

**Synthesis of the nanocrystalline platinum during Mn(II)–Mn(III) oxidation at 200–300°C and
P = 1 kb**

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Synthesis of metallic platinum in the hydrothermal media was described. The process is connecting with the Pt solubility against a background of manganese oxides evolution and evidence of synergy character.

Key words: synthesis, platinum, manganese oxides, experiment

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In preceding studies of metallic platinum dissolution in chloride aqueous solutions (200, 300°C; $P_{\text{tot}} = 1$ kb) [Plyusnina, 2002], new formed platinum microcrystals were deposited on hausmannite crystals. At present we describe the Mn(II)–Mn(III) oxidation kinetics and conditions needed for nanodisperse platinum crystallization.

Platinum solubility under elevated *PT*-parameters depends considerably from a redox potential [Gammons, 1995]. In this connection, for correct results, we are support the redox potential by means of solid phase mix assemblage compositions. Oxides of manganese variable valency have been used to reach the widest variation range of the redox potential in studied system. In runs carried out at 200–500°C, the following mixtures were used: MnO–Mn₃O₄, Mn₃O₄–Mn₂O₃, and Mn₂O₃–MnO₂ [Plyusnina et al., 2011]. Noteworthy, metallic platinum was crystallized in run products at 200–300°C only, when solid mixture contained MnO - unstable under 400°C [Hem, Lind, 1983].

The study was performed by ampoule method in the Ni-Ti alloy autoclaves. During dissolution the inner surface of sealed platinum ampoules (9 x 80 x 0.2 mm) served as the Pt source. Bidistilled water and 1m NaCl and 0.1m HCl solutions were placed into ampoules (according to P-V-T ratios for water at T of interest, and $P_{\text{tot}} = 1$ kb). At 200 and 300°C f_{O_2} was supported by the MnO–Mn₃O₄ mixture (200 mg).

The solid phase of run products was diagnosed by powder X-ray diffraction and its chemical compositions were determined by EVO-50 XVP scanning electron microscope analysis equipped with INCA 350 system of energy dispersive X-ray spectrometer. Pt concentration in quenched solutions was analyzed by a Shimadzu AA-6800 atomic spectrometer with 0.002 ppm sensitivity.

The runs products (200 and 300°C), which contained up to 5 wt % Pt_{met}, were studied by an electron microscope. Micrographs of disperse metallic platinum fix its crystallization in aggregates (3–5 μm cross sections) of complex geometric shapes. The aggregates were found on facets of idiomorphic hausmannite crystals and consisted of discrete isometric Pt_{met} grains (60–500 nm) with a complex “verrucous” surface (Fig. 1a). The energy dispersive spectrum of platinum microaggregates comprises peaks of C, O, Pt, and Mn (Fig. 1b). The carbon peak is due to a conductive carbon film sputtered to release charges in recording insulators. The oxygen and manganese peaks are associated with characteristic X-rays excited by the matrix manganese oxides.

As a result of Mn²⁺ instability, the oxidation of initial MnO to Mn₃O₄ was observed at 200 and 300°C, and takes place via spontaneous crystallization of metastable intermediates (Mn hydroxides) according to the Ostwald’s steps rule. The intermediate phase was feitknechtite (β-MnOOH). And its formation can be described by the protonation reaction: $2\text{Mn}^{2+} + 0.5\text{O}_2 + 3\text{H}_2\text{O} = 2\text{MnOOH} + 4\text{H}^+$ [Murray et al., 1995]. Feitknechtite was identified by the reflections (*d/n*): 4.63, 2.66, 2.37, and 1.99 Å (ASTM 18-804). In the 1 m NaCl and 0.1 m HCl solutions, kempite Mn₂(OH)₃Cl, pyrochroite Mn(OH)₂ along with MnOOH crystallized as intermediates identified by *d/n*: 5.75, 5.40, 4.31, 2.98, 2.91, 2.83, 2.39, 2.33, 2.17, 1.92, 1.78 Å (ASTM 25-1158) and 4.61, 2.48, 2.39, 1.82 Å (ASTM 18-787), the first and second respectively. These phases formation in aqueous chloride solutions may be

described by: $3\text{MnOOH} + 0.5\text{H}_2\text{O} + \text{HCl} = \text{Mn}(\text{OH})_2 + \text{Mn}_2(\text{OH})_3\text{Cl} + 0.75\text{O}_2$. This reaction is accompanied by oxygen discharge; as a result, $\text{Mn}(\text{OH})_2$ oxidizes to MnOOH via: $\text{Mn}(\text{OH})_2 + 0.25\text{O}_2 = \text{MnOOH} + 0.5\text{H}_2\text{O}$. Depending on the run duration, $\beta\text{-MnOOH}$ appeared in products periodically, together with $\text{Mn}_2(\text{OH})_3\text{Cl}$ and $\text{Mn}(\text{OH})_2$. Such periodicity of intermediate metastable phase's crystallization is synchronized with oscillations of the redox potential, water activity, pH values and ultimately leads to an increase in platinum solubility. In result the metallic platinum crystals ($d/n = 2.265, 1.96, 1.387, 1.183, 1.133 \text{ \AA}$) precipitate from solutions.

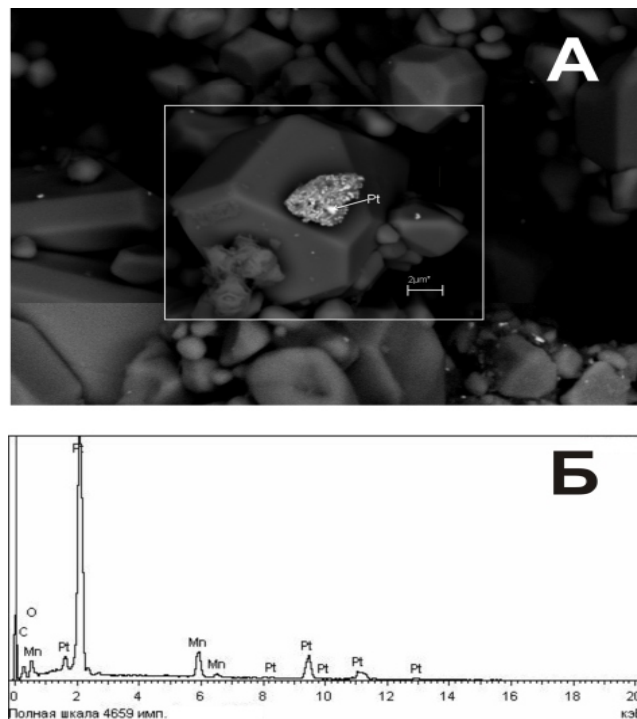


Fig. 1. Aggregates of ultrafine Pt_{met} grains on the hausmannite crystals (A), and energy-dispersive spectrum of one grain (B)

A direct correlation between the Pt solubility, intermediates behavior and metallic platinum crystallization is found. In the aqueous solution Pt_{aq} content varies ($-72 < \log \text{mPt} < -03$) depending on run duration (Figs. 2, 3).

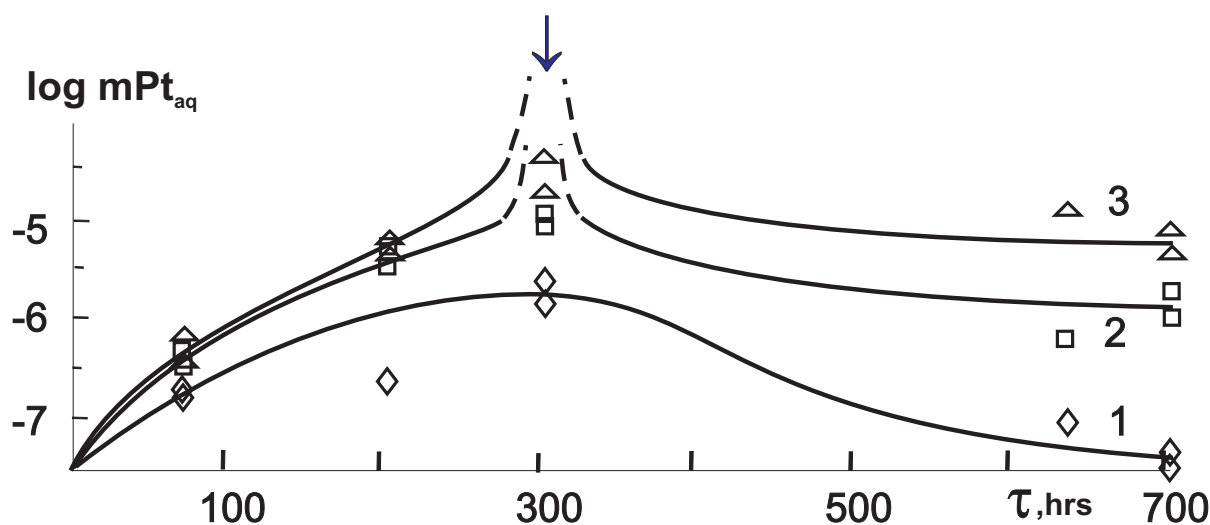


Fig. 2. Pt dissolution rate curves at 200°C ($\text{MnO-Mn}_3\text{O}_4$). 1 – in water, 2 – 1m NaCl, 3 – 1m HCl.

Along with the maximal Pt_{met} content the greatest MnOOH yield (up to 10% of solids) was observed and maximal intensity of the X-ray diffraction reflections of crystalline platinum. In the 0.1 mHCl solution $\log \text{mPt}_{\text{aq}}$ varies from -5.54 to -3.81. In the case, $\text{Mn}_2(\text{OH})_3\text{Cl}$ dominates, while

MnOOH amounts are under 5%. The most quantity of metallic platinum is observed in the chloride medium ($\log mPt_{\text{aq}} = -3.81$) along with increased content of kempite in the solid. Auto-oscillation wave processes are particularly intrinsic to chemical systems far from chemical equilibrium and are accompanied by periodic precipitation of reaction products [Bystray, Pivovarov, 1989]. The absence of manganese hydroxides in the long-term run products proves its intermediate character and nonequilibrium formation. In comparing platinum dissolution rate curves (Fig. 2, 3), we find that peak Pt concentrations in solutions coincides with period of intermediate phases crystallization. As the intermediates convert to stable hausmannite, the Pt content of solutions drops. At 400°C, MnO is stabilized and the MnO–Mn₃O₄ buffer mix is stable in the course of runs. In the case, there are no extremes on the Pt dissolution kinetic curves and the equilibrium Pt_{aq} content was established in the first four days (Fig. 4).

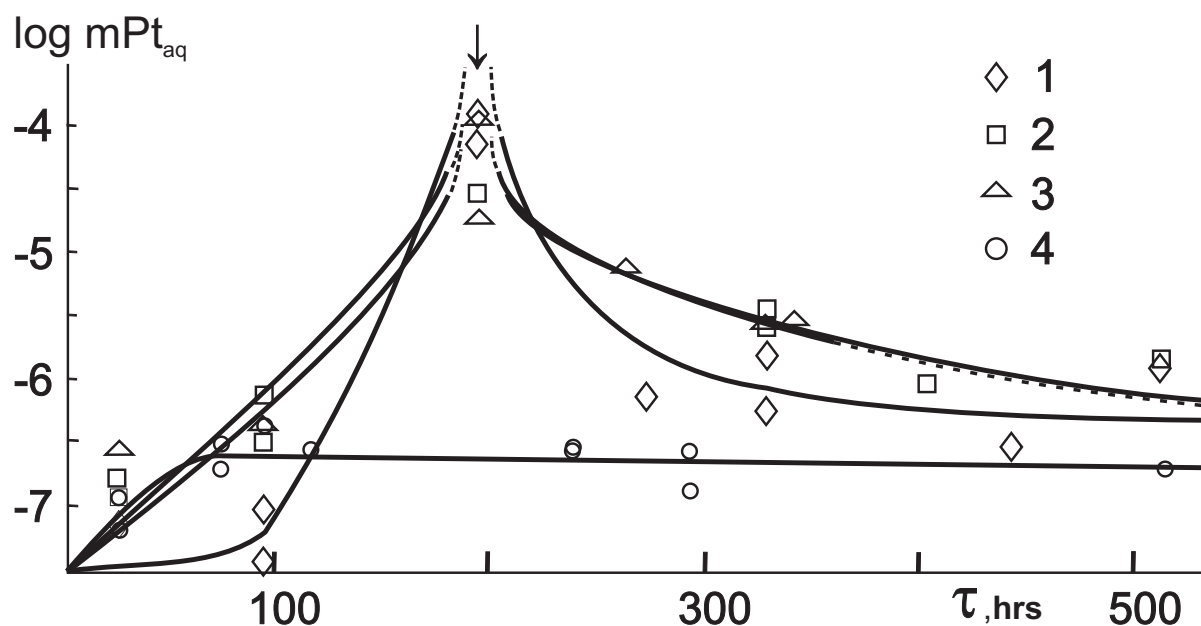


Fig. 3. Pt dissolution rate curves at 300°C (MnO–Mn₃O₄).
1 – in water, 2 – 1m NaCl, 3 – 1m HCl (), and 4 water buffered by Fe₂O₃–Fe₃O₄.

The relationship between crystallization of metastable Mn hydroxides and the Pt_{aq} concentration in solutions coexisting with these hydroxides is confirmed by run results at 300°C with Fe₃O₄–Fe₂O₃ buffer. Since these Fe oxides are stable at the temperature, new solid phases in products are lacking and an extreme is absent on the Pt dissolution kinetic curves (Fig. 3). X-ray for the products obtained at the 200°C in the presence of the MnO–Mn₃O₄ mixture reflects next order of changing mineral assemblages in dependence of run duration (days): MnO + Mn₃O₄ (start) → MnOOH + Mn₃O₄ + Pt (9th) → Mn(OH)₂ + Mn₃O₄ + Pt (15th) → Mn₂(OH)₃Cl + MnOOH + Mn₃O₄ + Pt (30th) → Mn₃O₄ (60th). At 300°C the change in mineral assemblages finished in platinum ampoules in 15 days.

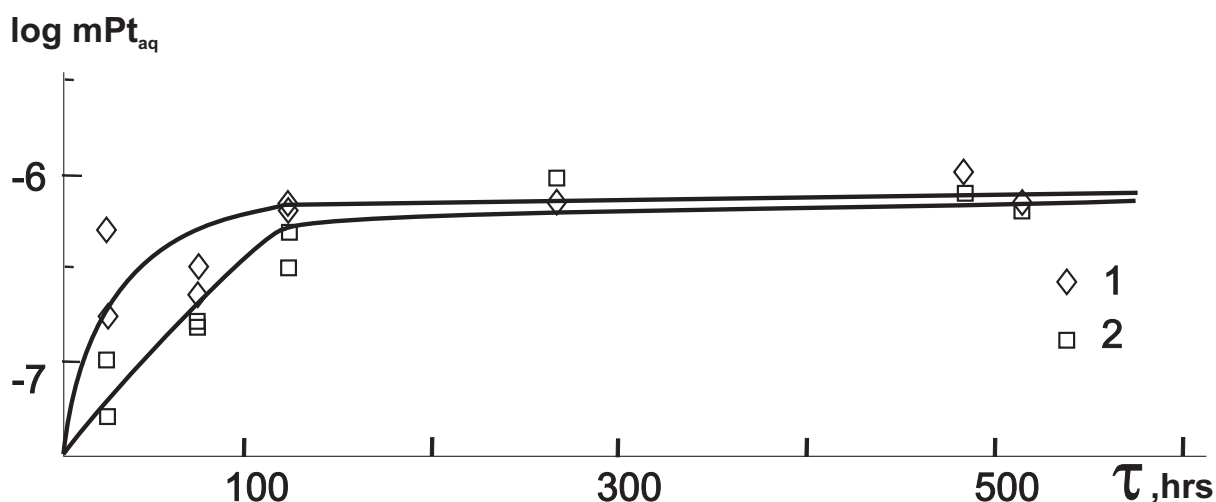


Fig. 4. Pt dissolution rate curves at 400°C, in the presence MnO–Mn₃O₄ (1), and Fe₂O₃–Fe₃O₄ (2)

The catalytic effect of Pt on Mn oxidation may be described by reactions involving dissolved Pt(OH)₂ and releasing free oxygen, which enhances Mn²⁺ oxidation: MnO + Pt(OH)₂ = MnOOH + Pt_s + 0.5H₂O + 0.25O₂; 3MnOOH + Pt(OH)₂ = Mn₃O₄ + Pt_s + 1.75O₂ + 2.5H₂O. The activation of oxidation processes, in turn, gives rise to anomalies in Pt solubility kinetics.

Noteworthy, a similar process of Pt adsorption onto Mn oxides occurs in natural settings, too. In Pacific substrates, for examples, ferromanganese nodules and crusts with elevated Pt concentration are widely spread. The described relationship between solid phase compositions and the Pt solubility in the Mn–H₂O–Cl system is confirmed by an elevated Pt/Mn ratio in sea water, which exceeds the respective value in the oceanic crust more than 300 times [Jacinto, Berg, 1989].

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References

- Bystray, G. P., et al. (2002). Disequilibrium systems (Izd-vo Ural'sk Univ., Sverdlovsk), 186 p. (in Russian).
- Gammons, C. H. (1995). Experimental investigation of the hydrothermal geochemistry of platinum and palladium, *Geochim. Cosmochim. Acta*, v. 59, p. 1665–1668.
- Hem, J. D., et al. (1983). Nonequilibrium models for predicting forms of precipitated manganese oxides, *Geochim. Cosmochim. Acta*, v. 47, p. 2037–2046.
- Jacinto, C. S., et al. (1989). Different behavior of platinum in the Indian and Pacific oceans, *Nature*, v. 338, p. 332–334.
- Plyusnina, L. P. (2002). Effect of phase transitions in the Mn–O₂–H₂O system on platinum and gold solubility at 200–400°C and 1 kb, *Geochimiya*, v. 80, No 1, p. 80–86 (in Russian).
- Plyusnina, L. P., et al. (2011). Mn(II)–Mn(III) oxidation kinetics and its effect on crystallization of Nanodisperse platinum at 200–300°C and 1 kbar, *Russian Journ. Inorganic Chem.*, v. 56, N 9, p. 1358–1362.