УДК 669.018:538.931

ATOMIC STRUCTURE AND DIFFUSION PERMEABILITY OF Ni – Al, Cu – Au, Ni – γFe INTERPHASE BOUNDARIES*

Sannikov A.V.*[1], *Postgraduate
Poletaev G.M.*[1], *Dr. Sci. (Phys.-math.), Professor, Head of the Chair (gmpoletaev@mail.ru)
Mikrukov V.R.*[2], *Cand. Sci. (Eng.), Candidates for a degree Dr. Sci. (Eng.)
Starostenkov M.D.*[1], *Dr. Sci. (Phys.-math.), Professor, Head of the Chair
Soskov A.A.*[2], *Postgraduate

[1] Altai State Technical University
(46, pr. Lenina, Barnaul, Altai Territory, 656038, Russia)
[2] Siberian State Industrial University
(42, ul. Kirova, Novokuznetsk, Kemerovo Region, 654007, Russia)

Аннотация. The atomic structure of Ni–Al, Cu–Au, Ni–γFe interface boundaries, oriented along planes (100) and (111), and diffusion mechanism along it in solid-contact were studied by the method of molecular dynamics. It was shown that on the boundary forming a net of edge misfit dislocations, which play key role in diffusion along interface boundary.

Ключевые слова: molecular dynamics, interface boundary, dislocation of discrepancy, diffusion mechanism, activation energy of diffusion.

At the interphase boundaries can occur a situation, qualitatively similar to that which occurs 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 – 4]. 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.

Earlier, in [5], in the study by computer simulation of diffusion along the Ni–Al interphase boundary in two-dimensional model was found that misfit dislocations play a key role in the migration of atoms near the boundary. It was mentioned that diffusion can occur due to the formation of cyclic displacements of atoms near the dislocation cores and formation of chains of atoms displaced from one core to the core of neighboring dislocation. In the simulation of diffusion along Ni–Al boundary in three-dimensional model [6], was found that the migration of atoms happens mainly along the cores of misfit dislocations which are formed, depending on orientation of the interphase boundary, the network of two or more sets of edge dislocations.

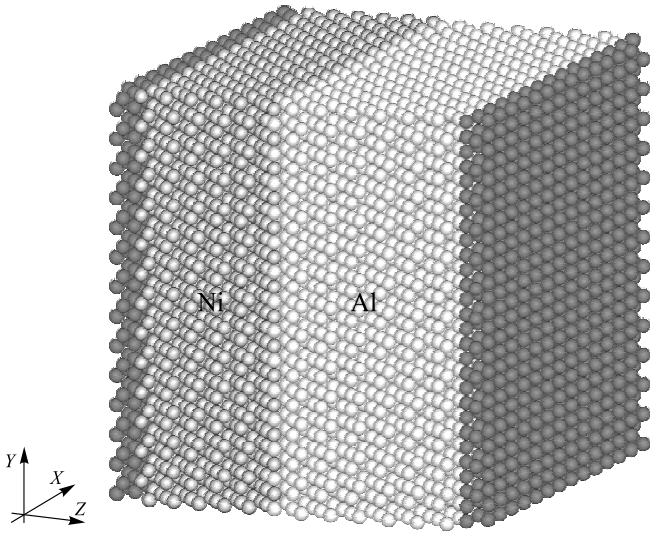
The present work is devoted to the study of the atomic structure of Ni–Al, Cu–Au, Ni–γFe interphase boundaries and diffusion mechanism along them in the condition of solid phase contact by the method of molecular dynamics. In the work the interphase boundary orientations in (100) and (111) planes were considered. As examples the fcc metals with lattice parameters were taken: Ni – 3.524 Å and Al – 4.05 Å (the difference – 14.9 %), Cu – 3.615 Å and Au – 4.078 Å (the difference – 12.8 %), Ni – 3.524 Å and γ-Fe – 3.637 Å (the difference – 3.2 %). The difference of the lattice parameters leads to the formation of misfit dislocations at the interphase boundary: the higher this difference, the higher density of dislocations is.

The interphase boundary was being created in the center of the simulation block (Fig. 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 Fig. 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 Fig. 1 fixed atoms are dark grey). The number of atoms in the calculation block is from 20 000 to 30 000.

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 [7].

When creating the interphase boundary disorientation contacting crystals was not made because it was found for

* The reported study was partially supported by RFBR, research projects No. 13-02-00301_a, No. 14-02-98000-r_sibir_a.



Calculation 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*)

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.

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 one of the contacting phases. 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.

In the relaxation process, during which conjugation of contacting metals occurred, at the interphase boundary formed misfit dislocations (Fig. 2). The dislocations formed in the result of lattice parameters mismatch.

Fig. 2 shows the distribution of free volume in the plane of Ni–Al (Fig. 2, *a*, *b*) and Ni–Fe (Fig. 2, *c*, *d*) interphase boundaries. 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. Black color corresponds to the presence of free volume near the atom, approximately equal to the volume of vacancies, that is, as if a vacancy was located near given atom.

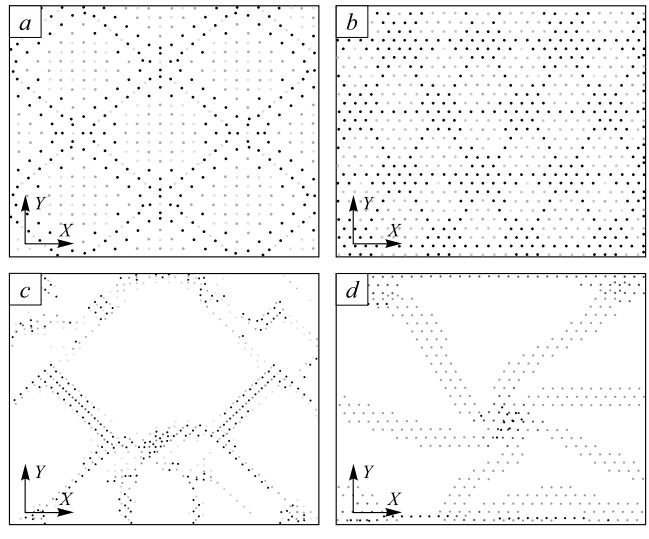
In Fig. 2 cores of misfit dislocations are seen, which in the case of Ni–Al (100) boundary form a network with square cells, consisting of two systems of edge dislocations, and in the case of Ni–Al (111) boundary – network with triangular cells, consisting of three systems of edge dislocations. For Cu–Au boundary similar pictures were obtained, with that difference that the cells size of dislocation networks was bigger in connection with the smaller difference of lattice parameters of Cu and Au.

The lattice parameters of Ni and γ-Fe have close values (the difference is only 3.2 %) and therefore, the density of misfit dislocations at Ni–Fe boundary was much lower than at the Ni–Al and Cu–Au boundaries. Furthermore, the dislocations had an unordered structure (Fig. 2, *c*, *d*): they did not form geometrically regular network as in the case of Ni–Al and Cu–Au boundaries. However, at larger area of Ni–γFe interphase boundary during structural relaxation should apparently expect the formation of the dislocation network similar those that formed at Ni–Al and Cu–Au boundaries.

In the study of diffusion along the interphase boundary for each given temperature at the end of the molecular dynamics experiment the diffusion coefficient was calculated separately for different types of atoms. The temperature during the computer experiment was kept constant. When calculating the diffusion coefficient was assumed that the width of the interphase boundary is 5 Å.

On the whole, along the (111) boundaries, despite the seemingly higher density of atoms in this plane, in all cases the diffusion proceeds strongly than along the (100) boundaries. Apparently, this is due to the higher density of misfit dislocations at the (111) boundary relative to the (100) boundary (Fig. 2).

In the case of Ni–Al system along the interphase boundary Al atoms migrated more intensively. This was due to the fact that Ni–Ni and Ni–Al bonds considerably stronger than Al–Al bond, whereby the defect areas (in the form of misfit dislocation cores) contained predominantly Al atoms, because of which they proved to be more mobile. Along the Cu–Au (100) and (111) boundaries more intensively Cu atoms migrated. In this case, the energy of Cu–Au bond higher than Cu–Cu, but less than the Au–Au. That is, as in the case of Al atoms on the boundary of Ni–Al, in the areas



The image of misfit dislocations at the Ni – Al (100) (*a*), Ni – Al (111) (*b*), Ni – Fe (100) (*c*), Ni – Fe (111) (*d*) boundaries using the free volume visualizator

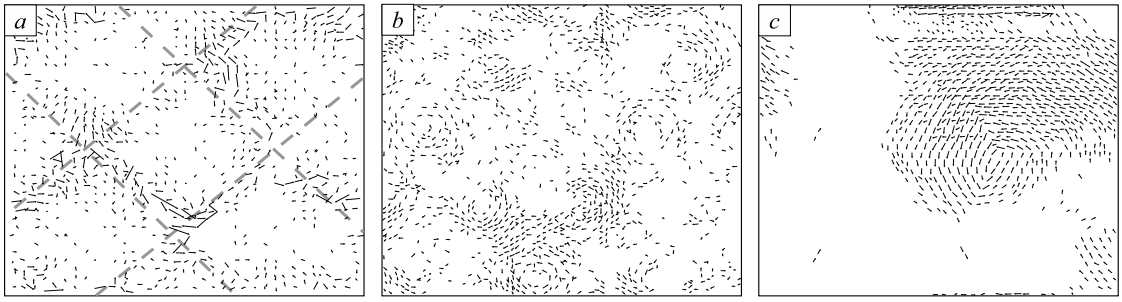


Рис. 3. Atoms migration in the interphase boundary plane (atoms displacement are depicted by black segments. Bold gray dashed lines show the approximate positions of misfit dislocations):
a – Cu – Au (100) at 900 K during 200 ps; *b* – Cu – Au (111) at 1000 K during 200 ps; *c* – Ni – γFe (111) at 1300 K during 200 ps

of dislocation cores Cu atoms proved more movable. When considering Ni–γFe boundary significant preponderance of the diffusion of atoms of different types was not observed. In this case, the energy of Ni–Fe bond is smaller than the energy of Ni–Ni and Fe–Fe bonds.

From the slope of dependences of ln(D) from T^{-1} diffusion activation energies were found separately for atoms of different types. Along the Ni–Al (100) interphase boundary: 0.5 eV for Ni and 0.3 eV for Al; along Ni–Al (111) boundary: 0.5 and 0.2 eV respectively. The obtained values are close to values of the activation energy of diffusion along grain boundaries in the Ni_3Al intermetallide [8]: depending on the misorientation angle of grains the migration energy of Al atoms is in the range 0.2 – 0,3 eV, Ni atoms – 0.1 – 0,3 eV. Consequently, the diffusion permeability of interphase boundaries is comparable to permeability of grain boundaries.

For Cu–Au (100) and (111) boundaries were obtained similar activation energy of migration of Cu and Au atoms: 0.1 eV and 0.2 eV respectively. For Ni–γFe (100) and (111) boundaries the activation energy of Ni and Fe atoms had similar values of the order of 0.1 eV.

Atomic diffusion mechanism was investigated by visualizator of atomic displacements in regard to the initial positions [9, 10]. Displacements of atoms were visualized by the program directly in the process of the computer experiment that allowed to observe the displacements of atoms in dynamics.

It was found that misfit dislocations play a key role in the diffusion near the interphase boundary in the condition of solid phase contact. This is consistent with the conclusions of [5, 6]. Fig. 3 shows examples of atomic displacements pictures along the interphase boundaries during the computer experiment.

As it is seen from Fig. 3, *a*, in the case of (100) boundary, displacements of atoms occur primarily along cores of misfit dislocations. Herewith, the higher density of atomic displacements was more frequently observed in the area of nodes of the dislocation network. For the (111) boundaries cooperative vortex displacement of atoms were typical, and the size of these "vortices" coincided with the cell size of the dislocation network (Fig. 3, *b*, *c*).

Thus, using the method of molecular dynamics in the present study shows that at Ni–Al, Cu–Au and Ni–γFe interphase boundaries it is form 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. If the energy of heterogeneous bond is higher than energy of homogeneous bond of the one of the contacting phases, then more intensity migrate along the boundary, as a rule, those atoms, homogeneous bond energy of which is lower – in this case they are often locate in defect areas (e.g., dislocation cores) and more mobile.

The boundaries which are oriented in plane (100) have a lower density of misfit dislocations in comparison with the (111) boundaries, therefore the diffusion along them is relatively less intense. In the case of (100) boundaries migration of atoms occurs mainly along the misfit dislocations. For the (111) boundaries are typical is the formation of cooperative vortex displacements of atoms, and the size of the "vortices" coincides with a cell size of the dislocation network.

REFERENCES

1. Bokshtein B.S. Diffuziya v metallah [Diffusion in Metals]. Moscow: Metallurgiya, 1978. 248 p.
2. Bokshtein S.Z., Bolberova E.V., Ignatova I.A. etc. Fizika metallov i metallovedenie. 1985. Vol. 59. № 5. Pp. 938–942.
3. Thorik Yu.A., Khazan L.S. Plasticheskaya deformaciya i dislokacii nesootvetstvija v geterojepitaksial'nyh sistemah (Plastic deformation and misfit dislocations in heteroepitaxial systems). – Kiev: Naukova Dumka, 1990. 321 p.
4. Starostenkov M.D., Poletayev G.M., Starostenkov D.M. Journal of Materials Science and Technology. 2001. Vol. 17. № 1. P. 59, 60.
5. Poletaev G.M., Kobzar' L.M., Kulabukhova N.A., Starostenkov M.D. Fundamental'nye problemy sovremennogo materialovedeniya. 2009. № 4. Pp. 111–115.
6. Poletaev G.M., Sannikov A.V., Mikrukov V.R. Fundamental'nye problemy sovremennogo materialovedeniya. 2013. Vol. 10. № 1. Pp. 112–116.
7. Tsaregorodtsev A.I., Gorlov N.V., Dem'yanov B.F., Starostenkov M.D. Fizika metallov i metallovedenie. 1984. Vol. 58. № 2. Pp. 336 – 343.
8. Kharina E.G., Starostenkov M.D., Poletaev G.M., Rakitin R.Yu. Fizika tverdogo tela. 2011. Vol. 53. № 5. Pp. 980–983.
9. Poletaev G.M., Starostenkov M.D. Fizika tverdogo tela. 2009. Vol. 51. № 4. Pp. 686–691.
10. Martynov A.N., Poletaev G.M., Starostenkov M.D. Pis'ma o materialakh. 2011. Vol. 1. № 1. Pp. 43–46.

Received January 16, 2014