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Influence of Carbon and Oxygen Impurities on the Migration Rate of ⟨110⟩ Tilt Boundaries in Austenite

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Abstract—The effect of impurity carbon and oxygen atoms on the migration rate of the tilt boundaries with the misorientation axis ⟨110⟩ in γ-Fe with fcc crystal lattice was studied by the method of molecular dynamics. Dependences of energy of the considered boundaries and rate of their migration at a temperature of 1600 K on the misorientation angle were obtained. The migration rate of ⟨110⟩ tilt boundaries under the same conditions turned out an order of magnitude lower than the migration rate of ⟨111⟩ and ⟨100⟩ boundaries, which is primarily due to the relatively low energy of ⟨110⟩ boundaries. In addition, the low-angle ⟨110⟩ tilt boundaries are unique compared to other tilt boundaries—grain-boundary dislocations in them are ordinary perfect edge dislocations with even cores that do not contain jogs periodically located on them as in ⟨111⟩ and ⟨100⟩ boundaries. The introduction of impurity carbon and oxygen atoms led to a significant decrease in migration rate of the grain boundaries. The binding energies of impurity carbon and oxygen atoms with grain-boundary dislocations in the austenite were calculated. The obtained values correlate well with the dependences of migration rate of ⟨110⟩ boundaries on the impurities concentration. Effect of impurities on migration of the boundaries in austenite turned out to be stronger than in the previously studied nickel and even more so in silver, which can be explained by the relatively low value of the electronegativity of iron atoms in comparison with nickel and silver. A higher value of the binding energy with dislocations in austenite and, accordingly, a greater effect on the migration rate of grain boundaries were obtained for carbon atoms.

Keywords: molecular dynamics, grain boundary, migration, austenite, impurity

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INTRODUCTION

Migration of grain boundaries is decisive in the recrystallization in many phase transformations. In spite of a long-term interest in the problem of migration of boundaries, the problems associated with the mechanism and features of migration of various types of boundaries are yet unsolved. It is considered that small-angle tilt boundaries migrate through the combined action of two mechanisms, such as sliding and climbing of grain-boundary dislocations [1]. For example, the authors from [2, 3] derive statement that climbing of grain-boundary dislocations is the main mechanism of migration of small-angle tilt boundaries. However, the results from [4, 5] indirectly indicate the predominance of sliding of dislocations during migration. In [6, 7], during computer simulation of tilt boundaries with misorientation axes ⟨111⟩ and ⟨100⟩, it was also stated that migration of these boundaries occurs primarily through sliding of grain-boundary dislocations.

Another important problem is the effect of various impurities, defects, and free volume on the mobility of grain boundaries. It is known that impurity atoms significantly slow down their migration after attaching to boundaries [8–11]. Grain boundaries (along with dislocations) accumulate clouds or so-called atmospheres of impurities, such as Cottrell atmosphere [12, 13]. The migration mobility of boundaries as a result of formation of cloud of impurities significantly decreases, because additional energy is required for the detachment of the boundary from cloud as in the case of dislocations. In the case of small-angle boundaries, the binding energy of the impurity atom with boundary is nearly equal to the binding energy with dislocation. For example, in [14, 15], the binding energies of carbon atom with dislocation in iron in the range of 0.4–0.7 eV were determined, while the value of 0.5 eV was obtained for the oxygen atom in zirconium in [16]. The order of value indicates a relatively high binding of impurity atoms both with dislocations and clearly with tilt boundaries.

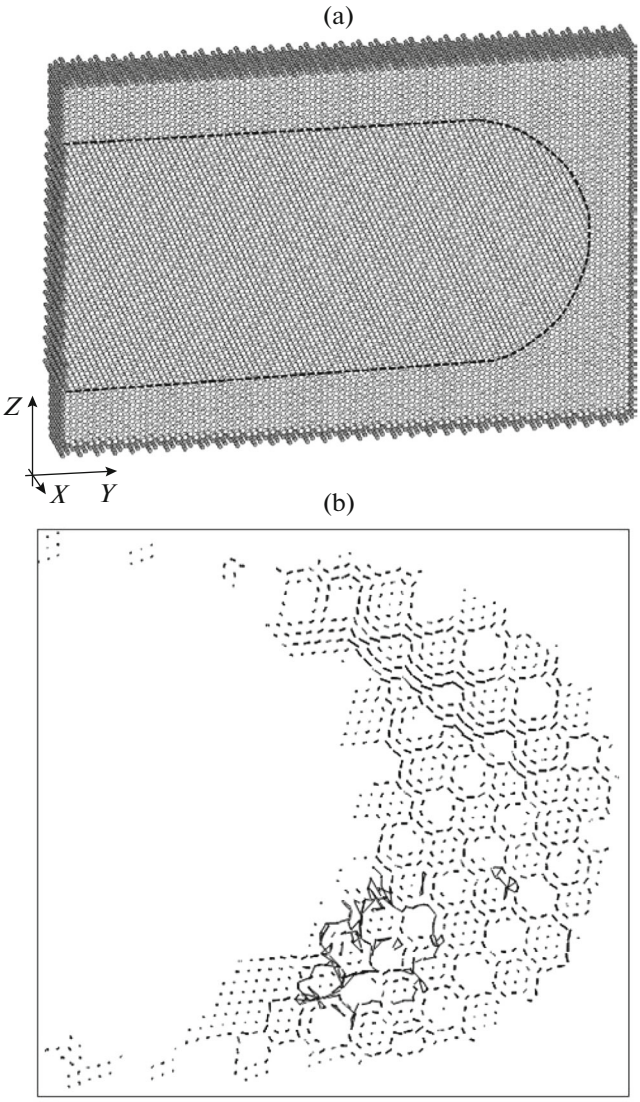

Fig. 1. (a) Calculated cell for modeling migration of ⟨110⟩ tilt boundaries and (b) atomic displacements (shown only by those who more than 0.08 nm) in the process of migration of ⟨110⟩ tilt boundary with orientation angle of 15° in austenite during 3000 PS at 1600 K.

The effect of impurities of carbon and oxygen on the rate of migration of tilt boundaries with misorientation axes ⟨100⟩ and ⟨111⟩ in fcc metals, such as nickel, silver, and aluminum, was previously investigated [17]. In particular, it was shown that introduction of impurity atoms of light elements results in a notable inhibition of the migration of grain boundaries. The boundaries with misorientation axis ⟨110⟩ were not considered. However, consideration of tilt boundaries ⟨110⟩ {111} is of great practical significance, because it is known that most boundaries in fcc metals are oriented in dense-packed planes {111} [18, 19], among which the tilt boundaries with the misorientation axis ⟨110⟩ appear most often [18–22]. This type of boundaries is also related to twins Σ3{111}⟨110⟩, which play a particularly important role in strain processes [23, 24].

This work is devoted to the molecular dynamics study of the effect of impurity carbon and oxygen atoms on the rate of migration of tilt boundaries ⟨110⟩ in austenite. Consideration of γ-iron, which has an fcc crystal lattice, is caused by its high practical significance as a base of a large class of austenitic steels.

DESCRIPTION OF MODEL

A procedure of study of the migration of tilt boundary of grains, which was suggested and developed in [1, 25], was taken as base. A clearly certified boundary in the form of loop or arc as shown in Fig. 1a is formed (shown by a black dashed line). The tension force of the boundary, which in analogy with surface tension arises due to the tendency of the boundary to minimize energy, is the reason for directed transfer of the boundary towards a decrease in its area (Fig. 1b). The force inducing migration depends on the misorientation angle (the energy of boundary usually increases with an increase in the misorientation angle) and curvature of boundary. In the considered model, the boundary was formed with a relatively high curvature so that the rate of migration would be sufficiently high to be measured by molecular dynamics. The force and rate of migration at constant temperature remained constant in the considered model during the motion of boundary gradually decreasing in the end of computer experiment.

The computational cell with the sizes of 20.4 × 13.8 × 2.5 nm contained nearly 60000 atoms. An infinite repeating of structure was simulated along the X axis (Fig. 1a); i.e., periodical boundary conditions were applied. At the edge of computational cell, grain boundaries should be fixed, which means the retention of the crystal lattice orientation of two different grains at the cell boundary. For this reason, the grain boundaries were tightly fixed along Y and Z axes for the fixation of the specified grain misorientation (atoms are colored in dark-gray color in Fig. 1a) and remained intact during computer simulation.

In order to describe the interaction of atoms in austenite, the known and tested Lau EAM potential was used [26]. In particular, in [27], it was tested in detail upon description of structural, energy, and elastic characteristics of austenite. To describe the interactions of atoms of impurities of light elements with metal atoms and impurity atoms with each other, the Morse pair potentials were used [28]. Both potentials proved themselves to be good in a number of calculations performed by molecular dynamics [28–30]. Parameters of the potentials for the description of interactions of impurity carbon and oxygen atoms with iron atoms were taken from [26, 28], where they were found assuming empirical dependences and known characteristics (such as melting point or temperature

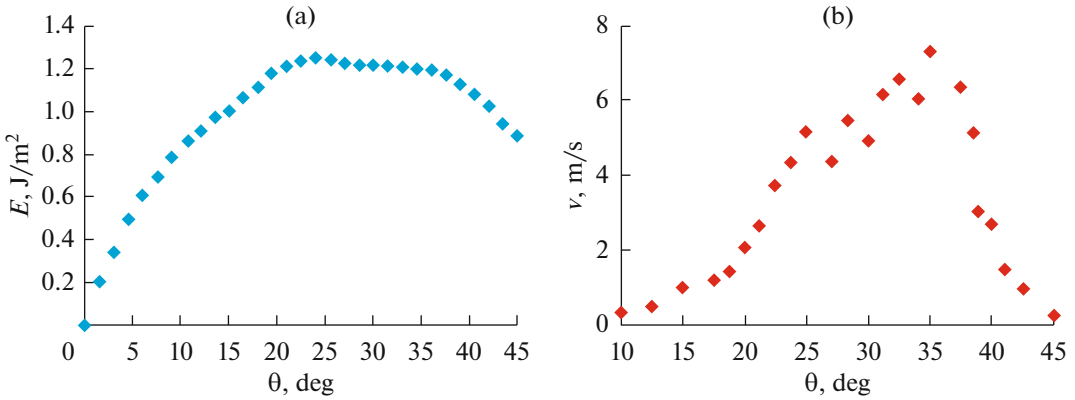

Fig. 2. (a) Energy of ⟨110⟩ tilt boundaries and (b) their migration rate at 1600 K depending on orientation angle θ in austenite.

of decomposition of corresponding chemical compound of metal with light element, activation energy of diffusion of impurity atom in the crystal lattice of metal). To describe the interactions of impurity atoms with each other in metals in [28], the potentials suggested by other authors were taken as a base. In the case of C–C bond, the pair potential from [31] was transformed into the Morse potential. In the case of O–O bond, the potential from [32] was used.

Impurity atoms were added to the computational cell containing grain boundaries randomly to octahedral voids. It is known that impurity atoms of light elements (such as carbon and oxygen) are located in octahedral voids in the fcc lattice of metals [8]. Modeling of the migration of tilt boundaries ⟨110⟩ was carried out at the temperature of 1600 K. Choice of the temperature near the upper boundary of existence of pure austenite is caused by the fact that the rata of migration of boundaries is largest at this temperature.

RESULTS AND DISCUSSION

Figure 2 shows the dependences of the energy E of tilt boundaries ⟨110⟩ and the rate v of their migration at the temperature of 1600 K from the misorientation angle θ. The angles from 0° to 45° were considered. The energy of boundaries was calculated as the ratio of the difference of the energies of computational cell with boundary and perfect crystal with the same number of atoms to the boundary area. Before calculation of energy, the relaxation of cell structure was performed. The obtained values agree well with the results of other authors [20, 21].

Small-angle tilt boundaries ⟨110⟩ are unique as compared to other tilt boundaries: grain-boundary dislocations in such boundaries represent ordinary perfect edge dislocations with direct cores without ruptures (steps) on them. On the tilt boundaries with other misorientation axes, for example, ⟨111⟩ and ⟨100⟩, grain-boundary dislocations are more complex: they are usually pair (the disloactions from two different sets with different sliding planes are combined in one core) and contain geometrically imperative ruptures [6, 7]. Dislocations in tilt boundaries ⟨110⟩ do not possess ruptures and contain less free volume and their energy is much lower than the energy of boundaries ⟨111⟩ and ⟨100⟩ at the same misorientation angles (Fig. 2a).

Migration of boundaries ⟨110⟩ occurred by nearly one order of magnitude more slowly than that of boundaries ⟨111⟩ and ⟨100⟩ [7] (Fig. 2b). It is evident that this is related to the relatively low energy of ⟨110⟩ boundaries. Under similar conditions, temperature and size of computational cell, the rate of migration of boundaries ⟨111⟩ and ⟨100⟩ with the misorientation angle of more than 30° for nickel in [7] corresponded to ca. 30–35 m/s. The peak of the rate of migration of grains ⟨110⟩ was observed for large-angle boundaries in the angle range of 22° to 37° (Fig. 2b). Then, the rate again decreased up to nearly zero at the misorientation angle of 45°.

As a result of migration of tilt boundary ⟨110⟩, trajectories of displacements of atoms formed "grids" (Fig. 1b), which are similar to those formed upon migration of boundaries ⟨111⟩ and ⟨100⟩ in [6, 7]. During migration of boundary in grain, towards which migration occurred, the domains of identical shape were formed, which are uniformly directed at the misorientation angle, the size of which in the case of small-angle boundaries depended on the distance between neighboring grain-boundary dislocations. The form of these cells of the grid is determined by crystallography; in the case of ⟨110⟩ boundaries, they possess nearly hexagonal shape. It should be noted that the character of atomic displacements in grain boundaries ⟨110⟩ is the same as that for the boundaries ⟨111⟩ and ⟨100⟩ [6, 7]. In all cases, migration occurred as a result of consistent sliding of grain-boundary dislocations. Climbing of dislocations, which is caused, for example, by diffusion, marginally contributes to the mechanism of migration of boundaries according to the studies.

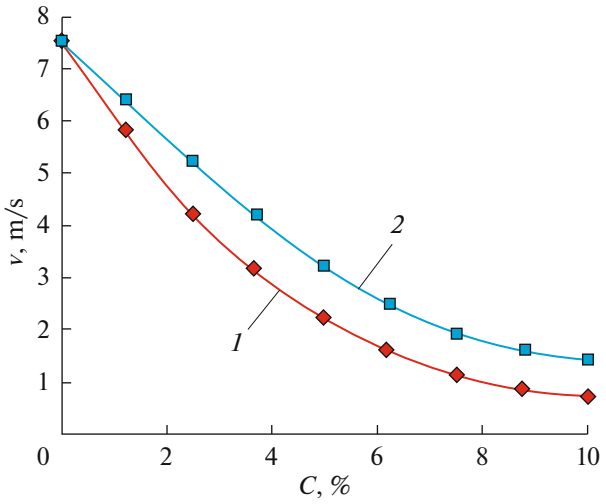

Fig. 3. Dependences of migration rate of ⟨110⟩ tilt boundaries with orientation angle of 35° at 1600 K on concentration of impurity (*1*) carbon atoms and (*2*) oxygen in austenite.

Introduction of impurity carbon and oxygen atoms resulted in a notable decrease in the rate of migration of grain boundaries, which is certainly caused by high binding energies of impurity atoms with them. Fig. 3 shows the dependences of the rate v of migration of tilt boundaries ⟨110⟩ with the misorientation angle of 35° at the temperature of 1600 K on the concentration of impurity atoms in γ-iron.

Effect of impurities on the migration of boundaries in austenite was stronger than those previously studied in nickel and particularly silver, which is caused by relatively low electronegativity value of iron atoms (1.83) as compared to nickel (1.91) and silver (1.93). In the case of γ-iron, larger binding energies of carbon and oxygen atoms with dislocations were obtained (0.79 and 0.66 eV, respectively) as compared to nickel (0.77 and 0.62 eV [7]) and particularly silver (0.30 and 0.10 eV) [7]. The found values of the binding energy agree well with the dependences given in Fig. 3.

The binding energy of impurity atom with grain-boundary dislocation was calculated as the difference of potential energy of computational cell containing small-angle boundary ⟨110⟩ and impurity atom in octahedral pore of crystal lattice at such a distance from each other, which excludes the interaction of dislocation and impurity atom, and the potential energy of computational cell containing impurity atom in the core of dislocation. In both cases, before calculation of the energies of computational cell, relaxation of structure was performed, after which the computational cell was cooled to 0 K. The position of impurity atom in the dislocation core was chosen in such a way that the binding energy is the highest; i.e., the energetically most favorable position of impurity in dislocation was chosen.

CONCLUSIONS

Using molecular dynamics, the effect of impurity carbo and oxygen atoms on the rate of migration of tilt boundaries with the misorientation axis ⟨110⟩ in γ-iron possessing fcc crystal lattice has been studied. Dependences of the energy of considered boundaries and the rate of their migration at the temperature of 1600 K on the misorientation angle have been obtained. It has been shown that the rate of migration of tilt boundaries ⟨110⟩ at the same conditions is less by one order of magnitude than the rate of migration of boundaries ⟨111⟩ and ⟨100⟩, which is primarily related to the relatively low energy of boundaries ⟨110⟩. In addition, small-angle tilt boundaries ⟨110⟩ are unique as compared to other tilt boundaries: grain-boundary dislocations in them represent ordinary perfect edge dislocations with flat cores, which do not contain periodically located ruptures, as in the boundaries ⟨111⟩ and ⟨100⟩.

During migration of boundary in grain, towards which migration occurs, the domains of identical shape are formed, which are uniformly directed at the misorientation angle, the size of which in the case of small-angle boundaries depends on the distance between neighboring grain-boundary dislocations. The migration of small-angle boundaries usually occurs through cooperative shifts as a result of consistent sliding of grain-boundary dislocations. Climbing of dislocations induced by diffusion marginally alters the mechanism of migration of boundaries.

Introduction of impurity carbon and oxygen atoms results in a notable decrease in the rate of migration of grain boundaries. In the case of impurity carbon and oxygen atoms, the binding energies with grain-boundary dislocations in austenite have been calculated. The obtained values correlate well with the dependences of the rate of migration of boundaries ⟨110⟩ on the concentration of impurities. The effect of impurities on the migration of boundaries in austenite is stronger than those in previously studied nickel and particularly silver, which is caused by relatively low electronegativity of iron atoms as compared to nickel and silver. A higher binding energy with dislocations in austenite and, accordingly, a larger effect on the rate of migration of grain boundaries have been obtained for carbon atoms.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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