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Full Articles

High-temperature X-ray diffraction study of thermolysis of the double complex salt $[Rh(NH_3)_5Cl][PtCl_4]$

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The formation process of a nanosize powder of the equilibrium solid solution $Pt_{0.50}Rh_{0.50}$ by thermolysis of the double complex salt $[Rh(NH_3)_5Cl][PtCl_4]$ under hydrogen or helium and *in vacuo* was studied *in situ* by X-ray diffraction and synchrotron radiation. The reduction temperature of the metals in the cationic and anionic moieties of the starting complex is the main factor responsible for the mechanism of solid solution formation.

Key words: double complexes, platinum, rhodium, solid solutions, nanosize powders, formation steps, high-temperature X-ray diffraction.

Heteroatomic metallic phases and composites with a crystallite size smaller than 100 nm can be prepared by crystallization of amorphous alloys and mechanochemical alloying,[1] as well as by decomposition of precursors containing atoms of two or more metals. Double complex salts, which consist of complex cations and anions containing various transition metals as the central atoms, serve as the starting compounds for the preparation of bimetallic powders. Nanosize powders with different phase compositions, including metastable oversaturated solid solutions, can be prepared by varying the coordination environment, the temperature parameters of the decomposition process of complex salts, and the gas medium.[2]

Investigation of the mechanism of thermolysis of double complex salts is of considerable practical interest, in particular, for the development of procedures for the preparation of supported catalysts.[3] Compared to conventional methods for the preparation of bimetallic materials, the latter method allows one to prepare metallic phases at substantially lower temperatures. Due to the fact that precursors contain metal atoms in a stoichiometric ratio and these atoms are already "mixed" at molecular level, the problem of preparation of homogeneous materials of strictly specified compositions, which are located in phase diagrams in the immiscibility region, has been successfully solved in some cases.

Earlier,[4] we have studied in detail thermolysis of the $[Pd(NH_3)_4][IrCl_6]$ salt under quenching conditions. In these experiments, we measured X-ray diffraction patterns of samples, which were quenched from the equilibrium state, at room temperature and also *in situ* in a high-temperature X-ray chamber. The formation steps of the

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metastable solid solution $Pd_{0.5}Ir_{0.5}$ at temperatures, at which a two-phase mixture should be formed according to the phase diagram, were described.

The phase diagram of the Pt—Rh system was examined in several studies.[5] The existence of a continuous series of solid solutions with possible ordering at a concentration of ~25 at.% Rh was noted. More recently,[6] a sharp inflection in the concentration curve of the magnetic susceptibility by analogy with the Pt—Ir, Pd—Th, and Pd—Ir systems has been attributed to discontinuity in solubility in the subsolidus region of the phase diagram. Based on this fact, the critical temperature of 780 °C was predicted. The proposed phase diagram was accepted as a recommended diagram.[7]

However, this fact was not experimentally confirmed. Even after annealing at 600 and 800 °C for 36000 h, samples of solid solutions remained homogeneous.[8] Quantum mechanical calculations[9] suggested that the enthalpy of mixing of the components in this system is negative, which is contradictory to the assumption[6] that decomposition can occur. Measurements of diffuse X-ray and small-angle neutron scattering from a Rh(47 at. %)—Pt single crystal, which was annealed at 650 °C, revealed local ordering in the solid solution.[10]

The procedure for the synthesis of $[Rh(NH_3)_5Cl][PtCl_4]$ and the final thermolysis products of this compound under argon and helium have been documented earlier.[11] In the present study, the mechanism of solid solution formation in the Pt—Rh system by thermolysis of this salt under hydrogen or helium, as well as *in vacuo* and in air, was examined *in situ*. In all cases, elimination of platinum metal was demonstrated to be the first step. However, further elimination of rhodium and the formation of the final product depend on the experimental conditions.

Experimental

Powder X-ray diffraction analysis of the precursor $[Rh(NH_3)_5Cl][PtCl_4]$ and its thermolysis products was carried out on a DRON diffractometer equipped with a SEIFERT-RM4 automated system (CuKα radiation, graphite monochromator, reflection mode, scintillation detector with amplitude discrimination). The samples were prepared by coating an ethanolic suspension onto a polished side of a standard quartz cell. Polycrystalline silicon (a = 5.4309 Å) prepared analogously was used as the external standard. The X-ray diffraction patterns were measured in the step-by-step mode in the 2θ angle range from 5° to 60° for the complex salt and from 5° to 135° for the thermolysis products. The X-ray diffraction patterns of the thermolysis products were indexed based on the data for pure metals and compounds retrieved from the PDF database.[12] The unit cell parameters of metallic phases were refined by the full-profile analysis based on all data with the use of the PowderCell 2.4 program.[13]

The *in situ* experiments were carried out in a high-temperature X-ray chamber on an X-ray diffraction station using time-resolved synchrotron radiation (VEPP-3 ring storage in the G. I. Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences, 5b beamline) and an OD-3 one-coordinate detector. The detector has 3328 channels and operates in the angle range of 30 deg.[14] The synchrotron radiation wavelength $\lambda = 1.504$ Å. Samples were prepared by pressing the starting compound into a cavity of a stainless steel cell. In some experiments, the samples were held up against the surface by a 100 μm thick beryllium foil to prevent bloating of the sample upon thermolysis, which leads to its deviation from the focusing plane.

Results and Discussion

Thermolysis of $[Rh(NH_3)_5Cl][PtCl_4]$ was studied by X-ray diffraction taking into account the data from thermogravimetric measurements. It was found[11] that decomposition of this complex under helium involves two steps in the temperature range of 280—350 °C, the steps being virtually indivisible. Under an atmosphere of hydrogen, the reaction proceeds in one step at 200—230 °C.

First, we performed experiments under an inert atmosphere. A weighed sample of the complex salt was heated in helium stream in a quartz boat placed in a flow reactor to a specified temperature and kept at this temperature. After cooling, the sample was weighed and the X-ray diffraction pattern was recorded at room temperature in air. Each next temperature point was obtained with the use of a new portion of the starting compound.

The first step of decomposition of the complex under helium starts at 280 °C and is accompanied by the endo effect. After storage at 300 °C for 1 h, the compound loses ~16% of the weight, which corresponds to approximately 89 atomic mass units (amu). The product obtained after completion of this thermolysis step contains platinum metal and a nonidentified phase (Fig. 1). After treatment of this product with water, the nonidentified phase goes into solution, and the insoluble precipitate consists of pure platinum. The amount of platinum corresponds to the total percentage of reduced metal in the anion of the starting compound $[PtCl_4]^{2-}$. The crystallite size in the resulting platinum powder determined by the Fourier profile analysis of individual diffraction peaks (WINFIT 1.2.1 program)[15] is 80—130 Å.

According to elemental analysis data, three ammonia molecules and one chlorine atom are removed in this step. The IR spectrum demonstrated that the bending band of the NH_3 molecules coordinated to rhodium is shifted to longer wavelengths by ~25 cm^{-1}. This change is characteristic of the formation of rhodium complexes containing a smaller number of NH_3 ligands in the coordination sphere. In addition, a weak band at 1400 cm^{-1} appears in the IR spectrum, which is indicative of the formation of the NH_4^+ ion.

The next step of weight loss starts at 310 °C and is also accompanied by the endo effect. After 1 h, the weight loss

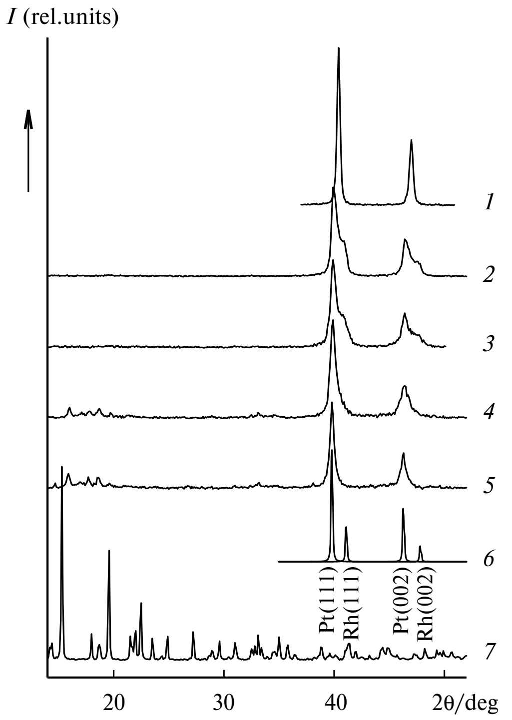

Fig. 1. Phase composition evolution during thermolysis of $[Rh(NH_3)_5Cl][PtCl_4]$ under helium at 750 (*1*), 350 (*2*), 320 (*3*), 310 (*4*), and 300 °C (*5*). X-ray diffraction patterns of a mixture of pure platinum and rhodium (*6*) and the starting complex (*7*) measured at room temperature.

in the sample is ~30%, which corresponds to the partial transformation in this step. The X-ray diffraction pattern of the intermediate product, like the above-described pattern, shows broadened asymmetric reflections of a face-centered cubic (fcc) phase (crystallite size is 60—80 Å) and the same unindexed reflections of residual compounds with much lower intensity. The refinement of the unit cell parameter of the fcc phase gave a = 3.915(3) Å, which differs from the lattice parameter of pure platinum (a_{Pt} = 3.9231 Å). This is indicative of the formation of a substitution solid solution. The composition of the solid solution determined according to Vegard's rule is $Pt_{0.95}Rh_{0.05}$. The fact that Vegard's rule is obeyed by this system was confirmed by experimental data[8,12] (Fig. 2).

A further increase in the temperature to 320 °C leads to a weight loss of ~44%. The X-ray diffraction pattern shows no reflections of residual compounds and an amorphous halo. The profiles of the reflections of the metal have a pronounced shoulder with half intensity on the side of large angles. The observed X-ray diffraction pattern is adequately described on the assumption that there are two fcc phases with the lattice parameters a_1 = 3.832(3) Å and a_2 = 3.914(3) Å (Fig. 3). These lattice parameters correspond to solid solutions of compositions $Pt_{0.25}Rh_{0.75}$ and $Pt_{0.90}Rh_{0.10}$, respectively.

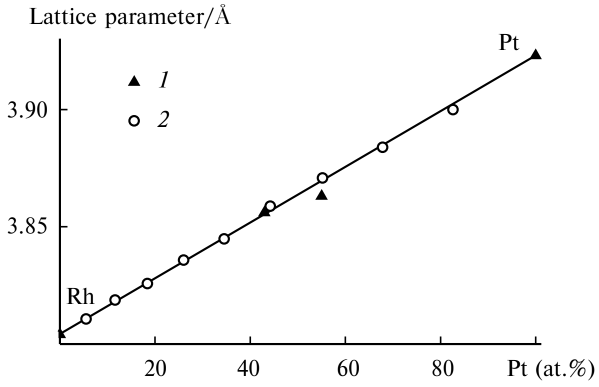

Fig. 2. Vegard's isotherm for the Pt—Rh system (experimental points): *1*, powder data from the PDF database;[12] *2*, results of the present study.[8]

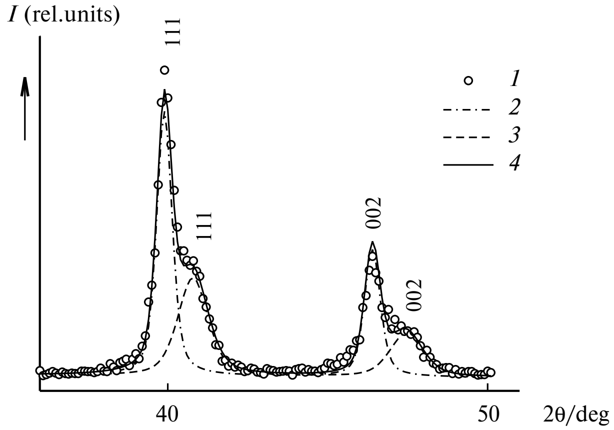

Fig. 3. Fragment of the experimental X-ray diffraction pattern of a metallic powder, which was prepared by thermolysis of $[Rh(NH_3)_5Cl][PtCl_4]$ in helium, at 20 °C: *1*, experimental points; *2*, the theoretical X-ray diffraction pattern of the solid solution $Pt_{0.90}Rh_{0.10}$, the crystallite size is 70—100 Å; *3*, the theoretical X-ray diffraction pattern of the solid solution $Pt_{0.25}Rh_{0.75}$, the crystallite size is 50—70 Å; *4*, the overall profile of two solid solutions (calculations).

The third step in the temperature range of 350—500 °C is characterized by very slow weight loss, which is not accompanied by noticeable thermal effects. During this step, the weight loss is ~4%, which corresponds to 19 amu. Thermolysis products isolated in this step contain metallic phases only. The Raman spectra of these samples show no vibrational bands corresponding to chemical bonds. The X-ray diffraction pattern of this sample is virtually identical to that of the product prepared at 320 °C. It should only be noted that the intensities of reflections corresponding to a rhodium-rich solid solution are somewhat higher.

According to the phase diagram, platinum and rhodium form a continuous series of solid solutions. Since the starting complex salt contains metals in a stoichiometric ratio, one would expect the formation of a homogeneous solid solution of composition $Pt_{0.50}Rh_{0.50}$. However, the phase composition of the powder remained virtually unchanged upon storage of the thermolysis product at 500 °C for 6 h. A rise of the temperature and annealing under helium at 750 °C for 1 h led to homogenization of the system. The lattice parameter of the fcc phase a = 3.868(2) Å is only slightly different from the parameter corresponding to a solid solution of composition 1 : 1 with $a_{1:1}$ = 3.864(2) Å in Vegard's isotherm (see Fig. 2). Upon homogenization, the particle size of the powder increased (crystallite size was 180—250 Å).

In the *in situ* study of the thermolysis process, X-ray diffraction patterns were recorded at 10 min intervals (exposure time was 1 min). In each case (decomposition of the complex in air, *in vacuo*, or under H_2), preliminary experiments were performed to more precisely determine the temperature range of transformations. Then a freshly prepared sample was placed in a high-temperature chamber and heated at a rate of 5 deg min^{-1}. In the vicinity of the temperature of the onset of decomposition of the complex, the rate of heating was decreased to 2 deg min^{-1}. After completion of the run and cooling of the sample to room temperature, X-ray diffraction patterns were recorded in a high-temperature chamber but without a shielding cover. Then, X-ray diffraction patterns were recorded on an X-ray diffractometer in a broad diffraction angle range for a more complete characterization of X-ray diffraction parameters of thermolysis products.

The results of experimental study of thermolysis of $[Rh(NH_3)_5Cl][PtCl_4]$ performed *in situ* under vacuum are presented in Fig. 4, *a*. The X-ray diffraction patterns show reflections of beryllium and beryllium oxide (BeO) and a weak reflection from a stainless steel cell. Thermolysis of the complex *in vacuo* is in many ways similar to the above-described process performed under He. Up to 235 °C, the structure of the starting complex remains unchanged. At 250 °C, the X-ray diffraction pattern already shows only broad and low-intensity reflections of platinum in the 2θ angle range of 25—55°, and the background level slightly increases at diffraction angles, whose positions coincide with those of the reflections of the solid solution $Pt_{0.50}Rh_{0.50}$. Further heating of the sample to 280 °C leads to complete decomposition of the anionic part of the complex and reduction of platinum, which is indicative of a substantial increase in the intensity of reflections of platinum. The crystallite size is 100—130 Å.

At 305 °C, reflections with increasing intensity appear on the side of the right shoulder of the platinum peaks. The composition of the resulting solid solution is difficult to precisely estimate because of the influence of thermal expansion on the unit cell parameters of the phases in the sample. Nevertheless, based on the positions of the peaks (111) and (002) of platinum and rhodium measured at room temperature, we can state with certainty that the Pt : Rh ratio is close to 1 : 1. A further rise of the temperature to 500 °C leads to destruction of the cationic coordination sphere and elimination of rhodium. However, rhodium is not isolated as an individual phase but reacts with platinum to form a solid solution of composition 1 : 1. The X-ray diffraction patterns show a successive increase in the intensity of reflections belonging to a solid solution phase and a decrease in the intensity of reflections of platinum. The process is completed at 550 °C to form a homogeneous finely dispersed phase. The lattice parameter of the resulting fcc phase measured at room temperature (a = 3.862(2) Å) is indicative of the formation of the solid solution $Pt_{0.50}Rh_{0.50}$ with the crystallite size of 150—250 Å.

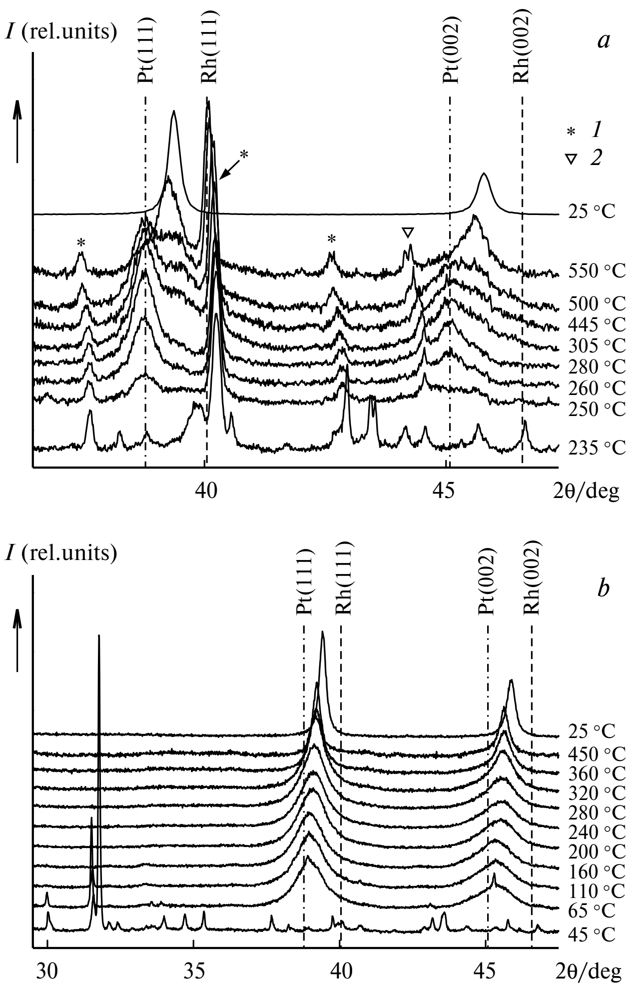

Fig. 4. Phase composition evolution during thermolysis of $[Rh(NH_3)_5Cl][PtCl_4]$ *in situ* under vacuum (*a*) and under hydrogen (*b*). The positions of reflections of platinum and rhodium at room temperature are indicated by dash-and-dot and dashed lines, respectively (synchrotron radiation wavelength λ = 1.504 Å): *1*, beryllium oxide (BeO); *2*, beryllium.

Reduction of $[Rh(NH_3)_5Cl][PtCl_4]$ under hydrogen starts and occurs at a substantially lower temperature. The X-ray diffraction patterns of intermediate steps of the process measured *in situ* are shown in Fig. 4, *b*. In this series, experiments were performed without the use of a beryllium foil, which made it possible to obtain the diffraction pattern free from redundant reflections. At 45 °C, the X-ray diffraction pattern contains only a set of reflections of the starting complex. However, the X-ray pattern measured at 65 °C shows already lines of the complex that remains undecomposed along with a set of broad reflections of a platinum-based fcc solid solution. Enlargement of the crystals of the starting compound resulted in a change in the relative intensities of the complex and the disappearance of some of them.

Under an atmosphere of H_2, as in the case of thermolysis under He, the anionic sphere starts to decompose earlier than the cationic moiety and platinum is the first to eliminate. However, the difference in reduction temperature of the metals in the anionic and cationic parts of the complex under hydrogen is substantially smaller and rhodium metal starts to form virtually immediately after elimination of platinum. The particle size of the solid solution formed at this temperature is 50—60 Å. Metal clusters of this size are virtually crystallite nuclei and have an excess free energy. Under these conditions, the rhodium atoms do not form an individual phase but are dissolved in the lattice of a platinum-based solid solution. During a further rise of the temperature, a gradual reduction of rhodium persists and solid solutions containing an increasingly higher percentage of this metal are formed. In the X-ray diffraction patterns, the positions of reflections of the fcc phase gradually shift to larger angles, whereas an increase in the lattice parameter with increasing temperature should lead to a slight shift of the peaks toward small angles. The process is completed in the temperature range of 320—360 °C as the composition of the solid solution reaches 1 : 1. A further increase in the temperature lead not only to an increase in the crystal lattice parameter of the solid solution but also to an increase in the crystallite size to 250—350 Å. The unit cell parameter of the resulting solid solution measured at room temperature (a = 3.864(1) Å) exactly corresponds to the composition $Pt_{0.50}Rh_{0.50}$ in Vegard's isotherm.

Therefore, study of thermolysis of the complex salt $[Rh(NH_3)_5Cl][PtCl_4]$ and the phase composition of the reduction products allow the conclusion that the formation of platinum—rhodium solid solutions and the formation of the final single-phase equiatomic solid solution occur through elimination of metal atoms. In spite of the fact that the platinum and rhodium ions in the starting precursor are "mixed" at atomic level, thermolysis does not lead to the formation of solid solution nuclei in the initial step of reduction of metals. The difference in thermal stability of the $[PtCl_4]^{2-}$ and $[Rh(NH_3)_5Cl]^{2+}$ complex ions plays the determining role in the mechanism of formation of thermolysis products, which is responsible for temperature-resolved reduction of each metal.

The formation of a solid solution under hydrogen differs from that under helium and *in vacuo*. In the presence of a reducing agent, the temperature of decomposition the coordination spheres and formation of metal atoms is substantially lower. On the one hand, this leads, to the formation of platinum metal species of substantially smaller size, which, consequently, have higher reactivity. On the other hand, rhodium atoms are also reduced at lower temperature and react with platinum before enlargement of species.

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