Development of n-body interatomic potentials for calculating the thermodynamic characteristics of V-Nb-Mo-W alloys

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Abstract. New interatomic potentials for Mo and binary systems V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W are constructed taking into account the angular dependencies of interatomic interactions. Together with the potentials constructed earlier in the same approach, a complete set of potentials for modeling alloys of the V-Nb-Mo-W system at any component concentrations is obtained. A tendency to narrow the range of values of the calculated enthalpy of formation and the volume of formation in equiatomic alloys of the V-Nb-Mo-W system with an increase in the number of components was found. Deviations from the Vegard's rule in the volume of formation of these alloys are shifted to the negative range of values when the number of components is more than two.

1. Introduction

The enthalpy of formation of a solid solution is one of the key values that determine the thermodynamic stability of high-entropy alloys, along with the configuration entropy (recent review [1]). To date, the experimental values of the enthalpy of formation have been determined for many binary systems, including alloys of refractory BCC metals (database [2] and references therein). However, there is still a challenge in establishing the enthalpy of formation of multicomponent alloys. The problem is related to the complexity of experimental work in this direction and the increase in CALPHAD errors with an increase in the number of components due to neglect of the details of the atomic structure. The missing information can be obtained by atomistic modeling. However, the use of such modeling for high-entropy alloys remains limited due to the insufficient development of potentials for multicomponent systems. One of the problems is the need to take into account the angular dependencies when the chemical bond is significantly covalent, which limits the use of a number of well-tested methods for constructing potentials, in which angular dependencies are not taken into account.

In this paper, we develop the V-Nb-Mo-W potentials in the framework of the recently developed n-body approach to constructing interatomic potentials for systems with metallic and covalent characters of chemical bonds, which correctly takes into account angular dependencies [3-5]. The reliability of the theoretical predictions of thermodynamic characteristics in this approach is achieved by including experimental and CALPHAD data on the formation enthalpy and volume of solid solutions at high homological temperatures in the construction of potentials [5]. The advantage of the approach [3-5] is its focus on modeling multicomponent systems at any concentration of components. For this, it is sufficient to construct interatomic potentials only for each pair of components of the system, since the potential functions in this approach depend only on one or two types of atoms [5].

Using the developed potentials, we further calculate the enthalpy of formation and the volume for a number of equiatomic alloys of the V-Nb-Mo-W system to determine the features of the dependence of these thermodynamic characteristics on the number of components in the alloys on the example of the considered system.

2. Methods

The potential energy E_{pot} of the atomic system of N particles depends on the interatomic distances and the angles between bonds according to the following equation [3,5]

$$E_{pot} = \sum_{i<j}^{N} \Phi_{ji}(R_{ji}) + \sum_{i}^{N} \sum_{k<j\neq i}^{N} \sum_{p,q}^{n_3} g_i^{pq}(\cos\theta_{jik})\, f_{ji}^{p}(R_{ji}) f_{ki}^{q}(R_{ki}) + \sum_{i}^{N} F_i(\bar{\rho_i}), \quad (1)$$

where

$$\bar{\rho_i} = \sum_{j\neq i} \rho_{ji}(R_{ji}) \quad (2)$$

and the indices i and j refer to atoms. The discussion of the terms in this expression, potential functions, and the method for optimizing potential parameters is presented in articles [3-5]. To construct interatomic potentials V-Nb-Mo-W, you must specify potential functions $\Phi_{ji}(R_{ji})$, $g_i^{pq}(\cos\theta_{jik})$, $f_{ji}^{p}(R_{ji})$, $F_i(\bar{\rho_i})$, and $\rho_{ji}(R_{ji})$ for pure elements and cross-potential functions $\Phi_{ji}(R_{ji})$, $f_{ji}^{p}(R_{ji})$, and $\rho_{ji}(R_{ji})$ for each pair of elements in the V-Nb-Mo-W system. We used the potentials of the monatomic systems V, Nb, Mo, W and the binary system V-W [5] that we constructed earlier. At the same time, we modified the potential Mo for a more accurate reproduction of the experimental equation of state and thermal expansion of the BCC lattice of Mo. In this paper, we have constructed potentials for binary systems V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W. The enthalpy of formation and the lattice parameters of the alloys were used as target values, as implemented in [5]. As a result, a complete set of potentials was obtained for modeling the V-Nb-Mo-W system at any component concentrations.

The enthalpies of formation of binary systems were calculated by molecular dynamics simulations in the framework of the supercell model containing 2000 atoms in the computational cell at a constant number of particles *N*, pressure *P=0*, and temperature *T* (*NPT* ensemble). We use the periodic boundary conditions, the velocity Verlet algorithm for the solution of the equations of motion, the Nose-Hoover thermostat, and the Berendsen barostat. The temperature was chosen to be equal to the temperatures for which the enthalpies of formation of the considered alloys were determined in known experimental studies or calculations using the CALPHAD method. In the case of studying the dependence of the enthalpy of formation and the volume of equiatomic alloys on the number of components, the method of molecular statics at 0 K was used.

3. Results and discussions

Figure 1 shows the results of our calculations of the equation of state for Mo and the enthalpies of formation for V-Nb, V-Mo, Nb-Mo, Nb-W, and Mo-W alloys as functions of the component concentrations. As can be seen from Figure 1, the new potential reproduces well the experimental equation of state for Mo, and the constructed potentials predict the enthalpies of formation of the considered binary systems in good agreement with the experimental and CALPHAD data at high homological temperatures.

Figure 2 shows the results of our calculations of the thermal expansion of Mo and the dependence of the lattice parameters of V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W alloys on the component concentrations.

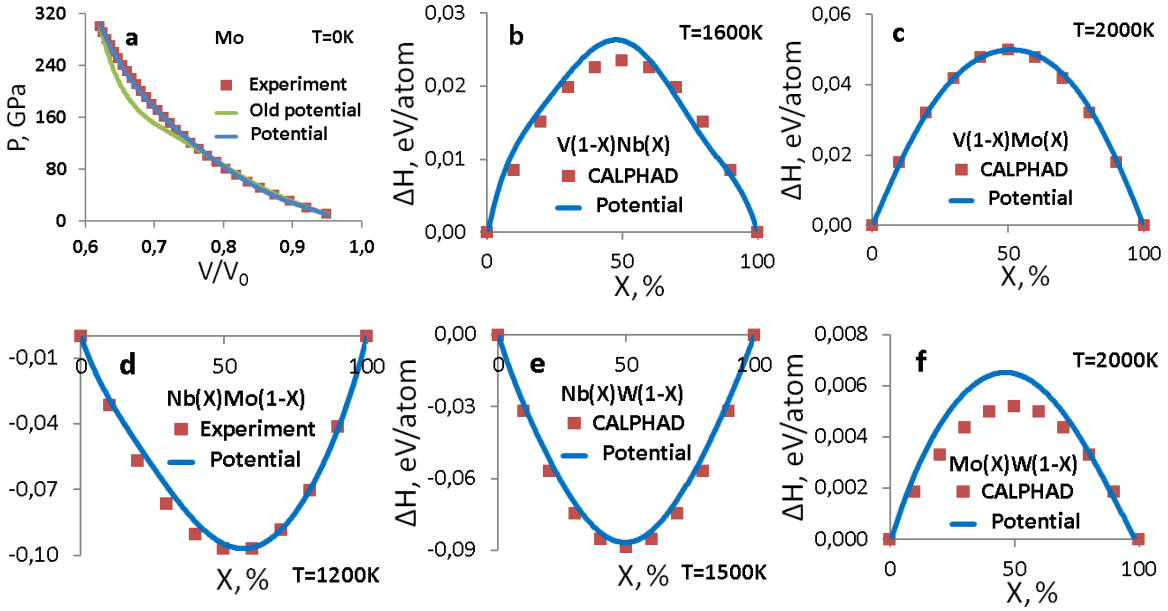

Figure 1. The results of our calculations of the equation of state for Mo in comparison with experimental data [6] and the formation enthalpies of V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W alloys as functions of the component concentrations.

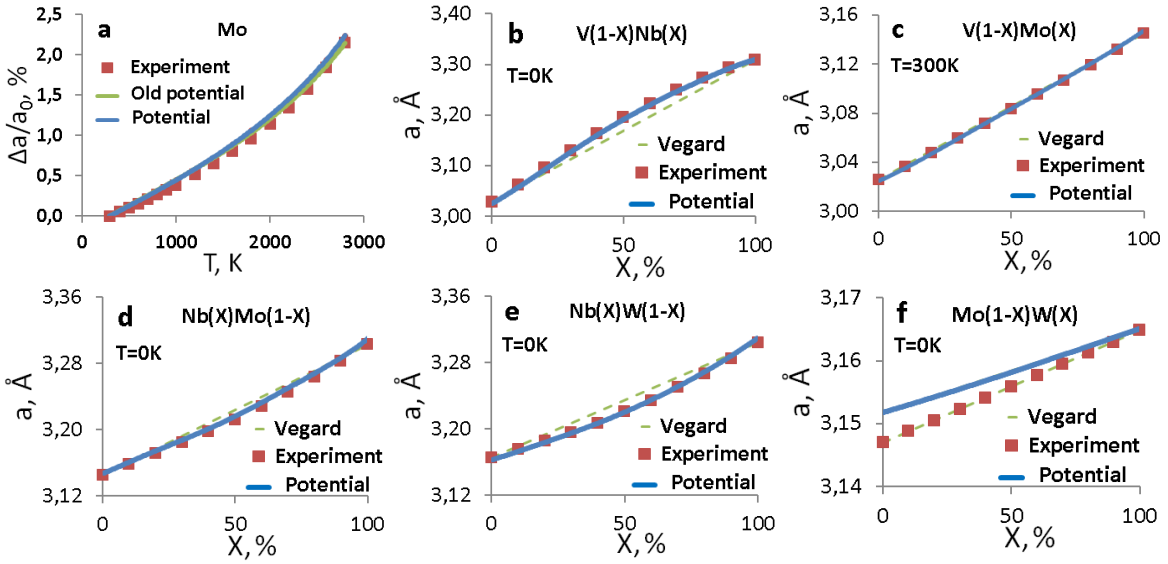

Figure 2. The results of our calculations of the thermal expansion of Mo in comparison with experimental data [7] and the parameters of the BCC lattice of V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W alloys as functions of the component concentrations.

Figure 2 shows a good agreement between the calculated values of the lattice BCC parameters and their known experimental values for all the systems considered. Deviations from the linear dependence of the lattice parameters on the concentration (from the Vegard's rule) are reproduced in detail. In the case of the Mo-W alloy, the potentials predict the exact execution of the Vegard's rule in accordance with the experimental results, which, however, showed a slight difference (of the order of 0.005 Å) between the calculated equilibrium parameter of the Mo lattice and the experimental value. Thus, the interatomic potentials of V-Nb-Mo-W predict thermodynamic characteristics, the enthalpy of formation and the

volume, in good agreement with experimental data and CALPHAD calculations for each binary alloy of the V-Nb-Mo-W system. This justifies the use of the potentials constructed by us for the prediction of thermodynamic characteristics of other alloys of the V-Nb-Mo-W system.

Figure 3 shows the results of our calculations of the volume of formation and the enthalpy for 2 -, 3 -, and 4-component equiatomic alloys of the V-Nb-Mo-W system. As can be seen from Figure 3, there is a slight narrowing of the area of the volume and enthalpy values with an increase in the number of components in the considered alloys. The volume deviation from the Vegard's rule has only negative values for alloys with more than two components.

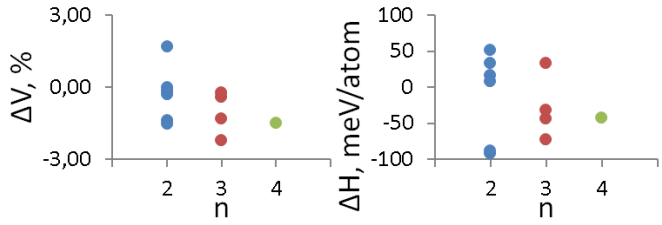

Figure 3. Calculated values of the deviation ΔV of the volume of formation from the Vegard's rule (left) and the enthalpy of formation ΔH (right) for n-component equiatomic alloys of the V-Nb-Mo-W system.

4. Conclusion

In this paper, interatomic potentials for Mo, V-Nb, V-Mo, Nb-Mo, Nb-W and Mo-W are constructed taking into account angular dependencies in interatomic interactions. The potentials reproduce the values of the enthalpy of formation and the lattice parameters of the considered alloys in good agreement with the known experimental data and the results of CALPHAD calculations. A complete set of potentials for modeling the V-Nb-Mo-W system at any component concentrations was obtained. Using these potentials, it is shown that the regions of the volume of formation and the enthalpy of equiatomic alloys of the V-Nb-Mo-W system become narrow with increasing number of components in these alloys. The volumes of formation of V-Nb-Mo-W alloys are characterized by negative deviations from the Vegard's rule for the number of components more than two. The developed new potentials can be used to study alloys of the V-Nb-Mo-W system in a wide temperature range using atomic simulation methods.

Acknowledgments

The work was supported by the Ministry of Education and Science of the Russian Federation under Project No.18-02-00585.

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