

# Nanostructural C-Pd coatings obtained in 2-steps PVD/CVD technological process

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Received 17.09.2009; published in revised form 01.12.2009

## Materials

### ABSTRACT

**Purpose:** The paper presents scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigation results of nanoporous coatings based on palladium and carbon, obtained in two steps process – first step – physical vacuum deposition (PVD) and second step chemical vacuum deposition (CVD).

**Design/methodology/approach:** Studies of topographical and structural properties of coatings obtained in the first and the second step of technological process.

**Findings:** Pd content included in the volume of a coating obtained in PVD process affects on a distribution and sizes of Pd nanocrystals. The diameter of Pd nanocrystals obtained for coatings with lower Pd content is lower than for coating with higher Pd content. Modification of these coatings in CVD process at temperature of 650°C leads to obtain a different form of the final coating: for coating with lower content of Pd, the CVD process causes formation of nanoporous C-Pd coating; for coating with higher Pd content, formation of bigger Pd crystals is found. Temperature higher than 650°C leads to coatings growth with non-porous structure.

**Practical implications:** Obtained coatings can be used as active layer in hydrogen and hydrogen compounds sensors or in hydrogen storage applications.

**Originality/value:** Two steps method of presented coatings obtaining was originally elaborated by our group in Tele- & Radio-Research Institute.

**Keywords:** Coating deposition; Structure and morphology; Electron microscopy; Nanoporous materials

#### Reference to this paper should be given in the following way:

M. Kozłowski, E. Czerwosz, P. Dłużewski, E. Kowalska, J. Radomska, H. Wronka, Nanostructural C-Pd coatings obtained in 2-steps PVD/CVD technological process, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 304-308.

## 1. Introduction

Nanoporous materials possess highly-developed surface and high pore volume. A highly-developed surface of nanoporous carbon coating promotes efficient adsorption process that allows

their use in various types of detectors [1-4]. Sensitivity of such detector depends on efficiency, reversibility and speed of desorption process. These phenomena of adsorption/desorption are connected with composition and structure of an active coating used in a detector. In case of nanoporous coatings based on palladium and carbonaceous nanostructures high efficiency of

adsorption/desorption processes and reactivity of palladium toward hydrogen allow for applications of such coatings in hydrogen detectors [5].

Such coatings based on palladium and carbon could be constructed in many ways, for example as Palladium Sub-Nanoparticle Decorated Bamboo Multi-Walled Carbon Nanotubes, Ultrafine Palladium Particles upon a Glassy Carbon, Palladium Nanoparticle-Loaded Carbon Nanofiber or Palladium Dispersed in Porous Carbon. Topography and morphology of such materials are studied by SEM and TEM.

In our paper we present results of investigation of two types of nanoporous carbon-palladium (C-Pd) coatings originally elaborated in Tele- & Radio Research Institute [6].

## 2. Experiments

C-Pd nanocrystalline coatings were obtained in a two-steps process. The first step was PVD process and the second - CVD process. The concentration of Pd in the studied coatings was 8 wt % and 26 wt %. In the PVD-step a thick coating composed of palladium nanocrystals embedded in carbonaceous matrix was obtained. The deposition process was performed from two separate sources: one containing fullerenes  $C_{60}$  powder and second containing palladium acetate  $Pd(C_2H_3O_2)_2$ . The temperature of the substrates during the growth processes was  $\sim 100^\circ C$  and growing time was 8 min.

The polycrystalline carbonaceous nano-Pd coating from PVD process was used as the catalyst support in the second step in which the pyrolysis of xylene ( $C_8H_{10}$ ) as a carbon source proceeded. The temperatures of pyrolysis process were 550, 650, 700 and  $750^\circ C$ . Xylene flow and duration time for CVD process were the same for all applied temperatures. As result of catalytic decomposition of xylene and carbonic vapour condensation on the substrate (CVD process) the polycrystalline coatings were obtained.

For our studies, we chose two types of coatings – one containing 8 wt% of Pd and second – containing 26 wt% of Pd. The studied samples description is shown in Tab.1.

Table 1.  
Description used for studied samples

Pd content [wt. %]	Sample obtained in technological step	
	PVD	PVD/CVD
8	PVD1	CVD1
26	PVD2	CVD2

Flame Atomic Absorption Spectrometry was applied for determining Pd content in coating.

The structure, topography and composition of obtained coatings were studied by SEM and TEM. SEM investigations were performed with FEG SEM (LEO 1530, and JEOL-JSM 7600F). TEM investigations were performed with the JEOL 2000EX electron transmission microscope operating at 200 keV incident beam energy. The electron diffraction from selected area (EDSA) method was also applied.

## 3. Results and discussion

SEM images of PVD1 and PVD2 COATINGS are shown in Fig. 1. The sizes of observed grains for these coatings are different. The size of grains for PVD2 coatings is smaller than the size observed for grains for PVD1 coatings.

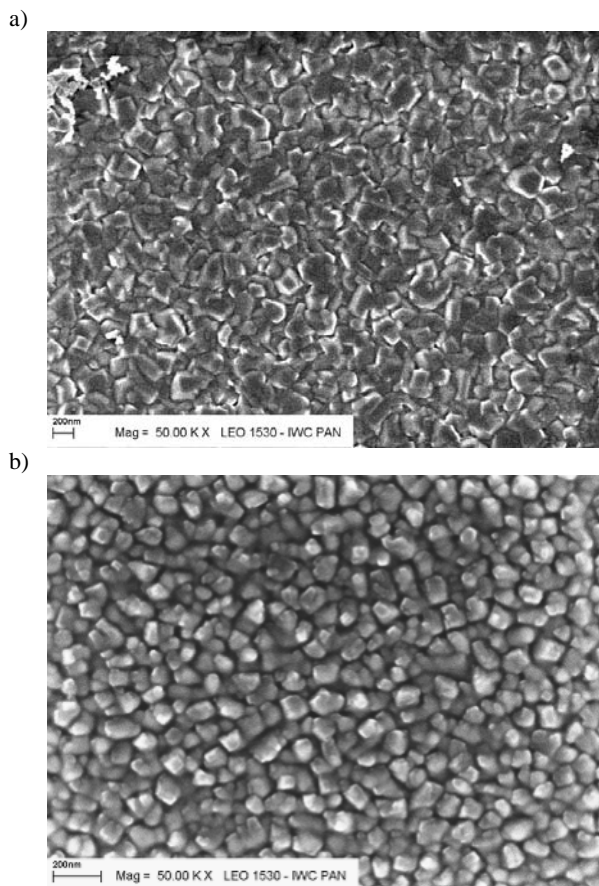


Fig. 1. Typical SEM image of Pd-C coating after PVD process for a) PVD1, b) PVD2 samples

Topographies of CVD1 and CVD2 coatings are shown in Fig. 2. For CVD1 higher porosity of carbonaceous matrix was found than for CVD2 coating, and the size of palladium nanocrystals found for CVD1 coating is higher than for CVD2 coating. In Fig. 2b image for CVD2 is shown. In the inset in Fig. 2b a nanoobject having a bright core and darker shell is presented.

In Fig. 3. SEM images show the coating surface observed in two different modes: Fig.3a - Secondary Electron Image (SEI) and Fig. 3b - Backscattered Electron Image (BEI). Typically, SEI mode informs about surface topography, when BEI informs about differences in chemical composition of various areas of the sample.

Fig. 3a (SEI image) shows objects of bigger sizes than the sizes of respective Pd nanocrystals seen in BEI image (Fig. 3b). BEI mode is sensitive to atomic number, and then clearly separates details of structure that has different atomic number. Pd nanocrystals have larger atomic number than carbon and are

visible as bright objects on the dark carbon background. If the shell was composed of structures containing Pd and C, then (this shell) it could be visible as grey object surrounding the Pd core. In BEI mode we can see Pd nanocrystals without carbon shell. For CVD2 coatings the shell of observed nanoobjects is much darker and then we suppose that it is composed only of carbon. Such interpretation allows us to determine the size of Pd nanocrystals (Fig. 3c). The histogram showing size distribution is shown in Fig. 3d and we can also determine the most numerous diameter as ~16.4 nm.

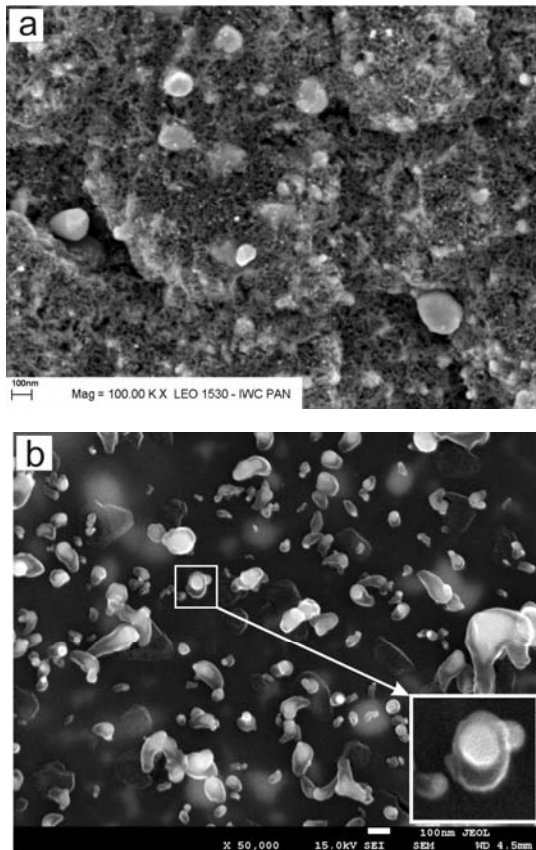


Fig. 2. SEM images for CVD1 (a) and CVD2 (b) samples

In Fig.4 TEM images and electron diffraction pattern for CVD1 coating are presented. For CVD1 coating the diameter of Pd nanocrystals is between 10-50 nm. The Pd nanocrystals are rarely dispersed in carbon matrix. Palladium core of nanoobjects is enveloped in carbon shells (Figs. 4c, d). Palladium core has *fcc* type of structure. In diffraction patterns (Fig. 4b) we observe rings originating from *fcc* Pd and graphite. The strongest ring originates from 00.2 planes of graphite.

Fig. 5 shows TEM images and electron diffraction pattern for CVD2 coating. The number of found Pd nanocrystals for CVD2 coatings is higher than for CVD1 COATING. The size distribution for these nanocrystals is wide (diameter from 10 to 100 nm). Palladium core in observed nanocrystals is enveloped in carbon shells (Fig. 6c). Palladium core has *fcc* type of structure. In TEM images (Figs. 4c, d and Figs. 5c, d) forming a multi-shell structure graphite planes are shown.

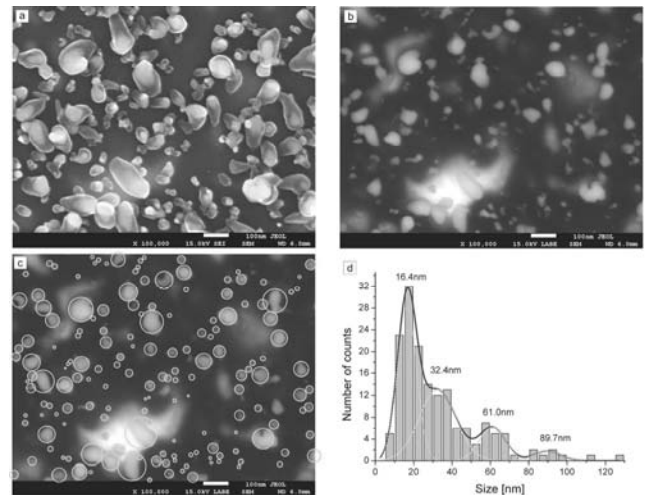


Fig. 3. SEM images of CVD2 sample: a) SEI mode; b) BEI mode, c) size analysis - circles circumscribed on nanocrystals represents its diameter, d) histogram of nanocrystals size distribution

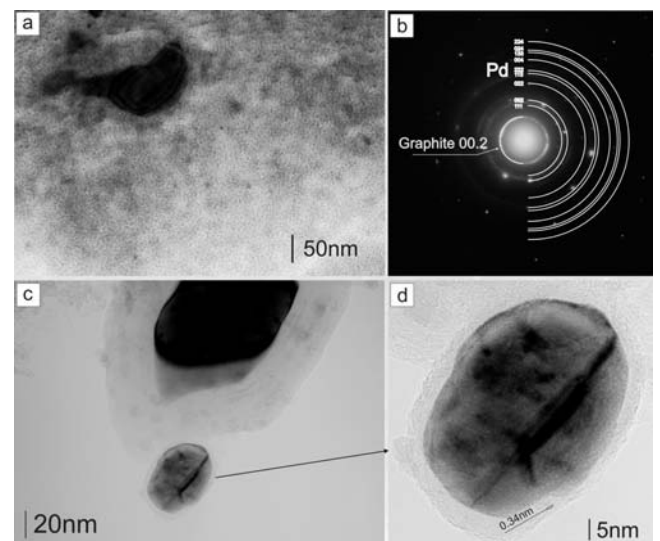


Fig. 4. TEM investigations of CVD1 sample, a) coatings structure, b) diffraction pattern c, d) Pd nanocrystals with visible graphite multi-shell

The shell protects Pd core from the influence of various chemical agents (e.g. oxygen). Graphite grains may be formed in a C-Pd coating because of conversion of residue  $C_{60}$  under the influence of temperature in the CVD process, as well as a result of decomposition of xylene.

Fig. 6, 7 presents SEM images of CVD1 coatings modified in CVD process at different temperatures (550, 650, 700 and 750°C).

SEM study of CVD1 coating modified at different temperatures shows that the optimal temperature for obtaining the coating of nanoporous structures with a highly developed specific surface area is 650°C.



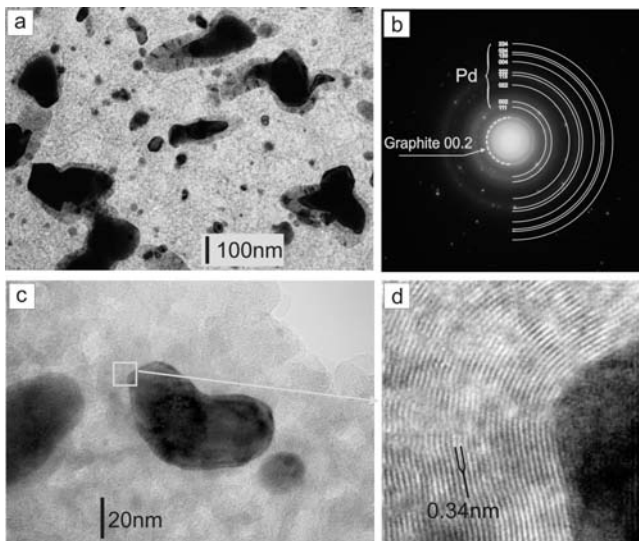


Fig. 5. TEM investigations of CVD2 sample, a) coatings structure, b) diffraction pattern, c, d) Pd nanocrystals with visible graphite multi-shell

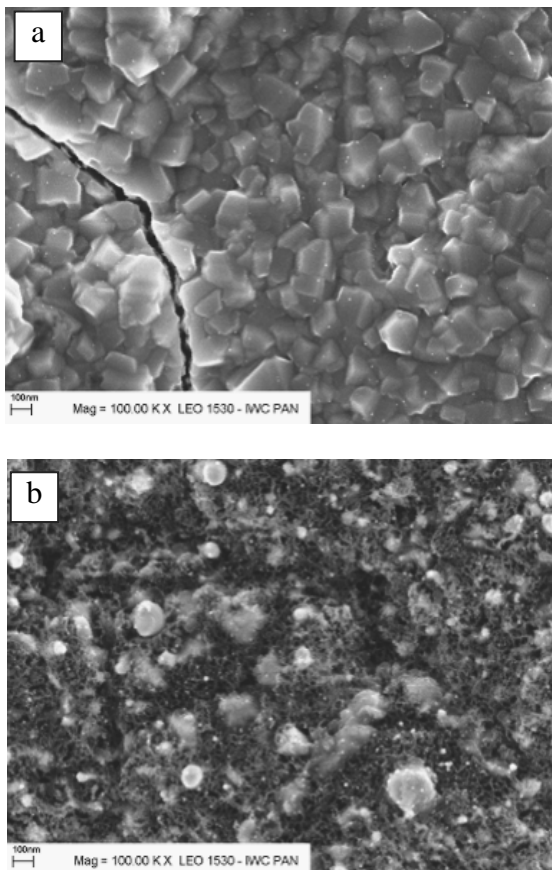


Fig. 6. SEM images of CVD1 coatings modified at different temperatures a) 550°C, b) 650°C

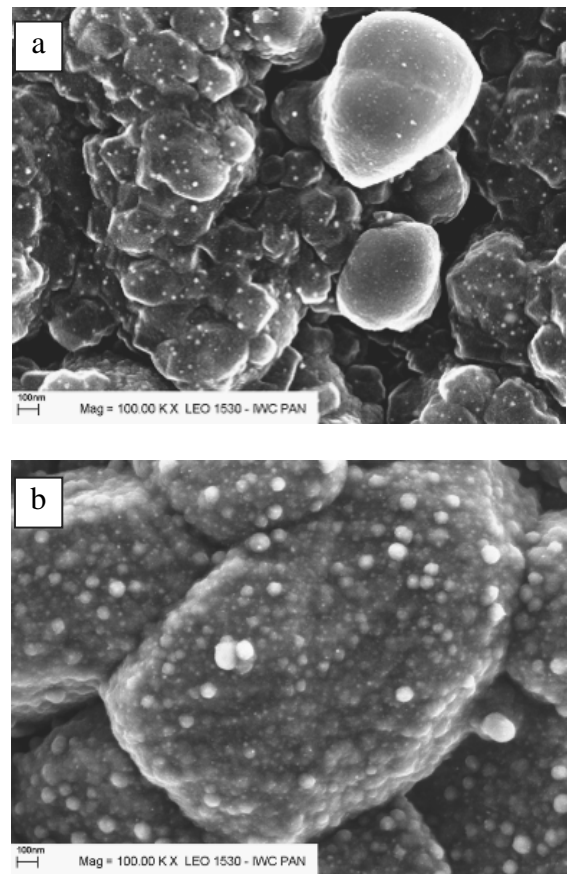


Fig. 7. SEM images of CVD1 coatings modified at different temperatures a) 550°C, b) 650°C, c) 700°C, d) 750°C

Formation of the carbon nanoporous coating containing Pd nanograins was observed at this temperature. This porous carbonaceous skeleton exhibits large specific surface area with open cell structures and it seems to be very promising material for hydrogen detection.

Temperature of 550°C is too low for synthesis of porous material. In this temperature PVD1 coating is only cracked (Fig. 6a) and grains characteristic for PVD coatings are still observed. This temperature is probably too low to cause catalytic reaction activating formation of porous carbonaceous structure and enveloped with graphite planes Pd nanocrystals.

The modification at temperatures of 700°C and 750°C seems to be too high for forming nanoporous structures (Figs. 7a, b) but is high enough to lead to a formation of bigger C-Pd crystalline forms. The final structure of these C-Pd objects is still under studies. In temperature range 700-750 °C boundaries between the clusters of grains are still visible.

## 4. Conclusions

Coatings obtained in PVD process exhibit various size distributions of Pd nanocrystals depending on Pd content in the

coating. The diameter of Pd nanocrystals obtained for coatings with lower Pd content is between 10-50nm while for coating with higher Pd content it is between 10 -100nm. Modification of these coatings in CVD process at temperature of 650°C leads to obtain a different form of the final coating. We found that for coating with 8 wt % of Pd the CVD process causes formation of nanoporous C-Pd coating. Temperature changes of CVD process lead to growth of coatings with non-porous structure.

## Acknowledgements

This research was co-financed by the European Regional Development Fund within the Innovative Economy Operational Program 2007-2013 (No UDA-POIG.01.03.01-14-071/08-00).

Researches being a basis of this publication were financed from financial resources of the West Pomeranian Province budget.



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