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PALLADIUM DEPOSITION ON MAGNESIUM IN PdCl₂ SOLUTIONS IN DMF

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Received: April 15, 2013 / Revised: April 25, 2013 / Accepted: October 30, 2013

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Abstract. Palladium deposition on rotational magnesium disk and magnesium powder *via* cementation has been investigated in 0.01 M PdCl₂ solutions in dimethylformamide. The reduction process started from 323–333 K without the induction period. Spheroidal micro-particles of palladium and its agglomerates were found to be formed on the magnesium disk surface. Particles in the form of needles and plates by the width of 80–120 nm were formed on the surface of magnesium powder. The deposited particles are characterized by high adhesion to the substrate surface.

Keywords: cementation, palladium, magnesium, dimethylformamide.

1. Introduction

The possibility of magnesium usage as an effective material for hydrogen storage in the form of MgH₂ and other hydrides on its basis were investigated for last two decades [1-7]. However, the hydrining-dehydrining rates may be too low for the practical use. The catalysts, namely *d*-metals – nickel [2-4], iron [3-5], cobalt [3] and palladium [6, 7] considerably accelerate the process of hydrining-dehydrining. At the same time the last works [7, 8] point the especial efficiency of nanostructured catalysts and composites. To ensure the uniform distribution of the catalyst over the magnesium surface (in volume) the Mg-Me systems are prepared using ball-milling in the absence of oxygen and moisture [4, 5, 8].

It is shown in [9, 10] that all metals which are active catalysts of the equilibrium process $Mg + H_2 \leftrightarrow MgH_2$ are easily deposited on the magnesium surface. Taking into account the considerable negative

magnesium standard potential ($E_{Mg^{2+}/Mg}^0 = -2.36$ V) the high values of cementation current are observed over microcathodes. This fact favors the high-dispersed deposits of metals, including nanostructured ones over the magnesium surface. However aqueous solutions and contact with air cannot be used for preparing Mg-Me system because it is the reason of the end-products pollution by oxides. The possibility of silver films contact deposition on the magnesium surface in the aprotic solvent – dimethylformamide (DMF) – is shown in [11].

The aim of the present work is to investigate the palladium deposition on the magnesium surface from the non-aqueous medium.

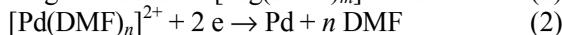
2. Experimental

Palladium was deposited on the surface of magnesium powder and magnesium disk in 0.01 M PdCl₂ in DMF solution at 323–333 K. The disk working part (the end with the diameter of 30 mm) was smoothed by the fine-grain emery and chemically polished in the acetate acid 5 % solution in glycerin. Then it was washed by distilled water, isopropanol and dried at 333 K. The magnesium powder (particles average sizes are 0.42x0.15x0.04 mm) was treated with 1 % isopropanol solution of the acetate acid, washed by isopropanol and dimethylformamide and put into the working solution. Palladium cementation was carried out in the thermostated glass vessel with the solution volume of 50 cm³ under hydrodynamic regime: using a rotational cylinder (1000 rpm) – according to the procedure described in [12] and the magnesium powder (stirrer rate of 500 rpm) – according to [13]. After the process the samples were washed in the organic solvent, isopropanol and dried at 333 K.

The morphology of palladium deposits on the magnesium disk surface and particles of magnesium powder was investigated using Zeiss EVO 40XVP scanning microscope. The images were obtained by the balance record of secondary electrons (BSE) using scanning by the cathode ray of 15 kV. During the investigations of kinetic regularities of palladium deposition from dimethylformamide solution the samples were withdrawn periodically and analyzed for the content of reduced metal using the atomic-absorption spectroscopy (atomic-absorption spectrophotometer AAS-IN in the air-propane-butane flame). The wave length was 340.5 nm.

3. Results and Discussion

The palladium reduction by magnesium is not observed at 293–303 K in 0.01 M PdCl₂ in DMF solution, though the difference between standard electrode potentials is great ($E_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.363$ V and $E_{\text{Pd}^{2+}/\text{Pd}}^0 = 0.915$ V). If compared with water, DMF is characterized by higher electro-donor properties (18 and 26). Therefore in DMF solutions the relatively stable surface complexes are formed on the magnesium surface due to the donor-acceptor bonding *via* O-donor atom of aprotic solvent molecule $\text{Mg} \leftarrow \text{:OCHN}(\text{CH}_3)_2$. This complicates the formation of microanodic and microcathodic zones in accordance with the reactions (1) and (2). The considerable cathodic polarization of palladium in DMF solutions retards the process (2). The same phenomenon is not observed for silver [14].



The increase of temperature weakens the factor of surface complexes and at 323–333 K the deposition takes place *via* the reaction (2) without the induction period (Fig. 1). The increase of temperature also favors the depolarization of palladium reduction on microcathodes. Thus, microanodic and microcathodic zones are formed already at the first seconds.

The same regularity in palladium deposition on the magnesium surface is observed in the solutions with conductive additives. The curve of palladium concentration change during its reduction on the magnesium disk in the solution of 0.01M PdCl₂ + 0.05M Bu₄NClO₄ in DMF is identical to that represented in Fig. 1. The deposit morphology is also almost the same. It means that palladium may be deposited on the magnesium surface only in the simple salt (PdCl₂) solution.

Microcathodes which are identical to the palladium nucleus are the particles with size of 90–300 nm and their agglomerates are uniformly distributed over the magnesium surface (Fig. 2a). At the same time the areas consisted of conglomerates of reduced metal micron particles (Fig. 2b) are formed. Obviously it is caused by the nonuniformity of the magnesium surface, in particular by the boundaries between crystallites, the same as during silver cementation [15].

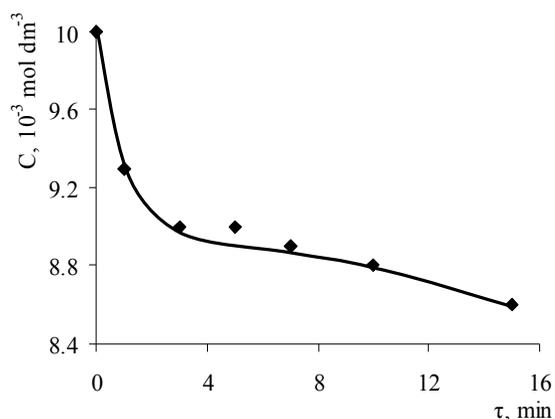


Fig. 1. Change of palladium ions concentration during cementation on the magnesium disk in dimethylformamide solution of PdCl₂; initial concentration is 0.01 mol·dm⁻³; temperature is 333 K

While palladium reduction 3D growth of the deposit in the form of agglomerates made of spheroid particles is observed (Fig. 3). With time the size of structural particles increases and the form remains constant. It indicates that the nuclei growth prevails over the nucleation process. Spheroid configuration of the particles is caused by the adsorption of high-donor molecules of the organic aprotic solvent on particles of palladium, the same as palladium deposit formation during electrolysis in DMF solutions [16]. The important factor is surface blocking due to the DMF molecules release owing to the microcathodic reaction (2).

On the surface of magnesium powder particles the palladium deposit is in the form of needles (Figs. 4a and b) and plates (Figs. 4c and d). The deposit densely covers the surface with good adhesion. Their thickness is within 80–120 nm so the deposit may be attributed as the nanoscale ones.

Such morphology of the palladium deposit is caused by the peculiarities of the magnesium powder topography compared with that of the magnesium disk. Thus, the particles of the magnesium powder are characterized by corrugation (Fig. 5a) which is preserved even after palladium deposition (Fig. 5b). Thereafter, the surface is electrochemically nonuniformed that eases microanodes and microcathodes forming in DMF solution of PdCl₂. Moreover, under hydrodynamic regime of cementation the turbulent movement of the solution is provided around microelectrodes, favorable for ions diffusion to the latter ones and high values of current density for microcathodes. The results are the weakening of donor-acceptor bond $\text{Pd} \leftarrow \text{:OCHN}(\text{CH}_3)_2$ and destruction of surface complexes analogously to palladium deposit formation during electrolysis [16]. Under the mentioned conditions and low concentrations of reduced metal ions the high-dispersed deposit is formed from the particles of metals in the form of needles and plates [9].

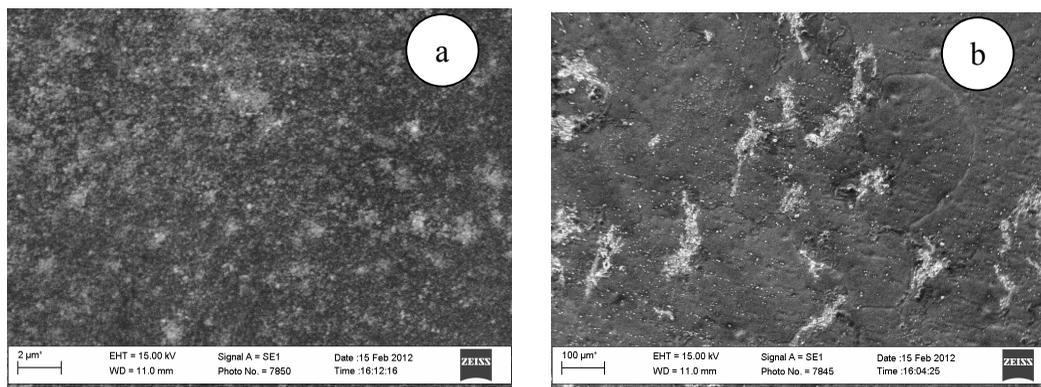


Fig. 2. SEM images of the magnesium disk surface after palladium deposition from 0.01 PdCl₂ in DMF at 333 K during 1 min

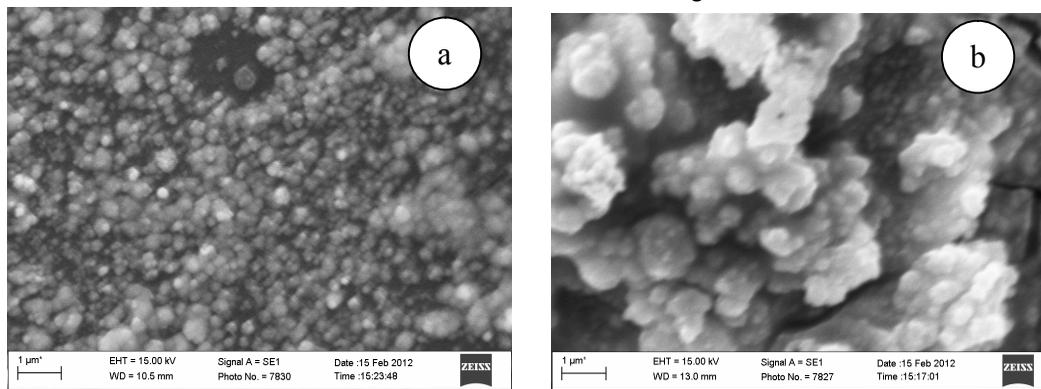


Fig. 3. SEM images of palladium agglomerates formed on the magnesium disk surface after deposition from 0.01 PdCl₂ in DMF at 333 K during 5 (a) and 10 (b) min

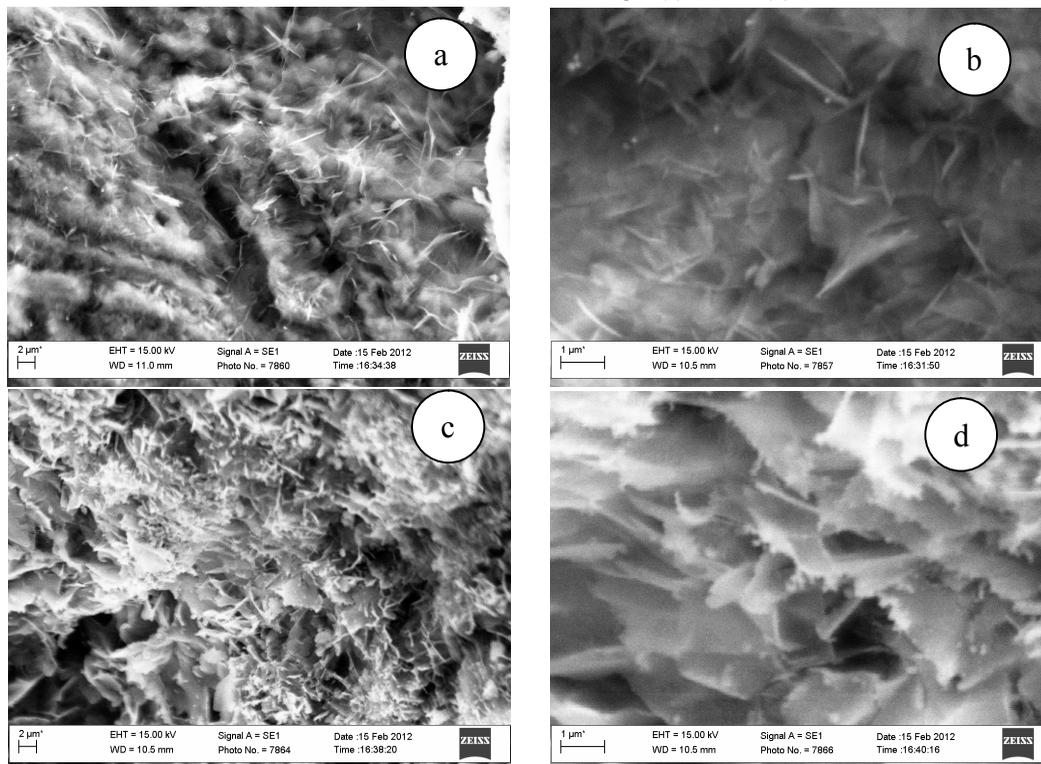


Fig. 4. SEM images of palladium deposited on the magnesium powder surface from 0.01 PdCl₂ in DMF during 5 min at 323 (a, b) and 333 (c, d) K

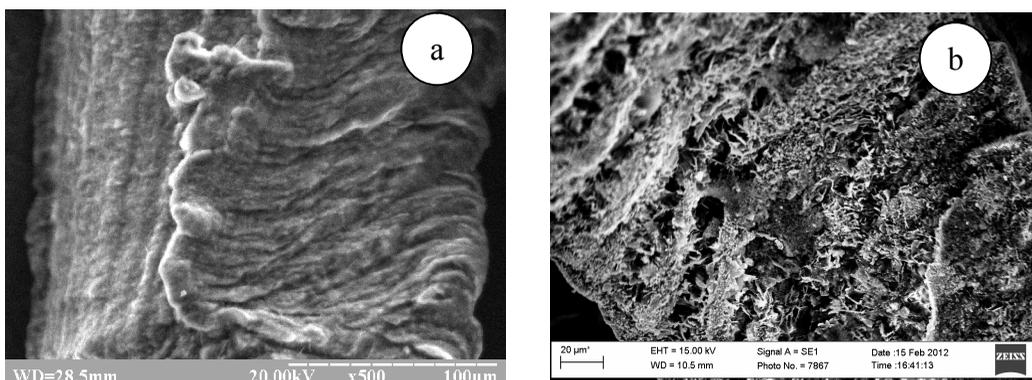


Fig. 5. SEM images of the surface of initial magnesium powder (a) and after palladium deposition (b) in 0.01 PdCl₂ in DMF

4. Conclusions

Micro- and nanosized particles of palladium and their agglomerates are uniformly deposited on the magnesium surface from dimethylformamide solutions of PdCl₂. They are characterized by high adhesion to the substrate. The process takes place at 323–333 K caused by the desorption of organic aprotic solvent molecules from the metal surface and surface complexes destruction. The palladium particles geometry is spheroid for the smooth surface of the magnesium disk. The particles in the form of needles and plates are typical on the corrugated surface of the magnesium powder as a result of electrochemical nonuniformity of the substrate and differences in hydrodynamic regime during deposit formation.

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ОСАДЖЕННЯ ПАЛАДІЮ НА МАГНІЙ У РОЗЧИНАХ PdCl₂ В DMF

Анотація. Досліджено осадження паладію на поверхні обертового магнієвого диску та магнієвого порошку цементацією у 0.01 M PdCl₂ в диметилформаміді. Показано, що процес відновлення кількісно починається за 323–333 K без індукційного періоду. На поверхні магнієвого диску формуються сфероподібні мікрочастинки паладію та їх агломерати, на поверхні магнієвого порошку – частинки у формі шпів на пластівців товщиною 80–120 нм. Осаджені частинки паладію характеризуються значною адгезією до поверхні підкладки.

Ключові слова: цементація, паладій, магній, диметилформамід.