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FEM modelling of nanoindentation experiment for nanostructural Me – carbon film (Me = Pd, Ni)

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ABSTRACT

This work presents a comparison of numerical simulation and experimental data for nanoindentation studies of nanostructural Me-carbonaceous films (where Me = Pd or Ni). Films containing palladium or nickel nanograins embedded in a carbonaceous matrix were synthesized by a PVD process. The topography of films was characterized by AFM and the mechanical properties were analyzed by nanoindentation. Nanoindentation experiments were performed with a tip made of diamond with a shape of a 90° cube corner three-sided pyramid in a Hysitron Triboscope. The finite element method (FEM) was used to simulate the indentation experiment in such heterogeneous material on nanoscale.

Keywords: nanoindentation, nano-crystals, Ni, Pd, Carbon, AFM, Hardness, FEM

1. INTRODUCTION

Nanostructural films are new materials with unique characteristics and structure other properties than conventional materials. Such films containing Ni or Pd nanocrystals exhibit many interesting properties such as: cold emission, self organization in electric field, in some condition catalytic properties. These types of films can be applied as active material for gas sensor and in nanoelectromechanical systems (NEMS) [1,2]. They are also of great significance in many areas including chemical catalysis, optical detection, and magnetic separation [3].

Their nanomechanical properties (nanohardness, reduce modulus) are studied with nanoindentation method. Nanoindentation is a new technique designed to measure the mechanical properties of materials on the nanoscale. [4].

In this paper we present results of AFM and nanoindentation measurements for nanostructural Me-carbon film (Me = Pd or Ni). The topography and nanomechanical properties of the these films were studied. Comparison of experimental data and Finite Element Method (FEM) was presented and quantitative accordance of these results was found. FEM was used for modeling structure and numerical simulation for nanoindentation studies of nanostructural Pd-carbonaceous films.

2. EXPERIMENTAL

In our experiment nanostructural Me-carbon film (Me = Pd or Ni) films composed of nano-size nickel or palladium grains embedded in a carbonaceous matrix were synthesized by a PVD process. This process were performed from two separated sources; one containing C₆₀ fullerenes and other containing Ni acetate or Pd acetate. Films were deposited on glassy substrates and their thickness was of about 300nm. Depending on the process parameters (temperature of substrates, temperature of sources, source-substrate distance, the rate of growth of nanostructures) the film composed of a matrix of carbon and metal grains of different sizes [5, 6]. Samples studied here are described in Tab.1.

Tab. 1 Characteristics of the samples

Sample No.	Me content in [wt %]	Me nanograins sizes [nm] ¹	Oxidized
5Ni	2,6	1,5-2	YES
8Ni	2,7	4	NO
Pd	23,6	4,5	NO

¹ Nanograins size was obtained from TEM image analysis [5, 6]

The first sample set 5Ni was obtained using untreated fullerenes and the second set 8Ni was produced with a pre-treatment of the fullerene raw material. For the 8Ni sample set, the C60 powder was heated up to a temperature of 200°C in the dynamic vacuum (10^{-5} mbar) for 2h before the depositions process to remove solvent residuals and to purify the material.

The morphology of the nano-composite films was characterized by atomic force microscopy (AFM). AFM experiments were performed with a Nanoscope IV multimode. A standard Si_3N_4 tip was used to image the surface in contact mode. The grain size investigation was performed by the section analysis tool.

Nanoindentation experiments were performed with a tip made of diamond with a shape of 90° cube corner (three-sided pyramid). A Hysitron Triboscope attached to a scanning force microscope the Nanoscope IV was used for the investigations. If nanoindentation is combined with surface imaging nanomechanical properties can be locally determined.

The nanohardness is defined by load over the projected contact area and reduce modulus of elastic by functions of stiffness at the initial point of the unloading curve in Oliver&Pharr's model [7, 8]. The maximum indentation depth is denoted by $h_{\max}$ and includes elastic and plastic deformation. The depth at which the applied forces becomes zero on unloading is called h_f . The depth h_c is the penetration depth at which the cross section area A_c is taken to calculate hardness and Young's modulus. The nanohardness of the sample (HN) is determined using the formula:

$$HN = \frac{F_{\max}}{A_c(h_c)}, \quad (1)$$

where $F_{\max}$ is the maximum applied load and A_c is the cross-sectional area corresponding to the depth h_c (see Fig. 2). The determination of the contact depth h_c is given by

$$h_c = h_{\max} - 0.75 \frac{F_{\max}}{S}, \quad (2)$$

where S is the contact stiffness

$$S = \frac{dF}{dh}, \quad (3)$$

with dF/dh being the slope of the unloading curve at the initial point of unloading. The reduced Young's modulus E_r is a measure of the elastic properties of the tip-sample system and can be calculated from the load-depth curves according to the formula

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_c(h_c)}} \frac{dF}{dh} \quad (4)$$

For elastically deformable indenters, the reduced modulus E_r can be generalised and is defined as

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_t^2}{E_t} \quad (5)$$

where

- E_s and ν_s stand for Young's modulus and Poisson ratio of the sample,

- E_t and ν_t stand for Young's modulus and Poisson ratio of the indenter tip.

Since E_t is much higher than E_s the value of E_r will hardly differ from E_s for soft materials.

3. RESULTS AND DISCUSSION

AFM image with grain size analysis for nanostructural Ni-carbonaceous films nanograins presented in Fig 1. Surface between nanocrystals was very flat. Size of separate nanograins with spherical shape (droplets like) were between 100-200 nm and their height was 8-12 nm. Root mean square of roughness RMS (Rq) was less than 0.5 nm.

Fig. 1 AFM image with grain size analysis for nanostructural Ni-carbonaceous films nanograins

Different surface was observed for the samples with Pd nanocrystals. AFM image of C- Pd films shown in Fig. 2 presents two level structure – big grains build from smaller grains. The diameters of big grains were between 300-400 nm and height was between 25-35 nm. While for small grains diameters were between 120-150 nm and height between 10-15 nm. Root mean square of roughness RMS (Rq) was 7.6 nm.

Fig. 2 AFM image with grain size analysis for nanostructural Pd-carbonaceous films nanograins

The mechanical properties (nanohardness and reduce modulus of elastic) were analyzed by nanoindentation. Load-displacement curves were obtained as a result of the nanoindentation experiment. A nanoindentation analysis results for two Ni-carbonaceous films nanograins samples 5Ni and 8Ni are presented in Fig.3.

Fig. 3 Load–displacement curves for nanoindentation into Ni carbonaceous films a) samples 5Ni, b) samples 8Ni

The load–displacement curves for samples with Ni nanocrystals show large pop-ins. A pop-in marks the sudden transition between elastic and plastic deformation during nanoindentation. The data for nanohardness and reduced modulus obtained from nanoindentation measurements are presented in tab.2.

Tab.2 Nanohardness and reduced modulus for Ni –carbon films

	Nanohardness [GPa]	Reduced modulus [GPa]
5Ni	NH = 2 NH _{max} = 3.4	E _r = 60 E _{r(max)} = 90
8Ni	NH = 1.5 NH _{max} = 2.4	E _r = 65 E _{r(max)} = 72

The maximum nanohardness is slightly larger for 5Ni films with 3.4 GPa in comparison to 8Ni films with a maximum hardness of 2.4 GPa. There is a hardness variation between 3.4 and 1.7 GPa for the sample 5Ni and 2.4 and 1.1 GPa for the sample 8Ni. In general the hardness is larger for the 5Ni sample. The reduced modulus for both Ni carbonaceous films shows similar features as the hardness variation [9].

Depth dependent indentation reduce modulus of elastic and nanohardness for sample 5Ni and 8Ni shown fig. 4.

Fig. 4 Depth dependent indentation a) reduced modulus, b) hardness for sample 5Ni (blue symbol) and 8Ni (pink symbol).

The load–displacement curves for Pd sample show plastic deformation. Pd-carbon films of nano-size palladium grains embedded in a carbonaceous matrix have an elastic indentation modulus 12 GPa and a hardness 0,24 GPa. (Fig. 5)

Fig. 5 a) Load–displacement curve for nanoindentation , carbonaceous film with Pd. b) Depth dependent indentation reduce modulus and c) hardness for sample.

4. FEM ANALYSIS

Nanoindentation experiments were performed with a tip made of diamond with a shape of 90° cube corner (three-sided pyramid). In practice, such indenter is not perfectly sharp but has a tip radius in the order of 100nm. Tip rounding becomes important when one wishes to perform indentations on thin films more than about 500nm thickness and when the maximum depth of penetration is on the order of 50nm. A real indenter can therefore be modeled as a spherical shaped indenter [8]. Model of spherical shaped tip in the simulated indentation process of the C60 film is shown in Fig. 6.

An indentation model was developed using ANSYS FEA software. This software allows calculating stress state in a material due to spherical tip of indenter. The diamond tip was modeled as a sphere. Fig. 6 shows introduction tip in layer and surface deformation as a result of penetration spherical tip.

Fig 6 a) Model of spherical shaped tip in the simulated indentation process of the C60 film. b) Deformation of the C60 film obtained in the numerical indentation experiment

Film was model as a volume with introduced into it several spherical objects that represents nanograins. Ratio of nanograin size and tip diameter determined a scale of problem. In our case chosen ration is connected to calculations performed in nanoscale. The influence of number and distribution of nanocrystals embedded in a carbonaceous matrix on the indentation experiment was analyzed.

3D problem was simplified as an equivalent to a planar model. The planar model makes shorter the analysis time. The diamond tip, that Young's modulus is $E = 1140\text{Gpa}$ and Poisson ratio is $\nu = 0.07$ was estimated as a circle.

Tip and specimen were meshed by PLANE82 - quadrilateral 8-node elements. Interaction of indenter tip and material was considered as a contact pair, for which target element (TARGE169) is applied to the tip and contact element (CONTA175) is applied to the specimen.

Fig. 7 Changes in numerical nanoindentation experiment versus to film morphology. Deformation of (a) C₆₀ film (b) carbonaceous-palladium film with 4 Pd-nanocrystals (c) carbonaceous-palladium film with many Pd-nanocrystal.

Fig. 7 presents very regular and symmetrical deformation of the C₆₀ film after unloading. Deformation for a carbonaceous-palladium film is different. This figure shows an example of an analyzed nanostructure and its subsequent deformation calculation. It seen that nanocrystals move in the carbonaceous matrix toward the film's surface and create

bigger piling-up on a surface in the contact area of penetration. Deformation inside the film's layer depends on the distribution of grains in the layer (compare Fig. 7b and Fig.7c).

Fig. 8 shows influence of the number and distribution on nanocrystals in film volume on Von Mises mechanical stress distribution and value of nanograins displacement. Nanocrystals were moving in the matrix without much stress. Stress occurs between the tip and the nanograins in the vicinity of the contact.

Fig. 8 Von Mises mechanical stress (a) C60 film (b) carbonaceous-palladium film with 4 Pd-nanocrystals (c) carbonaceous-palladium film with many Pd-nanocrystal.

4. CONCLUSIONS

From nanoindentation measurements:

- Various mechanical properties are connected to differences in structure and composition of these films.
- The load – displacement curves show typical pop-ins correlated with the heterogeneous nano-structure.
- The depth dependent hardness and indentation modulus vary according to the nano-composite structure and reflect the changes of the mechanical properties in the film
- Hardness and indentation modulus of Ni, Pd - carbonaceous films are much larger than in pure C60 films in which popins are not present.

From numerical experiment:

- Numerical results reflect experimental results
- Calculated load – displacement curves depend on distribution of metal nanograins in film volume as well as on film composition
- Metal nanograins move in film volume due to tip pressing on the film surface
- Metal nanograins displacement is biggest and stress is highest in the neighbourhood of the tip

5. ACKNOWLEDGEMENTS

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