

Entropy-stabilized binary alloys

Rafshan Ul Atik^{a,b}, Sufyan M. Shaikh^{a,b}, Hitanshu Sachania^a, Satyesh K. Yadav^{a,b,*}

^a Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, 600036, Tamil Nadu, India

^b Center for Atomistic Modeling and Materials Design, Indian Institute of Technology Madras, Chennai, 600036, Tamil Nadu, India

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ABSTRACT

Alloying W with Re is an effective method for improving its intrinsic ductility. The solubility limit of Re in W is $\sim 27\%$ at 851 K. However, this alloy possesses a high enthalpy of formation, which can result in phase-instability. Configurational entropy alone cannot stabilize this alloy as a single-phase solid solution. Recent research questions the importance of configurational entropy in determining the single-phase stability of “complex, concentrated solid solutions” and suggests that vibrational entropy may play a critical role. The question arises: Can vibrational entropy contribute significantly enough to ensure single-phase stability in a binary alloy? Our first-principles phonon calculations using density functional theory demonstrate that vibrational entropy is equally essential as the configurational entropy in promoting the formation of a single-phase solid solution in WRe binary alloys. This finding necessitates revisiting the role of vibrational entropy in the single-phase stability of binary alloys.

Historically, ductilization of W at low temperatures involves addition of HCP element Re [1–3]. Recently Shaikh *et al.* found that alloying with elements that decrease the unstable stacking fault energy (γ_{usfe}) of the alloys from their composition averaged value, $\Delta\gamma_{usfe}$ can enhance its intrinsic ductility [4]. Specifically, the equiatomic BCC WRe alloy displays a remarkable 35% reduction in γ_{usfe} . Furthermore, a strong inverse correlation between $\Delta\gamma_{usfe}$ and enthalpy of formation ($\Delta_f H$) has been found. The BCC W-25%Re alloy exhibits a high positive $\Delta_f H$ of 45 meV/atom [5]. The maximum solubility of 25%Re in W is found at a temperature of 581 K [6]. The contribution of ideal configurational entropy to the free energy at this temperature amounts to a mere 20 meV/atom, which is inadequate to render the alloy stable as a single-phase solid solution.

Using the Debye–Grüneisen model, Ma *et al.* found that the absolute value of vibrational entropy of equiatomic CoCrFeMnNi high entropy alloy is five times larger than configurational entropy [7]. They suggested that non-configurational entropies, while hitherto neglected, are salient to determining phase stability and can potentially contribute up to 50% to the total entropy of formation at 1200 K. However, the highest stabilizing effect of the vibrational entropy for any binary alloys is reported as 21% of the overall formation entropy at 1000 K in the equiatomic Ni-Rh alloy [8]. We hope that vibrational entropy may be equally significant as configurational entropy in the single-phase stability of WRe binary alloys due to the significant lattice distortion inherent

in them [9] and the dissimilar stable crystal structures of its constituent elements. Present study endeavors to ascertain the subtle balance of vibrational entropy, configurational entropy, and enthalpy of formation, along with their influence on the phase stability of the binary system of W-50%Re and W-25%Re alloys using first-principles phonon calculations via density functional theory (DFT).

For any solid solution, the stability of a phase under constant pressure is determined by Gibbs energy of formation ($\Delta_f G$), expressed as

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

where $\Delta_f S$ is the entropy of formation of the alloy. An alloy is thermodynamically stable as a single-phase solid solution when $\Delta_f G < 0$. Phase stability under constant volume is dictated by Helmholtz energy of formation $\Delta_f A$, which is given as

$$\Delta_f A = \Delta_f U - T\Delta_f S \quad (2)$$

Here $\Delta_f U$ denotes the internal energy of formation. All the extensive thermodynamic formation properties are evaluated based on the difference of extensive thermodynamic properties (Y , where $Y = H, S, U, A, G$) of the alloy from its composition-averaged value through the use of the expression

$$\Delta_f Y = Y_{\text{alloy}} - \sum_{i=1}^c x_i Y_i \quad (3)$$

* Corresponding author at: Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, 600036, Tamil Nadu, India.
E-mail address: satyesh@iitm.ac.in (S.K. Yadav).

where x_i is the atom fraction of component i in the solution, c is the total number of components present in the solution, Y_{alloy} and Y_i are the extensive thermodynamic property of the alloy in the required crystal structure and the individual components in their most stable phase respectively. It should be noted that Huang *et al.* [10] and Wróbel *et al.* [11] have computed the “enthalpy of mixing” for W-Re system, which is found to be negative. This is due to Re being modeled as BCC (same crystal structure as that of W-Re solid solution) despite the most stable phase of Re being HCP. In our study, we have calculated the “enthalpy of formation” for the alloy, which is evaluated by considering pure components in their respective most stable phases (BCC W and HCP Re). As a result, the “enthalpy of formation” for the W-Re solid solution is positive. Alloys having positive $\Delta_f H$ are susceptible to phase separation or may exhibit a miscibility gap at low temperatures unless the condition $|\Delta_f H| < |T\Delta_f S|$ is satisfied with $\Delta_f S > 0$. In such a scenario where entropic contribution $|T\Delta_f S|$ assists in overcoming a substantially large positive $\Delta_f H$ and enables the alloys to remain stable as a single-phase solid solution, we call such types of alloys as “entropy-stabilized alloys.”

The total entropy of formation ($\Delta_f S$) of an alloy has contributions from configurational ($\Delta_f S^{\text{conf}}$), vibrational ($\Delta_f S^{\text{vib}}$), electronic ($\Delta_f S^{\text{elec}}$) and magnetic entropy of formation ($\Delta_f S^{\text{mag}}$). The ideal configurational entropy of formation of any random substitutional solid solution is

$$\Delta_f S^{\text{conf}} = -k_B \sum_{i=1}^c x_i \ln x_i \quad (4)$$

where k_B is the Boltzmann constant, x_i is the mole fraction of component i in the solution. We have modeled WRe binary alloys as an ideal random solid solution. However, the configurational entropy value in real systems tends to be lower than ideal solutions due to local short-range ordering at low temperatures [12]. The $\Delta_f S^{\text{vib}}$ can either stabilize (positive value) or destabilize (negative value) the system, depending on the difference in the interactions between the alloy constituents [13]. Since WRe binary alloys and their constituents are all metallic, the contribution of $\Delta_f S^{\text{elec}}$ to the free energy (i.e., A and G) of formation is negligible. Hence, we can ignore $\Delta_f S^{\text{elec}}$. The $\Delta_f S^{\text{mag}}$ can also be conveniently ignored for the paramagnetic WRe system. Therefore, the equation that describes $\Delta_f S$ for WRe system can be expressed as

$$\Delta_f S = \Delta_f S^{\text{conf}} + \Delta_f S^{\text{vib}} \quad (5)$$

Special quasi-random structures (SQS) capture the chemical disorder present in a random substitutional solid solution. We used 64-atom BCC SQS of W-50%Re and W-25%Re alloy generated using the MC-SQS code as implemented in the Alloy Theoretic Automated Toolkit (ATAT) [14,15]. We were able to attain a perfect match of the pairs, triplets, and quadruplets correlation functions with a cut-off distance that equals to the BCC unit cell lattice parameter (the second nearest neighbor distance) with the random solid solution. Geometric relaxations of SQS were done in the framework of DFT using Vienna Ab-initio Simulation Package (VASP) with plane-wave basis cut-off of 520 eV and projector augmented wave (PAW) pseudopotentials [16–18]. We used Perdew-Burke-Erzerhoff generalized gradient approximation (PBE-GGA) exchange-correlation functional for the calculation [19,20]. Sampling of the Brillouin zone was done through the Monkhorst-Pack scheme using an automatically generated mesh with k-point spacing of less than $2\pi \times 0.03 \text{ \AA}^{-1}$ [21]. First-order Methfessel-Paxton smearing method with a width of 0.2 eV was utilized [22]. Relaxation was done until the forces on the atoms converged to 0.5 meV/\AA .

The resultant relaxed SQS were used for phonon calculation through the finite difference method implemented in Phonopy code [23,24]. For each SQS, 384 displaced structures were generated, with the displacement for each atom being 0.01 \AA in x-, y-, and z-direction. A strict energy convergence criterion (10^{-7} eV) was applied for the electronic relaxation of each displaced supercell. The computation of force constants, dynamical matrix, phonon frequencies, and eigenvectors with a q-point grid of $64 \times 64 \times 64$ was performed after calculating the Hellmann-

Feynman forces on each atom of the supercells. The calculated phonon frequencies are subsequently used to derive the phonon density of states (DOS) by numerically integrating over the Brillouin zone. Harmonic phonon energy of the crystal (U_{phonon}) at constant volume can then be obtained from the resulting phonon DOS based on the canonical distribution in statistical mechanics for phonon [25]. Vibrational entropy (S^{vib}) as a function of temperature can be calculated using thermodynamic relation [25]. Phonon contribution to the free energy at constant volume or Helmholtz energy for a unary system can then be evaluated using the expression

$$A_{\text{phonon}} = U_{\text{phonon}} - TS^{\text{vib}} \quad (6)$$

We introduced volume-dependence of phonon properties using quasi-harmonic approximation (QHA) of phonons [23], where the thermal property calculations were independently done at seven different volumes. The structure of a crystal at any temperature will be in a state of equilibrium with the lowest free energy. Thus Gibbs free energy G at constant pressure for the random solid solution can be evaluated as

$$G(T, p) = \min_V [U(V) + A_{\text{phonon}}(T; V) + pV - TS^{\text{conf}}] \quad (7)$$

where V and p are the volume and pressure respectively, $U(V)$ is the DFT total energy of the system at respective volume, and S^{conf} is the ideal configurational entropy of an alloy, which is inherently zero for its components.

We have examined the temperature-dependent behavior of the absolute values of vibrational entropy (S^{vib}) of W-50%Re and W-25%Re alloys, along with their constituent elements. The results, obtained through the harmonic approximation, reveal that despite having a similar mass, S^{vib} of Re consistently exceeds that of W by a significant margin across all temperatures, as shown in Fig. 1a. Furthermore, the W-50%Re alloy exhibits a higher S^{vib} than the W-25%Re alloy. The S^{vib} value of the W-50%Re alloy surpasses that of pure Re. This trend can be explained using the phonon DOS, which exhibits two salient peaks for all the systems at their respective equilibrium volumes. Pure Re has a large number of low-frequency phonons compared to pure W. This distinction is apparent in the phonon DOS, where the peaks of Re are situated at lower frequencies than those of W. Such disparity can be attributed to the presence of distinct stable phases of Re (HCP) and W (BCC) at $T = 0$ K. For both W-25%Re and W-50%Re alloys, there is a resemblance in the shape of the phonon DOS to that of BCC W. However, a noticeable shift towards lower frequencies has been noted for both peaks as the concentration of Re in W increases (see Fig. 1b). These findings are consistent with earlier investigations [26]. This observation suggests that adding Re in W weakens its bond strength due to phonon softening, consequently increasing the vibrational entropy.

In the framework of the quasi-harmonic approximation, it is observed that S^{vib} values for both the alloys and their constituent elements are higher than the values obtained under the harmonic approximation. Specifically, S^{vib} of Re demonstrates a more rapid increase at elevated temperatures compared to the alloy W-50%Re, as illustrated in Fig. 2a. However, the relative values of S^{vib} as a function of temperature remain consistent. Both the W-25%Re and W-50%Re alloys display a steep ascent in their S^{vib} with rising temperature, reaching the values of 0.74 meV/K.atom and 0.76 meV/K.atom , respectively, at 1200 K. These values exceed their corresponding configurational entropy (S^{conf}) by 15 and 13 times, respectively, highlighting the substantially large values of the vibrational entropy in these alloys at high temperatures. However, the absolute values of entropy are not significant in determining the phase stability of a solid solution. Rather, the entropy of formation is crucial in assessing the phase stability of the solid solution.

We have computed the entropy of formation ($\Delta_f S^{\text{vib}}$) for W-50%Re and W-25%Re as a function of temperature (see Fig. 2b). In both instances, under harmonic approximation, $\Delta_f S^{\text{vib}}$ initially exhibits a rapid increase with temperature. However, beyond ~ 100 K, this growth diminishes and subsequently maintains a constant value even as the

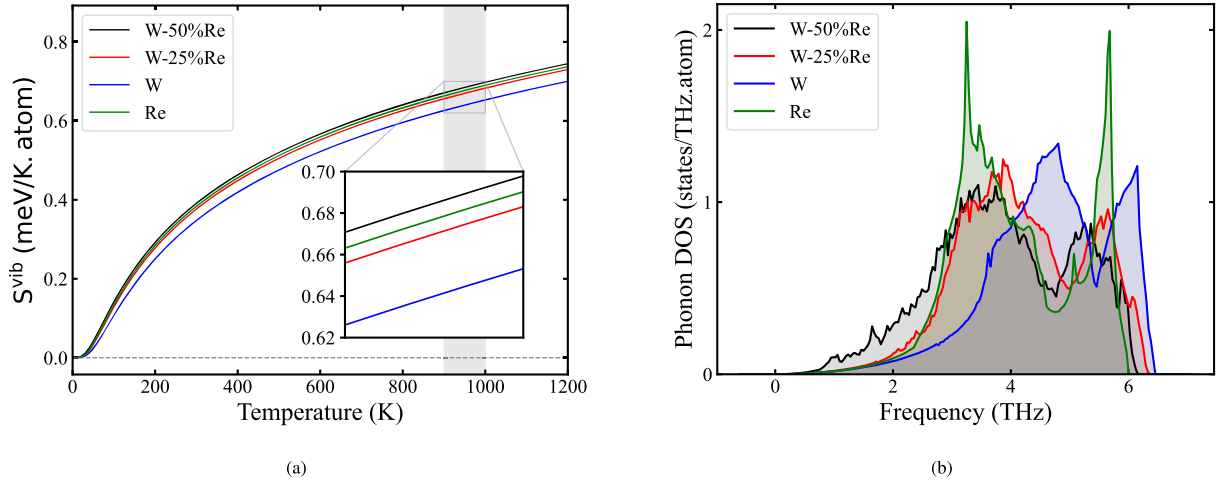


Fig. 1. Temperature dependence of (a) absolute vibrational entropy (S^{vib}) under harmonic approximation and (b) Phonon DOS plot for pure W, pure Re, W-50%Re, and W-25%Re alloy. Note that the DOS of all the systems is calculated at their respective equilibrium volumes at $T = 0$. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

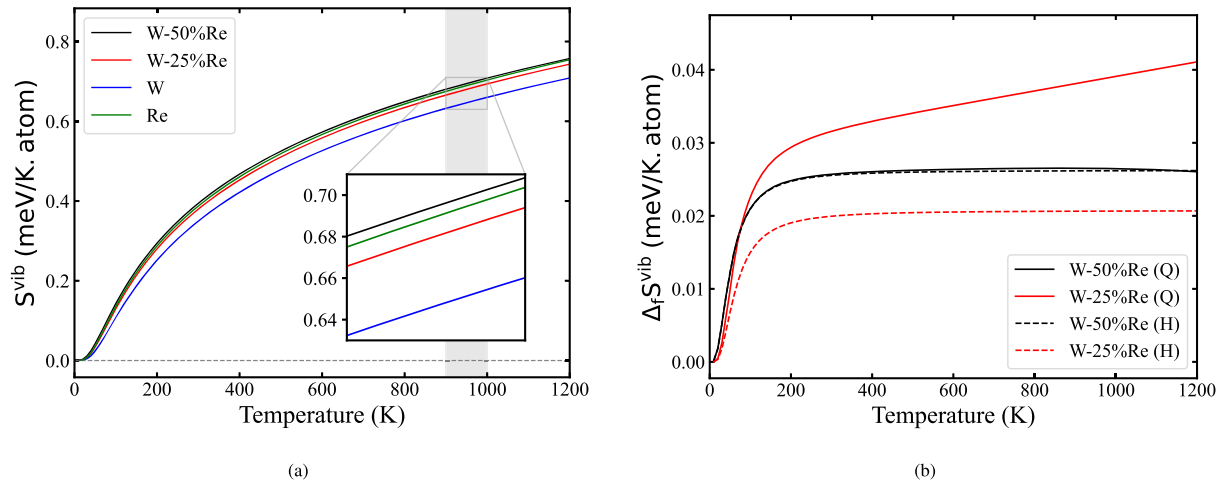


Fig. 2. Temperature dependence of (a) absolute vibrational entropy (S^{vib}) under quasi-harmonic approximation and (b) vibrational entropy of formation ($\Delta_f S^{\text{vib}}$) under harmonic (H) and quasi-harmonic (Q) approximation.

temperature continues to rise. Additionally, it was noted that the W-50%Re alloy displayed a greater $\Delta_f S^{\text{vib}}$ than the W-25%Re alloy across all temperature ranges. Nevertheless, a reversed trend is observed under quasi-harmonic approximation. Specifically, above ~ 100 K, W-25%Re exhibits a larger $\Delta_f S^{\text{vib}}$ compared to W-50%Re alloy. The $\Delta_f S^{\text{vib}}$ of W-50%Re, computed using the quasi-harmonic approximation, shows a negligible deviation in comparison to the values obtained through the harmonic approximation. However, $\Delta_f S^{\text{vib}}$ of W-25%Re under quasi-harmonic approximation is substantially larger than the values obtained from harmonic approximation. Moreover, $\Delta_f S^{\text{vib}}$ continues to rise as the temperature increases within the quasi-harmonic approximation.

We have calculated the percentage of the configurational entropy of formation ($\Delta_f S^{\text{conf}}$), and $\Delta_f S^{\text{vib}}$ that contributes to the total entropy of formation ($\Delta_f S$) for both W-50%Re and W-25%Re alloys. As shown in Fig. 3a, under quasi-harmonic approximation, $\Delta_f S^{\text{vib}}$ constitutes 32.4% of $\Delta_f S$ at 1200 K for W-50%Re alloy. Similarly, for W-25%Re alloy, $\Delta_f S^{\text{vib}}$ in $\Delta_f S$ is found out to be 45.88% at 1200 K (see Fig. 3b). Notably, the percentage of the vibrational entropy of formation in the overall formation entropy reported in this work exceeds similar find-

ings in the existing literature on binary random solid solutions, as documented by Manzoor *et al.* [8]. Although they calculated thermodynamic mixing quantities of binary alloys, all alloys (except for Pt-Ru) considered in the paper consisted of elements having identical crystal structures. In such instances, thermodynamic mixing and formation quantities are equivalent. Consequently, the percentage contribution of the vibrational entropy of formation of W-50%Re can be compared to that of the high percentage contribution of the vibrational entropy of mixing of Ni-50%Pd and Ni-50%Rh alloys. It should be noted that, for the Pt-Ru system, vibrational entropy destabilizes the alloy instead of stabilizing it. It could be due to Ru being considered as FCC rather than its most stable phase, HCP.

Here we have demonstrated through first-principles phonon calculations using DFT that the entropic contribution can overcome a significantly large positive enthalpy of formation of W-50%Re and W-25%Re. Moreover, we have provided quantitative insight into the vital role of vibrational entropy in stabilizing the W-50%Re and W-25%Re alloys as a single-phase solid solution. We have found the highest contribution of vibrational entropy to the overall formation entropy for a binary alloy, surpassing any existing report in the literature [8]. These findings com-

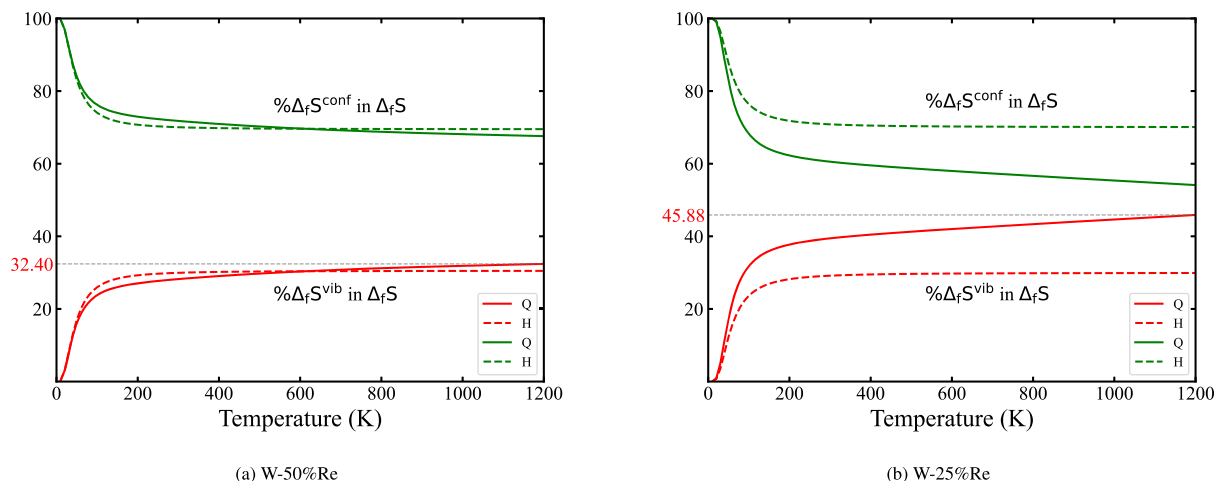


Fig. 3. Percentages of configurational entropy of formation ($\Delta_f S^{\text{conf}}$) and vibrational entropy of formation ($\Delta_f S^{\text{vib}}$) in the total entropy of formation ($\Delta_f S$) of (a) W-50%Re and (b) W-25%Re alloy under harmonic (H) and quasi-harmonic (Q) approximation.

pel us to reassess the significance of vibrational entropy in the stability of alloys as single-phase solid solutions.

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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