PtNiPd thin films obtained by Thermionic Vacuum Arc Method: synthesis and characterization

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PtNiPd thin films on glass substrates were obtained by Thermionic Vacuum Arc (TVA) method. The nanostructured PtNiPd films were characterized by Transmission Electron Microscopy (TEM), electron diffraction, High Resolution Transmission Electron Microscopy (HRTEM), Energy Dispersive X-Ray Spectroscopy (EDXS), tribological analysis and electrical measurements.

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1. Introduction

Lately Platinum Group Metal alloy catalysts are intensively studied for use as cathode materials for reduction of oxygen in polymer electrolyte fuel cells [1].

Thus, the ternary series PtCoZr nanostructured thin films prepared by co – sputtering technique [2] are of major relevance. As novelty, our paper presents the synthesis and charcterization of thin films of ternary PtNiPd series obtained by Thermionic Vacuum Arc (TVA) method in a three guns configuration.

One of the main advantages of this technology is the bombardment of the growing thin film just by the ions of the depositing material. Moreover, the energy of ions can be controlled. Thermo-electrons emitted by an externally heated cathode and focused by a Wehnelt focusing cylinder are accelerated towards the anode whose material is evaporated and bright plasma is ignited by a high voltage DC supply [3,4].

2. Films deposition. Methods of investigation

The PtNiPd thin films on glass substrate have been obtained by Thermionic Vacuum Arc method; the deposition consisted of two stages: the platinum - nickel deposition followed by the palladium deposition. The goal was to create a 20nm thick layer of PtNi on the glass substrate and then bombard it with Pd nanoparticles.

1. *The platinum - nickel deposition*. The filament current intensity had a value of *55.6A* for Pt and *34.6A* in the case of Ni evaporation during the *19min* and *40sec* deposition time. Internal pressure was $1.5\bullet10^{-5}$*torr* and the enclosure temperature *91.3°C*. The PtNi matrix thickness is approximately *20nm*.

2. *The palladium deposition*. Filament current intensity had a value of *45A* during the *224sec* deposition time. The formation of *5nm* diameter Pd nanoparticles that nucleate in the PtNi matrix was intended.

From the samples obtained by this procedure one random sample was chosen to undergo TEM, electron diffraction, HRTEM, EDXS, tribological and electrical analysis for morphology, crystalline structure, chemical composition and physical properties.

TEM and electron diffraction were performed using the Philips CM120ST microscope with MegaView III CSD camera. The TECNAI 30F G² S TWIN microscope was used for HRTEM and EDXS analysis. The sample was prepared using the scratch method for the TEM and electron diffraction investigation on the surface of the film while HRTEM and EDXS required the Ion Beam Thinning method to analyze the depth of the thin film.

For tribological characteristics determination, systematic measurements were performed using a ball-on-disc tribometer made by CSM Switzerland, with normal forces of 0.25N and 0.50N respectively. The stainless steel ball with a diameter of 6 mm had a linear speed of 2cm/s on the dry sliding distance of 50 m.

Ohmic contacts were attached to the sample for use in the electrical measurements. The electrical contact was guaranteed by a product consisting of 80% silver-filled two-component epoxy-based glue (0.0025 Ω/cm specific resistance) [5].

3. Results and interpretation

TEM investigations reveal that the investigated film has uniform morphology and polycrystalline structure. Fig.1 shows the electron diffraction image for the sample prepared by scratch method. The first ring corresponds to nickel oxide, the second to Pt or Pd while the third and fourth show Ni.

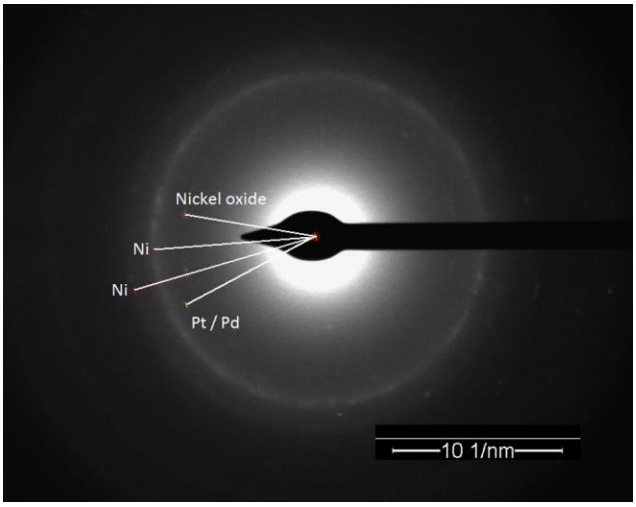

Fig. 1. Electron diffraction reveals the presence of Ni and Pt or Pd (100 kV accelerating voltage).

To perform EDXS and HRTEM investigations, the sample was prepared using the Ion Beam Thinning method consisting of a mecanical stage followed by an ion thinning stage.

The final appearance of the specimen due to the ion bombardment at a voltage drop of 3 – 5kV is presented in Fig. 2.

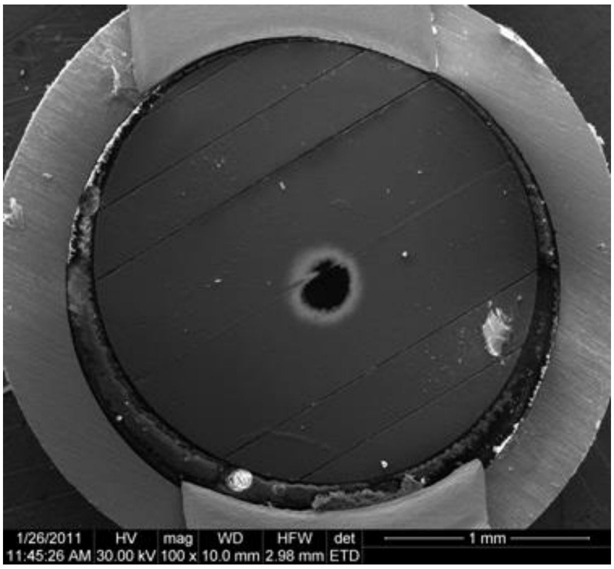

Fig. 2. Final aspect of the specimen

Small portions of the sample are suspended in epoxy resin as you can see in Fig.3; here the region where EDXS and HRTEM are made is indicated.

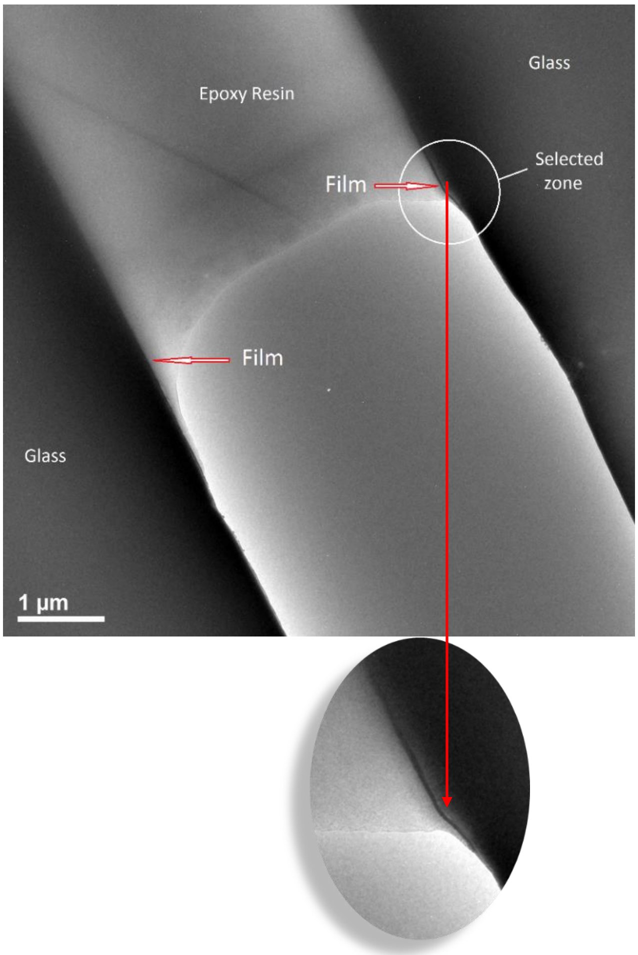

Fig. 3. The selected zone shows the thin film. This is the region where EDXS and HRTEM analyses are made.

A cross section in the sample chosen for the study is presented in Fig. 4. We can see a columnar growth of the 19nm PtNiPd thin film. The three regions for the EDXS investigation are marked.

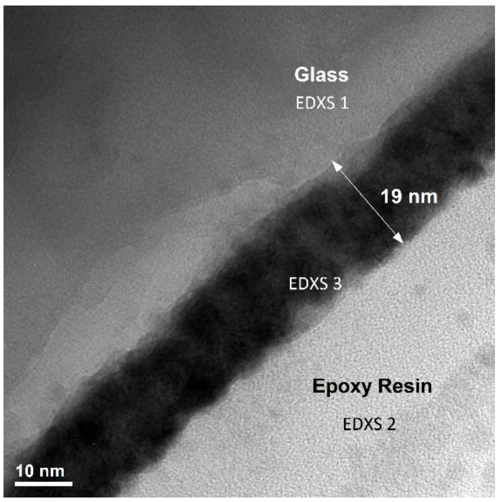

Fig. 4. The regions for the EDXS investigation on the studied PtNiPd sample

In Fig. 5 the Energy Dispersive X-Ray Spectroscopy graph for the selected region of glass, EDXS 1, is shown. The presence of O and Si is confirmed.

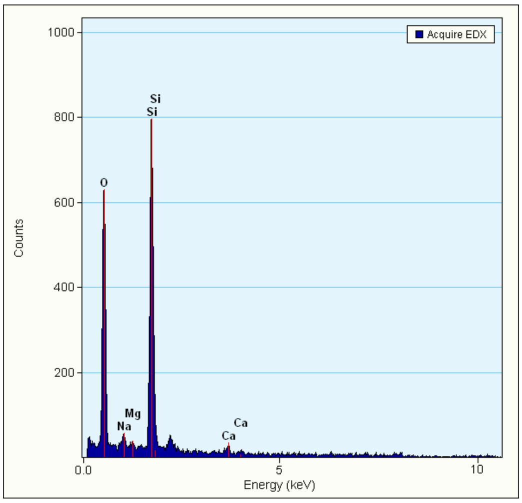

Fig. 5. EDXS graph for the glass region in Fig.4

Fig. 6 presents the analysis of the film region.

Ni is present at approximately 1.0 keV and 7.5 keV energies while Pt is found at 2.3 – 2.5 keV and around 8keV energy respectively.

The presence of Pd is confirmed at 3keV and again at 21keV.

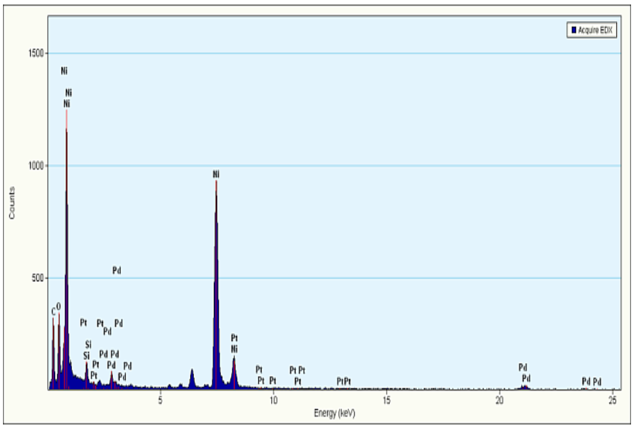

Fig. 6. EDXS graph for the film region in Fig.4

An up-close investigation of the film is illustrated in Fig. 7.

The presence of Ni is identified by the 2.07Å spacing between HRTEM bright interference fringes. Pd is located by the 2.22 Å interplanar spacing between two parallel planes. These values are compared to the ICDD database [6,7].

Most important is the inclusion or „nucleation" of approximately 5nm diameter spherical Pd nanoparticles in the PtNi matrix.

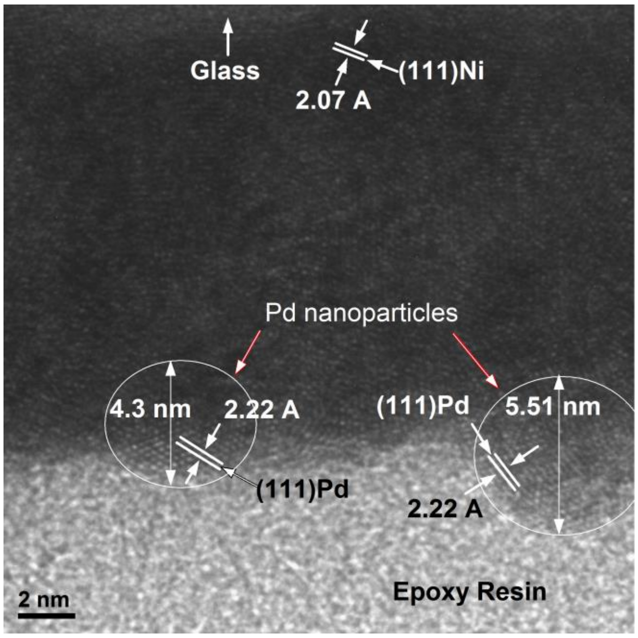

Fig. 7. HRTEM image of the thin film region

Another important aspect is the growth of Ni crystallites or grains during the TVA deposition in the matrix (Fig. 8).

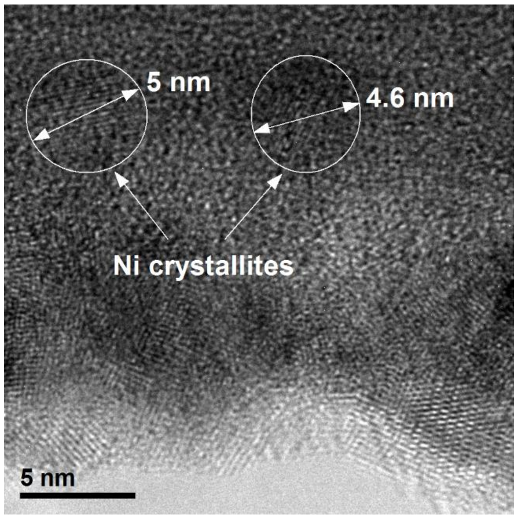

Fig. 8. HRTEM reveals the size of Ni grains to be 4 – 5nm

For tribological results interpretation an *accommodation regime* of 10m, until the stainless steel ball makes contact with the maximum surface possible, must be considered.

Correlated with the SEM image, in Fig. 9 it can be seen that for the normal force of 0.25N and the normal force of 0.5N respectively, for a sliding distance of 50m, the deposited layer is not removed by the ball and the glass substrate is not visible.

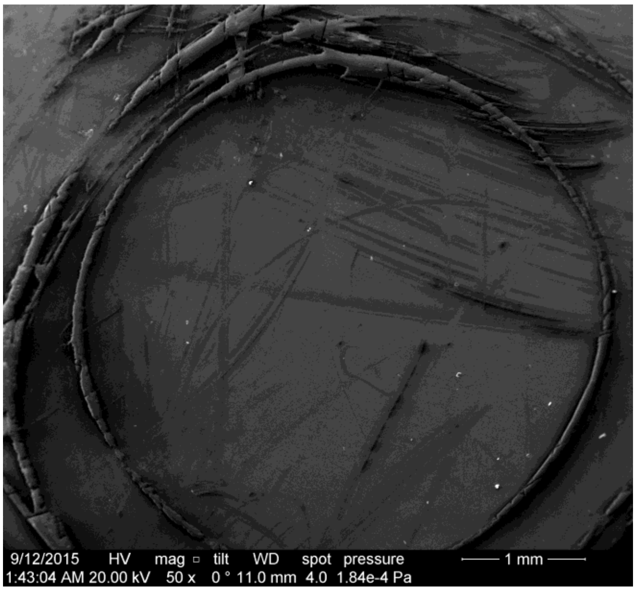

Fig. 9. The surface of the tribologically examinated PtNiPd film (50x magnification)

A decrease of the coefficient of friction with the increase of the normal force can be observed (Fig. 10). The values of the coefficient of friction (approximately 0.45 for 0.25N normal force and about 0.35 for 0.5N normal force) are within the limits of the specific values of metallic films [8].

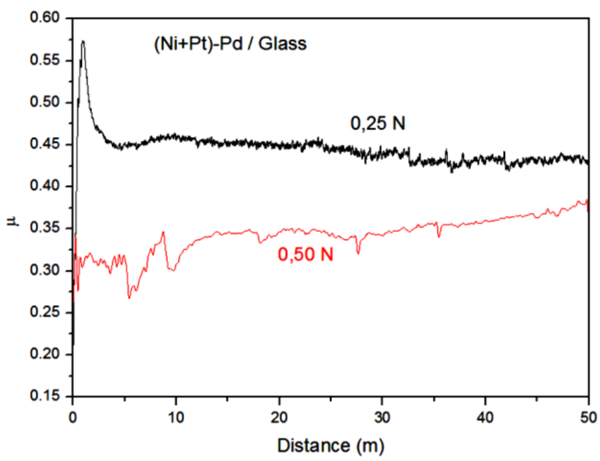

Fig. 10. The coefficient of friction μ as a function of distance and normal force

Electrical measurements investigate the conductivity of the sample. The resistance was measured by comparing the voltage drop on the sample to the voltage drop on a standard series resistance in constant current mode [4,5,9].

The conductivity was calculated using the formula:

$$\sigma = \frac{l}{R_x \cdot D \cdot d}$$

where ***l*** is the distance between contacts, $\boldsymbol{R_x}$ is the measured resistance, ***D*** is the diameter of the contacts attached to the sample while ***d*** is the 20nm thickness of the PtNi matrix.

Fig. 11 presents the average conductivity vs. temperature graph.

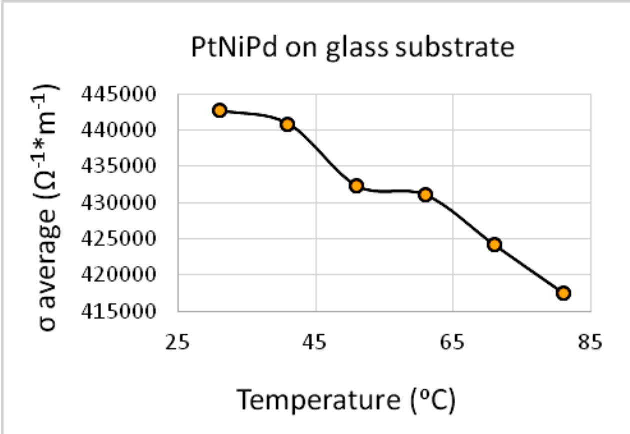

Fig. 11. Sample average conductivity vs. temperature graph

The electrical analysis illustrates the conductor behavior of the thin film, the average conductivity decreasing with temperature.

4. Conclusions

Nanostructured PtNiPd thin films on glass substrates were obtained by Thermionic Vacuum Arc method.

The electron diffraction image reveals the presence of Ni, Pt and Pd. The presence of these elements can be corroborated with the EDXS graph of the film which proves that Pd has diffused in the PtNi layer.

The HRTEM analysis revealed the nucleation of spherical Pd nanoparticles approximately 5nm in diameter in the PtNi matrix as intended. The size of the Ni crystallites or grains in the thin film is 4 – 5nm.

Tribological tests demonstrate the smooth and homogenous character of the film and a low value of the coefficient of friction. The deposited layer is not removed for either normal force thus the film has a very low mechanical attrition rate.

The thin film has a conductor behavior as shown by the electrical measurements.

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