

Role of point defects in self-diffusion along low-angle twist boundaries in fcc metals: A molecular dynamics study

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Abstract The interaction of point defects with low-angle (100), (110) and (111) twist boundaries in fcc metals Ni, Cu, Al and role of the point defects in self-diffusion along considered boundaries were studied by the molecular dynamics method. The binding energies of point defects with low-angle twist boundaries were calculated. It was found that the point defects are mainly fixed in the nodes of grain-boundary screw dislocations network. It was shown that the introduced vacancies play an important role in diffusion along twist grain boundaries. The contribution of introduced interstitial atoms to grain-boundary diffusion under thermodynamic equilibrium condition is less by several orders of magnitude in comparison with the contribution of vacancies.

Keywords Molecular dynamics; twist boundary; screw dislocation; point defects; vacancy; interstitial atom; diffusion.

1. Introduction

Grain boundaries in polycrystals are divided into two types: tilt boundaries and twist boundaries. In the first case, the misorientation axis, that is the axis around which one crystal grain is rotated relative to the other, lies in the plane of the boundary. In the case of twist boundaries, the misorientation axis is perpendicular to the plane of the boundary. It is known that low-angle tilt boundaries represent a system of geometrically necessary (grain-boundary) edge dislocations. Low-angle twist boundaries also have an ordered structure, which represents a network of screw dislocations [De Hosson *et al.*, 1990; Ghafoor *et al.*, 1998, 2001; Shallcross *et al.*, 2008; Belov *et al.*, 1999] (Fig. 1(a)). In [Poletaev *et al.*, 2010], we have carried out the identification of screw dislocations in twist boundaries oriented in the (100), (110) and (111) planes in metals with fcc crystal lattice Ni, Cu and Al. It was shown that the (100) boundaries contain a square network of $1/2\langle 110 \rangle$ screw dislocations; (110) boundaries — a rectangular network of screw dislocations of two types: $1/2\langle 110 \rangle$ and $1\langle 100 \rangle$; (111) boundaries — a hexagonal network of

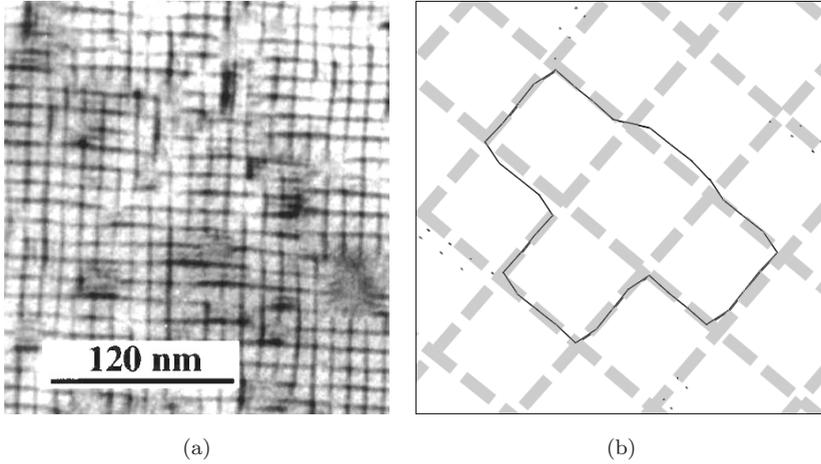


Fig. 1. Low-angle twist boundary in (100) plane: (a) the image obtained in [Poletaev *et al.*, 2010] with the help of an electron microscope; (b) closed chain of displaced atoms in the (100) twist boundary with a misorientation angle of 15° (the image was taken from [Martynov *et al.*, 2011], where it was obtained by modeling the diffusion along the boundary).

$1/4\langle 112 \rangle$ screw dislocations. With an increase in the misorientation angle of grains, the dimensions of the dislocation network cells decrease. In the center of the network cells, i.e., outside the cores of grain-boundary dislocations, the structure corresponds to an almost ideal crystal. In the same paper [Poletaev *et al.*, 2010], the dependencies of the energy of the considered twist boundaries on the misorientation angle were obtained using pair Morse and multiparticle Clery–Rosato potentials.

In [Martynov *et al.*, 2011], we studied by the molecular dynamics the self-diffusion along (100), (110) and (111) twist boundaries in Ni, Cu and Al. It was shown that self-diffusion over low-angle twist boundaries is realized by forming of chains of displaced atoms along the cores of grain-boundary screw dislocations, wherein the sites of initiation of the chains of displaced atoms are nodes of the dislocation network. The chains of atomic displacements often have a closed form (Fig. 1(b)). The formation of closed chains of atomic displacements along the cores of screw grain-boundary dislocations was explained in [Martynov *et al.*, 2011] by the recombination of a pair of excess defects — a vacancy and an interstitial atom formed at neighboring nodes of the dislocation network when atoms are displaced along the dislocation cores from one network node to the other. According to [Martynov *et al.*, 2011], the (110) boundaries have a relatively maximum diffusion permeability (and a minimum energy of self-diffusion activation), and the (111) boundaries have a minimum permeability. With the increasing misorientation angle, the diffusion activation energy decreases.

The results given above refer to structural “clean” grain boundaries which do not contain any “introduced” defects. In fact, in real polycrystals, grain boundaries are effective traps for various defects: dislocations, vacancies, interstitial atoms and

their complexes. Almost all boundaries contain some or other introduced defects, which to varying degrees affect to the grain boundary processes: diffusion, plastic deformation, etc. The concentration and type of these defects mainly depend on the conditions of the structure creation (deformation, rapid cooling or heating, radiation exposure, etc.). In practice, these are thermodynamically non-equilibrium states. Therefore, to predict the concentration and type of defects using the laws of equilibrium thermodynamics in many cases does not make sense. However, on the other hand, from the known values of the formation energy and energy of bond of the defect with the boundary, we can conclude on the concentration of various defects in the boundary, the probability of their appearance and fixation in it.

The present paper is devoted to the investigation of the interaction of point defects with low-angle (100), (110) and (111) twist boundaries and their role in self-diffusion over the considered boundaries in fcc metals Ni, Cu and Al.

2. Description of the Model

The study has been carried out with the help of the computer program MDR developed by our scientific group. The boundary was created in the middle of the crystal calculation block as a result of turning one half of the block relative to the other one by a given angle θ around an axis perpendicular to the boundary (Fig. 2). In the paper, we considered three variants of the orientation of the boundary plane in a fcc crystal: (100), (110) and (111). After the creation of the calculation block (in Fig. 2, it is separated by a dotted contour), the stage of structure relaxation was followed, when the structure near the grain boundary acquired a state with the lowest potential energy under the given conditions. During the structural relaxation, a geometrically necessary network of grain-boundary screw dislocations was formed

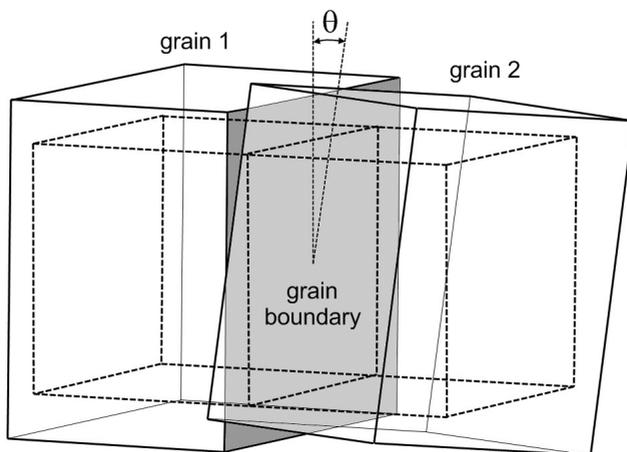


Fig. 2. Creation of the twist boundary in the model. θ — the misorientation angle of the grains. The final calculation block is separated by a dotted contour.

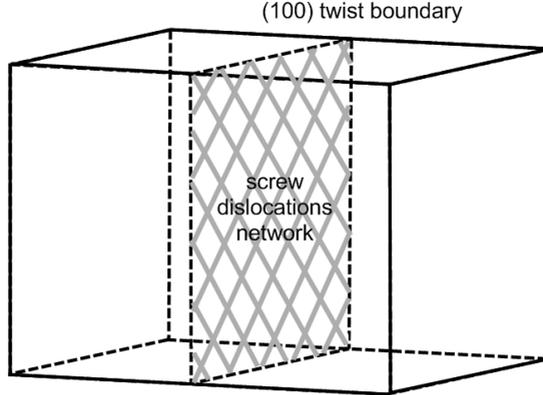


Fig. 3. Calculation block with (100) low-angle twist boundary and screw dislocations network after the structural relaxation.

at the boundary (Fig. 3). After the relaxation, the calculation block was cooled to 0 K.

Rigid boundary conditions were imposed on the borders of the calculation block, i.e., the atoms near the borders of the block were remained stationary during the simulation. This was necessary to keep the grain boundary with the specified parameters in the middle of the calculation block during the simulation. The calculated blocks had approximately the dimensions $80 \times 80 \times 65 \text{ \AA}$ and contained 30,000 atoms.

Interactions of metal atoms with each other in the molecular dynamics model were described by the multiparticle EAM Cleri–Rosato potentials [Clери and Rosato, 1993], built within the tight-binding model. In this case, the energy of the i th atom is found using expression

$$U_i = \sum_j A \exp \left(-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right) - \sqrt{\sum_j \xi^2 \exp \left(-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right)}. \quad (1)$$

Here A, p, q, ξ, r_0 are the potential parameters; r_{ij} is the distance between the i th and j th atoms. The parameters of the Cleri–Rosato potentials were taken from [Clери and Rosato, 1993].

This potential has proved itself well in a number of calculations of the structural and energy characteristics of metals performed by the molecular dynamics method [Poletaev and Starostenkov, 2010; Poletaev *et al.*, 2018]. The time step of integration of atomic motion in the method of molecular dynamics was equal to 5 fs. This step is sufficient for modeling the thermal motions of metal atoms up to the melting point [Poletaev *et al.*, 2013, 2016]. The temperature of the calculation blocks was set via the initial atomic velocities in accordance with the Maxwell–Boltzmann distribution. When setting the temperature, the thermal expansion of the metal was taken into account.

The molecular dynamics experiments of self-diffusion along the twist boundaries were carried out with duration of 0.3–0.5 ns. The temperature of the calculation block during these experiments was kept constant with the help of Nose–Hoover thermostat, i.e., in the molecular-dynamics model was used NPT ensemble. The diffusion coefficient was calculated through the mean square displacements of atoms by the formula (for the coefficient along the X -axis)

$$D_x = \frac{\frac{1}{N} \sum_{i=1}^N (x_{0i} - x_i)^2}{2t}, \quad (2)$$

here x_{0i} is coordinate of the initial position of the i th atom; x_i is the coordinate of the i th atom at time t ; N is the number of atoms in the calculation block.

Before calculating the diffusion coefficient, the calculation block was cooled to 0 K in order to eliminate the thermal (none-diffusion) displacements of the atoms. The calculation of the diffusion coefficient along the Y and Z axes was performed analogously. The mean self-diffusion coefficient was calculated as the arithmetic mean of the coefficients D_x , D_y and D_z . In the study of self-diffusion along grain boundaries, it was assumed that the boundaries have a diffusion thickness of 5 Å. Such a thickness was chosen not accidentally — as is well known, the main diffusion processes proceed along the boundaries in a small layer with a thickness of about 5 Å [Larikov and Isaychev, 1987]. The diffusion characteristics (the activation energy of diffusion and the pre-exponential factor in the Arrhenius equation) were determined from the dependences of $\ln D_b$ on T^{-1} , where D_b is the self-diffusion coefficient along the grain boundary and T is the temperature, according to the method described in [Poletaev *et al.*, 2018].

3. Results and Discussion

When studying the interaction of point defects with the considered twist boundaries, one vacancy or interstitial atom was introduced into different positions of “structurally correct” (i.e., not containing excess defects) boundaries. Three different positions of the point defect at the boundary were compared: at the node of the grain boundary dislocations network, at the dislocation core and at the center of the dislocation network cell (with an almost ideal crystal structure). After the insertion of the point defect into one or another position, the structure was relaxed with subsequent cooling.

It was noted that in most cases the point defects migrated to the nearest node of the dislocation network in the process of structural relaxation. This happened even without additional thermal activation. In Fig. 4, there are examples of atomic displacements as a result of such migrations of point defects at their initial introduction into the area of the dislocation core at the boundary $\theta = 6^\circ$ (100). The figures show that the atoms are displaced predominantly along the dislocation cores. Here-with, the parallel displacements of atoms in opposite directions occurred, typical for the motion of a screw dislocation.

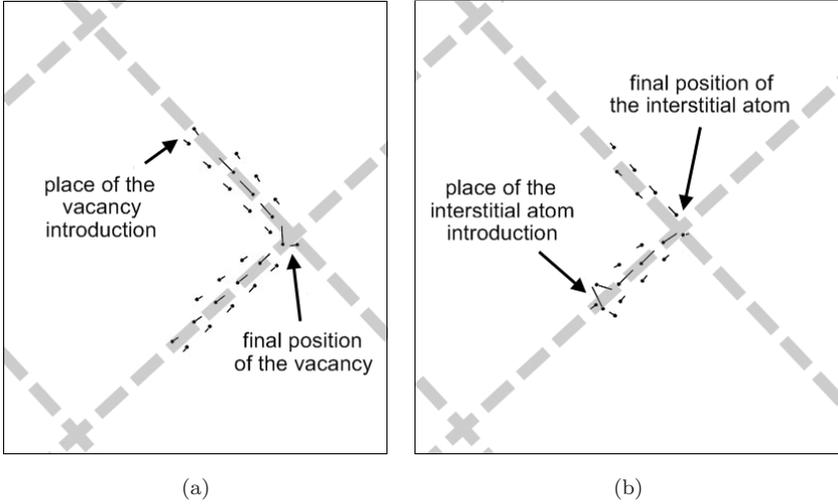


Fig. 4. Atomic displacements in low-angle $\theta = 6^\circ$ (100) twist boundary in Ni as a result of migration of the vacancy (a) and interstitial atom (b) with their initial introduction into the core region of the screw grain-boundary dislocation.

The binding energy of a point defect with a grain boundary is the work that must be expended in order to remove this defect from the boundary into the volume of the crystal. The binding energy E_b was calculated by formula

$$E_b = U_{bv0} - U_{bv}, \quad (3)$$

where U_{bv0} is the potential energy of the calculation block containing the grain boundary and the point defect in the grain volume (in the crystal) at a sufficient distance from the boundary; U_{bv} is the potential energy of the calculation block containing the grain boundary and the point defect located in the boundary at the node of the dislocation network. When the values U_{bv0} and U_{bv} were obtained, the structure was necessarily relaxed and subsequently cooled to 0 K (this was necessary to avoid the effect of thermal displacements of the atoms).

The energy of formation of a point defect in the grain boundary E_f is the work of creating this defect in the boundary. It can be calculated as the difference in the formation energy of the defect in the pure crystal E_{f0} and the binding energy of the defect with the grain boundary E_b :

$$E_f = E_{f0} - E_b. \quad (4)$$

The values of the vacancy formation energy in a pure crystal E_{f0} were taken from [Wollenberger, 1996; Shtremel, 1982; Orlov and Trushin, 1983]: 1.64 eV for Ni, 1.22 eV for Cu and 0.68 eV for Al. The energies of the formation of interstitial atoms (in the $\langle 100 \rangle$ dumbbell position) were taken from [Poletaev *et al.*, 2018], where they were obtained by the molecular dynamics method using the same potential as in the present paper: 4.98 eV for Ni, 3.58 eV for Cu and 2.25 eV for Al. Table 1 shows

Table 1. The formation energy of vacancy and interstitial atom in (100), (110) and (111) twist boundaries with misorientation angles of 6° , 15° and 24° (eV).

		(100)			(110)			(111)		
		6°	15°	24°	6°	15°	24°	6°	15°	24°
Ni	vacancy	0.57	0.47	0.74	0.03	0.10	0.23	1.35	1.58	1.60
	int. atom	2.09	1.93	2.22	0.51	0.77	0.62	4.09	4.12	4.30
Cu	vacancy	0.23	0.34	0.41	0.17	0.11	0.06	1.16	1.09	0.95
	int. atom	1.74	1.53	1.02	0.11	0.21	0.20	2.76	2.52	2.37
Al	vacancy	0.12	0.08	0.17	-0.06	0.07	0.11	0.57	0.59	0.63
	int. atom	0.91	0.87	0.93	0.19	0.23	0.16	2.01	1.92	2.12

the values of the formation energy of the point defects in (100), (110) and (111) twist boundaries obtained for three different misorientations: 6° , 15° and 24° .

According to the obtained data, for the twist boundaries oriented in the (110) plane, the energies of formation of point defects are the lowest. For the (111) boundaries, on the contrary, the formation energies are close to the values for the pure crystal. This correlates with the energy values of the grain boundaries themselves, obtained earlier in [Poletaev *et al.*, 2010]: the (111) boundaries have the lowest energy, the (110) boundaries – the largest among the considered orientations. In other words, the higher the energy of the boundary (and, hence, its “defectiveness”), the higher the binding energy of a point defect with the boundary and, consequently, its formation energy in the boundary. The angle of misorientation of the grains had practically no effect on the formation energy of the defects in the boundary.

The obtained results support the fact that (111) twist boundaries in real metals should contain the smallest concentration of excess defects and be a relatively weak trap for external point defects. The more effective traps are the (110) boundaries. With increasing misorientation angle, the density of the dislocation network nodes is higher. In this connection, it is obvious that the higher the angle of misorientation of the grains, the more effective trap for point defects is the boundary.

When studying the contribution of the introduced point defects to self-diffusion along the twist boundaries, one vacancy or one interstitial atom was introduced into the boundary. The grain-boundary self-diffusion coefficient D_b was determined at different temperatures, after which the activation energy and the pre-exponential factor in the Arrhenius equation were calculated from the dependences $\ln D_b$ OT T^{-1} . In connection with the cumbersome calculations (for one metal, it was necessary to obtain six temperature dependences of the diffusion coefficient — two (with the participation of a vacancy and an interstitial atom) for three different angles of misorientation 6° , 15° and 24°), calculations were carried out only for Ni. The results are shown in Table 2.

As can be seen from the table, the activation energy of self-diffusion is less when a point defect is introduced. In addition, the introduction of a vacancy or an

Table 2. The activation energy of self-diffusion in Ni along “structurally pure” and containing one excess point defect (100), (110) and (111) twist boundaries with misorientation angles of 6°, 15° and 24° (eV).

	(100)			(110)			(111)		
	6°	15°	24°	6°	15°	24°	6°	15°	24°
Pure	1.49	1.22	1.01	0.38	0.32	0.30	—	—	—
Vacancy	0.83	0.62	0.66	0.22	0.25	0.34	0.90	1.02	1.29
Int. atom	0.78	0.55	0.61	0.44	0.23	0.31	0.20	0.20	0.16

interstitial atom almost equally affects to the diffusion permeability of the (100) and (110) boundaries, whereas in the case of (111) boundaries, the introduction of an interstitial atom leads to a more significant decrease in the activation energy of diffusion compared with the introduction of a vacancy. This again indicates a high degree of ordering of the structure of (111) twist boundaries.

A quantitative estimate of the contribution of the introduced point defects to self-diffusion along the considered twist boundaries was carried out as follows. The probabilities that some part of the boundary will contain one vacancy or one interstitial atom, respectively, are equal to

$$p_v = n \exp\left(-\frac{E_{fv}}{kT}\right), \quad p_i = n \exp\left(-\frac{E_{fi}}{kT}\right), \quad (5)$$

where E_{fv} and E_{fi} are the formation energies of the vacancy and interstitial atom (Table 1); k is the Boltzmann constant; T is the temperature; n is the number of the nodes of the dislocation network (where the point defects are predominantly located) in the considered part of the boundary.

Then the probability that the part of the boundary will not contain the point defects:

$$p_0 = 1 - p_v - p_i. \quad (6)$$

The diffusion coefficient along the entire grain boundary is equal to the sum of the contributions of the diffusion over the parts without the defects D_0 , with the vacancy D_v and with the interstitial atom D_i :

$$D_\Sigma = D_0 + D_v + D_i. \quad (7)$$

These contributions can be found as multiplications of the diffusion coefficients in the considered parts and the corresponding probabilities of the presence of these parts in the boundary:

$$D_0 = p_0 D_0 \exp\left(-\frac{Q}{kT}\right), \quad D_v = p_v D_{0v} \exp\left(-\frac{Q_v}{kT}\right), \quad D_i = p_i D_{0i} \exp\left(-\frac{Q_i}{kT}\right), \quad (8)$$

where Q_v and Q_i are the activation energies of self-diffusion in the considered part of the boundary containing one vacancy or one interstitial atom (Table 2); D_v and D_i are the pre-exponential factors obtained from the dependences of $\ln D_b$ on T^{-1} when introducing one vacancy or one interstitial atom into the calculation block.

The relative contribution of the vacancy and interstitial atom to the self-diffusion are

$$V_v = \frac{D_v}{D_\Sigma} \cdot 100\% \quad \text{and} \quad V_i = \frac{D_i}{D_\Sigma} \cdot 100\%. \quad (9)$$

Temperature dependencies of the contribution of the introduced vacancies to self-diffusion along the (100) twist boundaries with misorientation angles of 6° , 15° and 24° are shown in Fig. 5. As can be seen from the figure, the contribution of vacancies is quite substantial. Moreover, for the (111) and (110) boundaries, the contribution of vacancies was close to 100%. That is, it can be said that diffusion along such boundaries proceeds mainly due to the introduced vacancies. Interstitial atoms, due to the high formation energy, make, in general, a small contribution compared to vacancies. Their contribution in most cases is close to zero, only for the (110) boundaries it sometimes reaches about 1%.

It should be borne in mind that the calculations carried out for “ideal” conditions: for “structurally correct” boundaries and for the equilibrium concentration of defects provided that there are no other defects introduced. It is known that grain boundaries in real polycrystals are often in a non-equilibrium state and include a number of introduced (excess) point defects and dislocations. Nevertheless, the carried-out calculations make it possible to judge qualitatively about the role of vacancies and interstitial atoms in diffusion along low-angle twist boundaries.

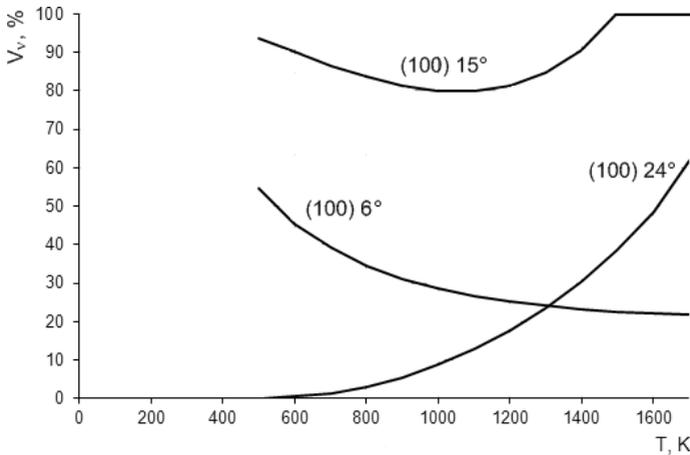


Fig. 5. Temperature dependencies of the contribution of the introduced vacancies to the self-diffusion along (100) twist boundaries with misorientation angles of 6° , 15° and 24° .

4. Conclusions

According to the calculations carried out in this paper using the molecular dynamics method, the introduced vacancies play an important role in diffusion along twist grain boundaries. The contribution of introduced interstitial atoms to grain-boundary diffusion is less by several orders of magnitude in comparison with the contribution of vacancies. The point defects are mainly fixed in the nodes of grain-boundary screw dislocations network. Diffusion with the participation of point defects proceeds by migration of the defects from one network node to another with the formation of a chain of displaced atoms.

When calculating the energy of formation of point defects in the twist boundaries, it was found that the higher the energy of formation of the boundary (the higher its “defectiveness”), the lower the energy of formation of point defects in it. The energy of formation of point defects turned out to be the lowest for the (110) boundaries. For the (111) boundaries, the energy of formation of the vacancy and interstitial atom is close to the formation energies in a pure crystal. The energy of formation of point defects was practically independent of the misorientation angle of the low-angle boundaries. However, their concentration in the boundaries with an increase in the misorientation angle obviously rises, because the density of the nodes of the grain-boundary dislocations network increases.

Judging from the obtained data, the (111) boundaries should contain the smallest concentration of point defects and be a relatively weak trap for external defects. At the same time, (111) twist boundaries have the lowest energy in comparison with other twist boundaries. The most effective traps for defects are, according to the results of this paper, the boundaries that have the greatest formation energy (from the considered twist boundaries, these are the (110) boundaries).

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