Chapter

Solid Phase Evolution of Nanodispersed Palladium Powders

Veronika Ivanovna Rozhdestvina

Abstract

The processes of solid phase evolution of nanodispersed palladium powder at low temperatures were studied. It has been established that the process of solid phase transformation, which develops over time, forms a hierarchically structured organization of palladium grains from a structurally loose atomic cluster to a micrograin—an encapsulated aggregate of hollow subgrains. The process of grain ordering unfolds at several scale levels. It starts with the inner walls of the hollow subgrains that form the channel structures of the microaggregate and then passes to their surface and the unified encapsulating grain shell. In the collective effects of self-organization, periodic activation of mass transfer is observed, in which nanoparticles of various mesoscale structure organization are involved.

Keywords: palladium, nanodispersed powders, solid phase evolution

1. Introduction

Palladium is one of the most versatile elements of the platinum group metals. Ultrafine palladium particles exhibit unique catalytic properties (extremely high activity and selectivity); they are used to create composite materials and are capable of absorbing large amounts of hydrogen [1]. Current trends in the study of nanostructured palladium are mainly aimed at the development of new methods for the manufacture and stabilization of nanoparticles [1–5] and control of sizes and shapes that determine the physicochemical properties [6]. Despite numerous theoretical and experimental studies, structural-reactional relationships and the understanding of mechanisms of the catalytic reaction on the surface of palladium nanoparticles remain controversial.

In the study of evolutionary interactions between nanoparticles of the solid phase, the emphasis is on the mass exchange theory, experimental and model studies of agglomeration in a dispersion medium (liquid or gaseous). Contact reactions occur when particles approach each other randomly or in a controlled manner [7–10]. Most studies of the contact interactions of metallic dispersed powders are performed on systems in highly excited states caused by deformation influences of thermally activated nature [11, 12]. As a result, processes go with high velocities, causing the contact melting effect—sintering between contacting surfaces.

However, very little attention is paid to the study of the subsequent solid phase evolution of a nanostructured system under conditions of surface energy dissipation, without deformation and thermal effects, since it is believed that solid phase processes are not large-scale and proceed with extreme slowness. In this regard, a
study of structural and morphological transformations of nanodispersed palladium powders at low temperatures is of both practical importance and fundamental scientific interest.

In the framework of this article, we studied the processes and mechanisms of solid phase transformations that occur in freely contacting nanodispersed palladium powders at low temperatures.

2. Materials and methods of study

We studied PdAP-0 nanodispersed powders manufactured by Krastsvetmet JSC (mass fraction of Pd min. 99.98%) obtained by chemical reduction of palladium from solution, followed by filtration, washing and drying, packed in glass ampoules (1 month from the date of manufacture to the beginning of the experiment). The powder was agitated in ethanol, and a drop of suspension was applied to a conductive carbon tape fixed to observation tables in an electron microscope. After the droplet dried, the samples were placed in a vacuum column of an electron microscope.

Among all elements of the platinum group, the Debye characteristic temperature Pd $\Theta_D = 274$ K is closest to the temperature of normal conditions. To observe changes in the morphostructural characteristics of a nanodispersed powder, the particles of which are in free contact; the following temperature regimes were chosen for experimental observations of solid phase transformation. The first temperature regime which is $293 \pm 5$ K exceeds $\Theta_D$ Pd by no more than 24°, that is, the increase in the vibration amplitude due to the temperature effects is insignificant. The second temperature regime is $258 \pm 1$ K, which is lower than $\Theta_D$ Pd by 16°. The amplitude of the natural vibrations of atoms is still significant under these conditions, but the temperature contribution to them is minimal. The third temperature regime is 77 K, which is lower than $\Theta_D$ Pd by 197°. The amplitude of natural vibrations of atoms is low, and interatomic interactions dominate.

The powder was placed in tightly closed ampoules, from which air was evacuated to prevent moisture condensation on the samples when operating at low temperatures. The one ampoule was kept at room temperature, the second in a cryostat ($258 \pm 1$ K) and the third in liquid nitrogen (77 K). The total duration of the experiment was 2 years. Control observations of evolutionary changes in the morphostructural features of palladium powders in ampoules were carried out after every 6 months of exposure of the samples to the respective conditions. After this period, the ampoules were removed and stabilized without opening to room temperature during the day. Powder samples were examined with an optical microscope for the occurrence of larger particles in the powder. If available, individual particles were extracted from the powder, and studies of their structural and morphological characteristics were carried out. Then the particles were again placed in ampoules from which air was evacuated, and the ampoules were again placed in the appropriate temperature conditions for the next holding period.

Systematic observations of solid phase transformation processes in finely dispersed palladium powders were performed using the device base of the Analytical Center of Mineralogical and Geochemical Research of the Institute of Geology and Nature Management, Far-Eastern Branch of the Russian Academy of Sciences: JEOL JSM 6390LV (Japan) scanning electron microscope and SIGMA (Carl Zeiss) scanning electron microscope with the X-Max INCA Energy (Oxford Instrument). X-ray diffraction studies were performed using a Shimadzu XRD-7000 MAXima. X-ray diffractometer (2.2 kW, Cu Target, Long Fine Focus (LFF)
3. Solid phase processes of self-organization of substance at nanolevel

In the chemical reduction of palladium from a solution at an early stage of nucleation, metal ions are reduced to a state with zero valency and, when approaching, are combined into atomic clusters to form irreversible nuclei (0.1–1 nm in size) [1]. These nuclei can increase in size due to the addition of other atoms or coagulation among them, forming flocules. To reduce the effect of coagulation and stabilization of nanoparticles, special agents are introduced into solutions that provide a monodisperse state and the required forms of nanoparticles [5, 6].

Thus, metal particles (dispersed phase) are released from the solution (dispersion medium), which are suspended in a liquid. The interactions between them lead to clustering (the first stage of substance integration). Clusters of various shapes gradually increase in size and form loose flocules. After liquid removal, the system also remains biphasic: solid particles in the form of flocules with a developed surface and gas (air) filling the spaces between them. The system is energy saturated, and it is in a non-equilibrium state. Metallic materials are dissipative systems capable of energy dissipation. This can be manifested in the activation of morphostructural solid phase transformations.

An analysis of the Debye powder diagrams obtained from the starting powders confirms their ultrafine state. The X-ray diffraction pattern of palladium powder is characterized by broadening of symmetric diffraction peaks for all crystallographic directions, with an increase in the degree of blurriness and intensity with an increase in the diffraction angle of reflection (Figure 1). Doublet (422) is not split. The diffraction broadening of reflections caused by a decrease in coherent dissipation blocks begins at crystallite sizes less than 100 nm. In the area of small angles, a wide halo is observed, which is characteristic of X-ray amorphous phases, due to the presence of a significant number of particles with sizes less than 10 nm. To study the degree of broadening of diffraction reflections, we used a method based on extracting from a graphical representation of the dependence of the intensity on the wavelength of a linear optical spectrum obtained by scanning X-ray diffraction patterns and then storing it in the form of a full-profile bi-dimensional description. It was found that the diffraction peaks have a symmetrical shape and the broadening is proportional to the tangent of the diffraction reflection angle, which indicates the dispersion of the powder under study. The lines with Miller indices \((hkl) h = k\) are approximated by Gaussian curves, which also indicates a high dispersion. An analysis of the degree of broadening of the diffraction reflections of the X-ray diffraction pattern of the initial palladium powder indicates that according to the size criterion of the composing particles, the powder can be divided into two dominant fractions of 30–60 nm and less than 10 nm.

Electron microscopic studies show that palladium particles are a quasi-amorphous substance in which isolated particles of two scale levels are identified: 5–20 nm and 40–150 nm (Figure 2). Among the first group, rounded particles with
fuzzy boundaries of 5.5–7 nm in size predominate; those larger than 15–20 nm are observed occasionally. The second group is mainly represented by particles of various configurations formed as a result of aggregation of particles of the first group or having a quasi-amorphous structure without isolation of individual elements with a predominant size of ~60 nm (Figure 2). At this stage, differentiation is already observed in the total mass of particles with the individualization of elements of a denser structure.

Figure 1.
X-ray diffraction patterns of palladium powder (T = 293 K)—initial state (a, b1) and state after 6 (b2), 12 (b3), 18 (b4) and 24 (b5) months. Changes in the preferred orientations of crystallites in palladium grains at different stages of conversion (state after 6 (c1), 12 (c2), 24 (c3) months).
The system is an ultrafine mixture of metal particles and gas (air) filling the spaces between them. The morphostructural organization of metal nanoparticles formed during synthesis is represented by clusters of various configurations (up to 2 nm) and floccules (5–20 nm). The floccule structure is locally heterogeneous with a pronounced gradient of density decrease from the centre to the periphery. In the solid phase, the integration process continues. Floccules have a developed contact surface; smaller clusters, forming contact with them, significantly increase floccules in size, due to the expansion of a structurally loose boundary. A small amount of substance covers a large amount of space. Floccules with many interpenetrating and point contacts coagulate and form aggregates. The system begins the processes of self-organization and structuring. Floccule nuclei become denser, their flocculent boundary outgrowths and smaller free clusters grow together to form a quasi-amorphous cement (Figure 3). Later, the floccules are acquire a spherical shape. The substructure of the cementitious substance becomes indistinguishable.

The process of interaction of nanoparticles with an active unfolded surface, which provides multiple contacts, contributes to the development of their collective effects aimed at self-organization and structuring of the system. As a result, new
structural units form in the form of plates, flakes of various configurations from the total mass of loose flaky substance. Due to the compaction of the substance, their edges are often curled up, and the plates are separated (Figure 2). The substructure of the flakes in the form of stacking spheres at this stage remains clearly distinguishable. Observation of the dynamics of the system showed that at room temperature, the process of separation of particles of the second scale level is gradually activated, and larger fragments up to 200 nm are also individuated. They acquire clear boundaries as they condense. Their structure is composed of denser spheres cemented by a quasi-amorphous loose substance.

Developing over time, the processes of structural self-organization evolve to the consequent scale level, where the main structural units are no longer floccules and clusters but nanosized lamellar formations (~50–180 × 5–15 nm) which are formed from them. The process develops according to the planar contact deposition of nanoplates (flakes). This determines the morphostructural specificity of this stage of transformation. The scales continue to condense, the relief is gradually smoothed out and they become more closely adjacent to each other (Figure 2). As a result, a multilayer thin surface structure is formed of contact superimposed flakes, the substructure of which is still quite pronounced. Since the density of the substance at this stage of conversion is still quite low, the processes of compaction and structuring are decisive.

Thus, in the area of nanolevel scales, the solid phase evolution of palladium powders proceeds at three meso-levels of structural organization. The first meso-level is characterized by the integration of substance with the formation of clusters up to 2 nm in size (point, linear, volumetric of various configurations, the substructure is filamentous, flocculent) and floccules—segregations with a relatively dense core and indefinite flaky boundaries (5–20 nm). The second is the integration of floccules and smaller clusters, densification and structuring with the formation of nanoplates (flakes) (~50–180 × 5–15 nm). The third is the integration of flakes (“tiling” of flakes), the formation of thin multilayer submicroscopic plates with a movable easily transformable substructure. All the transformations described above took place in a thin layer of powder placed on a carbon tape substrate which is put on an observation table in an electron microscope for 6 months of observation.

A study of palladium powders in a sealed ampoule for 6 months at 293 ± 5 K showed that larger formations appeared in them in the form of branched micrograins, which are intergrowths of subgrains of rounded elongated shapes (Figure 4). The microstructure of subgrains is composed of nanosized polydisperse
particles of varying degrees of compaction, on the surface of the subgrains without their mutual ordering and at the boundaries of intergrowth with other subgrains with polygonization elements (Figure 4). The particles are identical in their morphostructural features to the above-described particles which are formed in a thin layer of powder deposited on a conductive carbon tape.

4. Low-temperature solid phase self-organization processes

In finely dispersed palladium powders aged at negative temperatures, the integration processes take place at substantially higher rates than at a temperature of 293 ± 5 K. After 6 months of exposure to nanodispersed powders at a temperature of 258 ± 1 K, the occurrence of micrograins with sizes up to 250 μm is observed (Figure 5). The grains have a branched spongy structure, in the form of intergrowth of subgrains of rounded elongated shape with a diameter of 1–3 μm. The ratio of the volumes of voids and solids in the grains is comparable to each other. Many subgrains have end-to-end surface discontinuities, which indicate their hollow structure (Figure 6).

Studies of the structural organization of powder particles and palladium micrograins maintained at a temperature of 293 ± 5 K (T < ΘD Pd) showed that the main processes here also include coagulation, densification, the formation of thin flakes and their aggregation with the creation of larger forms of thin multilayer plates, but in structural organization, they advanced significantly further than powders kept at a temperature of 293 ± 5 K (T < ΘD Pd).

The surface of the plates (flakes) is more compacted, smoothed, with well-defined boundaries. Thin multilayer structural units gradually increase their area and, having reached micron sizes, begin to bend and twist, forming hollow, rounded, oval or tubular shapes (Figures 6–8). The multilayer structural organization of the plates (“tile laying” of the flakes) that form the walls of the hollow subgrains during bending provides them mobility due to the displacement of the layers relative to each other (Figure 7). With the increasing surface curvature, the upper plates move apart, revealing the inner layers with a quasi-amorphous surface. In this case, discontinuous discontinuities are often observed.
As a result of the processes of coagulation and compaction of the substance and the collective actions of nanoparticles of several scale levels, thin-walled hollow formations of rounded, oval, tubular shapes with a diameter of about 1–3 μm

Figure 5.
Transformations of palladium micrograins at a temperature of 258 ± 1 K: sponge aggregate formed from nanopowder (after 6 months) (a), grain with a dense structureless surface and sponge internal structure (after 2 years) (b), X-ray diffraction patterns of palladium grain (after 6 (c), 12 (d), 24 months (e) at 258 K) and changes in the preferred orientations of crystallites in palladium grains at different stages of conversion (state after 6 (f1), 12 (f2), 24 (f3) months).

As a result of the processes of coagulation and compaction of the substance and the collective actions of nanoparticles of several scale levels, thin-walled hollow formations of rounded, oval, tubular shapes with a diameter of about 1–3 μm
are formed (Figure 8). These formations are structural units of the microscopic organization of matter. The structure formed in this way has an unfolded inner and outer surface. The diameter of the internal channels is close to 1 μm. The thickness of the multilayer wall is 30–60 nm.

By approaching each other, hollow micrograins grow together according either contact or bridge mechanism (Figures 9 and 10). The first mechanism is due to direct contact of curved surfaces (Figure 9). When the curved surfaces of two thin layers come into mutual contact, the layer thickness in the contact zone doubles. The scales composing the walls of the hollow grains come into motion due to the collective effects of the interaction. Mass transfer is directed away from the contact area (Figure 9). The outflow of particles causes opening of the cavity, the internal channels are combined and the wall thickness is levelled. The intergrowth process is not a sintering process with an increase in thickness in the contact area, but the unification and expansion of the thin channel internal structure.
The second aggregation mechanism, aimed at expanding the thin channel system, ensures the intergrowth of hollow thin-walled structures that do not contact each other. This mechanism is due to the effects of long-range bonds. When the curved surfaces of thin-walled (~30–60 nm) hollow formations are located at a distance comparable to the diameter of the internal channels (~1 μm) between the dispersed particles from which they are composed, collective effects aimed at combining the surface also appear. Collective actions of particles are manifested in mass transfer to the area of maximum approximation of surfaces (Figure 10). In this zone, a thin “bridge” begins to form, either in the form of a whisker-like outgrowth or a twisting effect forming an outgrowth cone that extends to contact with each other. After the formation of the bridge, mass transfer is activated. The contact bridge expands, and the transverse size becomes comparable with the size of the channels. The rupture structures and partings between the plates and scales are
smoothed, forming concentric bands similar to growth zones. A single expanded channel system is being formed.

Thus, the palladium grains formed at this stage are a two-phase mixture consisting of a solid phase (Pd) and two types of voids (air). The first type is a void encapsulated in the internal cavities of micrograins and complex branched channels (~1 μm) formed when they merge. The second type is a spongy volumetric structure formed during the intergrowth of hollow microparticles. A void is almost evenly distributed over the grain volume.

The formed system has a developed inner and outer surface; it is energetically saturated and metastable. The structural configuration of the dissipative system involves its further transformation. The activation of interactions between hollow subgrains is characterized by two processes occurring simultaneously: the formation of new contacts and the destruction of previously formed ones. The constant movement of matter associated with the formation of new contacts often results in rupture of the surface and opening of channel structures. Viscous deformation discontinuities, shears and disruptions without visible deformations of the accretion boundaries are observed (Figure 11). Microcracks appear along the boundaries of intergrowth, new contacts form and open-channel cavities are closed. The system is transformed in a mobile way, reducing the volume of second type voids.

The processes of structural self-organization of particles in thin-walled bodies quickly form geometrically regular shapes (negative crystals) on the inner side of the channel wall, the outer surface is a multilayer packing of flakes and sometimes ordering effects are also observed in their arrangement, with the formation of face shapes (Figure 12). Particles whose structural organization is constructed in this way (tubes, spheres whose walls consist of nanostructured particles in a quasi-amorphous phase) are energetically saturated and have a high degree of freedom for further transformation.

Opening of internal channels causes collective effects in the system aimed at closing them. The process is due to transformations of the substance in the area of the open hole and depends on the mechanism of rupture. If a rupture occurred due to tensile forces, leading to the formation of a tension zone and a thin isthmus at the time of the rupture, the boundaries of the rupture have thin ragged edges, with a significant number of nanosized separation protrusions. Such discontinuities are
closed as a result of the convergence of the walls and smoothing of the displacement formed during the rupture (Figure 13). When the size of the holes formed, for example, as a result of shear forces, corresponds to the diameter of the channel, their closure occurs mainly due to the effects of quasi-viscous flow (Figure 13). Incrusted structures grow, gradually closing the hole. This type of closure is most common in the studied system. The convergence of the walls in the rupture
boundary area is also observed; the outer diameter of the hole decreases until contact interactions between the particles of the surface layer are established, causing the processes of restoring the integrity of the outer layer and the formation of a common shell (Figure 13).

The development of the compaction process over time leads to the convergence of the boundaries of hollow subgrains. When there are several surfaces of hollow formations at a critical distance at a time, a unified surface is formed forming structural units of the next scale level in the form of intergrowth of rounded bodies with sizes of 3–30 μm, which gradually form curved surfaces preserving the boundaries (Figure 14). Their surface also has a scaly lamellar structure with elements of polygonization, and there are residual pores of the second type, which gradually decrease in size.

The main mobile structural units of the surface layer of subgrains are scaly lamellar formations. They do not lose their structural identity for a long time (Figure 15). After the merging of the hollow subgrains and the formation of rather extensive zones with denser intergrowth, the process of surface transformation is activated. Initially, the borders and shapes of the scales are structurally separated, and then spicule-like elements appear in the structure of the scales with the ordering effect in their location; the relief contours are softened and smoothed. Then, scales are flattened and boundaries are merged. Consequently, zones with structural corrugated bands are formed (Figure 16) which are gradually smoothed out levelling the surface. On the surface, the elements of polygonization are manifested, with the development of the process at the neighbouring subgrains.

In the processes of surface transformation, the key role is played by the size effect. The collective actions of ultrafine particles determine the order of transformations that develop over time. In the initial stages, in spite of the volumetric filling of space with particles, ordering has a planar distribution. Consequently, the transformation process goes to the sub-grain level, and then it is activated in the contact zones. With the coalescence of micrograins, the intergrain zones are also involved in the collective processes of surface transformation, the boundaries gradually disappear, and the structural organization of the surface becomes unified (Figure 16). At later stages, the surface topography is smoothed and acquires soft forms, and then banded and other forms with a relatively smooth relief appear. A structure identical

Figure 12. Recrystallization of the inner wall of hollow channel structures in palladium grains and elements of ordering of the outer layer.
Figure 13.
Closures of discontinuities in channel structures in palladium grains: walls convergence and displacement smoothing, quasi-viscous flow effect and recrystallization.

Figure 14.
Different densities of micrograin intergrowths and stages of surface transformations.
to the structures of the growth planes is revealed (Figure 17). A relatively stable state is organized in which slow processes occur, aimed at ordering between the particles of a thin layer—the shell. Subgrains lose their structural identity; former contact zones acquire smoothed shapes.

The next important stage in the structural transformation of palladium micrograins is associated with the creation of a unified grain shell as a whole. After
the formation of a micrograin (50–300 μm) of a spongy structure, the compaction processes contribute to its transformation as a whole, separating it from the rest of the fine powder. Since the aggregation and occurrence of grains have a progressive character with the simultaneous presence of both a finely dispersed phase and already formed grains in the system, particles of various sizes and degrees of compaction were found at various stages of the study. Transformation processes are aimed at the individualization of each individual grain, the creation of a common shell (the microencapsulation effect). When the displacement of voids of the second level is activated, resulting in compaction of the substance, the most active merging of particles occurs on the grain surface. A grain, as a whole object, tends to acquire a single, generalized surface. The individuality of the substructural components is first smoothed out due to effects similar to a viscous-flowing state, and then sod-deformed, smoothed, worn-out forms are formed, gradually closing the internal porous channel structure (Figure 18). The organized outer shell loses smoothness, becomes fine-grained and is worn smooth. The microencapsulation effect is aimed at organizing a common surface on which one can only detect relics of a structural organization that has undergone significant evolutionary transformations. The surface acquires a structure that is described as rounded with deformation elements (Figure 18). However, despite the presence of an external dense shell, the internal organization of the grain remains nanoporous.

Stabilization of the temperature regime at temperatures below the Debye palladium characteristic temperature favours the occurrence of preferred orientations of crystallites in palladium grains (Figures 1, 5 and 19). If the spongy grains, whose crystallites do not exceed 1 μm, are kept at room temperature, no increase in crystal size will be recorded. Radiographs are characterized by sharp lines (Figure 19a), and the intensity distribution is identical to the theoretical radiograph. The X-ray structural characteristics of palladium grains maintained at various temperature conditions are presented in Table 1.

The unit cell parameters for palladium grains transforming at room temperatures are approximately 3.882 Å. This value is reduced relative to the unit cell parameters of native palladium, which indicates the incompleteness of the transformations in the system of its metastability. And for samples aged under freezing temperatures, the parameter values are as close as possible to the values for native palladium. For negative temperatures close to the Debye characteristic
temperature of palladium, the ordering process is accelerated, and the crystallite sizes increase. It is likely that further transformation processes will lead to a single crystal state. However, the presence of internal channels/voids leaves the system

Figure 18.
Grain encapsulation and surface transformation.

Figure 19.
Radiographs characterizing the changes in the preferred orientations of crystallites in palladium grains, aged at 293 ± 5 K (a), at 258 ± 5 K (b) and at 77 K (c) (shooting at the Collective Use Centre of the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences).
open. A significant decrease in temperature (77 K) promotes rapid encapsulation (Figure 20), the formation of a dense shell, in which ordering occurs only at the micro level. That is, the processes of separation of each individual grain in this state are predominant over the processes of general ordering.

Thus, studies of interactions between ultrafine particles of palladium in free contact showed that their aggregation leads to the formation of thin channel structures with a channel diameter of ~1 μm and a wall thickness of ~30–100 nm. The sizes of the coherent dissipation blocks and the wall thickness of the channel structures are identical; their inner surface has flat faces in the form of negative crystals, which indicates the ordering between the particles composing them. The established effect of enlargement of coherent dissipation blocks and the occurrence of preferential orientations are probably associated with ordering in the arrangement of channel structures and their alignment in a certain order. Microencapsulation favours an orderly distribution of voids in the grain volume.

Dissipative processes in dispersed objects contribute to the development of long-range coherence in the system [13]. The determining parameter in this process, in our opinion, is the ratio of the sample holding temperature to the Debye characteristic temperature of palladium $\Theta_D = 274$ K. The Debye characteristic temperature is the temperature at which crystal lattice vibrations of all possible frequencies are realized. A further increase in temperature does not lead to the occurrence of new vibration modes but only leads to an increase in the amplitudes of existing ones, that is, the average vibration energy increases with the increase in temperature. At temperatures of the system $T < \Theta_D$, the atoms oscillate near a certain equilibrium position, the intensity and amplitude of which depend on the difference between the Debye characteristic temperature of the substance and the temperature of the system ($\Delta T = \Theta_D - T$). According to Debye, with a decrease in temperature in the area $T < \Theta_D$, the energy of each individual vibrator decreases; moreover, the vibrations of more and more new vibrators gradually decrease.

Thus, under conditions when $T < \Theta_D$, interatomic interactions become predominant. Long-range bonds are established between the atoms of matter; the collective actions of atoms are aimed at ordering and tending of the system towards the perfection of its crystal structure. The structure of the substance becomes denser.

| Table 1. X-ray structural characteristics of palladium grains aged in various temperature conditions. | Sample | For all available reflections | In the precision area |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $a \pm 0.001 \ \text{Å}$ | $V, \text{Å}^3$ | $\Delta d^*$ | Mn** | $a \pm 0.0001 \ \text{Å}$ | $\Delta d^*$ | Mn** |
| Pd 00-046-1043 | | 3.89019(2) | | 3.89019(2) | |
| Pd 293 ± 5 K | 1 | 3.882 | 58.482 | 0.00276 | 80.044 | 3.8831 | 0.00027 | 200.688 |
| | 2 | 3.882 | 58.512 | 0.00351 | 68.080 | 3.8839 | 0.00019 | 292.893 |
| | 3 | 3.881 | 58.467 | 0.00244 | 85.800 | 3.8825 | 0.00040 | 164.194 |
| Pd 258 ± 1 K | 1 | 3.887 | 58.717 | 0.00135 | 85.196 | 3.8871 | 0.00087 | 62.679 |
| | 2 | 3.890 | 58.870 | 0.00163 | 98.430 | 3.8911 | 0.00042 | 135.758 |
| | 3 | 3.890 | 58.857 | 0.00112 | 165.352 | 3.8906 | 0.00022 | 274.520 |
| Pd 77 K | 1 | 3.890 | 58.870 | 0.00096 | 153.662 | 3.8909 | 0.00007 | 906.799 |
| | 2 | 3.889 | 58.816 | 0.00072 | 183.220 | 3.8894 | 0.00024 | 233.847 |
| | 3 | 3.888 | 58.765 | 0.00125 | 127.889 | 3.8885 | 0.00034 | 162.065 |

$\Delta d^*$, average deviation of the calculated interplanar distances from the measured ones; Mn**, reliability criteria after de Wolf.
Further lowering the temperature reduces the amplitude and energy of the natural vibrations of the lattice, thereby contributing to even greater structuring of the substance.

5. Conclusion

Thus, studies of interactions between finely dispersed palladium powders that are in free contact under dissipative conditions of low temperatures indicate the group behaviour of particles at various scale levels. Structural aggregation takes place in stages, with the allocation of an aggregation field area at each scale level:

- Lack of structure
  - Small-scale clustering
- Prestructuring
  - Medium-scale aggregation and divergence of cluster types in the aggregate
  - Large-scale aggregation
- Structuring
  - Aggregate formation and shell formation (microencapsulation)
  - Recrystallization at the subgrain level
  - Recrystallization at grain level

In the collective effects of self-organization, periodic activation of mass transfer is observed, in which nanoparticles of various mesoscale structure organization are involved. The solid phase finely dispersed substance evolves mobile in the process.
of dissipation of surface energy, which takes on new forms at every scale level of the organization while maintaining the structural identity of its constituent particles. The manifestation of a multiscale structure, close relationship and mutual influence of various scale levels is one of the key points in the processes of mass transfer in contact interactions.

Conflict of interests

The author states having no conflict of interests.

Author details

Veronika Ivanovna Rozhdestvina
Institute of Geology and Nature Management FEB RAS, Blagoveshchensk, Russia

*Address all correspondence to: veronikapts@yandex.ru

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