METHODS FOR ANALYSIS OF SURFACE MODIFIED METAL ALLOYS

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Abstract: *In the last decades, there is interest in the fabrication of nanostructures suitable for different applications. Physical and mechanical properties of the nanoscale particles are novel, different from those in the bulk materials.*

This review deals with the latest techniques developed to perform the analysis of coatings on alluminium alloys or steel, classical and novel measurements for complementary characterization of the surfaces.

The topography of the surfaces of the metals and applied coatings are tested using atomic force microscopy (AFM), scanning electron microscope (SEM) and optical microscopy (OM) analysis. Coating defects and pores are demonstrated on 2D and 3D images.

МЕТОДИ ЗА АНАЛИЗ НА ПОВЪРХНОСТНО МОДИФИЦИРАНИ МЕТАЛНИ СПЛАВИ

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Резюме: *През последните десетилетия нараства интересът към получаването на наноструктури като допълнителна фаза за разнообразие в приложенията. Физичните и механични свойства на наноразмерните частици са нови, различни от тези на плътните материалите.*

Изследването разглежда най-новите разработени техники за анализ на покрития върху алуминиеви сплави или стомана, класически и нови измервания за характеризирзне на повърхността.

Топографията на повърхността на металите и нанесени покрития се тества с атомно силова микроскопия (AFM), сканиращ електронен микроскоп (SEM) и оптичен микроскоп (OM) за металографски анализ. Забелязани дефекти и пори се демонстрират на 2D и 3D изображения.

"We live in an era where some huge discoveries are really the result of giant collaborations, with major contributions coming from very large numbers of people.
Kip S. Thorne *on how Nobel Prize in Physics (2017) was a remarkable team effort*

1. Introduction

Nanostructured materials come in morphology as nanometer phase materials and as additional phase in matrix or coatings. Typical coating phases are usually nanograined materials with approximately sizes 1-100 nm.

A chromium nitride coatings have been deposited on stainless steel substrates by magnetron sputtering at constant temperature in [1]. The phase composition and lattice parameter of the coatings are determined by XRD analysis. Mechanical properties hardness and Young's modulus also are measured. The influence of bias voltage on phase composition and internal stresses of the coatings are discussed [2, 3].

The delamination function defined in paper [4] based on impedance data agrees very well with the degree of delamination determined visually according to ASTM D 610 [4].

The use of electroless Ni–B baths reduced with sodium borohydride and stabilized with thallium nitrate or lead tungstate allowed homogeneous thin or thick Ni–B deposits on aluminium 1050 or AS7G06 substrate to be realized in [5]. F. Delaunois & P. Lienard to improve the mechanical properties of electroless nickel–boron deposits various heat treatments are applied. The authors note that at low temperatures, no fundamental changes in the deposit structure are observed, only an improvement of adhesion on aluminium substrate. The values of the Knoop microhardness obtained on these heat-treated deposits are near 600 hk100. The thickness and the quality of the deposits are estimated using optical microscopy and SEM analysis. The use of an energy selection X-ray spectrometer allows the identification of the different chemical elements present in the Ni–B deposit, such as Ni, Tl, Pb, P and Al (map scanning). Boron, which is a very light element, cannot be detected due to matrix effects. To increase the microhardness measuring precision a Knoop diamond penetrator is used.

Many studies have proven that Ni-B and Ni-W-B coatings are amorphous at as-plated condition. By virtue of heat treatments applied on Ni-B and Ni-W-B coated 7075 aluminum alloy, microhardness values are increased which procures lower wear rates and give rise to be at crystallographic condition as referred in related works.

In [6] Ni-B and Ni-W-B coatings were applied on 7075 aluminum alloy by electroless deposition technique using solutions including lead tungstate as a stabilizer and sodium tungstate as tungstate former. Zincate treatment is a substantial process of aluminum alloys before the electroless deposition of Ni-B and Ni-W-B coatings. In order to increase wear resistance and fatigue life of coated specimens, heat treatments should be executed. Three different temperatures (125, 150 and 175 °C) were picked considering aging time of 7075 aluminum alloy. On the SEM micrographs the authors finds that Ni-B coated specimen has a ‘cauliflower’ like microstructure after heat treatments which enable the coated system to perform lower wear rates.

Nickel–phosphorus (NiP) coatings produced by autocatalytic (electroless) deposition tend to be extensively used as wear-resistant materials for engineering components. The ability of these coatings to be deposited on a large variety of materials including metallic and non-metallic substrates is known. Most of the papers were performed NiP coatings deposited on steel substrates. The behaviour of autocatalytic nickel coatings towards wear when deposited on a soft substrate such as, aluminium or its alloys was not evaluated [7]. To assess any improvement of the abrasive wear resistance of the nickel deposits, without sacrificing aluminium substrate characteristics, a low heat treatment temperature (220 °C) has been selected. The heat treatments were carried-out in an air circulation furnace. Similar measurements, that is, the abrasive wear resistance as a function of the applied load and phosphorus content for the as-deposited NiP–SiC coatings, are shown. The results of this study consistently showed that the abrasive wear resistance and the hardness of NiP particle-free deposits could be increased by decreasing phosphorus content and by applying a heat treatment at 220 °C for 1 h. This may indicate possible phase changes in the deposits structure, determined by the different phosphorus content and temperature which, in turn, can influence their response to wear and hardness. The phase composition of NiP and NiP–SiC coatings was analyzed by X-ray diffraction. The XRD patterns of as-deposited particle-free and composite coatings as a function of their phosphorus content are represented – low phosphorus contents 2.5 and 3.9 wt. % P. These textures were more distinct for the 2.5 wt. % P coating.

The formation of chromate/fluoride conversion coatings composed mainly of amorphous hydrated chromia, on model, solid-solution, binary Al–Cu alloys, of a range of compositions, and on 2014-T6 aluminium alloy are studied in [8].

Topographies of the coated 2014-T6 alloy were investigated by atomic force microscopy in [8]. The authors are focused on the role of copper on the integrity of the coating. They present AFM images (Fig. 1) of the conversion-coated 2014-T6 alloy for 5 min. There is a relatively uniform coating with a nodular texture, over most of the surface (z < 1 um).

The mechanism of electroless Ni-P plating is discussed briefly and the literature on the effect of crystallization and phase transformation behavior on the microstructure and material properties of electroless Ni-P deposits is critically reviewed. In [9] a comparison with other commonly used engineering deposits such as electroplated nickel and hard chromium is made. The advantages of electroless Ni-P are outlined. The use of heat treatment to tailor properties for specific industrial applications is described in [9].

The AFM and SKPFM techniques (scanning Kelvin probe force microscopy) are used to reveal the evolution of the surface topography and volt potential distribution after corrosion tests. The initial topography and potential map of the AA2024 are depicted in [10]. The alloy surface is relatively flat and only small hills are present in the places of hard intermetallic particles.

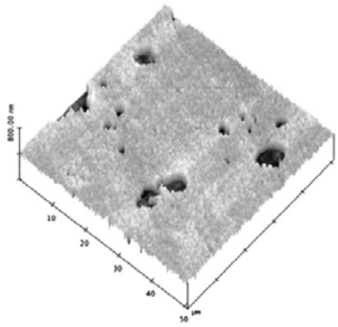


Fig. 1. AFM image of 2014-T6 alloy following conversion coating in a chromate/fluoride bath for 5 min [10]

The structural analyses [11] indicate that Ni–B coatings are amorphous in their as deposited state. However, addition of CeO2 into Ni–B matrix considerably improves the crystallinity of the deposit. The surface morphology study reveals the formation of uniform, dense and fine-grained deposit in both Ni–B and Ni–B–CeO2 composite coatings. However, Ni–B–CeO2composite coatings exhibit high surface roughness. The authors (R. A. Shakoora et al.) note that the addition of CeO2 particles into Ni–B matrix results in remarkable improvement in mechanical properties (hardness and modulus of elasticity) which may be attributed to dispersion hardening of Ni–B matrix by CeO2 particles.

The unique porous surface of the ceramic coating on aluminum [12] was revealed by the AFM images, as shown in Fig. 2.

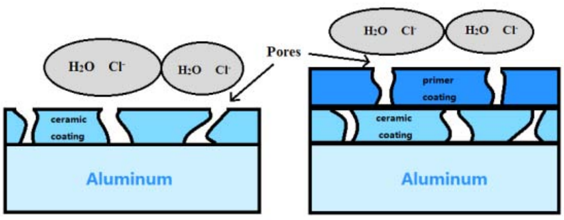


Fig. 2. Sketches of the pore distributions of coatings on the aluminum alloys in the context of polarization resistance [12]

The authors [12] provide a good example of how more detailed local information can be obtained by using AFM to explore the microtopography, homogeneity and defects of applied coatings (Fig. 3).

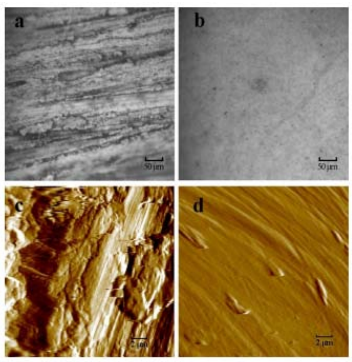


Fig. 3. OM and AFM images of sample A (bare aluminum alloy) and sample C (coated with chromate and epoxy coating) [12]

A. Fathy at al. produce Cu–ZrO_2 nanocomposites by the thermochemical process followed by powder metallurgy technique [13]. Microstructure development during fabrication process was investigated by X-ray diffraction, field emission scanning electron microscope and transmission electron microscope. The authors show distribution of zirconium dioxide (ZrO_2) nanoparticles (45 nm) in the copper matrix, which resulted in the improvement of mechanical properties of Cu–ZrO_2 composites. The nanocomposite with 9 wt-% ZrO_2 possesses the highest hardness (136.5 HV) and the compressive strength (413.5 MPa).

2. Experimental data and results

In the department "Space material science" ultrafine diamond particles for nickel coatings on metal alloys are synthesized [14, 15]. Detonation nanodiamonds are used as strengthening particles for improving the mechanical properties of materials. Also Authors in [16] study austempered ductile iron with nanosized additives.

The influence of deposited within nickel-phosphorus matrix cubic nano- and micro-sized particles (nanodiamond and micron cubic boron nitride) on the structure of the composite coatings/steel (Ni+cBN/17CrNiMo6) is investigated. Electroless nickel bath is used to prepare nickel composite coatings from a suspension. The particles have influence on the composition.

The structure, morphology and hardness are analyzed to study the samples. The influence of thermal processing of the samples properties is investigated.

The advance measuring techniques includes optical microscopy, SEM and scanning probe microscopy at the level of nano- and micrometer scale.

The samples are examined after polishing and special processing of the materials.

2.1. Optical microscopy

The microstructure is observed by metallographic microscope Neophot 32. A coating thickness of 7 to 9 um is determined. There are changes in microstructures after the heat treatment (Fig. 4).

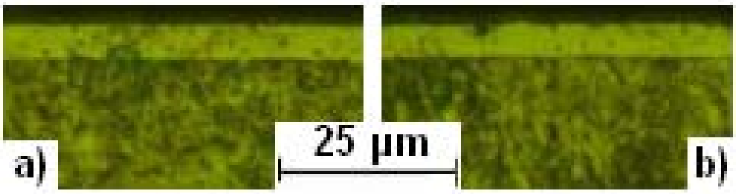


Fig. 4. Coatings Ni+cBN on steel 17CrNiMo6: a) with thermal processing; b) without thermal heating [14]

The hardness of the coatings is associated with the crystalline transition of nickel layer and formation of a new phase of Ni_3P.

Microhardness measurements are observed with a Knoop testing $HK_{0,02}$ = (712-1264). The low values reflect the influence of the residual porosity on the "soft" gray areas of the structure (Fig. 5).

2.2. SEM analysis

Samples structure is characterized by SEM and XRD. The SEM micrographs of surfaces of Ni+cBN on steel 17CrNiMo6 with/without thermal processing 290 °C (TO) are shown in Fig. 5. Two kinds of structures are found.

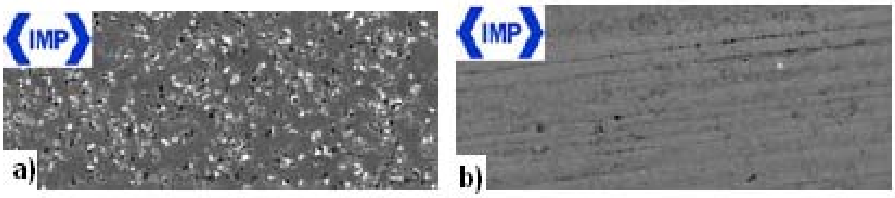


Fig. 5. Morphology of Ni+cBN on steel 17CrNiMo6: a) with TO; b) without TO [14]

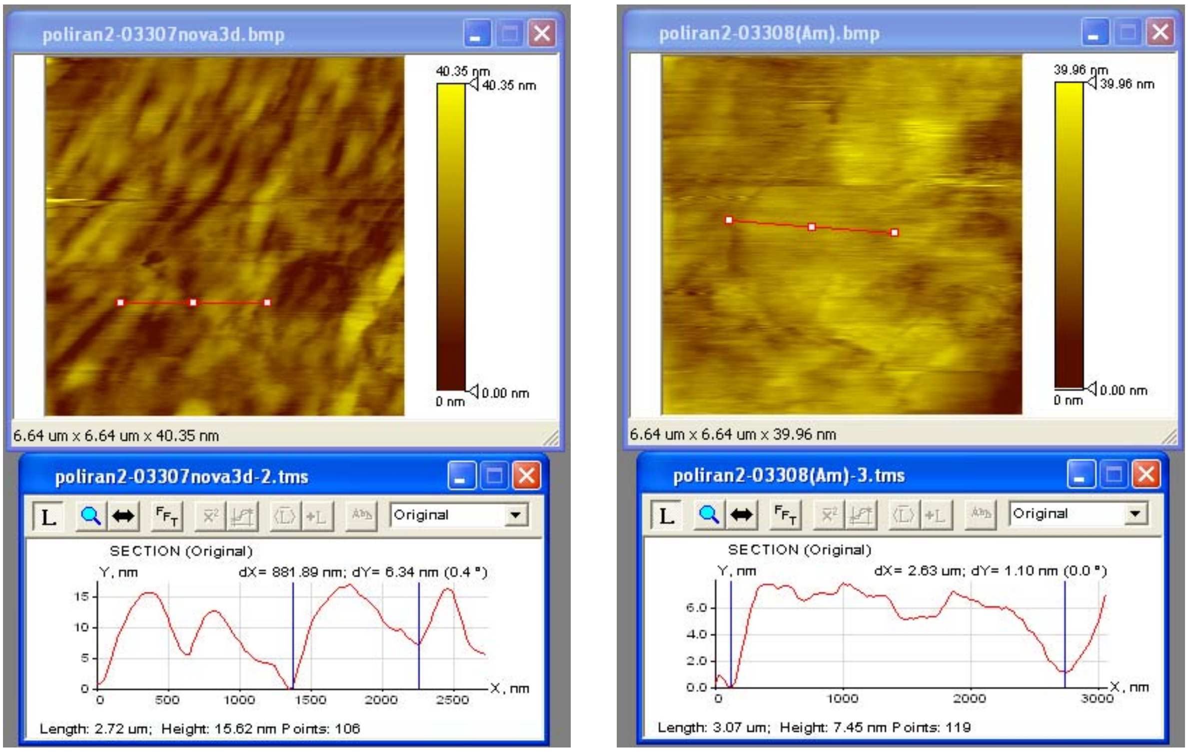
In the structures, obtained SEM investigations are revealed the chemical content of bulk metal regions. EDX allows information on the chemical composition of the sample. The white particles are cNB.

2.2. Nanoscan analysis of surfaces topology

Scanning testers of *"NanoScan"* family (Technological Institute for Superhard and Novel Carbon Materials, Russia) has been developed on principles of scanning probe microscopy (SPM) [17].

Fig. 6. Diamond tip

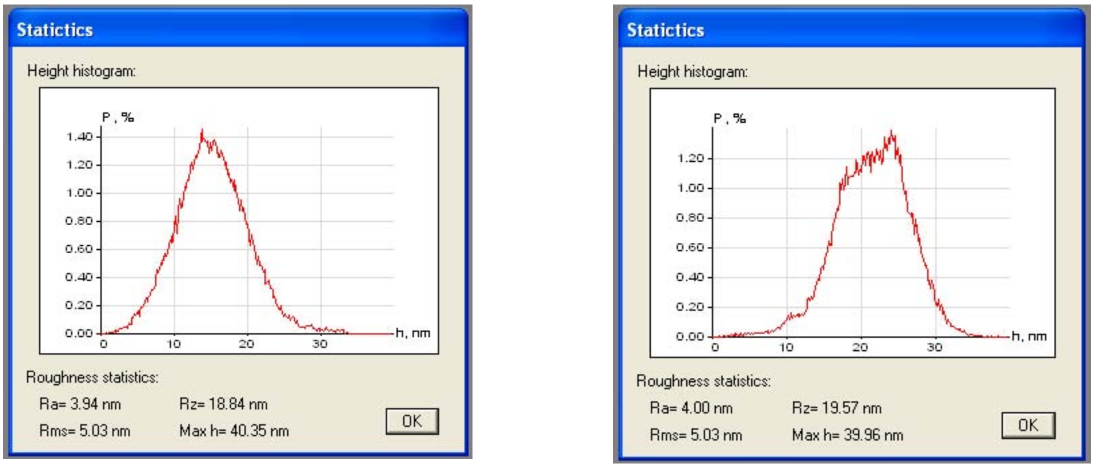
The main characteristic feature of *NanoScan* is the use of piezoresonance probe sensor having high bending stiffness of the cantilever 5-50 kN/m and resonant frequency 12 kHz (Fig. 6). The use of the regime of resonance oscillations allows tracking of contact between the probe tip (diamond indentor) and the surface on two parameters: change of amplitude and frequency of the cantilever oscillations. The investigation technique of structure using NanoScan allows to investigate the structure and quality of the surface (standard tapping mode). It gives possibility to calculate different parameters of surface roughness [18-22].



a) b)

Fig. 7. Topography of the surface:
a) 2D image and a cross-section along line of sample Ni+cBN on steel 17CrNiMo6 with TO 290 °C;
b) 2D image and a cross-section along line of sample Ni+cBN on steel 17CrNiMo6

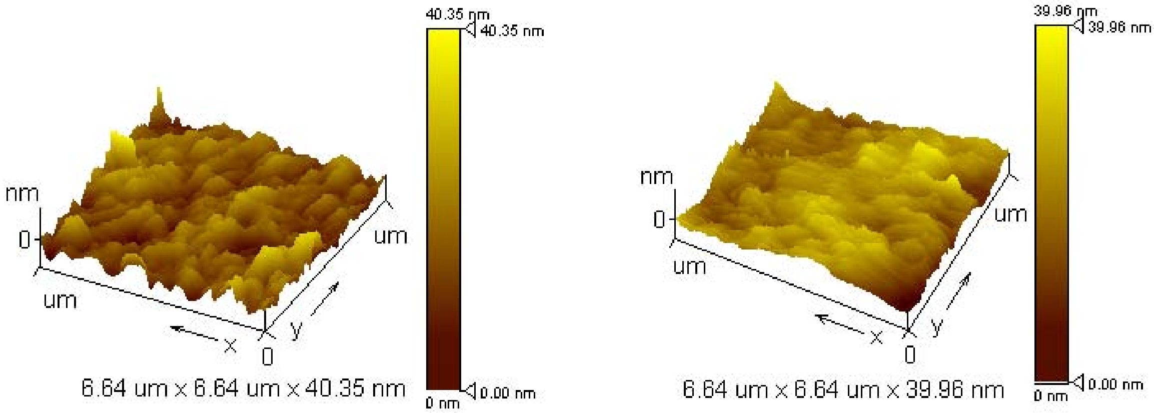
Texture is the surface that forms the threedimensional topography of the surface with roughness (nano- and microroughness), waviness (macroroughness), pores and defecs. Nano- and microroughness are formed by fluctuations in the surface which are characterized by hills (maxima) and valleys (minima) of varying amplitudes (Fig. 7). Liners are peaks in a profile (two dimensions) and in a surface map (three dimensions).



a) b)

Fig. 7. Roughness statistics: a) sample Ni+cBN/17CrNiMo6 with TO; b) sample Ni+cBN/17CrNiMo6

Surface roughness is characterized by calculating the roughness parameters. These parameters are derived from programma NanoScan Control. Ra is average roughness (the arithmetic mean of the absolute values of the height of the surface profile). Rms = 5,03 nm (root mean square roughness) parameter is the standard deviation of the surface heights values within a given area. Roughness Depth Rz is the arithmetic mean of the highest peaks added to the deepest valleys over the evaluation length measured. Rz is more sensitive to occasional high peaks or deep valleys. Surface profile analysis of samples includes Rz and maximum depth Max h. The cross-sectional line of the coatings is examined (Fig. 7).



a) b)

Fig. 8. 3D images: a) sample Ni+cBN/ 17CrNiMo6 with TO b) sample Ni+cBN/17CrNiMo6

AFM micrographs reveal that the samples are with smooth surface (Fig. 8). The surface roughness of both samples (with and without TO) is identical.

3. Conclusions

The advance measuring techniques include microhardness and roundness testing at the level of nano- and micrometer scale. Nanomeasurement techniques are important to improve the chemical technology and quality of surface characterization. Increasing the hardness of the nickel-phosphorus-cBN composite coating is obtained after heat treatment.

The electroless nickel depositions and electroless composite coatings whit reinforcing particles will be of great help in the future study of unknown coating properties, coating structures, new reinforcing particles in composite coatings, for new potential aerospace applications and project proposals.

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