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# Method of molecular dynamics investigation of diffusion in solid solutions with consideration of ordering effects on the example of V50W50 and V90W10 alloys

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**Abstract.** This paper presents the development of methods for the theoretical study of diffusion processes in solid solutions based on molecular dynamics (MD), taking into account the effects of ordering. The influence of concentration and temperature on the features of diffusion characteristics in substitution alloys is studied using the example of solid solutions V50W50 and V90W10. Modeling has shown that the V-W ordering is associated with the separation of plates enriched with tungsten in the planes (100). Vanadium atoms are more mobile and the difference in diffusion coefficients decreases with the equalization of component concentrations and temperature increases.

## 1. Introduction

At present, considerable attention is paid to establishing the diffusion characteristics of solid solutions (recent works [1,2] and references therein) due to their significant influence on the properties of such materials. In some cases, diffusion characteristics are obtained from experimental studies [1,2], which, however, are often limited by methodological complexity and insufficient resolution of the instrument base [3]. The missing information about the diffusion characteristics of solutions can be compensated by the predictions from the results of atomistic simulation. In this case, it is important to take into account the ordering effects for the correct setting of the atomic structure, which depends on the temperature of the solid solution.

A well-known approach to accounting for ordering is the MC/MD method [4] based on a combination of Monte Carlo (MC) and molecular dynamics (MD) methods. In the MC/MD method [4], the calculation of the change in potential energy when rearranging atoms of different types for the implementation of MC steps is carried out without taking into account the relaxation in the position of the atoms caused by the permutation. Therefore, it remains relevant to develop a new practical implementation of the MC method, which, along with using the advantages of the MD method, would take into account local relaxation to reduce the number of MC steps necessary to achieve equilibrium. Also, the MC/MD method [4] does not use direct modeling of the *NPT* ensemble, which does not guarantee the achievement of an equilibrium of the atomic system corresponding to the minimum Gibbs energy at a given number of particles  $N$ , pressure  $P$ , and temperature  $T$ .



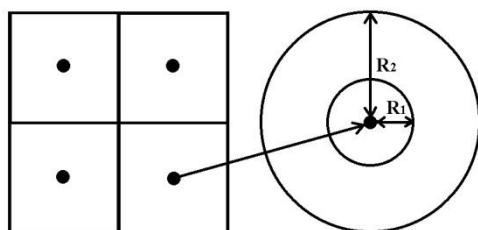
In this paper, we develop a new method for obtaining the equilibrium atomic structure of a solid solution based on a combination of MD and MC (MD+MC) methods. The new method correctly implements the achievement of the equilibrium of the atomic system as a result of modeling the  $NPT$  ensemble. Model samples obtained by the MD+MC method are used to study diffusion in solid solutions by the MD method. A new method for studying diffusion in solid solutions, taking into account the effects of ordering, is tested on the example of two alloys of the V-W system, which forms the basis of many modern metal materials for use at high operating temperatures. To define interatomic interactions of V-W, we use potentials [5-7].

## 2. Methods

The MD+MC method is based on the equivalence of the MD and MC methods in obtaining the microstates of the  $NPT$  ensemble. The microstate of the solution is defined by two constituents: 1) the position of the atoms in local equilibrium, which change as a result of diffusion jumps over significant times in comparison with the periods of vibrations of the atoms; 2) the displacement of the atoms from these positions due to thermal vibrations. The MD+MC method is implemented as an algorithm for sequential actions.

Action 1. In the superlattice model, we set the calculation cell of a random solution containing  $N_i$  atoms of each type  $i$  in accordance with the given  $C_i$  concentrations. We perform MD simulation during 20 ps at a given temperature  $T$  and pressure  $P (=0)$  until the ensemble's  $NPT$  equilibrium is reached. We use the velocity Verlet algorithm for the solution of the equations of motion, the Nose-Hoover thermostat and the Berendsen barostat.

Action 2. Do  $n_{MC}$  ( $=20$ ) steps of MC. To do this, we apply a uniform grid of  $n_{point}$  points to the calculation cell with a random position of the starting point of the grid in the cell within periodic boundary conditions as illustrated in figure 1.



**Figure 1.** A schematic representation of a uniform grid of points in the calculation cell and the selection of a sphere of atoms near each point with radius  $R_2$ . Within a sphere of a smaller radius  $R_1$ , mobile atoms are marked, which will participate in a permutation with an atom in the center of the sphere.

Next, select the atom closest to each point and cut a sphere from the cell containing all the atoms within the distance  $R_2$  from the selected atom. Inside the cut-out sphere, we mark about 100 atoms located within the distance  $R_1$  from the atom in the center of the sphere, which will be mobile during MD simulation of the sphere of radius  $R_2$ . The coordinates of atoms located at distances ranging from  $R_1$  to  $R_2$  from the central atom are fixed in the MD modeling process. The requirement  $R_2 - R_1 > R_c$  is imposed, where  $R_c$  is the radius of interatomic interaction for the possibility of parallel modeling of each sphere without their mutual influence. The radius  $R_c$  of interatomic interactions in the V-W system made it possible to select a  $2 \times 2 \times 2$  point grid in the calculation cell of 2000 nodes. MD simulation of each sphere is performed during  $n_{MD}$  steps to perform one MC step in it to exchange places of the atom  $i$  in the center with an atom of another type  $j$ , randomly selected among the atoms in the sphere of radius  $R_1$ . The MC step is performed with the Metropolis algorithm according to the change in potential energy  $\Delta U = U - U_0$ , where  $U_0$  is the average potential energy of the simulated sphere with the initial position of the atoms and  $U$  is the average potential energy of the same sphere, but after the rearrangement of atoms  $i$  and  $j$ .

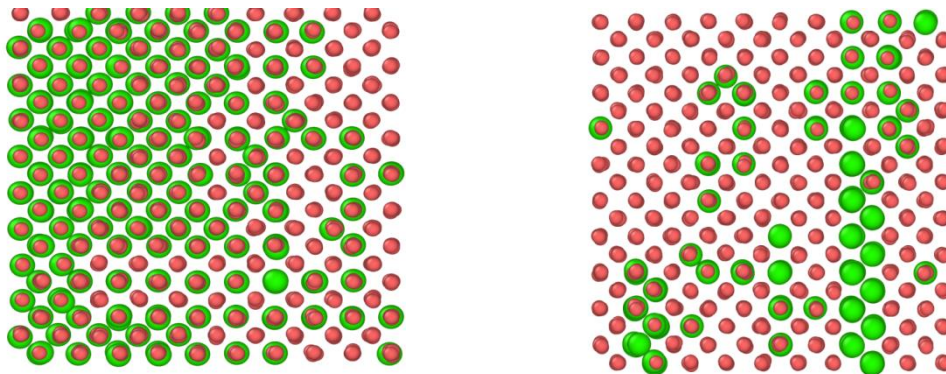
Action 3. Modeling the  $NPT$  ensemble of the entire cell as a whole with the accepted permutations of atoms by the MD method during  $N_{MD}$  ( $=2000$ ) steps to achieve equilibrium. Calculation of the average enthalpy, volume, and other current characteristics of the system using the MD method.

Calculation of the value of the order parameter, configuration entropy, and other values associated with configurations of atoms of different types by cluster variation method. Sequential repetition of steps 2 and 3 is one step of the MD+MC method. The values of MC and MD steps are selected after test calculations with a number of values as a variant with the smallest values of MD steps, which slightly change the result of modeling. To achieve equilibrium in V-W alloys, 100 steps of the MD+MC method are sufficient (the enthalpy, order parameters, and other values change near the average values during further MD+MC modeling).

Model diffusion experiments were performed using MD simulation (*NPT* ensemble) for 32 ns. In the initial calculation cell containing 2000 nodes, one atom was removed to create a vacancy. We used 400 points of mean square displacement of atoms in time for the temperature range 300-2100K. To smooth out random fluctuations, the obtained points were averaged over 20 sets of configurations, the starting points of which are 80 ps apart in time.

### 3. Results and discussions

The feature of the atomic structure associated with the formation of short-range order in V-W is illustrated in figure 2, which shows the projections of the positions of vanadium and tungsten atoms on the crystallographic planes (100) and (010) in the calculation cell of a V90W10 solid solution at a temperature of 300 K. As can be seen from figure 2, the ordered V90W10 alloy contains areas rich in tungsten. A characteristic feature of these regions is the formation of tungsten plates oriented in the

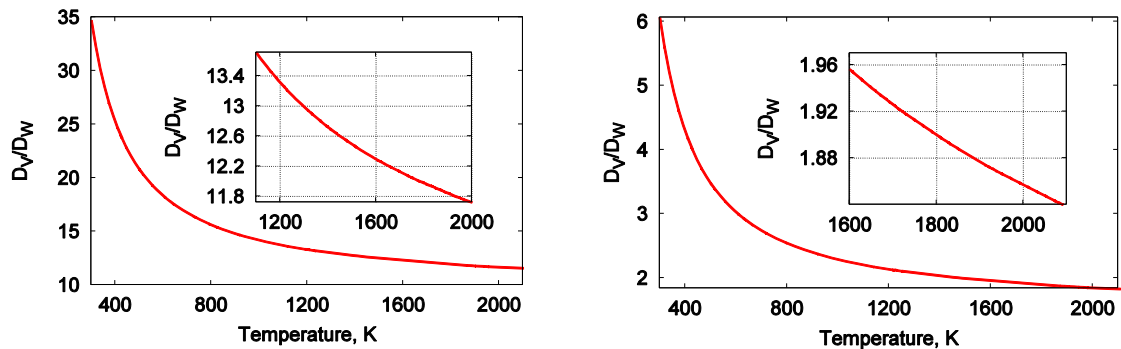


**Figure 2.** Projections of positions of vanadium atoms (red) and tungsten atoms (green) on the crystallographic plane (100) on the left and the plane (010) on the right in the calculation cell of V90W10 at a temperature of 300K.

crystallographic plane (100) of the BCC lattice. We also observed similar regions at higher temperatures. However, as the temperature increases, the size of areas rich in tungsten decreases. Similar areas were also observed in the V50W50 alloy, but the size of the tungsten plates decreases with increasing tungsten concentration. Here we note that it is possible in principle to observe the formation of tungsten plates in vanadium by atom probe tomography. During the MD+MC simulation, a decrease in the Gibbs energy calculated as the contributions of enthalpy and configuration entropy was always observed from the initial state of a random solution.

As a result of smoothing the calculated values of the diffusion coefficients for a number of temperatures by the Arrhenius dependence, we found that the activation energy of the diffusion process in the V90W10 alloy leaves  $1.08 \pm 0.04$  eV for vanadium atoms and  $1.12 \pm 0.04$  eV for tungsten atoms. The calculated activation energies in the V50W50 alloy were  $1.2 \pm 0.2$  eV for vanadium diffusion and  $1.3 \pm 0.1$  for tungsten diffusion. Thus, within the margin of error, the effective activation energy of vanadium diffusion in the V90W10 alloy corresponds to that of the V50W50 alloy with an equiatomic composition. A lower value of the activation energy of the tungsten diffusion in the V90W10 alloy is due to the diffusion of tungsten atoms along the plate surfaces that are released in the V90W10 solid solution (see Figure 2).

Figure 3 shows the calculated ratio of vanadium and tungsten diffusion coefficients as a function of temperature. As can be seen from figure 3, the diffusive mobility of vanadium atoms significantly exceeds that of tungsten in the V90W10 alloy. At the same time, this ratio of the diffusion coefficients in V50W50 is an order of magnitude less.



**Figure 3.** Calculated ratio of vanadium diffusion coefficient to tungsten diffusion coefficient in V90W10 (left) and V50W50 (right) as a function of temperature.

#### 4. Conclusion

The MD+MC method makes a significant contribution to theoretical predictions of the results of diffusion processes in solid solutions and can be used for the study of multicomponent systems, including high-entropy alloys. A decrease in the specific Gibbs energy in the MD+MC simulation from the initial state of a random solution was found, which justifies the reliability of the MD+MC simulation results in achieving thermodynamic equilibrium of alloys at a given temperature and pressure. It is shown that in the considered V-W alloys, ordering is associated with the selection of areas enriched with tungsten. The structure of these regions is characterized by the predominant formation of plates located in the (100) BCC lattice planes. This indicates the possibility of dispersed hardening of vanadium alloys due to alloying with tungsten. The results of MD simulation of diffusion showed that there is a tendency to a faster diffusion of vanadium atoms in comparison with tungsten atoms. With equalization of concentration and an increase in temperature, the difference in the diffusion coefficients of V-W alloy components decreases.

#### Acknowledgments

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