Simulation of structure of special tilt boundary and grain-boundary self-diffusion in Ti

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Abstract

Symmetric tilt boundary $[2\bar{1}\bar{1}0](01\bar{1}2)$ in HCP titanium has been investigated by computer simulation methods using the embedded atom potential. The structure and energies of the considered boundary and the energies of formation of vacancies in it have been calculated by the method of molecular-static simulation. The stability of the boundary at elevated temperatures has been investigated by the molecular dynamics method, and the coefficients of grain-boundary diffusion have been calculated.

Keywords

Grain boundaries, atomistic simulation, point defects, diffusion, titanium

1. Introduction

Titanium is widely used in medicine and is the most important metal in aerospace engineering. The properties of polycrystalline titanium directly depend on the structure and properties of grain boundaries (GBs). High-angle grain boundaries determine such properties of polycrystalline fine-grained titanium as ductility and strength. This study is aimed at the investigation of the structure of high-angle special tilt grain boundaries in α-titanium, which has a hexagonal close-packed (HCP) structure. The main goals were to calculate the energies of formation of vacancies in grain boundaries, to estimate the relationship between the energy of formation of a point defect and the degree of the accompanying relaxation of the structure, and to calculate the self-diffusion coefficients. The consideration was carried out on an example of $[2\bar{1}\bar{1}0](01\bar{1}2)$ boundary with a misorientation angle of 86.62º.

2. Methods

To study the grain boundary structure, the molecular statics method was used, in which the static GB configuration is obtained. In this method, there is no motion by default; therefore, it is assumed that the absence of temperature corresponds to the conditional 0 K. The atomic interaction was described by the potential of an embedded atom Ti_3 from [1], for which the energy of formation of point defects in titanium is close to the values determined based on the first-principle calculations by the pseudopotential method.

Simulation was carried out using computational cells consisting of two grains with periodic Born-Karman boundary conditions in all three directions. The scheme for constructing a special boundary was similar to that used in [2, 3]. When constructing a model of a special grain boundary, two modeling blocks (grains) were created, which were turned one relative to the other at a special angle corresponding to the theory of lattices of coinciding nodes. To form the geometry of the modeled block, the ATOMSK program was used [4]. The OVITO program [5] was used as a visualizer for the analysis of structures.

The simulation cell has two crystallographic identical GBs: GB1 is repeated at the upper and lower boundaries of the cell due to the use of periodic boundary conditions, and there is GB2 in the middle of the cell (Fig. 1).

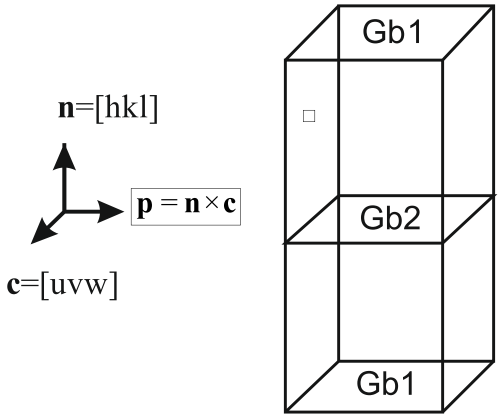


Fig. 1: Scheme of a three-dimensional periodic bicrystal computational cell with designation of the crystal orientation: **c** - tilt axis, **n** - normal to the boundary plane.

The GB structure relaxed at 0 K was determined by molecular statics. The GB energy, E_{GB}, was determined as the excess energy of the microstructure localized in the inter-grain region:

$$E_{GB} = \frac{E_p - N \times E_{coh}}{2S}, \tag{1}$$

where E_p is the total potential energy of a relaxed bicrystal, N is the number of atoms located in the computational region, E_{coh} is the cohesion energy (binding energy per atom of the defect-free lattice of a single crystal), S is the GB area. A factor of 2 in the denominator takes into account the presence of two boundaries.

The structure and energy of a GB were calculated for various initial configurations by searching for a local energy minimum using the conjugate gradient method. For further analysis, we used the structure corresponding to the global energy minimum.

Molecular statics lattice simulation generates a boundary structure that corresponds to a minimum energy at 0 K. Thermal fluctuations present at elevated temperatures can be sufficient to allow GBs to relax to a lower energy structure. If this is the case, it means that the structure constructed as a result of molecular-static modeling has no physical meaning, since it will be unstable at elevated temperatures. A similar criterion for the stability of the GB structure was used in [4].

To check the stability of the structure of GBs built by the molecular statics method for 0 K, they were annealed at finite temperatures by the method of molecular dynamics simulation. A stable structure is defined as a structure in which the positions of the atoms do not change after annealing. Annealing was carried out as follows. The initial state was a structure simulated by the molecular statics method. Next, heating was performed from 0 K to a given temperature for 500 picoseconds (500,000 steps). This was followed by holding at a constant temperature for 100 picoseconds (100,000 steps), after which the procedure for minimizing the energy of the GB at 0 K was started. An isotherm-isobar (NPT) ensemble was applied. The temperature change was controlled using a Nose-Hoover thermostat [7].

The energies of formation of vacancies in different positions in the grain boundary and at different distances from the boundary plane were calculated. The energy of formation of vacancies, E_V, was calculated by the formula:

$$E_V = E_f - (N_0 - 1) / (E_i / N_0), \tag{2}$$

where E_i is the initial energy of the system, before an atom removal; N_0 is the total number of atoms; E_f is the energy of the system after an atom removal, and this is the energy of the system of N_0-1 particles; E_i/N_0 is the energy per atom.

In this work, we performed calculations of grain-boundary diffusion at temperatures at which the boundary is stable. In this case, it was assumed that grain-boundary diffusion proceeds according to the vacancy mechanism. This assumption is based on the earlier Mössbauer studies, which showed that if the diffusing atom is close in size to the matrix atom, the vacancy mechanism of grain boundary diffusion is realized [8]. Consequently, we can confidently assert that grain-boundary self-diffusion should proceed according to the vacancy mechanism.

Self-diffusion was calculated by the molecular dynamics method. Before the calculation, one vacancy was created in the grain boundary at the position corresponding to the minimum energy of vacancy formation, and the simulation was started. The step time was chosen of an order of 1 femtosecond. The simulation time was several nanoseconds. In this case, the collective mean-squared displacement of atoms in the grain boundary was calculated, the width of which was taken to be 1 nm.

$$D = \frac{\sum \left[\left(x_i - x_{i0} \right)^2 + \left(y_i - y_{i0} \right)^2 + \left(z_i - z_{i0} \right)^2 \right]}{6nt} \cdot \frac{n}{N} \tag{3}$$

x_i, y_i, z_i are the coordinates of individual atoms at a given time, x_{i0},, y_{i0}, z_{i0} are the initial coordinates of atoms, n is the number of atoms in the GB in simulation block, N is the number of atoms per 1 vacancy, and t is the total MD simulation time. The n/N factor has been added to take into account that the number of atoms in the GB in the simulation block differs from the number of atoms per a vacancy. The calculation of collective mean-squared displacement in the absence of a vacancy showed that it is close to zero, which is also a confirmation of the vacancy diffusion mechanism. The number of atoms per a vacancy was calculated as the reciprocal of the equilibrium vacancy concentration, C_V:

$$N = 1/C_V \tag{4}$$

The equilibrium concentration of vacancies was calculated by the formula:

$$C_V = \exp\left(-\frac{E_{V\min}}{kT}\right), \tag{5}$$

where $E_{V\min}$ is the minimal energy of vacancy formation in a grain boundary.

3. Results and discussion

Figure 2 demonstrates the relaxed structure of $[2\bar{1}\bar{1}0](01\bar{1}2)$ GB, θ=86.62°. The structure of the boundary is shown perpendicular to the tilt axis. Black and light circles indicate the positions of atoms in alternating planes perpendicular to the tilt axes. Dotted lines encircle structural elements. It can be seen that the boundary is formed by one type of structural elements. Therefore, it belongs to the type of the so-called "preferred" boundaries. Its energy is 0.63 J/m^2.

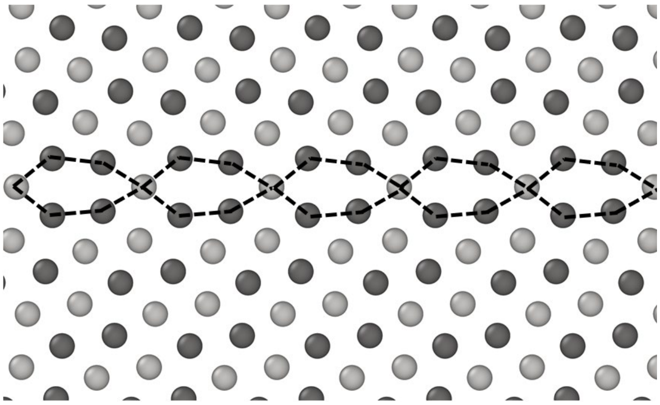


Fig. 2: Calculated relaxed structure of $[2\bar{1}\bar{1}0](01\bar{1}2)$ grain boundary, θ=86.62°

Calculations were made of the energy of formation of vacancies as a function of the distance from the boundary plane. The dependence of the vacancy formation energy on the distance from the plane of the boundary is shown in Fig. 3. The width of the near-boundary region, for which the vacancy formation energy is substantially lower than the vacancy formation energy in the bulk, is approximately 1 nm. Almost the same value is given in [9]. This is approximately twice as large as the structural and diffusion width of the GB [10, 11]. The minimum energy of vacancy formation is 1.42 eV. It should be noted that the positions of vacancies in the GB region can have an energy higher than in the volume. A similar situation was observed in [12].

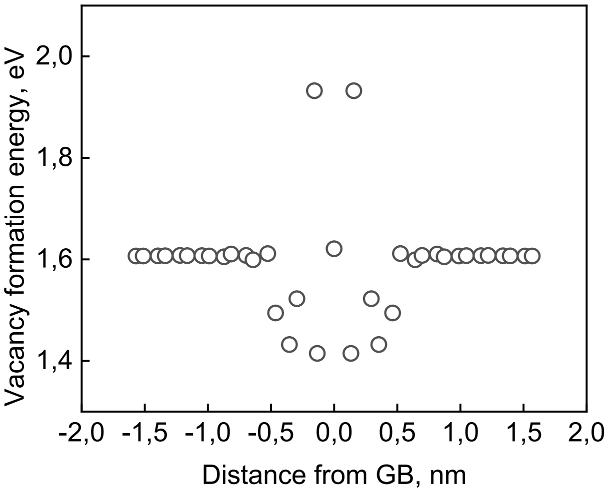
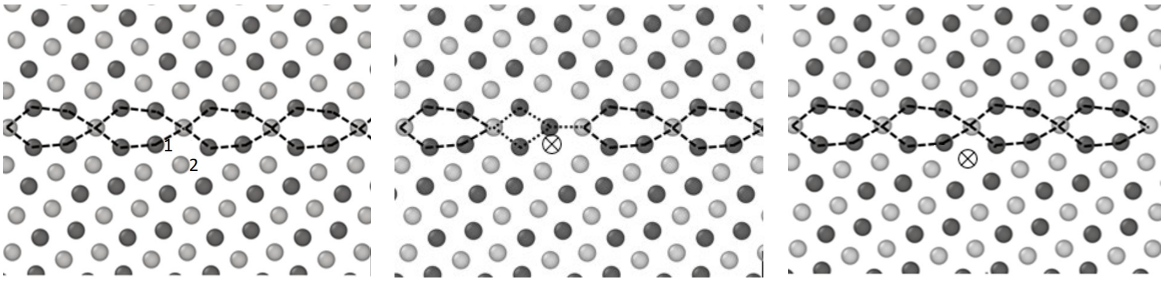


Fig. 3: Dependence of the vacancy formation energy on the distance from the boundary plane.

The dependence of vacancy formation energy on the subsequent relaxation of the structure in the vicinity of the boundary was analyzed. Figure 4a shows the initial relaxed structure, in which the positions of vacancy formation are indicated by numbers 1 and 2. After the removal of an atom in the grain boundary, relaxation was performed. The energies of formation of vacancies in positions 1 and 2 were 1.42 eV and 1.52 eV, respectively. Figures 4b and 4c show the structures of the boundary after the formation of vacancies in the indicated positions and relaxation. Markers show the positions from which the atoms were removed. It is seen that the highest structural relaxation corresponds to the vacancy with the lowest vacancy formation energy.



a b c

Fig. 4: Initial relaxed structure of $[2\bar{1}\bar{1}0]\,(01\bar{1}2)$ boundary (a), and its structure after the formation of vacancies in positions 1 (b) and 2 (c) and subsequent relaxation. In fig. 4a, the numbers show the positions of formation of vacancies. In figs. 4b and 4c, the markers show the starting positions of vacancies.

In this work, the grain-boundary diffusion coefficients in the considered boundary have been calculated. The stability of this boundary at temperatures for which the calculation of the diffusion coefficients was carried out was previously checked. It was found that the structure of the boundary is generally stable up to 1000 K, although, starting from the temperature of 600 K, certain distortions of the boundary structure are recorded. We calculated the grain-boundary diffusion coefficient for several temperatures and compared the obtained values with the experimental values of the grain boundary diffusion coefficient determined in the work by Herzig et al. [13].

In [13] the following expression for double product, δD_{gb}, was given:

$$P = 9.2 \cdot 10^{-14} \exp\left(\frac{-153 \pm 12 \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right), \text{ m}^3\text{s}^{-1} \qquad (6)$$

Assuming that the diffusion width of a grain boundary is 0.5 nm, this expression can be used to obtain the following formula for the coefficient of grain-boundary self-diffusion in HCP Ti:

$$D_{gb} = 1.8 \cdot 10^{-4} \exp\left(\frac{-153 \pm 12 \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right), \text{ m}^2\text{s}^{-1} \qquad (7)$$

Figure 5 shows a comparison of calculated values of the grain-boundary self-diffusion coefficient in HCP Ti with the experimental temperature dependence of this parameter described by expression (7).

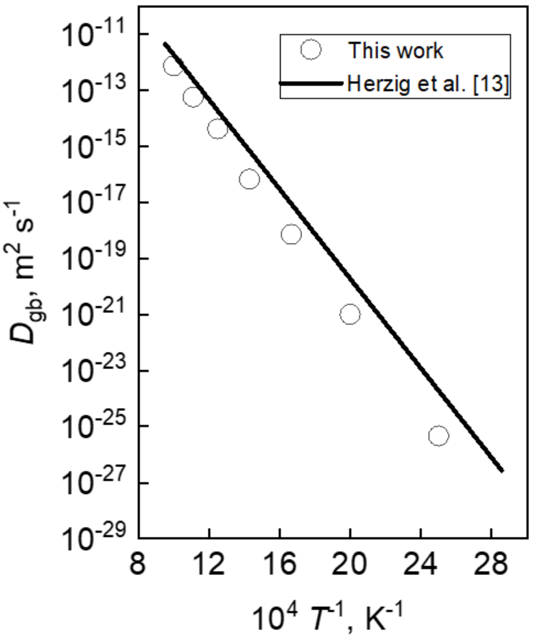


Fig. 5: Comparison of calculated values of the coefficient of grain-boundary self-diffusion in the HCP Ti and the experimental temperature dependence of this parameter obtained in [13].

It can be seen that in the entire temperature range for which the calculations were performed, there is a reasonable agreement between the calculations and the experiment. In this case, the calculated values of the self-diffusion coefficient are noticeably lower than the experimental ones. Apparently, this is explained, in particular, by the fact that the experiment was carried out on titanium samples with grain boundaries of general type, and the calculation was performed for a special boundary. At the temperature of 400 K, the difference reaches an order of magnitude, and with increasing temperature, it decreases. Perhaps, this is due to the fact, that with an increase in temperature, the structure of the special boundary is somewhat distorted and its properties approach the properties of high-angle boundaries of general type.

3. Conclusions

The structure and energy of symmetric tilt boundary $[2\bar{1}\bar{1}0](01\bar{1}2)$ in HCP titanium and the energies of formation of vacancies in it have been calculated by the method of molecular-static simulation.

The dependence of the energy of formation of vacancies on the distance from the boundary plane has been analyzed. It is shown that the width of the near-boundary region, for which the energy of vacancy formation is substantially lower than the energy of vacancy formation in the bulk, is approximately 1 nm.

The dependence of the vacancy formation energy on the subsequent relaxation of the structure in the vicinity of the boundary has been analyzed, and it is shown that the highest structural relaxation corresponds to a vacancy with the lowest formation energy.

The thermal stability of grain boundaries at elevated temperatures has been verified by molecular dynamic annealing, and it has been shown that the structure of the boundary is generally stable up to 1000 K.

The coefficient of grain boundary self-diffusion in HCP Ti has been calculated for several temperatures, and the results obtained are compared with the available experimental data in the literature. It is shown that there is a reasonable agreement between them.

Acknowledgments

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