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# Computation of entropies and phase equilibria in refractory V-Nb-Mo-Ta-W high-entropy alloys

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ABSTRACT

We have applied the first-principles phonon method to the refractory V-Nb-Mo-Ta-W high-entropy alloys (HEAs) to predict the major phase separations in the temperature-compositional space and hence the associated entropy changes within the systems, taking into account vibrational, electronic, and configurational contributions to the total entropy. The first-principles calculations covered 178 phases ranging from pure elements, the ordered B2, B32, $B2_3$, $B2_2$, hR8, hR7, tI6, C15, and $D0_3$ binary phases, two ordered MoNbTaW quaternary phases, and the partially disordered and completely disordered bcc phases. By sorting their relative phase stabilities with the Dantzig's simplex minimization algorithm, the possibilities of phase separation for the refractory quaternary and quinary HEAs were thermodynamically found in the temperature range of 500–907 K.



## 1. Introduction

Over the last few years, a class of metallic materials, called high-entropy alloys (HEAs) [1–3], have been receiving increasing attention both experimentally and theoretically, due to their potential applications as sustaining alloys, wear-resistant materials, and diffusion barriers [4]. HEAs are in essence solid-solution phases, usually made of solutions of multicomponent elements capable of mutual chemical substitution with equimolar or near-equimolar ratios. The term, HEAs, was coined by Yeh et al., in 2004 [5,6] based on the fact that the configurational entropy of solution increases with the number of constituent elements as $k_B \log M$ per atom where $k_B$ is the Boltzmann constant and $M$ is the number of components. For the known high-entropy alloys, see the very recent review by Miracle and Senkov [3].

At present, the relative phase stability [7] and hence phase ordering/separation in the temperature-compositional space are among the major research concerns in HEAs. In principle, all normal HEAs should undergo phase ordering/separations when temperature is lowered, knowing the fact that the role of the configurational entropy vanishes approaching 0 K. However, for all refractory HEAs, no signature of ordering has ever been experimentally observed [8,9]. This could be attributed to the fact that, commonly to most HEAs [10], experiments generally cannot achieve true equilibrium at temperatures far below the melting temperature [11] due to low atomic mobility.

As a solution, first-principles calculation can help accessing all phases that are not achievable through conventional experiments. In this regard, phonon calculation is especially helpful for the accurate prediction of entropy at finite temperature in addition to that the thermal electronic effects are accounted for simultaneously at high temperature. Meanwhile, regular comparison of the individual Gibbs energies at different compositions has become rather tedious due to the rapid increase in the number of phases, in terms of unary, binary, ternary, quaternary and etc, Dantzig's simplex minimization algorithm [12–14] makes it a lot easy to evaluate

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the relative phase stabilities among multiple phases no matter how many phases or components are involved.

With the great advances in both computer power and the computational efficiency of first-principles packages [15,16] in recent decades, first-principles approach based on the electronic density functional theory [17,18] is becoming a conventional tool for predicting the properties of a material with a given crystal structure. For example, Wang et al. [19] reported studies of several HEAs integrating the cluster + glue-atom model with electron work function (EWF) predicted from first-principles calculations. Wang et al. [20] also analyzed the local atomic arrangement in the bcc quaternary HEAs WMoAB (A,B = Ta, Nb, and V). Widom et al. [9,21] performed a hybrid Monte Carlo and molecular dynamics simulation to evaluate the temperature-dependent chemical order in the Mo-Nb-Ta-W system. Niu et al. [22] studied spin-driven ordering of Cr in an equal-molar face-centered-cubic (fcc) NiFeCrCo system [23]. Starovoytov et al. [24] presented comparative studies of the ground state properties for Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20. Li et al. [25] published the *ab initio*-predicted micromechanical performance of refractory ZrNbHf, ZrVTiNb, ZrTiNbHf, and ZrVTiNbHf. Körmann and Sluiter [8] studied the possible B2 ordering in NbMoTaW with the finite temperature effects being accounted for with the Debye model.

The current challenge is how to take into account the vibrational contributions to the entropy. For ordered phases, the first-principles phonon approach has demonstrated in many cases by the accurate predictions of entropies comparable with experimental data [26–29]. Meanwhile, phonon calculations for HEAs are rarely reported [11] (see the section of Note). In this work, we present a first-principles phonon approach, in combination with Dantzig's simplex algorithm, to predict the major phase transitions and hence the entropy changes in HEAs using the refractory V-Nb-Mo-Ta-W high-entropy system as a prototype.

## 2. First-principles calculations of free energy

It is known that the Gibbs energy [30] $G = F + PV$, where $F$ is Helmholtz energy, $P$ the pressure, and $V$ the volume. For HEAs, the expression for the Helmholtz energy of individual phase as a function of temperature $T$ and volume $V$ can be formulated as a slight modification of that commonly employed for ordered systems [26,29,31],

$$F(V,T,\sigma) = E_c(V,\sigma) + F_{vib}(V,T,\sigma) + F_{el}(V,T,\sigma) - TS_{cfg}(\sigma) \quad (1)$$

where $\sigma$ labels an individual phase, $E_c$ is the 0 K static total energy per atom, $F_{vib}$ is the vibrational free energy, and $F_{el}$ is the thermal electronic contribution to the Helmholtz energy. The configurational mixing entropy $S_{cfg}$ equals to zero for a completely ordered system and for the completely disordered system it can be approximated as

$$S_{cfg}(\sigma) = -k_B \sum_{i}^{M} x_i(\sigma) \ln x_i(\sigma) \quad (2)$$

where $M$ represents the number of components and $x_i$ are the compositions normalized to one. To calculate $F_{vib}$, we adopt the quasiharmonic phonon approximation [29] by which the anharmonicity is handled through the volume dependence of the phonon density-of-states (p-DOS). To calculate $F_{el}$, we adopt the Mermin statistics [31,32].

### 2.1. Structures

We consider a total of 178 phases. These include 137 ordered phases. They are 5 pure elements and 50 equal-molar binaries spanning the ordered B2, B32, $B2_3$, $B2_2$, and hR8 structures, 20 ordered hR7 type binaries with composition $A_3B_4$, 20 ordered tI6 type binaries with composition $AB_2$, 20 ordered C15 type binaries with composition $AB_2$, 20 ordered $D0_3$ type binaries with composition $AB_3$, and Mo2Nb1Ta2W2 and Mo2Nb2Ta1W2 quaternary phases. The B32 and $B2_3$ structures are from the calculations of Blum and Zunger [33] where the B32 structure (NaTl structure) is an $A_2B_2$ (antiphase) superlattice of B2 along the (111) atomic plane and the $B2_3$ structure is an $A_3B_3$ superlattice of B2 made of antiphase boundaries in every third (110) plane. The $B2_2$ structure is an $A_2B_2$ superlattice of B2 made of antiphase boundaries in every second (110) plane, inspired by the $B2_3$ structure. The tI6, hR7, and hR8 structures are based on the calculations of Huhn and Widom [21]. The C15 structure is based on the $TaV_2$ Laves phase [34–36]. The $D0_3$ structure is from the Materials Project [37]. Mo2Nb1Ta2W2 and Mo2Nb2Ta1W2 quaternary phases are based on the prediction by Widom [11].

The disordered phases cover 26 phases. They are 10 disordered binaries, 10 ternaries, 5 quaternaries, and 1 quinary. All the disordered phases are described using the special quasirandom structures (SQSs) [38]. The present criteria in searching for the SQSs include matching the correlation coefficients of the random alloys and minimizing the supercell sizes for the calculations of p-DOS. When doable, it is also considered the additional condition that if a cubic supercell with size less or equal 256 atoms for phonon calculations can be built, so that the cubic symmetry (including those rotational ones) can be restored for the calculations of phonon dispersions following the approach developed in the previous work [39]. For the Mo-Nb-Ta-V-W system, we prepared the SQSs following the previous work [40,41]. The sizes of the SQSs are 16, 18, 16, and 25 atoms, respectively, for the disordered binary, ternary, quaternary, and quinary. These SQSs can match the ideal random alloys up to the first 6, 11, 15, and 14 pair correlation coefficients, respectively.

The partially disordered B2-based phases can have 15 phases, considering all the possible combinations. They are inspired from the recent calculations for the ordering of MoWNbTa by Körmann and Sluiter [8] and Widom et al. [9,21]. The SQSs have 32 atoms with the disordering being restricted to occur within each of the two sublattices, i.e., mixed occupancy between the two sublattices is not allowed.

The primitive unit cells of 16 prototype structures of the compound phases are given in Fig. S1 in the Supplementary Materials. For the convenience of discussion in this work, we will use the following name conventions to label the phases with multiple compositions: ordered B2, B32, tI6, hR7, hR8, C15, $B2_2$, $B2_3$ and $D0_3$ phases by the prefix "B2, B32, tI6, hR7, hR8, C15, B22, B23, and D03" followed by the respective chemical formula, partially disordered equal-molar B2-based quaternaries by the prefix "B4" followed by the chemical formula, and disordered binaries by the prefix "A2, A3, A4, and A5" followed by the chemical formula.

### 2.2. First-principles calculations

We employed the projector-augmented wave (PAW) method [15,16] implemented in the Vienna *Ab-initio* Simulation Package (VASP, version 5.3). Both the standard PBE [42] and the PBEsol [43] exchange-correlational functionals were examined. For the pseudopotentials, we have chosen those recommended from VASP 5.2. In particular, they were Mo_pv, treating Mo 4p5s4d shells in the