Molecular dynamics study of diffusion along Ni-Al interphase boundary in the conditions of deformation

G Poletaev and A Sannikov
1Altai State Technical University, Department of Mathematics and Mathematical Modeling, Barnaul, 656038, Russia
E-mail: gmpoletaev@mail.ru

Abstract. The structural changes on Ni-Al boundary with orientations (100) and (111) and diffusion along it were studied by the method of molecular dynamics in the conditions of uniaxial compression-tension deformation. It was shown that during deformation the misfit dislocations network is distorted. Tension leads to a decrease of diffusion activation energy and to intensification of diffusion along the interphase boundary. During compression, on the contrary, the activation energy increases. Anisotropy of the diffusion along the interphase boundary under uniaxial deformation was not observed.

1. Introduction
At the interphase boundaries a situation can occur, that is qualitatively similar to that taking place at one crystal phase boundary, i.e. at the grain boundaries. As a result, in certain conditions, the acceleration of the matter diffusion transportation along the interphase boundaries is possible, that is proved experimentally [1, 2]. The fundamental difference between the phase boundaries and grain boundaries is that the second phase exists in many cases as an isolated inclusion in the matrix, i.e. phase boundaries do not form a united ramified network like grain boundaries. Dislocations that are typical for coherent interphase boundaries are formed not only as a result of contacting crystals disorientation (as in the case of grain boundaries), but as a result of mismatch of lattice parameters of the phases (so called misfit dislocations) [2, 3]. In [1, 2] it is highlighted because of structure imperfection the phase boundaries can detect high diffusion permeability, in some cases even higher than the grain boundaries. It is believed that the reverse case is also possible, and when the diffusion near the phase boundary is slower than in the grain volume.

In this paper the Ni-Al coherent boundary with two different orientations is considered: in (100) and (111) planes. The lattice parameters of contacting fcc metals are different (3.52 Å for Ni and 4.05 Å for Al), that leads to the formation of a high density of misfit dislocations at the Ni-Al interphase boundary. Earlier, in [4], using the method of molecular dynamics, we have shown that at the Ni-Al interphase boundary forms the network of edge misfit dislocations (with square cells of two systems of dislocations for the (100) boundary and with triangular cells of three systems for the (111) boundary), which play a key role in the diffusion along the interphase boundary at solid phase contact. It was found that the atoms migrate preferentially along the dislocation cores. Herewith Al atoms diffuse along the boundary more intense than Ni atoms. Activation energies of diffusion along the interphase boundary of Al and Ni atoms were found: 0.22 and 0.48 eV for the (100) boundary, 0.32 and 0.52 eV for the (111) boundary, respectively. Diffusion along the (111) boundary proceeded less intense than along the (100) boundary.
The present work is devoted to the study of the structural changes on Ni-Al boundary with orientations (100) and (111) and diffusion along it by the method of molecular dynamics in the conditions of uniaxial compression-tension deformation.

Previous research was carried out for a similar study for low-angle tilt [5, 6] and twist [7] boundaries in fcc metals. It was found that tension leads to an increase of diffusion intensity along grain boundaries, and on the contrary to decrease of diffusion intensity under compression. In [5-7] it was explained by a corresponding change of the free volume in the boundaries during deformation.

2. Description of the model

The interphase boundary was being created in the center of the simulation block (Figure 1). The boundary had orientation (100) or (111) in both contacting crystals. The block dimensions were chosen so that periodic boundary conditions could be used along the interphase boundary, i.e. along the X and Y axes in Figure 1 the endless repetition of the simulation block was imitated. Along the Z axis rigid conditions were imposed - atoms near the boundaries of the calculation block was parallel to the plane of the interphase boundary in the computer experiment remained motionless (in Figure 1 fixed atoms are dark grey). The number of atoms in the calculation block was about 30000.

![Figure 1. Simulation block containing Ni-Al (100) interphase boundary. The periodic boundary conditions were imposed along X and Y axes. Dark grey atoms remained motionless in the computer experiment (rigid boundary conditions along the axis Z).](image)

To bring the structure of simulation block in the equilibrium state (at these conditions) structural relaxation was carried. As a result of the relaxation, the temperature of the block increased, so after its completion the block was cooled to 0 K. Integration time step in the molecular dynamics method was equal 5 fs. Interatomic interactions were described by Morse pair potentials, parameters of which were taken from [8].

When creating the interphase boundary disorientation contacting crystals was not made because it was found for Ni-Al boundary, that at any disorientation aluminum near the boundary aim to imitate the crystal orientation of nickel. As a result, when Al was initially disoriented relatively Ni, in Al the grain boundary parallel to the interphase boundary was formed. This phenomenon is apparently due to the relatively high energy of Ni-Al bonds in comparison with the Ni-Ni and Al-Al bonds.

Uniaxial compression or tension deformation was set by a corresponding change of the interatomic distances along the X or Y axis (Figure 1), i.e. deformation along the interphase boundary was considered. After the deformation of the calculation block structural relaxation and the subsequent cooling to 0 K was carried out again.
Investigating the diffusion and the mechanism of atom migration at the interphase boundary computer experiments 100-300 ps duration were held at different temperatures of the calculation block from 300 K to the melting point of aluminum. Temperature of the calculation block was set through the initial velocity of the atoms according to the Maxwell-Boltzmann distribution. Herewith total impulse of atoms in the calculation block was zero.

3. Results and discussion
In the relaxation process, during which conjugation of Ni and Al phases occurred, at the interphase boundary edge misfit dislocations formed (Figure 2). The dislocations formed, as already mentioned above, in the result of lattice parameters mismatch.

![Figure 2. Misfit dislocations projected onto the plane (110) in the simulation block containing Ni-Al (100) boundary.](image)

Figure 3 shows the distribution of free volume in the plane of Ni-Al (100) (Figure 3a) and (111) (Figure 3b) interphase boundaries at the absence of deformation. The visualization of free volume was carried out by calculating the average distance between nearest atoms. If the average distance was not significantly different from the distance corresponding to the ideal crystal, the atom was not depicted. Otherwise the atom was painted in one or another shade of grey.

In Figure 3 cores of misfit dislocations are seen, which in the case of Ni-Al (100) boundary form a network with square cells, consisting of two systems of edge dislocations, and in the case of Ni-Al (111) boundary - network with triangular cells, consisting of three systems of edge dislocations.

![Figure 3. The image of misfit dislocations at the Ni-Al (100) (a) and (111) (b) boundaries using the free volume visualizer at the absence of deformation.](image)
The dislocation network structure changed during the deformation. Figure 4 shows examples of misfit dislocation networks in the (100) (Figure 4a) and (111) (Figure 4b) boundaries at 3% compression along the X-axis. It was distortion of the networks and in the case of the (100) boundary there was a significant breach of the ordered arrangement of dislocation cores. For the (111) boundary the disorders of dislocations arrangement also observed, but to a lesser extent compared with the (100) boundary.

A measure of order of misfit dislocations arrangement at the interphase boundary depends largely on two factors: mismatch of lattice parameters of the contacting crystals (and hence the average distance between dislocations) and the bond energy of dissimilar atoms. The higher these values the higher the probability of formation of ordered dislocation network. In this case, in the result of the same deformation of the contacting phases, in Ni and Al different in magnitude tensions appeared (due to the difference of elastic moduli), which led to a curvature of the dislocation network.

![Figure 4](image.png)

Figure 4. The image of misfit dislocations at the Ni-Al (100) (a) and (111) (b) boundaries using the free volume visualizer at 3% stress deformation along the X-axis.

In the study of diffusion along the considered Ni-Al boundary, as in [4], a more intensive diffusion of Al atoms in comparison with the atoms Ni was observed. This is due to the fact that Ni-Ni and Ni-Al bonds are considerably stronger then Al-Al bond, whereby the defective areas (in the form of misfit dislocations cores) preferably contain Al atoms.

Atomic diffusion mechanism was investigated by a visualizer of atomic displacements relative to the initial positions. Displacements of atoms visualized by the software directly during the computer experiment allowed observing the atomic displacements in the dynamics.

Figure 5 shows examples of paintings of atomic displacements along the (100) and (111) interphase boundaries. The trajectories of the atomic displacements have directions as the cores of misfit dislocations. However, as can be seen from the figures, these displacements often did not coincide with the start positions of the cores corresponding to the absence of deformation, which indicates displacement of the dislocations, i.e. curvature of the dislocation network as a result of deformation.

For different values of the temperature at the end of the molecular dynamic experiment, the diffusion coefficient was calculated separately for the atoms of Ni and Al. The temperature during the computer experiment was kept constant. The diffusion coefficients in the XY plane (plane of the boundary), to determine the presence of diffusion anisotropy, were calculated separately along the X and Y axis:
$$D_z = \frac{\sum (x_{i0} - x_i)^2}{2tN}, \quad D_y = \frac{\sum (y_{i0} - y_i)^2}{2tN},$$

where $x_{i0}$, $y_{i0}$ – coordinates of the initial position of $i$-th atom; $x_i$, $y_i$ – coordinates of $i$-th atom in the time $t$; $N$ - number of atoms in the simulation block.

**Figure 5.** Migration of atoms in the plane of Ni-Al interphase boundary: a) (100) boundary at temperature 700 K for 250 ps; b) (111) boundary at temperature 900 K for 300 ps. Displacements of atoms are depicted by black segments. Gray bold dashed lines show the positions of misfit dislocations at the absence of deformation.

In the calculation of the diffusion coefficients the width of the interphase boundary was assumed equal 5 Å. The same width was assumed in the study of grain boundary diffusion in [5-7].

From the slope of dependences $\ln(D)$ on the $T^{-1}$ the activation energies of diffusion were found. The obtained values are shown in Table 1. This study was conducted for the values of compression and tension deformation of 3%.

| Type of deformation | (100) | (111) |
|---------------------|-------|-------|
| Ni                  | $E_x$ | $E_y$ |
| Al                  | $E_x$ | $E_y$ |
| Ni                  | $E_x$ | $E_y$ |
| Al                  | $E_x$ | $E_y$ |
| normal state        | 0.48  | 0.22  |
| 3% X tension        | 0.24  | 0.32  |
| 3% X compression    | 0.52  | 0.42  |
| 3% Y tension        | 0.36  | 0.25  |
| 3% Y compression    | 0.50  | 0.53  |

The scatter of the data (caused, in particular, the different distortion of the dislocation network at different temperatures) is quite large, making it difficult to assess the qualitative regularities. Nevertheless, the table shows that tension leads to a decrease of diffusion activation energy and to intensification of diffusion, compression - conversely (referring, of course, not talking about the deformations corresponding to the formation of intense plastic shears). In the papers [5-7], devoted to the study of diffusion along grain boundaries, this was explained by a corresponding change of the free volume within the boundaries during deformation. In addition, the table shows that the activation
energy of Al atoms is smaller than for Ni atoms. Diffusion anisotropy was not detected, which may be explained by a large spread of the obtained values. However, atomic displacements (for example, Figure 5) also indicate the absence of a pronounced anisotropy of diffusion along the interphase boundary under uniaxial deformation.

4. Conclusion
Using the method of molecular dynamics in the present study it is shown that at Ni-Al interphase boundary network of edge misfit dislocations forms (with square cells of two systems of dislocations for the (100) boundary and with triangular cells of three systems for the (111) boundary), which play a key role in the diffusion along the interphase boundary at solid phase contact. The atoms migrate preferentially along the misfit dislocation cores. It was found that Al atoms diffuse along the boundary more intense than Ni atoms.

During deformation the misfit dislocations network is distorted. Tension leads to a decrease of diffusion activation energy and to intensification of diffusion along the interphase boundary. During compression, on the contrary, the activation energy increases. This is related, apparently, with the change of the free volume in the boundary. Anisotropy of the diffusion along the interphase boundary under uniaxial deformation was not observed.

It should be noted that the studies are devoted to the structurally correct (equilibrium) interphase boundaries. In fact contacting phases at the boundary contains various imperfections. Their role in the diffusion will be considered in subsequent studies.

Acknowledgment
The reported study was partially supported by RFBR, research projects No. 13-02-00301_a, No. 14-02-98000-r_sibir_a and No. 14-08-90416-Ukr_a.

References
[1] Bokshtain B S 1978 Diffusion in metals (Moscow, Russia: Metallurgiya)
[2] Bokshtain S Z, Bolberova E V, Ignatova I A, Kishkin S T and Razumovsky I M 1985 Fizika metallov i metallovedenie (Rus) 59 938
[3] Poletaev G M and Starostenkov M D 2003 Technical Physics Letters 29 454
[4] Poletaev G M, Sannikov A V and Mikrukov V R 2013 Fundamental’nye Problemy Sovremennogo Materialovedenia (Rus) 10 112
[5] Rakitin R Y, Poletaev G M, Aksenov M S and Starostenkov M D 2005 Fundamental’nye Problemy Sovremennogo Materialovedenia (Rus) 2 46
[6] Starostenkov M, Poletaev G, Rakitin R, Sinyaev D 2008 Materials Science Forum 567-568 161
[7] Poletaev G M, Martynov A M, Dmitrienko D V and Starostenkov M D 2012 Izvestiya Vysshikh Uchebnykh Zavedenij. Chernaya Metallurgiya (Rus) 6 64
[8] Tsaregorodtsev A I, Gorlov N V, Demyanov B F and Starostenkov M D 1984 Fizika Metallov i Metallovedenie (Rus) 58 336