How atoms of polycrystalline $Nb_{20.6}Mo_{21.7}Ta_{15.6}W_{21.1}V_{21.0}$ refractory High-Entropy Alloys Rearrange during the Melting Process

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For current HEA compositions, the interactions among five elements Nb, Mo, Ta, W, and V should be considered by the 2NN MEAM potential. Since the potential form and all parameters of 2NN MEAM have been completely introduced in original 2NN MEAM papers [1-5], we do not repeat the introduction on the detailed theoretical part of 2NN MEAM potential here. The 2NN MEAM parameter sets for Nb, Mo, Ta, W, and V elements shown in Table S1 were used [5]. However, the cross-element parameters are not available in the related literature, so the parametrization process on the 2NN MEAM cross-element parameters should be conducted. The following is the detailed introduction about the parameterization process for Nb-Mo-Ta-W-V system

by using the reference data obtained from the DFT calculation.

Reference data preparation

The CASTEP package was used for all DFT calculations, and the generalized gradient approximation (GGA) with the parameterization of RPBE was used [6]. For the electronic step, the energy tolerance in the self-consistent field calculation was 1.0×10^{-6} eV. For the ionic step, the energy, force, and atomic displacement tolerance were 1.0×10^{-5} eV, 3.0×10^{-2} eV/Å, and 1.0×10^{-3} Å, respectively. Table S2 lists the experimental and DFT predicted lattice constants as well as related errors. Most errors are lower than 2%, indicating the current DFT setting can predict reliable structural properties of Nb, Mo, Ta, W, and V. It also implies these DFT settings are reliable for the Nb-Mo-Ta-W-V multiple element system for current HEAs.

To obtain the cross-element 2NN MEAM parameters, the B2 structures of NbMo, NbTa, NbW, NbV, MoTa, MoW, MoV, TaW, TaV, and WV element pairs were used as the reference structures in the DFT calculations for the parametrization of 2NN MEAM potential. Figure S1 shows the NbTa B2 unit cell as an example, and ten B2 binary alloys were used for the Nb-Mo-Ta-W-V system. Besides the binding energies of B2 structures, the binding energies of the following reference structures were also used for the parametrization process:

1. The binding energies of all B2 structures having one atom void as the example structure shown in Fig. S2. The total number of atoms for each case is 53.
2. The binding energies of (100), (110), and (111) surfaces as well as the generalized stacking fault energies (GSFE) for all B2 structures. For the GSFE cases, the upper seven layers of the (112) surface were consecutively moved along the [11-1] direction were conducted. Ten consecutive structures for a lattice period along the[11-1] direction were used for the parametrization. The example structures can be seen in Figs. S3(a)-(c) for (100), (110), and (111) surfaces, and in Fig. S3(d) for the GSFE model.
3. The Nb-Mo-Ta-W-V HEA structure optimized by the DFT calculation as shown in Fig. S4. The total atom number of Nb-Mo-Ta-W-V HEA is 54 and the initial HEA structure was built by the maximum entropy theory.
4. Using the optimized Nb-Mo-Ta-W-V HEA, the structures of the corresponding GSFE profiles for the (112) plane along [11-1] direction, the (110) plane along [010] direction, the (111) plane along [1-10] direction, and (112) plane along [11-1] direction. Figure S5 shows the example structure of the GSFE for (112) plane along [11-1] direction and the total atom number is 72. For the HEA GSFE cases, the upper two layers were moved along the corresponding direction and ten consecutive structures for a lattice period were used for the parametrization

process.

5. The binding energies of structures generated by the molecular dynamics simulation at the NPT ensemble. The MD simulations were conducted for 100 steps with a time step of 2.5 fs, and the temperatures of 300, 600, and 900 K were considered at 0 GPa for all cases. The B2, L12, and HEA structures were considered, and the example structures can be seen in Fig. S6.

LGSCPSO method

To find the best 2NN MEAM parameter set for the Nb-Mo-Ta-W-V high-entropy alloy (HEA), a systematic global minimum search method should be used. In the current study, a local and global combine particle swarm optimization (LGSCPSO) algorithm was used to fit the required 2NN MEAM parameters according to reference data prepared by the density functional theory (DFT) calculation or experimental data [7]. The LGSCPSO algorithm can significantly improve the local domain search for all particles by introducing the local best particles, compared to the original PSO algorithm. The large-scale atomic/molecular massively parallel simulator (LAMMPS) [8] was used for obtaining the corresponding properties during the LGSCPSO process. For the current LGSCPSO search for 2NN MEAM parametrization, 96 particles were used and the search iteration was terminated when the standard deviation of fitness value is lower than 10^{-5}. Particle *i* possesses the information of 2NN MEAM parameter

values (a total number of 195 for Nb-Mo-Ta-W-V HEA), which form a 195-dimensional position vector X_i as follows:

$$X_i = (x_{i\text{-}1}, x_{i\text{-}2}, \ldots, x_{i\text{-}195}),\ i = 1, 2, \ldots, 96 \qquad (1)$$

A 195-dimensional velocity vector V_i of Particle i is also provided as follows:

$$V_i = (v_{i\text{-}1}, v_{i\text{-}2}, \ldots, v_{i\text{-}195}),\ i = 1, 2, \ldots, 96 \qquad (2)$$

In Eqs (1) and (2), for example, $x_{i\text{-}1}$ and $x_{i\text{-}2}$ (also for $v_{i\text{-}1}$ and $v_{i\text{-}2}$) correspond to the first and second fitted 2NN MEAM parameters of Particle i. The initial values of X_i and V_i were randomly generated between their corresponding lower and upper bounds. The fitness of each particle is the square of the difference between the data from 2NN MEAM and DFT calculation shown in the following formula:

$$\text{Fitness} = \sum_1^n w_n \times (E_{lammps}/E_{DFT})^2 \qquad (3)$$

Where E_{lammps} is the formation energy of lammps, E_{DFT} is the formation energy of DFT and w_n is the weight of reference structure.

If the new fitness is lower after a new LGSCPSO iteration, three parameter sets could be updated according to the following criterion:

1. If the fitness is lower than that of the last iteration, the corresponding X_i is used to update the best particle position $P_i = (p_{i\text{-}1}, p_{i\text{-}2}, \ldots, p_{i\text{-}195})$, which is a 195-dimensional vector .
2. If the fitness is lower than that of the current local best particle that particle I

belongs to, the corresponding X_i is used to update the local best position Pl = (pl_1, pl_2, . . . , pl_{195}) , which is a 195-dimensional vector.

3. If the fitness is lower than that of the current global best particle, the corresponding X_i is used to update the global best position Pg = (pg$_1$, pg$_2$, . . . , pg$_{195}$), which is a 195-dimensional vector.

After finding these three best values at iteration k, the next LGSCPSO iteration (k+1) updates its velocity and position with the following formulas:

$$v_{i\text{-}d}(k+1) = w{*}v_{i\text{-}d}(k) + c1{*}r1\{\alpha * (p_{i\text{-}d}(k) - x_{i\text{-}d}(k)) + (1-\alpha) * (pl_d(k) - x_{i\text{-}d}(k))\} + c2{*}r2\,(pg(k) - x_{i\text{-}d}(k)) \quad (4)$$

$$x_{i\text{-}d}(k+1) = x_{i\text{-}d}(k) + v_{i\text{-}d}(k+1) \quad (5)$$

$$\mathrm{w} = \mathrm{w}_{max} - \mathrm{iternation(i)} * (\mathrm{w}_{max} - \mathrm{w}_{min}) / \text{ total\_iterations} \quad (6)$$

w_{max} = 1.2, w_{min} = 0.4

where w is an inertia weight, which is calculated by Eq. (6) and decreases with the increasing iteration number from 1.2 to 0.4. The value of α is used to adjust the relative weights for the differences of the best position of Particle i and the local best position to current particle position. The variables $c1$ and $c2$ are acceleration constant, and 1.49445 and 1.49445 are used for these two parameters, respectively. Table S3 lists upper (maximum) and lower (minimum) bounds for 2NN MEAM potential parameters during the LGSCPSO.

Topology for SLR neighborhood method

For the neighborhood population of LGSCPSO, the singly-linked ring (SLR) topology was used to establish the communication paths of a neighborhood among its members [9]. In the SLR topology for the current study, the neighborhood structure with the members of 4 was adopted. For particle k, its neighborhood members are particles k+1, k-2, k+3, and k-4. If k-2 or k-4 is negative, this value adds the total number of particles. If k+1 or k+3 is larger than the total number of particles, this value is deducted by the total particle number. For examples, there are 96 particles used in the current study. For Particle 1 (i.e. k = 1, the smallest particle ID), its neighborhood members are Particles 2, 95, 4, and 93. For Particle 96 (i.e. k = 96, the largest particle ID), its neighborhood members are Particles 1, 94, 3, and 92. Consequently, the neighborhood population is 96 and the diversity becomes more significant with the increasing LGSCPSO iteration.

Parametrization evaluation

Figure S7 shows the binding energy relationship between the DFT calculation and 2NN MEAM potential with the LGSCPSO fitted parameters. The solid line in Fig. S7 is the guide for the eyes to indicate the equal value of both horizontal and vertical axes.

It can be seen most data are very close to the solid black line, and the discrepancies of L12 structures relatively larger compared to the other structures. Figure S8 displays the distribution of error percentage for the binding energies obtained by the DFT calculation and 2NN MEAM potential with the LGSCPSO fitted parameters. The data with the error percentage within $\pm 5\%$ is about 84.5% of the total reference data for the parametrization. Using the fitted 2NN MEAM potential parameters, the MD simulation of the BCC single crystal $Nb_{20.6}Mo_{21.7}Ta_{15.6}W_{21.1}V_{21.0}$ RHEA at the isothermal-isobaric (NPT) ensemble (300 K and 0 GPa) was conducted for 50 ps. The structure of BCC single crystal $Nb_{20.6}Mo_{21.7}Ta_{15.6}W_{21.1}V_{21.0}$ RHEA maintains the 100% local BCC structure, and the predicted density is about 11.9 g/cm^3, which is very close to the related experimental value of 12.3 g/cm^3 [10]. The MD results verify the reliability of NbMoTaWV 2NN MEAM potential with the fitted parameters by the LGSCPSO. All 2NN MEAM parameters for the Nb-Mo-Ta-W-V system in the LAMMPS format are also provided with the supporting file (NbMoTaWV_ref.lib for single element parameters and NbMoTaWV_crosselement.mean for the cross-element parameters).

Table S1. 2NN MEAM parameter sets for Nb, Mo, Ta, W, and V elements [5].

	E_C	r_e	B	A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{max}	C_{min}	d
Nb	7.47	2.860	1.73	0.72	5.08	1.0	2.5	1.0	1.7	2.8	-1.6	2.80	0.36	0.00
Mo	6.81	2.725	2.65	0.46	7.03	1.0	1.0	1.0	0.5	3.1	-7.5	2.80	0.64	0.00
Ta	8.09	2.860	1.94	0.67	4.49	1.0	1.0	1.0	1.7	2.1	-3.2	2.80	0.25	0.00
W	8.66	2.740	3.14	0.40	6.54	1.0	1.0	1.0	-0.6	0.3	-8.7	2.80	0.49	0.00
V	5.30	2.625	1.57	0.73	4.74	1.0	2.5	1.0	3.3	3.2	-2.0	2.80	0.49	0.00

Table S2. The experimental and DFT predicted lattice constants for Nb, Mo, Ta, W, and V unit cells.

Element	**Exp (Å) [11]**	**DFT (Å)**	Error (%)
Nb (BCC)	3.296	3.333	1.123
Mo (BCC)	3.144	3.173	0.922
Ta (BCC)	3.301	3.371	2.121
W (BCC)	3.162	3.200	1.202
V (BCC)	3.028	3.042	0.462

Table S3. The 2NN MEAM parameter ranges in the lammps format for LGSCPSO.

2NN MEAM parameters	Maximum	Minimum
C_{max}	2.8	2.0
C_{min}	0.99	0.1
rho0	1.0	1.0
Ec, Re	1.1 * DFT value	0.9 * DFT value
Attar, repul	-0.1	0.1

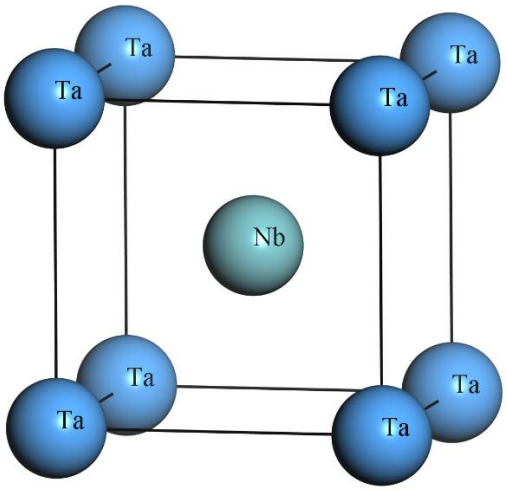

Figure S1. The schematic diagram of a B2 unit cell for the NbTa binary system, and the B2 is used as the reference structure for the 2NN MEAM potential. There are 10 groups of binary pairs for the Nb-Mo-Ta-W-V system, and only the structure of NbTa pair is shown for an example.

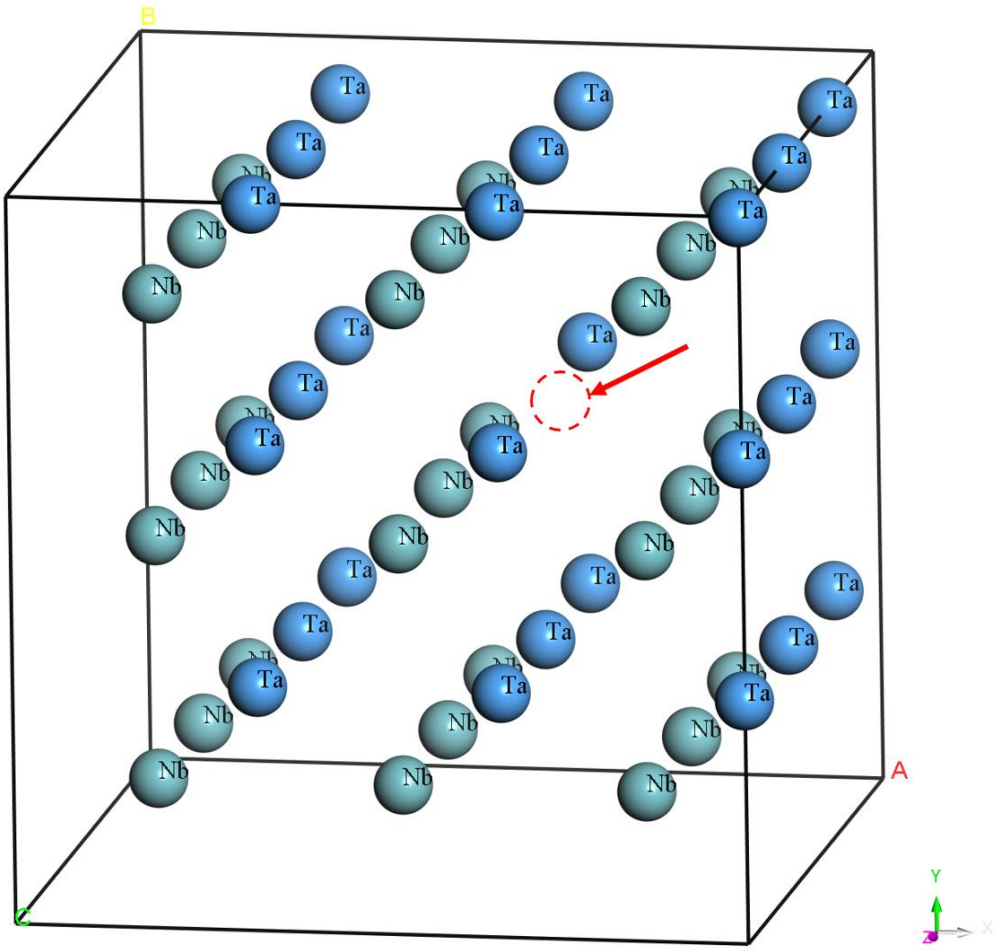

Figure S2. The schematic diagram of the binary system with one atom void. There are 10 groups of binary pairs for the Nb-Mo-Ta-W-V system, and only the structure of NbTa pair with the Nb void (indicated by an arrow) is shown as an example. The total number of atoms is 53.

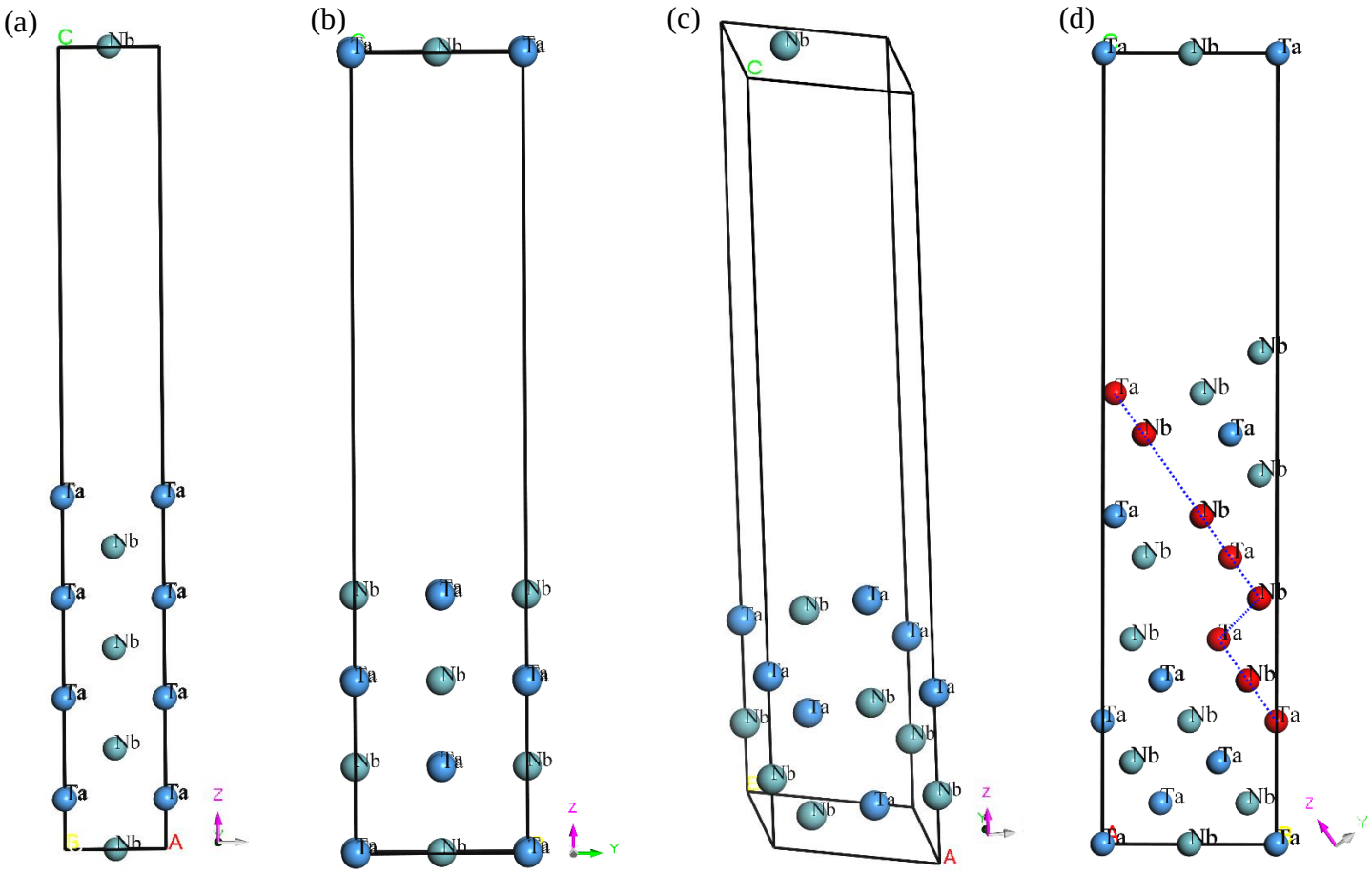

Figure S3. The schematic diagram of (a) (100), (b) (110), and (c) (111) surfaces as well as the schematic diagram for (d) the GSFE of (112) plane along [11-1] direction. Only the NbTa structure is shown, and the total numbers of atoms in (a)-(d) are 8, 8, 8, and 26, respectively.

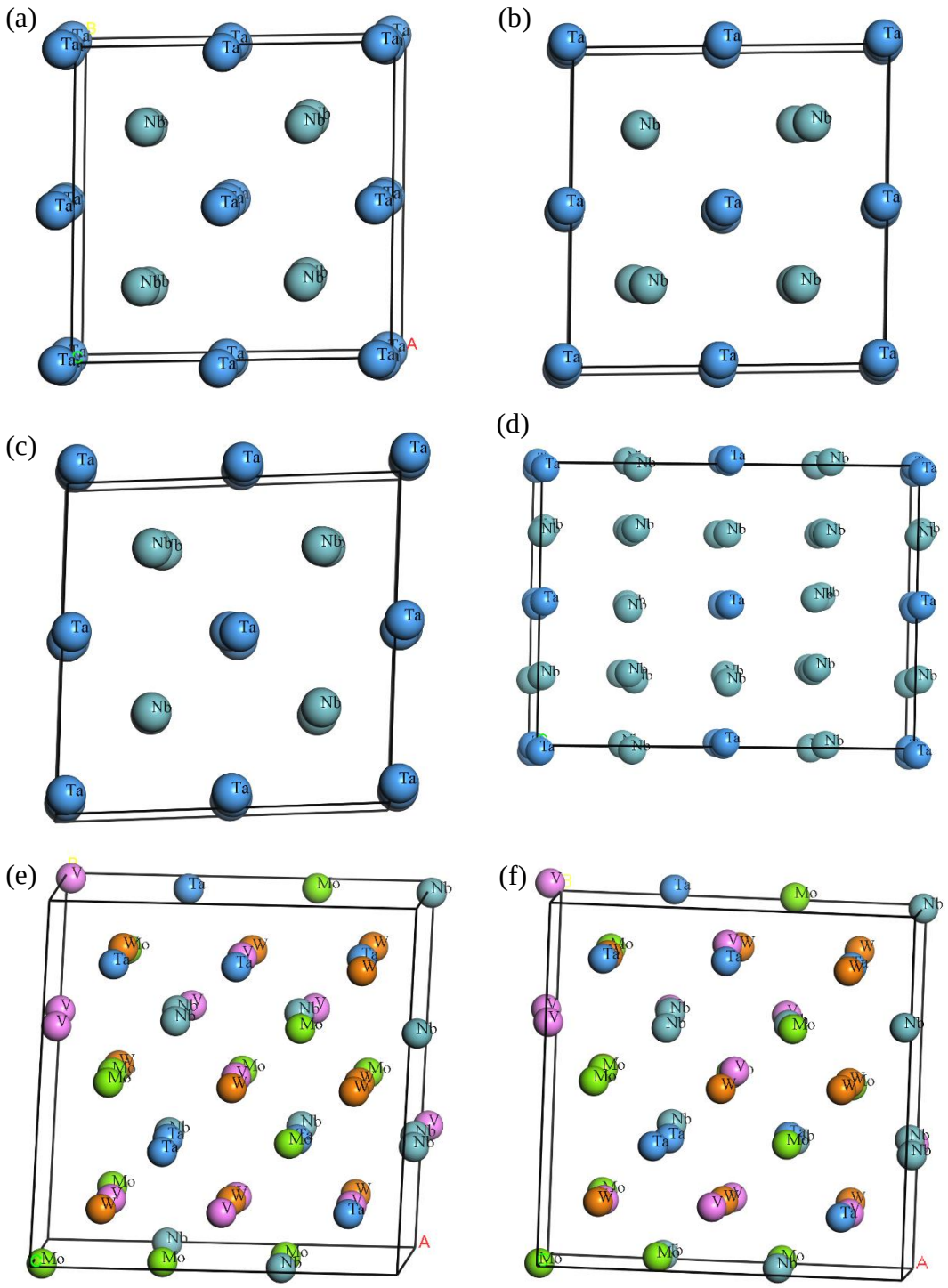

Figure S6. Schematic diagrams of structures after the NPT MD simulations for (a) B2 NbTa at 300 K, (b) B2 NbTa at 600 K, (c) B2 NbTa at 900 K MD. (d) 900K MD of binary Nb_3Ta_1 (L12) (e) 300K MD of HEA (f) 900K MD of HEA. The total number of atoms is 16, 16, 16, 32, 54 and 54, respectively

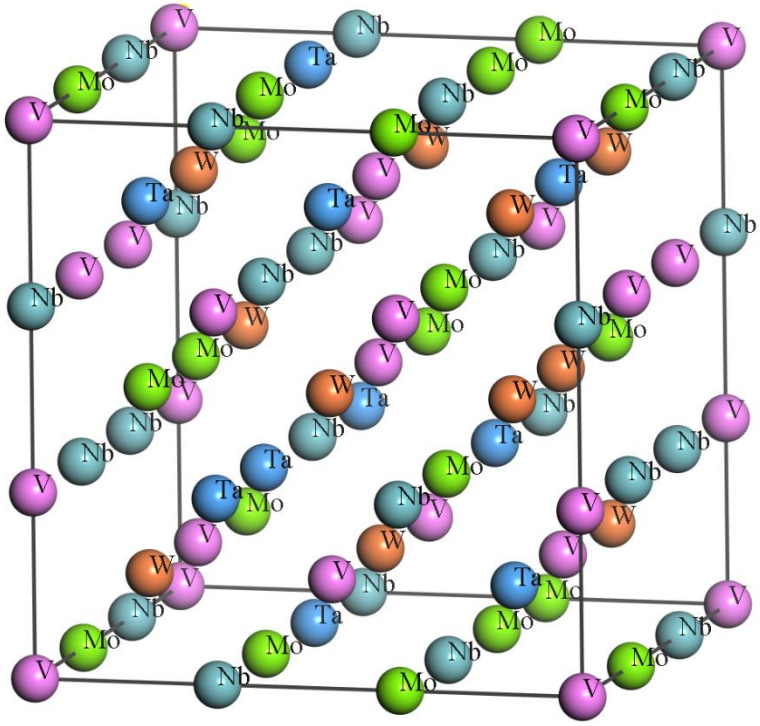

Figure S4. The schematic diagram of Nb-Mo-Ta-W-V HEA in the BCC arrangement, the total number of atoms is 54.

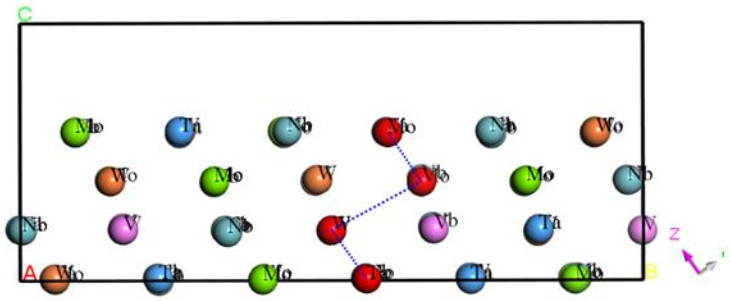

Figure S5. The example structure of the GSFE for (112) plane along [11-1] direction.

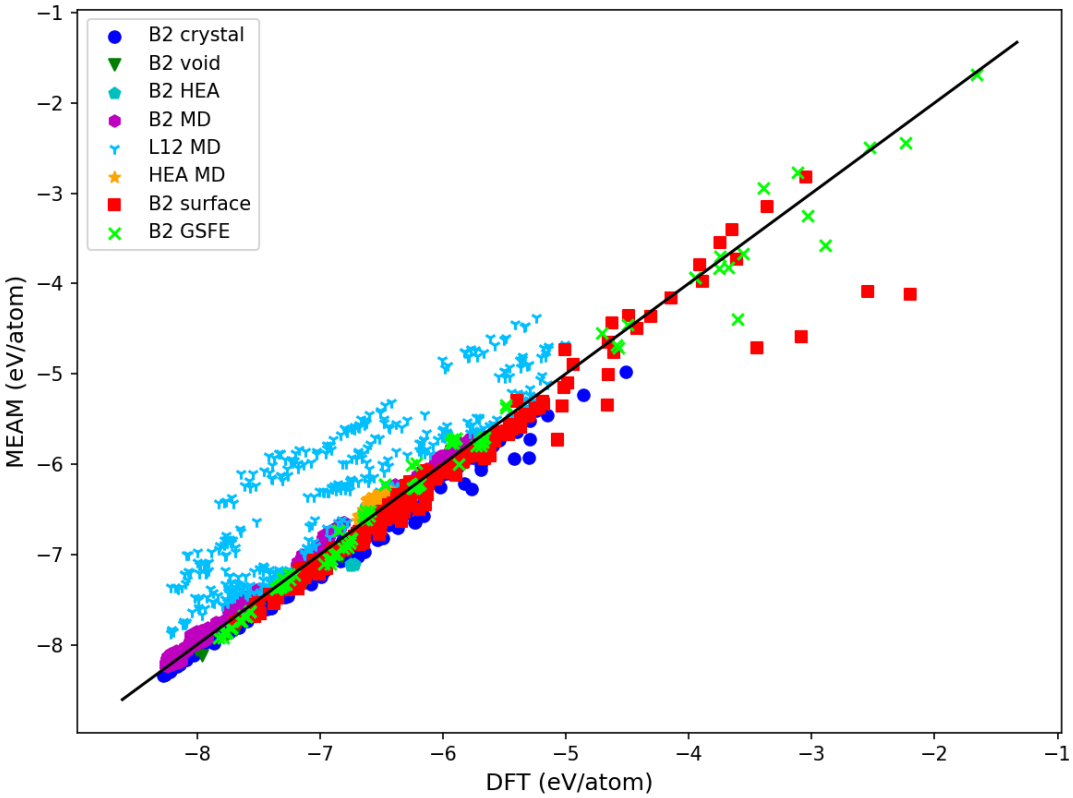

Fig. S7. The binding energies obtained by the DFT calculation and 2NN MEAM potential with the LGSCPSO fitted parameters. The solid line is used to indicate the equal value of the horizontal and vertical axes.

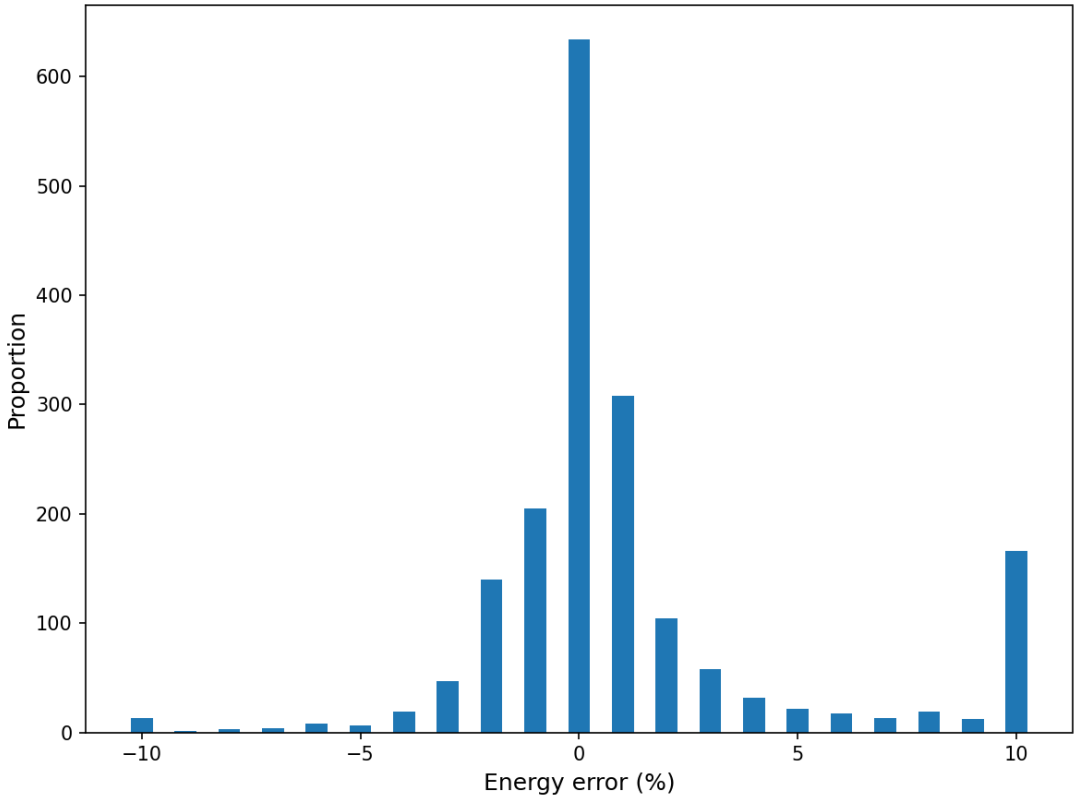

Figure S8. The distribution of error percentage for the binding energies obtained by the DFT calculation and 2NN MEAM potential with the LGSCPSO fitted parameters.

2NN MEAM Parameter file:

NbMoTaWV_crosselement.mean

NbMoTaWV_ref.lib

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