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On the mechanism of ordering of the solid solution of the Cu−Pd system according to the B2 type

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Based on the results of studying the structure of the membrane foil using X-ray diffractometry, high-energy electron diffraction and high-resolution transmission electron microscopy, the temperature dependence of electrical resistance, hydrogen permeability, crystal-chemical criterion and the electronic structure of the components, the mechanism of ordering the Cu−Pd system according to the B2 type is substantiated.

Keywords: CsCl type structure, palladium alloys, $\alpha \to \beta$ transformation, transformation mechanism, composition dependence.

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1. Introduction

Cu−Pd alloy has a relatively broad concentration range of type B2 ordering (formation of a CsCl type structure) [1,2], which is important for the creation and operation of deep hydrogen purification membranes. It is known from the literature data [3] that if Cu−Pd alloy is in a disordered structure (α-phase), then the activation energy of hydrogen diffusion in it is 0.23 eV, and the activation energy of hydrogen diffusion in an ordered structure (β-phase) is 0.035 eV. There are other reasons for the practical application of the alloy: there is no hydridization and, consequently, dilation does not occur; a multiple change of electrical resistivity as a result of $\alpha \leftrightarrow \beta$ transformations. It is impossible not to take into account the economic factor.

Fundamental studies of the kinetics of the processes of ordering and disordering, its dependence on the composition of the solid solution are continued by using various methods [4–8]. It was found in Refs. [9–11] that approaching the equiatomic composition results in an extremely low rate of ordering. This is justified in Ref. [12] by the spatial stratification of the components of a solid solution based on the results of high-resolution transmission electron microscopy studies of the structure.

The effect of large deformation has been found in Refs. [13–16] which manifests itself in an increase of the rate of $\alpha \to \beta$ transformation and minimization of the electrical resistivity of the sample.

It was found in [17], that the phase composition and texture of the foil formed by successive rolling stages (from 5 mm to 20 mm,μm) are preserved; the orientation ratios between β- and α-phases are close to the Nishiyama–Wasserman ratio [18,19].

The effect of rapid (0.3−1 s) photonic treatment with xenon lamp radiation (wavelength 0.2−1.2 μm) has been established, which manifests itself in a multiple acceleration of the process of disordering and stabilization of α-phase (quenching) [20,21]. This made it possible to compare the mechanical properties of a foil of the same elemental composition with the structure of β- and α-phases.

The substructure of two-phase samples is studied at the submicron level using transmission electron microscopy [22]. The interphase boundary $\alpha-\beta$ has been studied by the molecular dynamics method [23]. It is shown in [24] within the framework of the density functional theory that an increase of the concentration of Pd vacancies in an ordered structure should lead to an increase of the hydrogen permeability.

At the same time, there are still no experimental data on the mechanism of $\alpha \to \beta$ transformations, taking into account the observed effects: spatial stratification of components, changes of the electrical conductivity and hydrogen permeability.

The purpose of this report is to detail the process of nucleation of β-phase at the atomic level based on a set of experimental data and crystal chemical concepts.

2. Crystallochemical positions and experimental results on the substantiation of the ordering mechanism

1. The statement made in Ref. [9] about the discrete multiple nucleation of the β-phase according to the Bain model and its growth within the grains of the α-phase can be proved by the fact that the X-ray image (Figure 1) contains expanded reflections of the β-phase (a manifestation of the dimensional diffraction effect) along with the narrow reflections of the α-phase after rolling of 57 at.% Cu−Pd sample.

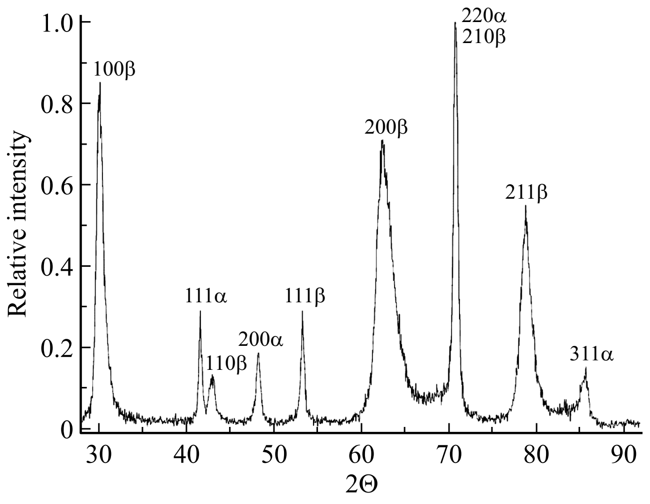

Figure 1. X-ray diffraction pattern of 57 at.% Cu−Pd foil after rolling.

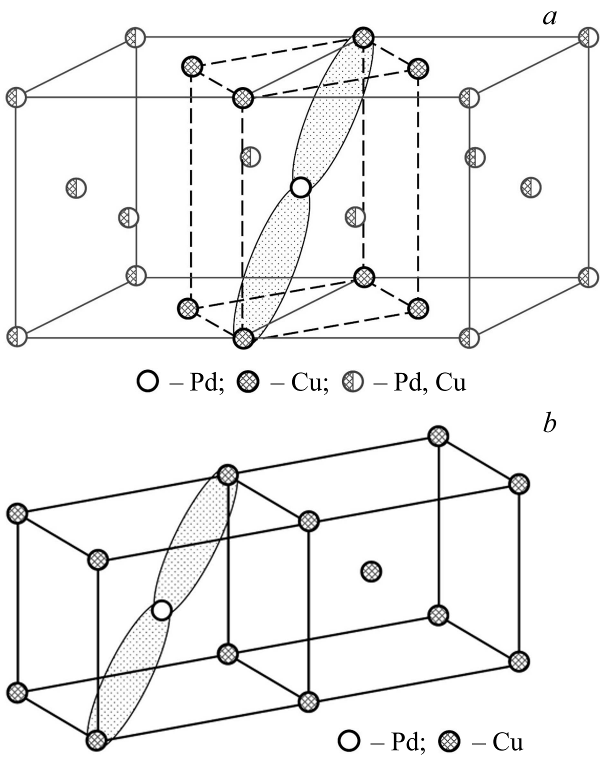

Figure 2. The model of transformation of structural units BCT → BCC: *a*) „pre-nucleus“, *b*) a cell of the CsCl type structure and a BCC-Cu cell coherently conjugated with it.

2. The possibility of the B2 type ordering of the solid solution of Cu−Pd system is justified by the basic crystallo-chemical criterion for electronic systems [25]: $K = \frac{P_A+q_B}{A+B}$ (here A and B — the percentage of atoms of each component, P and q — the number of electrons involved in the formation of compounds) should be close to 1.5 for the equiatomic composition. In particular, $K = 1.47$ for the composition 53 at.% Cu−Pd.

3. The elementary act of $\alpha \rightarrow \beta$ transformation according to the Bain model is controlled by the probability of discrete formation in the α-phase of structural units of lattice cells — body-centered tetragonal (BCT) „pre-nuclei“ of lattice cells of β-phase: a Pd atom surrounded by 8 Cu atoms (Figure 2, *a*). The choice of the Pd atom in the center of the lattice cell in the model is determined by the large size of its radius ($r_{\mathrm{Pd}} = 137$ pm, $r_{\mathrm{Cu}} = 128$ pm). Experimental fact: the rate of $\alpha \rightarrow \beta$ transformation increases with a deviation of the composition towards an increase of the content of copper atoms, which contributes to an increase of the probability of formation of a „pre-nucleus“.

The $\alpha \leftrightarrow \beta$ transformation process is realized by division of d-electrons into two groups with states ensuring the strongest coupling along directions $\langle 111 \rangle$ (a consequence of the octahedral potential of the shell p^6).

Figures 3 and 4 show diffraction patterns qualitatively characterizing samples with composition 63.6 at.% Cu−Pd and 51 at.% Cu−Pd.

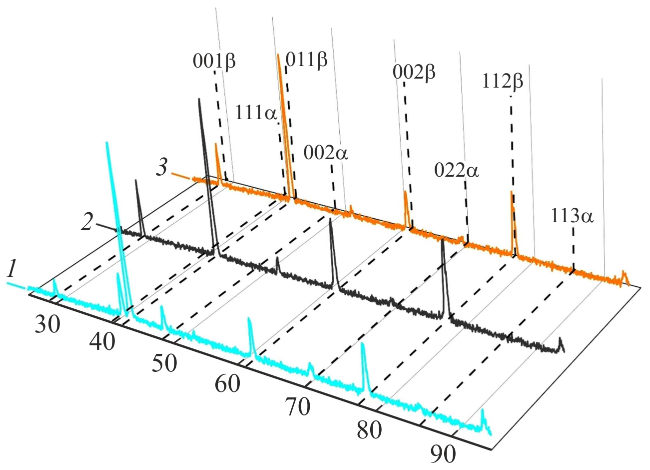

Figure 3. X-ray diffraction patterns of 63.6 at.% Cu−Pd sample (cycle heating to 700°C — cooling to room temperature (curve *1*) and exposure at 350°C for 2 h (*2*) and 24 h (*3*).

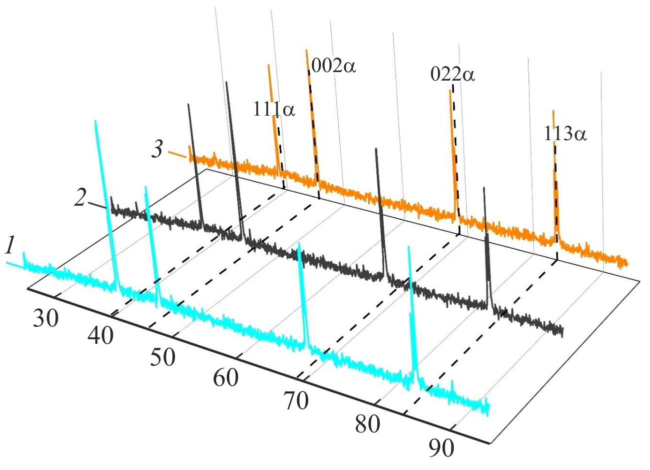

Figure 4. X-ray diffraction patterns of 51 at.% Cu−Pd sample after a cycle of heating to 700°C — cooling to room temperature (curve *1*) and exposure at 400°C for 4 h (*2*) and 20 h (*3*).

4. The alloy structure corresponds only to a centered cubic structure of the CsCl type when the composition deviates towards an increase of the proportion of copper (63.6 at.% Cu−Pd), as a result of a complete $\alpha \rightarrow \beta$ transformation (X-ray diffraction pattern in Figure 3). Vacancies in palladium (13.6%) can, in principle, be filled with copper atoms to form body-centered cubic (BCC) Cu structural units. It was concluded in [12] that BCC-Cu structural units are formed with an excess of Cu atoms (Figure 2, *b*). The invariance of the diffraction pattern is attributable to the fact that, according to the structural factor, the totality of reflections from the CsCl type structure overlaps the reflections corresponding to BCC-Cu structural units. The formation of BCC-Cu structural units is consistent with the conclusions of Ref. [26] when discussing the permeability of hydrogen in a 53 at.% Cu-Pd membrane.

5. No ordering occurred in the cycle of „heating 700°C, subsequent cooling to 350°C and holding at this temperature“ for 2 and 24 h in a foil with a composition close to the equiatomic (51 at.% Cu-Pd) (X-ray diffraction patterns Figure 4). This result is a consequence of the segregation of the atomic composition [12], which leads to a significant decrease of the probability of β-phase nucleation and a decrease of the rate of the ordering process. This is consistent with the data provided in Ref. [27]: when the alloy composition changes from 40 at.% Cu−Pd to the equiatomic composition, the mutual diffusion coefficient decreases by 2.6 times.

6. The decrease of the hydrogen permeability of a foil with a composition close to the equiatomic is explained in Ref. [12] by a delay of the diffusion of H atoms within zones with an excess content of Pd and transition zones accommodating nanodomains of different compositions. This conclusion correlates with the results of Ref. [25], in which the delay of single hydrogen atoms on defects in the palladium structure is shown by the method of molecular dynamics.

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Conflict of interest

The authors declare the absence of conflicts of interest.

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