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The structure of grain boundaries in the ordered solid solution of a Ni-Al system of equiatomic composition (molecular dynamics)

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The article presents the results of molecular dynamic simulation of the grain boundary structure in the β-phase of a Ni-Al solid solution (CsCl type structure). It is established that the structure of the torsion grain boundary ($\langle 001\rangle$, $\theta = 8^\circ$) is structurally unorganized, the thickness is 0.29 nm (one layer of each grain). The small-angle torsion boundary ($\langle 001\rangle$, $\theta = 36.9^\circ$) is organized to form a grid of helical super-dislocations (Burgers vectors $a\langle 100\rangle$), the structural thickness of the boundary is 0.85 nm (3 layers of each grain).

Keywords: ordered solid solution with CsCl type structure, grain boundaries, molecular dynamics.

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1. Introduction

Representations about an atomic structure of grain boundaries have been successfully developed mainly on examples of single-component structures that were metal in the great majority: small-angle structures with compensation of orientation mismatch by full Burgers vector dislocations (until coalescence of dislocation nuclei); large-angle structures — within the framework of a concept of the coincidence site lattice (CSL) and the O-lattice (coincidence sites with the same internal coordinates within crystal lattices of a grain pair) and grain-boundary dislocations (GBD) [1–6].

For different axis-angle pairs, there is a respective set of local energy minimums (i. e. special large-angle boundaries) with the largest statistics, which is given in the studies [6,7].

Studies of a structure of grain boundaries in the ordered structure of the CsCl type are limited by the first results of molecular-dynamic simulation of the small-angle and large-angle boundaries in the system Pd-Cu [8–13][1]. It has been found that in the grain boundaries (the small-angle $\langle 001\rangle$, $\theta = 8^\circ$ and large-angle $\langle 001\rangle$, $\theta = 36.9^\circ$ torsion boundary, the large-angle inclination boundary is $\langle 100\rangle$, $\theta = 36.9^\circ$) boundaries of the structure-unorganized type and an intermediate quasi-amorphous phase are formed in the ordered structure of the system Pd-Cu (β-phase).

As shown by results of the molecular-dynamic simulation, the hydrogen atoms are held on crystal-construction defects, in particular, in Pd on small-angle inclination and torsion grain boundaries, on the large-angle boundary that is close to a special one [14]. Therefore, a grain boundary structure issue is also fundamental in terms of real hydrogen permeability of a membrane foil of the system Pd-Cu and founding manifestation of special features of the electron structure in various solid solutions that are ordered by the CsCl type.

It was shown in the studies [15,16] by the molecular statics method that a model including the special large-angle inclination boundary ($\langle 100\rangle$, $\theta = 36.9^\circ$) in the solid solution Ni-Al was not stable and the smaller energy belongs to boundaries, in which the atoms are shifted by slight distances within the boundary plane in relation to positions in CSL.

We still do not know studies on investigating the relaxed atom structure of the grain boundaries in other systems with the CsCl-type structure.

The aim of the present study: to reveal patterns of structural organization of the intergranular small-angle and large-angle torsion boundaries; to substantiate the obtained results in terms of developed representations about specific features of dislocations in the systems ordered by the B2 type (as applied to the small-angle boundaries) and in terms of an electron structure of the surface of the solid solution Ni-Al.

2. Research procedure

The models are presented by two mating planes (001) of the crystals of the β-phase of an equiatomic composition with mutual disorientation around the axis $\langle 001\rangle$ (the torsion boundary) by the angle of 36.9° (the large-angle boundary) and $\theta = 8^\circ$ (the small-angle boundary). A size of the models for the two boundary types was the same and selected to be enough for visualizing the boundary structure.

The system was statically relaxed after creation of the models, which was followed by isothermal annealing at a given temperature with a time step of $\Delta t = 1.5 \cdot 10^{-15}$ s for $100000\Delta t$, i. e. the annealing duration was $1.5 \cdot 10^{-10}$ s.

[1] The system Pd-Cu with the wide temperature range of ordering (up to 598 °C) within the concentration interval (36−47 at.% Pd) was discussed from one year to another in the different aspects of application [9−13].

The annealing temperature was 27, 327, 527 and 727 °C for the large-angle boundary model and 27 °C for the small-angle boundary model. The calculation method consisted of numerical integration of the equations of motions of atoms using the Verlet algorithm [17]. The interatomic interaction in the system was calculated using the embedded atom method [18].

3. Results and discussion

3.1. Large-angle boundary.

Figure 1 shows an image contacting grain layers in the β-phase of the solid solution of the system Ni-Al after annealing at the temperature of 27 °C. Hence, it follows that this system forms a structure-unorganized grain boundary, wherein, unlike the system Pd-Cu [13], there is no mixing between layers of the various grains and atomic rearrangements affect mostly Ni atoms in the first layer. It can be related to specific features of the electron structure of NiAl, which is determined by d-electrons of Ni [19]. A structure width of the boundary, which is determined as a distance, within which atom coordination differs from atomic coordination in the grains, i.e. a total thickness of the contacting layer, is one atomic layer of each grain (0.29 nm). The boundary distinguishes fragments (Figure 1, b, c) that include structure elements of the two types — corresponding to parallel orientation of each of the grains, but their number is low (they include $\sim 16\%$ of the atoms). The system Ni-Al is characterized by the fact that the ordered phase exists up to the melting temperature (1638 °C) unlike the system Pd-Cu, which made it possible to simulate at the higher temperatures (327, 527 and 727 °C) within limits of existence of the β-phase. It is found that the boundary has a structure that similar to the structure produced at the temperature of 27 °C.

A single-component Ni nanoparticle on the surface of the Pd single crystal was simulated in the similar conditions [20] to show that for formation of the special boundary ($\langle 001 \rangle$, $\theta = 36.9°$, $\Sigma = 5$) MD annealing for $3 \cdot 10^{-11}$ s is sufficient, which is in 50 times less than annealing done in the system Ni-Al.

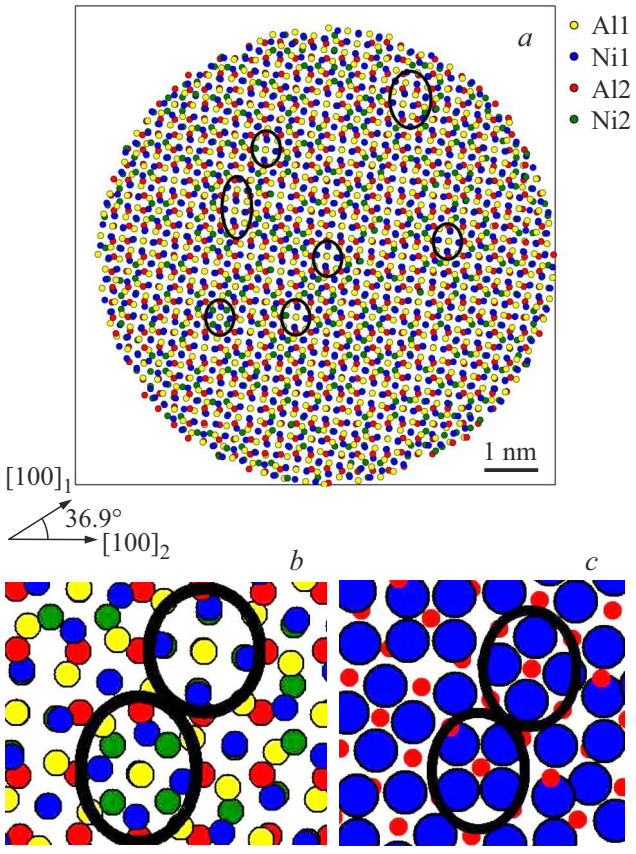

Figure 1. Contacting layers of the grains of the model that includes the large-angle boundary in the β-phase of the system Ni-Al, after annealing at the temperature of 27 °C (a) and a magnified fragment that includes structure elements of the two types (b, c). The figures a and b show two layers of each grain, while the figure c shows one layer of each grain. A size of the circles is conditional and selected for better perception of the image. The digits 1 and 2 designate grain numbers.

3.2. Small-angle boundary.

Figure 2 shows an image of the contacting layers of the grains in the β-phase of the solid solution of the system Ni-Al after annealing at the temperature of 27 °C. It follows from it that in this system orientation mismatch is compensated by formation of a dislocation net. A period of the dislocation net is ~ 2 nm, while a modulus of the Burgers vector is ~ 0.28 nm, which corresponds to the modulus of the vector $a\langle 100 \rangle$, i.e. a superdislocation vector. A structure of the internal layers of the grain was analyzed to show that besides the first layers structure distortions also affect the second and third layers of the grains. Thus, the structure width of the small-angle boundary is 6 atomic layers, i.e. 0.85 nm.

An obtained difference in the structure width of the boundaries agrees with results of the studies [21,22]. Molecular-dynamic simulation of the Pd bicrystal including the small-angle grain boundaries $\langle 001 \rangle$, 8° and $\langle 110 \rangle$, 8° showed [21] that the structure width of the small-angle boundary is 4 and 18 atomic layers, respectively; while the structure thickness of the large-angle special boundary in a gold bicrystal is 4 layers [22].

It is shown in the study [23] that Au segregation on the torsion boundary (001) of the film Fe bicrystals results in a change of the type of the boundary dislocation structure: the boundaries in the pure bicrystal consisted of regular dislocation nets with the Burgers vectors $\mathbf{b}_{1,2} = a/2\langle 111 \rangle$. In the bicrystal of the film of the composition Fe — 0.18 at.% Au, the boundary is formed by dislocations along the directions $\langle 100 \rangle$ with the Burgers vector $a\langle 100 \rangle$, respectively. An assumption that the observed transformation in the small-angle boundary is related to segregation of the Au atoms in it is confirmed by two methods of analysis

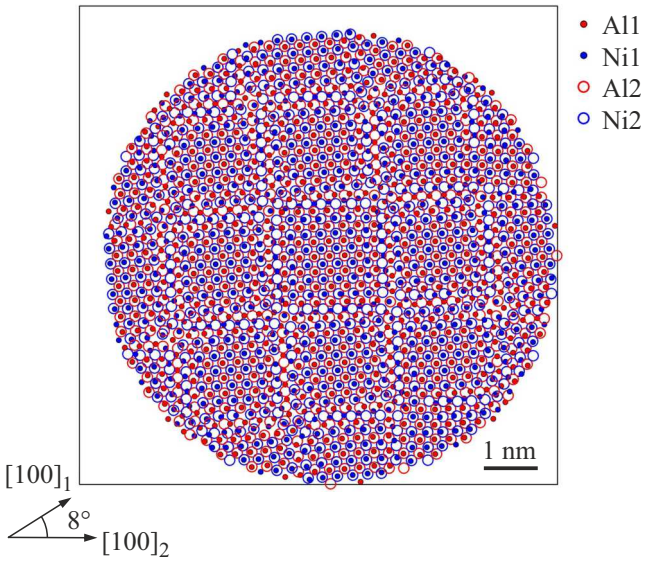

Figure 2. Contacting layers of the grains of the model that includes the small-angle boundary in the β-phase of the system Ni-Al, after annealing at the temperature of 27 °C. Two layers of each grain are shown and the digit means the grain number. A size of the circles is conditional and selected for better perception of the image

of a local elemental composition: Rutherford backscattering spectrometry and X-ray spectrometry.

Formation of the dislocation structures of the small-angle torsion boundary in the system NiAl confirms a stronger interatomic bond as compared to the system PdCu (according to a state diagram, the former still keeps ordering up to the melting point).

In terms of results of photoelectron spectroscopy [19], the electron structure and the spectral properties of the surface (001)NiAl are determined by the *d*-electrons of Ni (in the model of the contacting plane of a single grain) and a *d*-zone on the surface is narrowed and shifted into the higher energies by $\sim 2/5$ eV in relation to the atoms of the Ni layer in the volume, which can activate the atoms of this layer and its disordering processes at the boundary. Finally: the large-angle torsion boundary is formed as a structure-unorganized one and, accordingly, the concept of CSL, the O-lattice and GBD is unacceptable for characterizing the large-angle boundaries.

4. Conclusions

The small-angle torsion boundary is organized with formation of the a net of screw superdislocations (the Burgers vectors $a\langle 100\rangle$) and the structure thickness of the boundary is 0.85 nm (by 3 layers of each grain).

The large-angle torsion boundary is formed as a structure-unorganized one and, accordingly, the concept of CSL, the O-lattice and GBD is unacceptable for characterizing the large-angle boundaries.

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Authors' contributions

Calculations by molecular dynamics were performed by A.S. Prizhimov, the systems were simulated and the images were constructed by A.I. Dontsov and S.V. Gorbunov, problem formulation, result analysis and editing of the article were performed by V.M. Ievlev.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] D.G. Brandon, B. Ralph, S. Ranganathan, M.S. Wald. Acta met. **12**, 813 (1964).
[2] D.G. Brandon. Acta met. **14**, 1479 (1966).
[3] W. Bollmann. Phil. Mag. **16**, 363 (1967).
[4] Atomnaya struktura mezhzerennykh granits / Pod red. A.N. Orlova. Mir, M. (1978) 291 s. (in Russian).
[5] V.M. Kosevich, V.M. Ievlev, L.S. Palatnik, A.I. Fedorenko. Struktura mezhkristallitnykh i mezhfaznykh granits. Metallurgiya, M. (1980). 256 s. (in Russian).
[6] B.B. Straumal. Fazovye perekhody na granitsakh zeren. / Otv. red. E.V. Suvorov. Nauka, M. (2003) 327 s. (in Russian).
[7] Struktura vnutrennikh poverkhnostei razdela / Pod red. B.S. Bokshteina. Nauka, M. (1988) 272 s. (in Russian).
[8] V.M. Ievlev, A.I. Dontsov, A.S. Prizhimov, S.V. Gorbunov. Physics of the Solid State **66**, *11*, 1778 (2024).
[9] H.T. Hoang, D. Tong, F.C. Gielens, H.V. Jansena, M.C. Elwenspoek. Mater. Lett. **58**, 525 (2004).
[10] A.Yu. Volkov, N.A. Kruglikov. Physics of Metals and Metallography **105**, *2*, 202 (2008).
[11] A. Basile, F. Gallucci, S. Tosti. Membrane Sci. and Technol. **13**, 255 (2008).
[12] A.Yu. Volkov, O.S. Novikova, B.D. Antonov. Inorganic Materials **49**, 43 (2013).
[13] V.M. Ievlev, A.I. Dontsov, V.I. Novikov, D.A. Sinetskaya, S.V. Gorbunov, N.R. Roshan, G.S. Burkhanov. Russian Metallurgy (Metally) **9**, 854 (2018).
[14] V.M. Ievlev, A.S. Prizhimov, A.V. Boldyreva. Inorganic Materials **54**, *5*, 421 (2018).
[15] E.G. Sverdlova. Evolyutsiya defektnykh struktur v kondensirovannykh sredakh. Sb. tezisov 4-i Mezhdunar. shkoly seminara. Izd-vo AltGTU: Barnaul. (1998). S. 55 (in Russian).
[16] M.D. Starostenkov, B.F. Demyanov, S.L. Kustov, E.G. Sverdlova, E.L. Grahkov. Materials Science Forum. **294–296**, 215 (1999).
[17] L. Verlet. Phys. Rev. **159**, 98 (1967).
[18] M.S. Daw, M.I. Baskes. Phys. Rev. B: Solid State. **29**, 6443 (1984).

[19] O.I. Dubrovskii, S.I. Kurganskii, E.P. Domashevskaya. V sb.: Rost i struktura tonkikh plenok i nitevidnykh kristallov, VPI: Voronezh. (1989). S. 16–22. (in Russian).
[20] A.V. Evteev, V.M. Ievlev, A.T. Kosilov, A.S. Prizhimov. Physics of the Solid State **49**, *4*, 785 (2007).
[21] A.S. Prizhimov, V.M. Ievlev, A.V. Evteev, A.T. Kosilov. V sb.: Fizikochimiya ul'tradispersnykh (nano-) sistem. Materialy VIII Vserossiiskoi konferentsii. Izd-vo BelGU: Belgorod. (2008). S. 198. (in Russian).
[22] J. Budai, W. Gaudig, S.L. Sass. Phil. Mag., A. **40**, 757 (1979).
[23] J.A. Eastman, K.E. Sickafus, S.L. Sass. Trans. Jap. Inst. Metals. **27**, 147 (1986).

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