T ln}\left(\frac{\sum_{i=1}^{n}\frac{1}{m}e^{\frac{-\Delta \mathrm{H_f^v}(i)}{\mathrm{k_B T}}}}{n}\right) \tag{12}$$

where $\Delta\mathrm{H_f^v}(i)$ is the enthalpy of vacancy formation for the ith observation, and n is the number of observations. We compute the effective $\mathrm{H_f^v}$ for MoNbTaTiW and HfNbTaTiZr using **equation 12**. **Figure 5a** depicts the temperature dependence of the effective $\mathrm{H_f^v}$ for MoNbTaTiW. An effective H_f^v below 3.14 eV for MoNbTaTiW implies that monovacancies form much more easily at lower temperatures than if a simple average $\mathrm{H_f^v}$ is used. Similarly, **Figure 5b** illustrates effective $\mathrm{H_f^v}$ for HfNbTaTiZr. In both cases, the effective $\mathrm{H_f^v}$ is significantly lower than the mean $\mathrm{H_f^v}$ (MoNbTaTiW: 3.14 eV; HfNbTaTiZr: 1.04 eV).

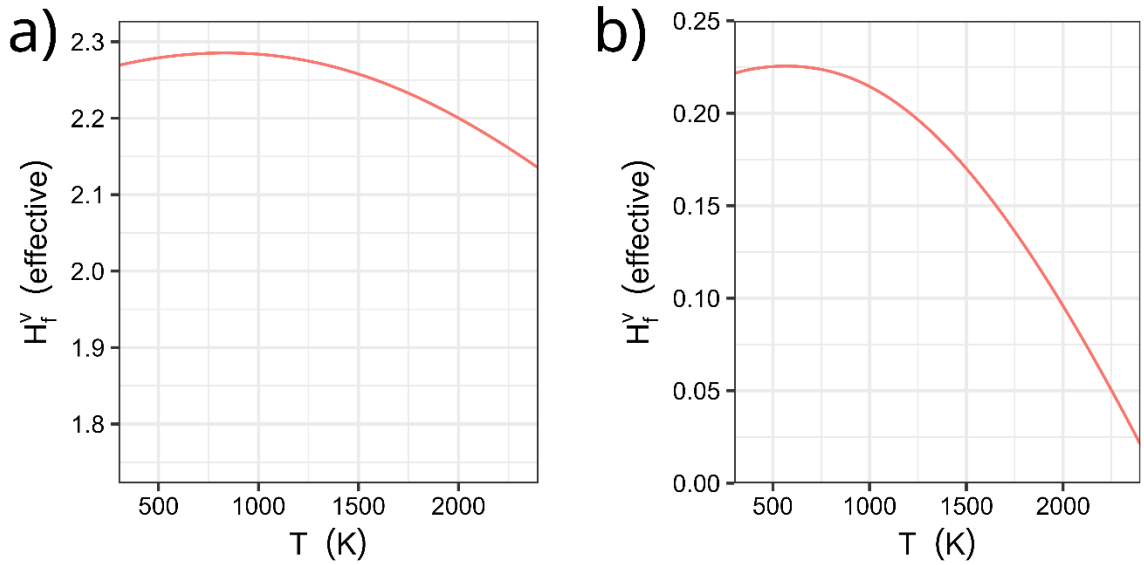


Figure 5. Effective $\mathbf{H_f^v}$ versus temperature. For a) MoNbTaTiW; and b) HfNbTaTiZr.

Our findings indicate that the higher equilibrium concentration of monovacancies observed experimentally in HEAs is primarily driven by the spread of vacancy formation enthalpies (H_f^v) inherent in these materials. Specifically, the deviation of the effective H_f^v from the mean H_f^v increases with the spread of H_f^v values (for example, shown in **Figure 2**), resulting in more vacancies than those predicted for simple pure metals and conventional alloys.

Summary

In this work, we examine the vacancy formation enthalpies and associated equilibrium vacancy concentrations of quinary alloys in the Hf-Mo-Nb-Ta-Ti-W-Zr system using density functional theory calculations. It is shown that while configurational entropy reduces vacancy concentration in these multicomponent systems, the lower tails in the enthalpy distribution caused by complex local environments around each vacancy lead to superabundant vacancies. This mechanism is likely to be active in both ordinary alloys and compositionally complex materials. This work provides insight into vacancy formation and equilibrium vacancy concentrations of high entropy alloys. Future analyses will investigate local ordering of elements and its effect on vacancy concentration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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