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Grain boundary structure in the β-phase of Pd-Cu 55 at.% solid solution (molecular dynamics)

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The results of molecular dynamic simulation of the grain boundary structure in the β-phase (ordered CsCl type structure) of a Pd-Cu 55 at.% solid solution are presented. It is shown that in the grain boundaries (small-angle $\langle 001 \rangle$, $\theta = 8^\circ$ and large-angle $\langle 001 \rangle$, $\theta = 36.9^\circ$ the torsion boundary, large-angle tilt boundary $\langle 100 \rangle$, $\theta = 36.9^\circ$) a boundary phase with an unordered structure is formed.

Keywords: interatomic interaction, large-angle boundaries, small-angle boundaries, B2-ordered solid solution.

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1. Introduction

A solid solution of the Cu-Pd system, ordered according to type B2 (β-phase, structure of type CsCl [1]), is promising for the manufacturing of deep hydrogen purification membranes: the activation energy of hydrogen diffusion (0.035 eV) is many times less than for α-phases (face-centered cubic structure, 0.33 eV [2]).

It has been established by the method of molecular dynamic modeling that the presence of grain boundaries in a crystal can delay the diffusion of hydrogen [3].

It is known [4–7] that the energy dependence of large-angle boundaries on the angle of grain misorientation is nonmonotonic, and local energy minima correspond to special grain boundaries, the structure of which for monatomic polycrystals of metals is characterized within the framework of the concept of a coincidence site lattice (CSL), 0-lattices (complete overlay lattice, COL) and grain boundary dislocations (GBD).

It was shown in Refs. [8,9] using the example of a NiAl alloy with an ordered CsCl type structure, that a model based on a coincidence site lattice corresponding to a special orientation $\langle 100 \rangle$, $\theta = 36.9^\circ$, characteristic of grain boundaries with a volume-centered cubic structure, is unstable. There is no data on the structure of grain boundaries in the β-phase of Pd-Cu solid solution.

Systematic studies of the grain boundary structure in Pd-Cu alloys ordered by type B2 have not been conducted. They could explain the significantly lower hydrogen permeability of the membranes (comparable) to that observed for pure and doped Pd [10,11] than expected from the activation energy of hydrogen diffusion [2], and the higher hardness of the foil with the β-phase structure compared to α-phase [12,13].

The purpose of this study is to identify the structural features of grain boundaries in a B2-ordered foil of the Pd-Cu 55 at.% alloy within the framework of the molecular dynamics method.

2. Research methodology

The model containing the torsion boundary is represented by two conjugating crystals of β-phases with Pd — 55 at.% Cu composition, planes (001) with mutual misorientation at an angle $\theta = 8^\circ$ (small-angle boundary) and 36.9° (large-angle boundary). The model of the special tilt boundary is represented by crystals with mating planes (013), misoriented relative to the axis of rotation [100] by an angle $\theta = 36.9^\circ$.

Static relaxation of the system was performed after creation of the models, followed by isothermal annealing at a given temperature (27 and 327°C) with a time step of $\Delta t = 1.5 \cdot 10^{-15}$ s during $100\,000\Delta t$, i.e., the annealing duration was $1.5 \cdot 10^{-10}$ s. The calculation method consisted of numerical integration of the equations of motion of atoms using the Verlet algorithm [14]. The interatomic interaction in the system was calculated using the immersed atom method [15].

3. Results and discussion

Large-angle torsion boundary. Figure 1 shows images of adjacent grain layers after annealing at a temperature of 327°C, which implies that atoms are mixed in the contacting layers, i.e. the structure of atomic layers characteristic of the β-phase is disrupted.

Figure 2 shows the structures of the 1st and 4th layers of the 1st grain (a, b) and the 20th layer of the 2nd grain (c). They show that a disruption of the ordered structure

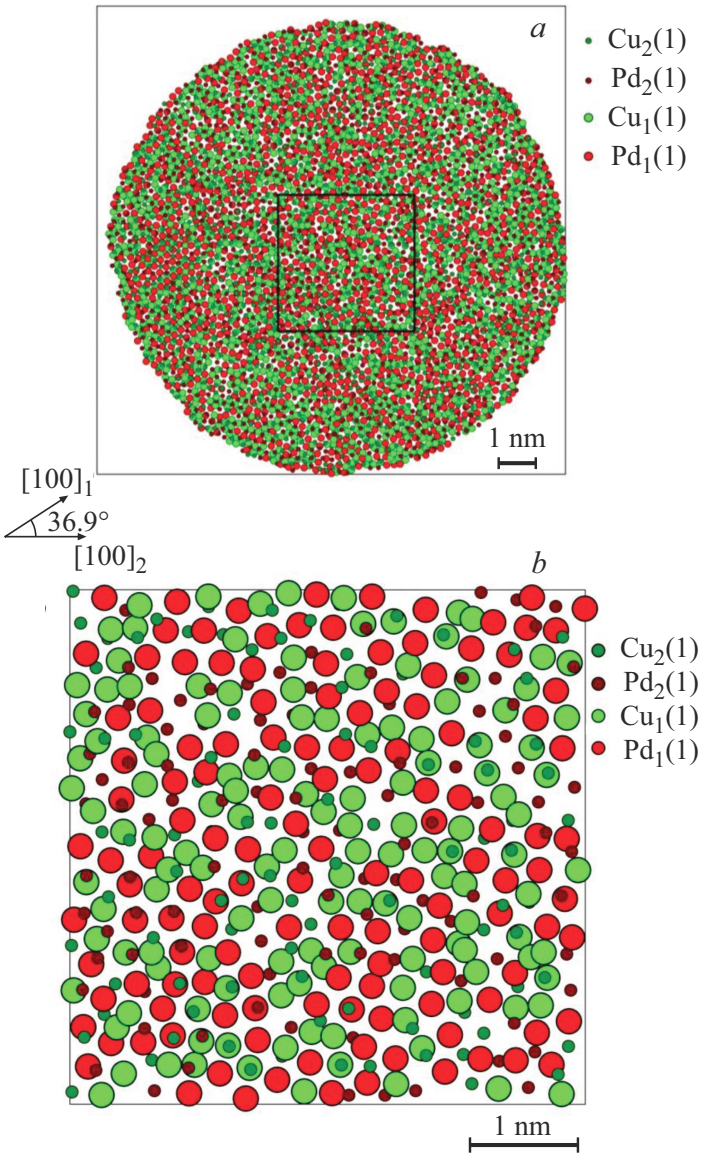

Figure 1. Adjacent layers of contacting grains of the model containing a large-angle torsion boundary, *a*) after annealing at a temperature of 327°C and *b*) enlarged fragment. The numbers in parentheses indicate the number of the layer within the grain, the subscript indicates the grain number (1 or 2).

affects a large number of layers of each grain (about 15), and the structure of the β-phase is maintained only in the 20th layer.

Figure 3 shows histograms of the distribution of atomic coordinates in both grains along the direction perpendicular to the boundary (in the direction of the axis of rotation) — initial, after static relaxation and after annealing. The initial histogram clearly shows a clear alternation of the atomic layers of copper and palladium (the columns corresponding to palladium are slightly lower due to the higher concentration of copper in the solid solution). It can be seen that the process of disordering begins in the contacting layers already during static relaxation. An intermediate phase with a disordered structure is formed as a result of MD annealing that consists of approximately 15 atomic layers of each grain. The width of this phase is about 5 nm.

Large-angle slope boundary. Figure 4 shows a projection of the model containing the slope boundary after MD annealing at a temperature of 27°C. It can be seen that the boundary is an intermediate phase with a disruption of the order (within 10 layers of each grain, i. e. the width of the boundary is about 5 nm). The adjacent planes $\langle 001 \rangle$ are misoriented to 36.9° in the initial state.

Figure 5 shows the function of the radial distribution of atoms of the model after annealing. It can be seen that a peak of the α-phase ($r = 3.55-3.65$ Å) appears in addition to the peaks of the β-phase. The peaks split as

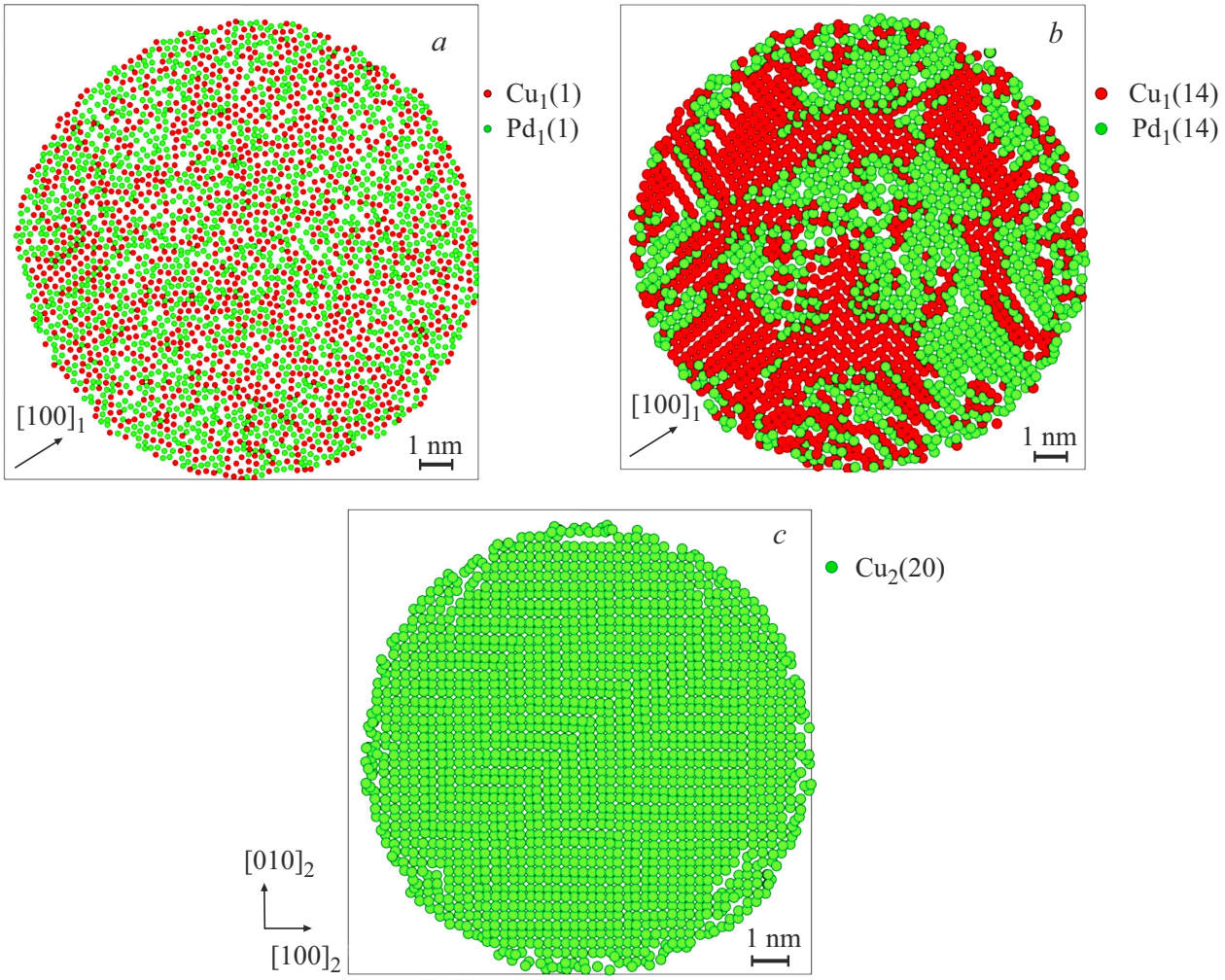

Figure 2. *a*) The first and *b*) the fourteenth layers of the first grain, *c*) the twentieth layer of the second grain. The numbers in parentheses indicate the number of the layer within the grain, the lower index indicates the grain number.

the temperature increases which indicates the stratification of the system into components (the peaks are close to the location of the peaks of copper and palladium).

It is possible to make the following conclusion from the above: a special boundary characteristic of single-component body-centered cubic crystals is formed. Modeling of a single-component nanoparticle under similar conditions showed that a special boundary is formed and the nanoparticle is rotated to a position corresponding to a special orientation ($\langle 001 \rangle$, $\theta = 36.9°$, $\Sigma = 5$) [13].

Small-angle torsion boundary. Figure 6 shows adjacent grain layers after static relaxation. It can be seen that the formation of a characteristic grid of dislocations begins, similar to that shown in Ref. [16] when modeling a Pd bicrystal with a small-angle torsion boundary. However, disordering occurs in the contacting layers (Figure 7) in the process of molecular dynamic annealing at a temperature of 27°C and an intermediate phase similar to the large-angle boundary is formed. The histograms of the distribution of atomic coordinates along the direction perpendicular to the boundary have a similar appearance to the case of a large-angle torsion boundary and confirm the formation of an intermediate phase.

4. Conclusion

The concept of CSL, COL, and GBD is not acceptable for characterizing grain boundaries in type-ordered B2 alloys.

The orientation mismatch at the grain boundaries is compensated through the formation of an intermediate structurally disorganized phase characterized by the stratification of components.

The results of the study substantiate the unattainability of the expected hydrogen permeability in the β-phase foil due to delayed diffusion of hydrogen atoms in a disordered structure and clarify the task of studying foil samples using high-resolution transmission electron microscopy.

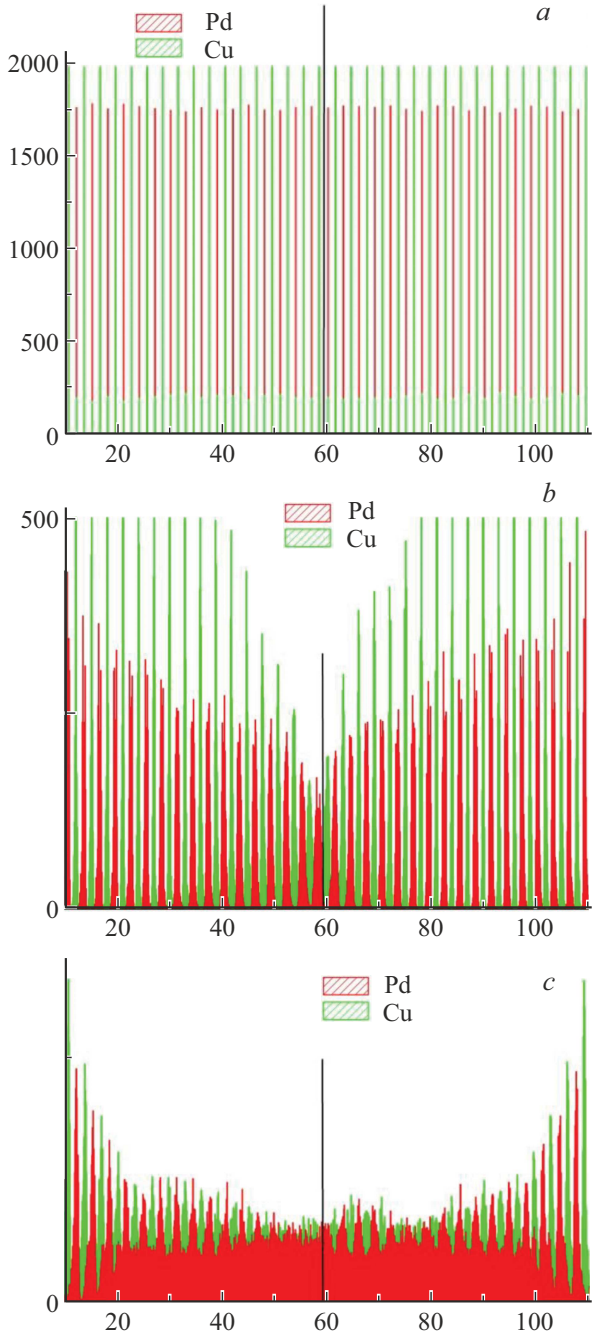

Figure 3. Histograms of the distribution of atomic coordinates along the direction perpendicular to the boundary (the black line shows the initial position of the boundary before annealing).

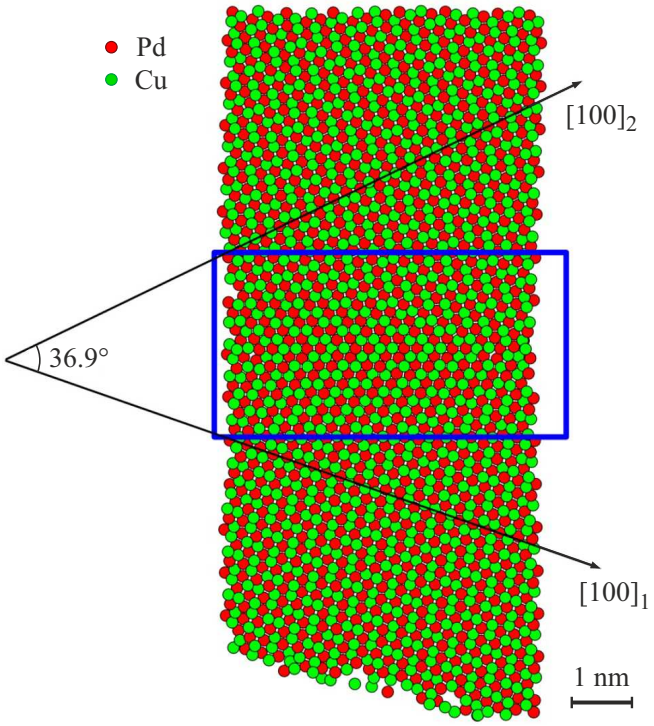

Figure 4. Projection of the model containing the slope boundary after molecular dynamic annealing. The lower index indicates the grain number.

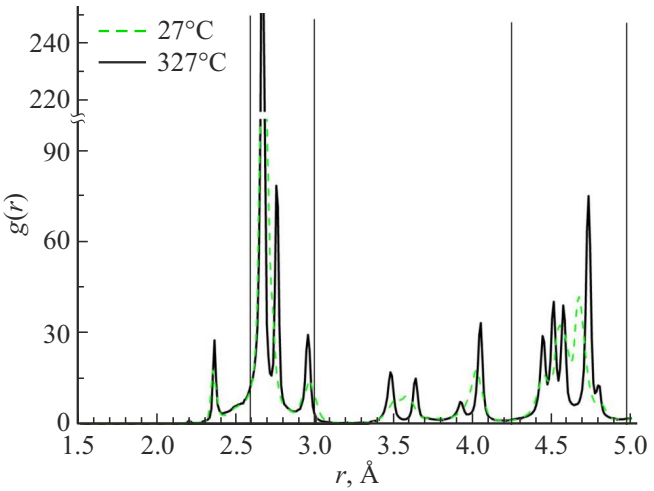

Figure 5. The paired function $g(r)$ of the radial distribution of atoms of the model containing the slope boundary after annealing at a temperature of 27°C (dotted line) and 327°C (solid line). The vertical lines indicate the peaks of the ideal crystal.

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Authors' contributions

Calculations using the molecular dynamics method were carried out by A.S. Prizhimov, system models and images were created by A.I. Dontsov and S.V. Gorbunov, problem statement, analysis of results and editing of the article was performed by V.M. Ievlev.

Conflict of interest

The authors declare that they have no conflict of interest.

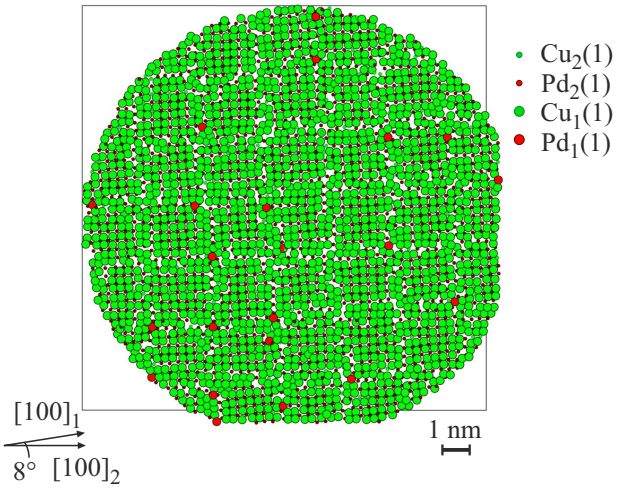

Figure 6. Adjacent grain layers after static relaxation of a model containing a small-angle torsion boundary. The numbers in parentheses indicate the number of the layer within the grain, the lower index indicates the grain number.

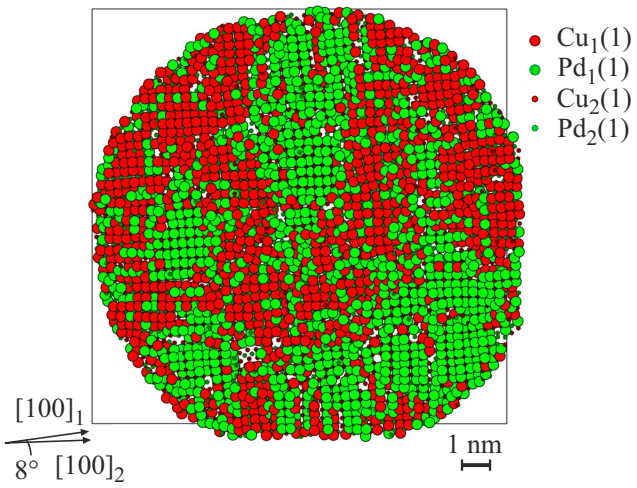

Figure 7. Adjacent grain layers of a model containing a small-angle torsion boundary. The numbers in parentheses indicate the number of the layer within the grain, the lower index indicates the grain number.

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