Entropy assisted stabilization as a way to improve deformability of refractory alloys

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Abstract

The deformation behavior of BCC alloys is sensitive to temperature, strain rate, and alloying elements which alter their unstable stacking fault energy (USFE). Effect of substitutional alloying elements in significant fractions have not been explored in detail for refractory BCC alloys. Substitutional elements may decrease USFE, which can improve their deformability. Special quasirandom structure (SQS) supercells are widely used to calculate the USFE of alloys. Such SQS attempt to mimic the random occupancy of each lattice site by the constituent elements. This approach does not guarantee the same stoichiometry in the shearing interface as in the alloy formula, which results in considerable variation in calculated USFE depending on the type and number of atoms in the two planes being sheared. Here we propose a modified SQS methodology with correct shearing interface chemistry to reliably calculate the USFE of concentrated alloys. In present work, enthalpy and ductility parameter is calculated using First-principles Density Functional Theory simulation. USFE of (110)<111> slip system is calculated for Group IV, V, VI elements & their 30 equiatomic binary alloys using a modified SQS methodology which reduces the number of DFT jobs required from the current 81 to 9. The deformability of refractory BCC alloys is correlated with their thermodynamic stability.

Keywords: stacking fault energy, deformability, high entropy alloys, special quasirandom structures
1 Introduction

The continued cost-pressures and ever stringent environmental norms have pushed aerospace and power generation industries to improve the overall efficiency of their jet-engines and gas-turbines [1]. Higher operating temperatures would lead to better thermodynamic efficiency in these propulsion and energy conversion systems [2, 3]. The Ni-based superalloys have ruled this application domain for the past more than six decades [4]. The melting point of the base metal Ni (T$_m$=1455°C) limits the highest operating temperature of these Ni-based superalloys [1, 5]. This emphasizes developing alloys which can sustain temperatures beyond current working temperatures of Ni-based superalloys [1]. The alloy developers are being pushed to look beyond traditional Ni-based superalloys for such high-temperature applications. Alloys based on refractory metals show great potential in this domain due to their ability to maintain mechanical properties at temperatures higher than current Ni-based superalloys [5].

Refractory alloys are based on Group IV, V, and VI metals [6–8]. These elements have very high melting-points (T$_m$>>1800°C) and BCC crystal structure which restricts their ductility at ambient temperatures. The lack of deformability at lower temperatures makes them difficult to manufacture, which creates a bottleneck in developing refractory alloys for various applications. Many approaches have been reported to ductilize refractory metals and alloys. Mo and W are made deformable after alloying with low stacking-fault energy elements [9, 10]. W is made deformable with Re addition which decreases shear resistance [11]. W is also made deformable by changing the nature of interaction between alloying elements [12]. Refractory alloys are explained to become deformable with HCP alloying additions which reduces the VEC [6, 13]. Nb-based refractory alloys are made deformable by altering the lattice distortion with appropriate alloying additions [14].

There have been conflicting suggestions about alloying additions to make W deformable. Qian et al. [12] suggests, “...addition of Mo, Re, and Os increases the ductility of W and decrease its GSFE as well as restoring force, whereas the effects of Ti, Ta, and V are contrary to those of Mo, Re, and Os. The above different effects of alloying elements may be primarily due to the fundamental repulsive/attractive nature of interaction between W and alloying element.” On the contrary, Shaikh et al. [6] and Sheikh et al. [13] suggests alloying with Ti, Zr, Hf, and Re (HCP elements) should ductilize the refractory alloys. None of the previous strategies discuss about the thermodynamic stability of these alloys. This calls for a comprehensive study on the role of various alloying elements on deformability and thermodynamic stability of refractory alloys.

A general theme in the existing refractory alloy ductilizing studies has been to add low stacking-fault energy ($\gamma_{sfe}$) elements to reduce the overall unstable-SFE ($\gamma_{usfe}$) of the alloy. Inadvertently, many of these studies conclude that the rule-of-mixtures (ROM) is a correct method to predict the $\gamma_{usfe}$ of alloys. Earlier studies have also suggested the amount of elements to be added to get the maximum ductilizing effect partially based on rule-of-mixtures (ROM) values. Most of the earlier studies selected alloying elements to get maximum decrease in the overall $\gamma_{usfe}$ of the alloy, without much consideration to the thermodynamic stability of the final alloy. There are many reports where the ROM has overestimated the final $\gamma_{sfe}$ of the alloy by an order of magnitude for FCC alloys (Table 1). Large decrease in $\gamma_{sfe}$ of FCC alloys due to alloying has already been observed in CoCrNi,
CoCrFeNi, CoCrFeMnNi as compared to their average $\gamma_{sfe}$ value (Table 1, [15–17]). However, there is a lack of comprehensive study on the effect of alloying additions on the deformability and thermodynamic stability of refractory alloys. Present work addresses these issues using first-principles density functional theory (DFT) simulations. Present study gives a strategy to select alloying elements which give maximum ductilizing effect along with thermodynamic stability of the final alloy.

Table 1: Comparison of ($\gamma_{sfe}^{(111)}<110>$, mJ/m$^2$) values of Ni, Fe, and NiFe (ROM-Rule-of-mixtures, DFT-Density functional Theory, TEM-Transmission electron microscope). Check for CoCrFeNi numbers. Calculate the Cr-FCC SFE and then use that value to calculate the average SFE of CoCrFeNi purely based on our DFT numbers.

| Metal/Alloy | ROM  | DFT   | TEM  |
|------------|------|-------|------|
| Fe-FCC     | –    | 260 [18] | –    |
| Ni         | –    | 127 [19] | 125 [20] |
| NiFe       | 193  | 102 [21] | 103 [20] |

2 Methods

Ti, Zr, Hf, V, Nb, Ta, Mo, W, Re, and their 30 equiatomic binary alloy systems (excluding alloys made up of only HCP elements) are studied using first-principles density functional theory simulations. Lattice parameter (a, Å), enthalpy of formation ($E_f$, eV/Atom), unstable stacking fault energy ($USFE, \gamma_{usfe}^{110}$, mJ/m$^2$), and surface energy ($\gamma_s^{110}$, mJ/m$^2$) is calculated for V, Nb, Ta, Mo, W, and 30 equiatomic binary alloys in BCC symmetry. For Ti, Zr, Hf, and Re, ($\gamma_{usfe}^{0001}$, mJ/m$^2$) is calculated for \{0001\}<1120> slip system, surface energy ($\gamma_s^{0001}$, mJ/m$^2$) is calculated for \{0001\} plane, lattice parameter (a, c, Å), and enthalpy of formation ($E_f$, eV/Atom) are calculated for HCP crystal structure. Experimental values of lattice parameters are taken from Ref.[22].

2.1 Special Quasirandom Structure

Special quasirandom structures (SQS) are used to capture chemical disorder in the alloys. SQS are generated using MCSQS code from Alloy Theoretic Automatic Toolkit (ATAT) [23, 24]. Pairs, triplets, and quadruplets correlations equal to the BCC unit cell lattice parameter are considered. We were able to get perfectly random correlations well within 48 hours. The enthalpy of formation ($E_f$) and lattice parameter are calculated with 128 atoms SQS generated using a BCC regular unit cell repeated four times each in <100> directions. In real alloy systems, the atoms do not remain at their ideal lattice sites due to stress fields of different chemical species present around each of the lattice sites. This deviation from ideality is calculated as root-mean-squared-deviation of the atoms from their ideal lattice sites. We have termed it as RLD in units of Å. The code to calculated RLD is given in Ref. [25].
2.2 First-principles calculations

The first-principles density functional theory (DFT) calculations were performed using Vienna Ab-initio Simulation Package (VASP) with plane-wave basis and projector augmented wave (PAW) pseudopotentials [26–28]. The electronic exchange-correlation effects were calculated by Perdew-Burke-Ernzerhoff generalized gradient approximation (PBE-GGA) [29, 30]. Methfessel-Paxton smearing method with 0.2eV width is used [31]. Structural relaxation is terminated when the forces on atoms become less than $10^{-4}$ eV/Å. Tetrahedron method with Blöch correction is used for accurate energy calculation [27].

3 Results

Refractory equiatomic binary alloys made from Group-IV (Ti, Zr, Hf), Group-V(V, Nb, Ta), Group-VI(Mo, W), and Group-VII(Re) elements are studied. The workflow to calculate lattice parameter, enthalpy of formation, root mean squared lattice distortion, unstable stacking fault energy, and surface energy is presented in Figure 1. The results are shown in the form of heat maps in Figure 2. Additional information can be found in supplementary information document.

3.1 Enthalpy of formation ($E_f$)

The enthalpy of formation ($E_f$) plays an important role in dictating the relative thermodynamic stability of alloys. $E_f$ is calculated with the relation [32],

$$E_{f}^{AB} = E_{AB} - \frac{E_A + E_B}{2}$$

where $E_{f}^{AB}$, $E_{AB}$, $E_A$, and $E_B$, are the enthalpy of formation of alloy AB, energy per atom of relaxed supercell of alloy AB in BCC symmetry, the energy of relaxed supercell of constituents A and B, respectively, all values are in the units of eV/Atom. The 9 alloying elements form a total of 36 equiatomic binary alloys. Out of these 36 alloys, 6 systems containing both the constituents being HCP, have been ignored. Figure 2a shows the enthalpy of formation ($E_f$, eV/Atom) values in the form of heat map. We have not considered VRe [33], TaRe [34], ZrW [35], VHf [36], VZr [37], having $E_f$, -0.2456, -0.1942, 0.1477, 0.1631, 0.1710 meV/Atom respectively, for subsequent analysis as they do not form stable BCC solid solutions at low temperatures at equiatomic concentration. The $E_f$ varies from -0.1232 eV/Atom for TaMo to 0.1114 eV/Atom for HfW. NbTa has the $E_f$ of -0.0067 eV/Atom which is closest to 0 eV/Atom.

$E_f$ plays an important role in defining the deformability of these alloys as depicted in Figure 4. The negative slope of the red line in Figure 4 shows the inverse correlation of enthalpy of formation with the change in unstable stacking-fault energy ($\gamma_{usfe}$) of alloys from their average values. $E_f$ defines the mutual attraction or repulsion between the constituents of the alloys. The more positive the $E_f$, the larger the repulsion between the constituents, which enhances the relative glide of slip planes over each other. Conversely, the more negative the $E_f$, the larger the attraction between the constituents, which hinders the easy glide of
the slip planes relative to each other. The present analysis proves our hypothesis that the
enthalpy of formation of alloys gives a fairly reliable idea about deformability of refractory
alloys apart from dictating their thermodynamic stability.

3.2 RMS lattice distortion (RLD)

Lattice distortion in the crystal is quantified using the radial distribution function (RDF),
a Fourier transform of the XRD curve [38]. The peak width of the RDF curve qualitatively
gives information about the deviations around the 1NN neighbor distance at which an atom
can be located. The RDF curve does not give accurate picture of the real lattice distortion
happening in real crystals.

Here we have used “root-mean-square lattice distortion (RLD)” method which is similar
to MSAD [39], to quantify the lattice distortion. Root-mean-squared lattice distortion
(RLD) captures the deviation of the crystal structure from its ideal BCC symmetry. RLD
is calculated using the relation,

\[
RLD = \sqrt{\frac{1}{N} \sum_n \sum_i (R_{ni}^n - R_0)^2}, \quad R_0 = \frac{a_0 \sqrt{3}}{2}
\]

where, \(R_{ni}^n\) is the distance between \(n^{th}\) atom and its \(i^{th}\) first nearest neighbor (1NN), \(R_0\) is
the ideal 1NN distance, \(a_0\) is the bulk lattice parameter of alloy in BCC symmetry, \(i\) is the
total number of 1NN for each lattice site (equal to 8 in BCC), \(n\) is the total number of atoms
in supercell (equal to 128), \(N\) is the total number of 1NN in the supercell (equal to 1024,
8 for every atom in the supercell). This approach ensures that the negative and positive
distortions in the crystal are captured correctly and are not canceled out by the opposite
signs of either distortions. We have calculated the RDF of an ideal NbTi crystal with lattice
parameter of 3.278 (unrelaxed). For an ideal crystal there should not be any peak-width in
the RDF curve. However we observe a peak width of 0.235Å. With our RLD code [25], we
get the correct lattice distortion of 0Å.

Figure 2b shows the RLD values in the form of heat map for alloys. The RLD value
ranges from 0.00Å for VW to 0.29Å for VZr. The RLD is higher for alloys having positive
\(E_f\) (larger diameter circles in Figure 4) and vice-versa. It means very positive \(E_f\) can lead to
large distortion in the crystal and may alter the BCC symmetry of the lattice. Therefore we
have put a threshold of ±0.12eV/Atom on \(E_f\). This criteria ensure that the alloys remain in
BCC symmetry with minimum lattice distortion. Alloys having \(E_f<0.12\) eV/Atom are not
considered in present study as they may form ordered intermetallics which could be brittle.
Similarly, alloys having \(E_f>0.12\) eV/Atom are not considered in the present study as they
may lead to extremely large lattice distortions.

3.3 Unstable stacking-fault energy \((\gamma_{usfe})\)

The chemistry of the shearing interface affects the overall \(\gamma_{sfe}\) of the alloy in concentrated
solid solutions [40]. The intrinsic \(\gamma_{sfe}\) of alloys can vary over a large range of 150mJ/m² [40].
Earlier reports did not consider the chemistry of the shearing interface which influences the
\(\gamma_{usfe}\) of the overall alloy [12, 20, 41–49].
For $\gamma_{\text{usfe}}$ calculation of pure elements the supercell had 48 atoms with 10 Å vacuum. The x, y, z axes of supercell of pure BCC elements were aligned in $<111>$, $<11\bar{1}>$, and $<110>$ directions respectively. The x, y, z axes of supercell of pure HCP elements were aligned in $<2\bar{1}10>$, $<1120>$, and $<0001>$ directions respectively. The $<111>$ slip direction of BCC crystal is similar to $<2\bar{1}10>$ slip direction of HCP crystal. Therefore, the $\gamma_{\text{usfe}}^{\{111\}<111>}$ of BCC elements is reported along with the $\gamma_{\text{usfe}}^{\{0001\}<2\bar{1}10>}$ of HCP elements.

For $\gamma_{\text{usfe}}$ calculations of alloy, the supercell had 120 atoms and 9 shearing interfaces. The x, y, z axes of supercell were aligned in $<111>$, $<11\bar{1}>$, and $<110>$ directions of a regular BCC unit cell respectively. The supercells are manipulated using Atomsk [50]. A vacuum of 10 Å is added perpendicular to the slip planes (along $<111>$ direction) to prevent interactions between faults due to periodic boundary condition. Equiatomicity is maintained at the shearing interface by shifting the respective planes towards the centre of the supercell. The atoms in top two planes and bottom two planes are fixed in all directions, whereas, the remaining atoms from the middle six planes are fixed only in slip direction. The supercells are sheared by one complete $\vec{b}=<111>$ vector to get four different $\gamma_{\text{usfe}}$ values as shown in Figure 1. For every supercell, the energy difference between before and after one complete slip along $\vec{b}$ is calculated. A total of four differences are calculated as shown in Figure 1. $\gamma_{\text{usfe}}$ is calculated for shearing direction having the lowest difference between no-slip and full-slip. The entire process is schematically represented in Figures 1 and in supplementary file. $\gamma_{\text{usfe}}$ is calculated using the relation given below,

$$\gamma_{\text{usfe}} = \frac{E_{\text{faulted}} - E_{\text{pristine}}}{(\text{Area of Plane})}$$

where the $E_{\text{faulted}}$ is the energy of supercell having unstable stacking fault and the $E_{\text{pristine}}$ is the energy of pristine supercell.

Figure 2c shows the $\gamma_{\text{usfe}}$ calculated using first-principles DFT method (for pure metals), and using rule-of-mixtures (for alloys) in the form of heat map. The $\gamma_{\text{usfe}}$ values of pure metals ranges from 1773 mJ/m$^2$ (W) to 457 mJ/m$^2$ (Zr). WRe (1670 mJ/m$^2$) has the highest $\gamma_{\text{usfe}}$ value whereas, TiZr (460 mJ/m$^2$) has the lowest $\gamma_{\text{usfe}}$ value. Figure 2d shows the $\gamma_{\text{usfe}}$ calculated using First-principles DFT method, in the form of heat map for pure elements and the alloys under study. MoW (1681 mJ/m$^2$) has the highest $\gamma_{\text{usfe}}$ value whereas, TaZr (454 mJ/m$^2$) has the lowest $\gamma_{\text{usfe}}$ value. Figure 2e shows the % change in $\gamma_{\text{usfe}}$ values of the alloys from their average values. The percentage change in $\gamma_{\text{usfe}}$ values from their average value ranges from -41% (MoRe) to 20% (MoV). The largest percentage reduction in $\gamma_{\text{usfe}}$ value is for MoRe (41%) and WRe (34%). The smallest percentage reduction in $\gamma_{\text{usfe}}$ is for NbTa (4%). The largest percentage increase in $\gamma_{\text{usfe}}$ is for MoV (20%) and the smallest percentage increase is for MoW (5%).

The present analysis shows many possible alloy combinations which can lead to reduced $\gamma_{\text{usfe}}$ in refractory binary alloys from their average values. This study leads to various alloy chemistries, which can give enhance deformability (by having low $\gamma_{\text{usfe}}$ and a large reduction in $\gamma_{\text{usfe}}$ once alloyed). There are numerous studies on deformability studies on Al/Nb/Mo-Ta-Ti-Zr-Hf-V alloy and its sub-systems [13, 51–55]. NbTaTiZrHf is reported to have more than 50% room temperature ductility [56, 57]. $A_{0.5}NbTa_{0.8}Ti_{1.5}V_{0.2}Zr$ is reported to be the most ductile refractory alloys with BCC-B2 microstructure, which is analogous to $\gamma-\gamma'$ type
microstructure of Ni-based superalloys [58]. Our previous study has shown that there are many potential refractory alloy systems having good combination of strength and ductility [59]. The alloys having good ductility/deformability contains Ti/Zr/Hf elements [59]. These HCP elements inherently have low $\gamma_{\text{usfe}}$ which reduces the alloy’s $\gamma_{\text{usfe}}$ and in turn improve its deformability (Figure 2). Once added to the alloy, they reduce the overall $\gamma_{\text{usfe}}$ of the alloy and in-turn make the alloy ductile/deformable. Adding Ti/Zr/Hf could improve the overall deformability of refractory alloys at the cost of decreased oxidation resistance as these HCP elements are susceptible to oxygen absorption [60, 61].

### 3.4 Surface energy ($\gamma_s$)

Our approach ensures that only the surface having equiatomic composition is exposed to vacuum. $\gamma_s$ is calculated using the supercells used to calculate the $\gamma_{\text{usfe}}$. The equiatomic shearing interface of the supercell is exposed to vacuum of 10Å. $\gamma_s$ is calculated using the relation given below,

$$\gamma_s = \frac{E_{\text{with-vacuum}} - E_{\text{no-vacuum}}}{2 \times (\text{Area of Plane})}$$

For Ti, Zr, Hf, and Re, the $\gamma_s$ is reported for (0001) plane. The $\gamma_s$ of pure metals ranges from 1586 mJ/m$^2$ (Zr) to 3267 mJ/m$^2$ (W). In alloys, MoW (3045 mJ/m$^2$) has the highest $\gamma_s$ value whereas, NbZr (1662 mJ/m$^2$) has the lowest $\gamma_s$ value.

### 3.5 Deformability parameter (D)

Deformability parameter is defined as the ratio of surface energy to unstable stacking fault energy [62, 63].

$$D = \frac{\gamma_s}{\gamma_{\text{usfe}}}$$

- $D > 1 \implies \gamma_s > \gamma_{\text{usfe}} \implies \text{Ductile}$
- $D < 1 \implies \gamma_s < \gamma_{\text{usfe}} \implies \text{Brittle}$

It quantifies the competition between the energy cost of creating a new crack surface and the energy cost of nucleating new dislocations in the stress field of the crack tip. The D also captures the brittle-to-ductile-transition of refractory alloys (BDT) [64–66] if the similar calculations are done across various temperature ranges. Present study uses first-principles density functional theory simulations to calculate D-parameter at absolute zero temperature. It may not give the complete picture of the deformability of these alloys as we are not calculating these properties across range of temperatures. However, the present study correctly captures the relative thermodynamic stability and deformability of these alloys.

Figure 2f shows the ductility parameter calculated for pure metals and alloys in the form of heat map. The D-parameter of pure metals ranges from 1.64 (Re) to 4.21 (Ti). TaTi (4.16) has the highest D-parameter value whereas, MoW (1.81) has the lowest D-parameter value. The improved deformability of WRe(D=3.15) and MoRe(D=2.70) does not look so large if we observe only their average $\gamma_{\text{usfe}}$ and $\gamma_s$. However, their improved deformability is well depicted in Figures 2f.
4 Figures

Figure 1: Workflow.

 Alloy

Calculate enthalpy, lattice parameter, RMSD

Generate SQS with pairs, triplets, and quadruplets

Relaxed SQS + 10Å Vacuum

Select equiatomic shearing interface

Shear

Exposure to 10Å vacuum

Calculate $\gamma_{usfe}$ for min. $\Delta_i$

$\gamma_{alloy} / \gamma_{usfe}$

$D = \frac{\gamma_{surface}}{\gamma_{usfe}}$
|   | Ti | Zr | Hf | V  | Nb | Ta | Mo | W  | Re |
|---|----|----|----|----|----|----|----|----|----|
| Ti | 0.07 | 0.03 | 0.11 | 0.06 | 0.07 | 0.10 | 0.00 | 0.07 | 0.01 |
| Zr | 0.17 | 0.06 | 0.11 | 0.05 | 0.05 | 0.13 | 0.00 | 0.07 | 0.01 |
| Hf | 0.16 | 0.06 | 0.11 | 0.01 | 0.11 | 0.05 | 0.00 | 0.07 | 0.01 |
| V  | 0.07 | 0.03 | 0.06 | 0.06 | 0.07 | 0.10 | 0.00 | 0.07 | 0.01 |
| Nb | 0.03 | 0.06 | 0.05 | 0.07 | 0.07 | 0.06 | 0.00 | 0.07 | 0.01 |
| Ta | 0.11 | 0.16 | 0.07 | 0.07 | 0.10 | 0.06 | 0.00 | 0.07 | 0.01 |
| Mo | 0.09 | 0.03 | 0.01 | 0.01 | 0.12 | 0.06 | 0.00 | 0.07 | 0.01 |
| W  | 0.03 | 0.06 | 0.06 | 0.07 | 0.07 | 0.06 | 0.00 | 0.07 | 0.01 |
| Re | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 | 0.01 | 0.00 | 0.07 | 0.01 |
|   | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |

(a) Enthalpy of formation (eV/Atom).

(b) RLD (Å)

(c) Average \( \gamma_{usfe} \) (mJ/m²)

(d) \( \gamma_{usfe} \) DFT (mJ/m²)

(e) Change in \( \gamma_{usfe} \) (%)

(f) Ductility parameter, D

Figure 2: Heat maps. Alloys containing both HCP constituents are not considered.
Figure 3: $\{110\}<111> \gamma_{usfe}$ of (a)Nb with Ta and (b)Nb with Ti. Numbers in blue show the change in $\gamma_{usfe}$ from the average value.

Figure 4: Change in $\gamma_{usfe}$ as compared to the average value vs enthalpy of formation ($E_f$). Lower enthalpy of formation helps improving the deformability of refractory binary alloys. RLD is shown as circle with different diameters.
Figure 5: (a) Comparison between $\gamma_{usfe}$ values calculated from same supercell but across shearing interfaces for WRe. Numbers on right shows the shearing interface. Numbers on left shows the $\gamma_{usfe}$ value. Upper inset shows the range of $\gamma_{usfe}$ obtained from the same supercell. Lower inset shows the energy difference between before and after 1 complete slip by $\bar{b} = \frac{a}{2} <111>$. (b) Chemistry of the shearing interfaces.
Figure 6: HCP slip system comparison. (a) Zr (0001)<11\bar{2}0> slip curve, (b) Zr (0001)<11\bar{2}0> slip direction projection along <0001> direction, (c) Zr (0001)<\bar{1}100> slip curve, (d) Zr (0001)<\bar{1}100> slip direction projection along <0001> direction.
5 Discussion

5.1 Why equiatomic?

Figure 3a and 3b shows the $\gamma_{usfe}$ values for Nb$_x$Ta$_{1-x}$ and Nb$_x$Ti$_{1-x}$ ($x \in [0,0.25,0.75,1]$) respectively. In Figure 3a, the numbers in blue show the reduction in $\gamma_{usfe}$ of Nb$_x$Ta$_{1-x}$ alloy from the average value. The largest reduction in $\gamma_{usfe}$ occurs at equiatomic concentration (-43 mJ/m$^2$). Similarly, the largest reduction in $\gamma_{usfe}$ (-163.5 mJ/m$^2$) of Nb$_x$Ti$_{1-x}$ occurs at equiatomic concentration (Figure 3b).

We have analyzed the alloys made from both the BCC-BCC (Nb-Ta) and BCC-HCP (Nb-Ti) elemental combination. The highest reduction in $\gamma_{usfe}$ value occurs at the equiatomic concentration, irrespective of the prior BCC/HCP crystal structure of the pure metal constituents. The highest reduction in $\gamma_{usfe}$ gives a direction for improving the deformability of refractory alloys with appropriate alloying additions. Present analysis is similar to an earlier study done by Yang and Qi in Ref. [10] where W-Ta and W-Re alloy systems become intrinsically ductile at equiatomic concentrations. The enhancement in intrinsic ductility is concluded to be due to the preference for dislocation emission in $\frac{a}{2}<111>\{\bar{1}10\}$ slip system at crack tip. That means the largest ductilizing effect of alloying elements is possible at equiatomic concentrations. Therefore we have considered only the equiatomic alloys in present study.

5.2 Shearing interface chemistry

Special quasirandom structures (SQS) have been extensively used to predict the SFE of alloys due to their simplicity in capturing the inherent chemical disorder present in the alloys [67]. There have been numerous reports on SFE of concentrated alloys calculated using SQS, albeit without any consideration to the shearing interface chemistry [12, 20, 41–49]. There has been significant deviations in the literature about the reported $\gamma_{usfe}$ values even for the pure metals [9, 16]. The literature talks about the accuracy of SQS method for planar defect calculations, but the shearing interface chemistry was not considered [68]. This emphasises the need for a reliable methodology to calculate $\gamma_{usfe}$ and $\gamma_s$ of concentrated alloys. The SQS are generated, considering the correlations of pairs, triplets, quadruplets. Figure 5 shows how the generated SQS can lead to incorrect composition at the shearing interface. However, the composition at the shearing interface 5,6 and 8,9 is same as required, i.e. equiatomic (Figure 5b). Therefore the USFE value should be calculated for the shearing interface 5,6 and 8,9 (Figure 5b).

Figure 5 shows how the same SQS can give a range of $\gamma_{usfe}$ values depending on the chemistry of the shearing interface for WRe alloy. The upper inset in Figure 5a shows the $\gamma_{usfe}$ values. The lower inset shows the energy difference between before and after 1 complete slip by $\bar{b}=rac{a}{2}<111>$. The $\gamma_{usfe}$ varies from 906 to 1199 mJ/m$^2$. Similarly the energy difference between before and after 1 complete slip varies from 0.5 to 109 mJ/m$^2$ (Figure 5a). It means that the $\gamma_{usfe}$ of WRe alloy can be any value between 905.5 to 1308 mJ/m$^2$. Such large variation in $\gamma_{usfe}$ poses a challenge as to which value to be selected for further analysis. Our current methodology eliminates this ambiguity by maintaining equiatomicity at the shearing interface and ensuring that only those curves are studied for which the energy
difference between 0-slip and 1-slip remaines within ±3meV/Atom. The concentration at the shearing interface always remains same as formula composition of the alloy therefore our current methodology minimizes the errors associated with the incorrect chemistry at the shearing interface which helps in accurately predicting the $\gamma_{usfe}$ and $\gamma_s$ of concentrated alloys.

5.3 Slip system

The $<111>$ slip direction of BCC crystal is similar to $<11\overline{2}0>$ slip direction of HCP crystal (Figure 6a,6b). Both the slip direction has only one peak in their slip curve. Generally in literature, the $<1\overline{1}00>$\{0001\} (Figure 6c,6d) slip curve of HCP metals and alloys is emphasized as the slip in this direction leads to a stable stacking fault. However, the BCC crystal system does not have any stable stacking fault for $<111>$\{110\} slip system. Therefore, we believe the $\gamma_{usfe}^{\{110\}<111>}$ of BCC elements/alloys should be compared with the $\gamma_{usfe}^{\{0001\}<11\overline{2}0>}$ of HCP elements/alloys for correct analysis.

5.4 $E_f$ vs. Deformability of alloys

The $E_f$ defines the relative thermodynamic stability of an alloy. $E_f$ also describes the bonding characteristics of the alloy constituents. Highly negative $E_f$ means stronger bonds between the alloy constituents and vice-versa. Strong interaction between the alloy constituents also means their resistance to deformation will be high and vice-versa. Very large negative $E_f$ also means that the alloy is no longer an disordered mixture of its constituents, rather it has been converted into an ordered intermetallic, which are extremely brittle, e.g. ordered-Ni$_3$Al in superalloys [4]. Figure 4 shows how increased $E_f$ leads to large reduction in $\gamma_{usfe}$ of alloys. Figure 2f shows the large variation in the D-parameter value of various alloys.

6 Conclusion

In the present work, we have researched a strong correlation between the thermodynamic stability of refractory alloys and their deformability. We have developed a methodology to select alloying elements which help make alloys deformable without much loss in their strength. We have developed a reliable and scalable framework to accurately predict stacking fault energies, surface energies, and in turn deformabilities of concentrated alloys. Our present work sheds light on the long standing controversy surrounding the effect of valence electron concentration which was supposed to dictate the ductility of refractory alloys. Here we have proved that VEC may not be the most accurate measure of deformability of refractory alloys. Our present work helps simultaneously tackle 2 major issues associated with refractory alloy development for high temperature applications:

1. There exists an inverse correlation between the enthalpy of formation and the deformability of refractory alloys. Slight positive enthalpy of formation can improve deformability without much compromise on the thermodynamic stability of refractory alloys.
alloys. The increase in the temperature will only lead to improved stability of the alloys by $\Delta G = \Delta H - T\Delta S$ type relationship. We believe our findings will further be reinforced once a similar study is done at higher temperatures.

2. Earlier methods did not focus on the chemical composition of the surface and shearing interface while calculating surface energies and stacking fault energies. Our method ensures that we are accurately capturing the correct formula chemistry of the alloys while predicting those properties.

7 Declarations

7.1 Funding

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7.2 Competing interest

The authors declare no competing interests.

7.3 Authors’ contributions

S.M.S. performed the calculations and drafted the initial manuscript. S.M.S. and S.K.Y. developed the initial hypothesis. S.M.S., S.K.Y., and B.S.M. together discussed the results. S.K.Y. and B.S.M. supervised the project. All authors contributed to the manuscript writing.

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