

Structure and properties of nanocomposite polymer coatings

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Abstract. We investigate the surface morphology and structure formations of nanocomposite polymer (polytetrafluoroethylene, polyurethane) coatings obtained by vacuum plasma method. We present data about the influence of coating composition and deposition conditions onto coating properties and structure.

1. Introduction

Thin polymer based nanocomposite coatings obtained by vacuum methods demonstrate unique properties enabling possibilities to solve different technical problems [1, 2]. Their properties are known to be dependent on various structural factors, e.g. form, concentration, and size distribution of the embedded metal or polymeric nanoparticles as well as molecular structure of polymeric matrix [3, 4].

Effective methods of composite coating deposition are thermal evaporation or laser evaporation and subsequent precipitation of complex compound vapours on substrates [1]. Generation of active gas phase by electron beam evaporation or dispersion of bulk polymers is perspective technology. This method is effective, especially for deposition of coatings with complex structure and composition. Electron beam impact on polymer surface and evaporation of low-molecular fragments leads to the forming of numerous active particles in gas flow [5]. Additional activation of particles in the gas flow can be performed by means of glow discharge excitation. The main goal of the present work is investigation of morphology and properties of nanocomposite polymer-polymer and metal-polymer coatings deposited from the active gas phase under the conditions of additional plasma activation.

2. Experimental

Morphology and adsorption properties of polytetrafluoroethylene (PTFE), polyurethane (PU) coatings containing different nature polymer or metals of nanosize particles were investigated. Coating forming was performed from the active gas phase formed by electron beam dispersion of initial materials.

Activation of the volatile products was performed in glow discharge. Discharge parameters were 1500 V and 20 – 60 mA. Typical deposition rate of the coating was 5-10 nm/s and the thickness of the films was 500 nm. Surface morphology of coatings was investigated by atomic force microscopy with «Nanotop-203» measuring system. Scanning of the surface was executed in a tapping mode.

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Additional mathematical analysis of cluster formation images was carried out. Fractal analysis of the images was performed according to the algorithm proposed by Feder [6]. Scanning electron microscopy (Hitachi S-806 device) was employed to investigate the morphology of coatings formed. Fracture of these coatings was carried out in liquid nitrogen. Tribotechnical tests were performed using a microtribometer operating in sphere-plate friction scheme. Speed of the indenter during friction measurement was $3.3 \cdot 10^{-6}$ m/s, normal component of the force 0.2 N.

3. Results and discussion

3.1. Nanocomposite polymer-polymer coatings

It is established that composite coating structure and properties are different from those of homogenous coatings. Figure 1 shows the SEM images of coating surfaces and corresponding profiles. As one can see PTFE coating surface has low roughness but contains micropores of 0.15 μm size.

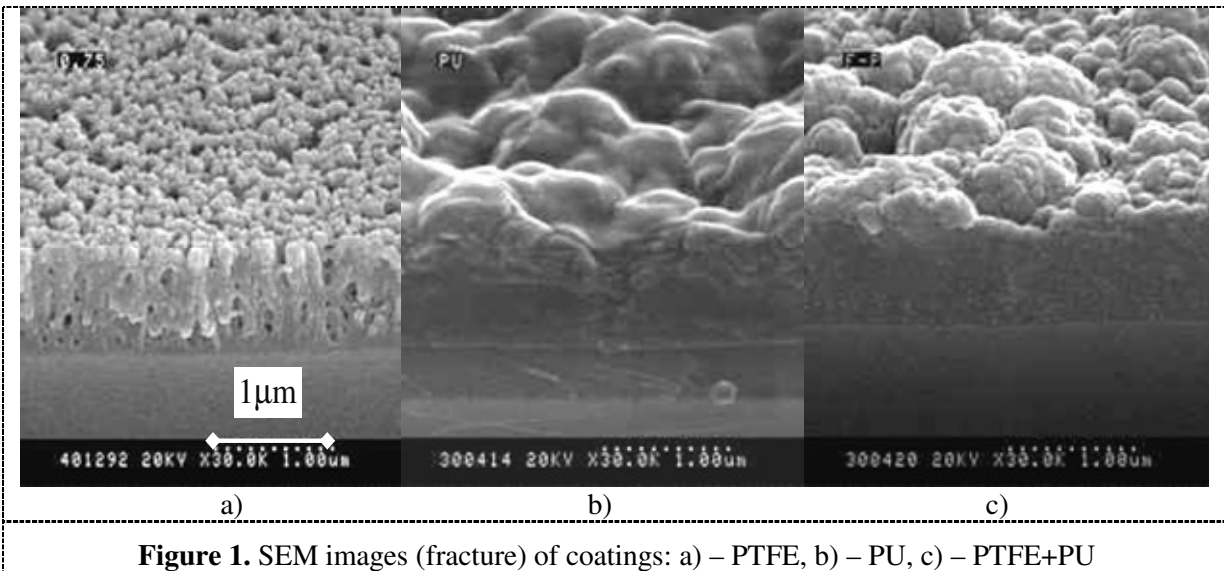
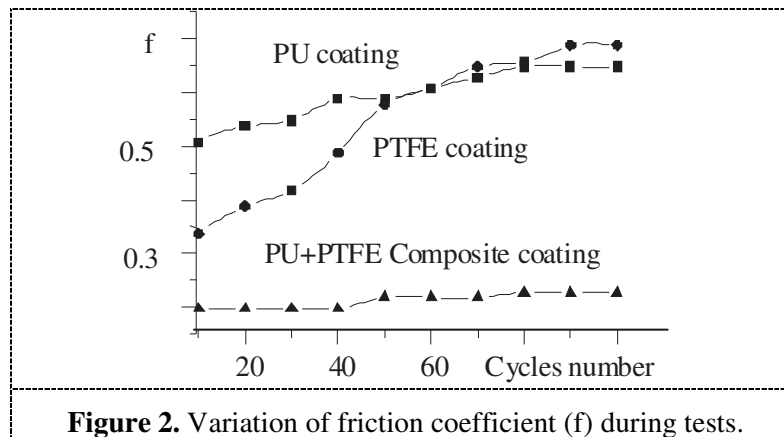


Figure 1. SEM images (fracture) of coatings: a) – PTFE, b) – PU, c) – PTFE+PU

Formation of these pores is a result of polymer phase synthesis under the condition of active particle deficiency. Structural elements with normal orientation to the surface are well visible in the coating profiles. PU coating has a developed structure. It contains globular micro formations of about 0.1 μm size. These formations have no evident orientation.

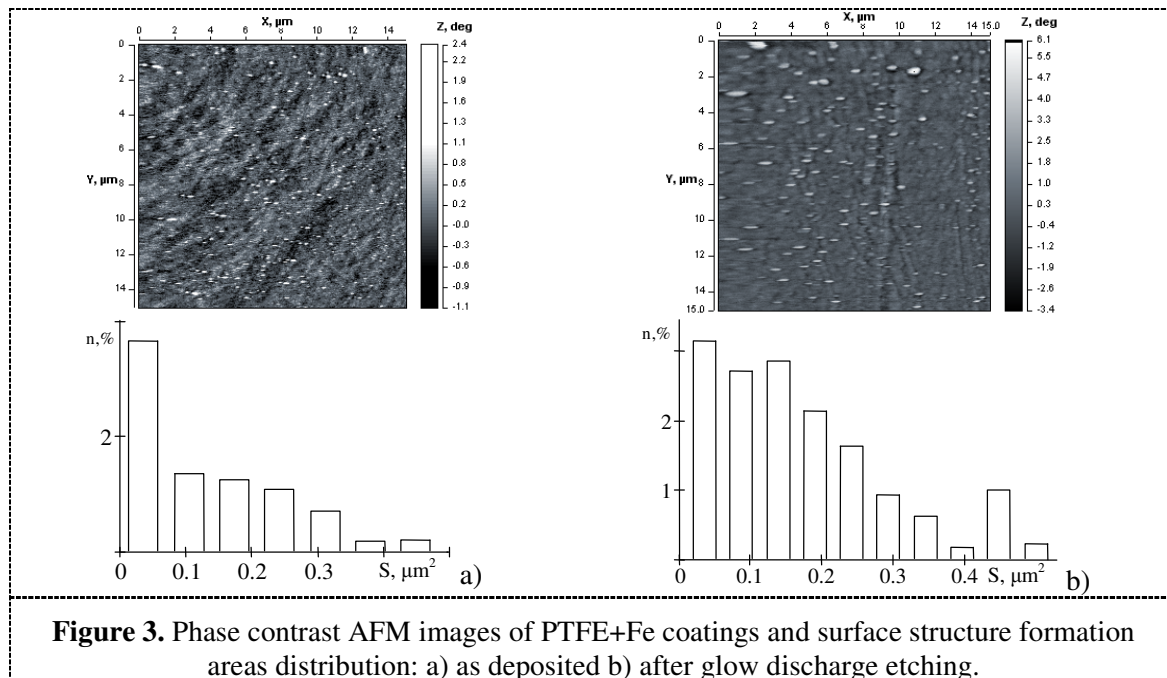
Co-dispersion of PTFE and PU leads to formation of coating that can be described as nanosized polymer mixture. On the SEM images of composite coating profiles and surfaces we can see both morphological elements that are typical for the structures of homogenous coatings. It means that the composite coating structure is the mechanical mixture of homogenous polymer nanoparticles.

Vacuum deposition of thin polymer coatings is an effective way to decrease the friction coefficient. According to our results polymer coating nature and structure have a strong influence on friction properties (figure 2). As shown in figure 2, composite coatings have much lower and more stable friction coefficient as compared to the single polymer coatings. SEM image of a friction path shows the smoothing of the nanocomposite coating surface relief. No cracks were detected in the composite coating after abrasion. Such coatings are worn without peeling or scuffing. Friction of homogenous polymer coatings leads to coating destruction after 60 -70 cycles of abrasion.



3.2. Metal-polymer nanocomposite coatings.

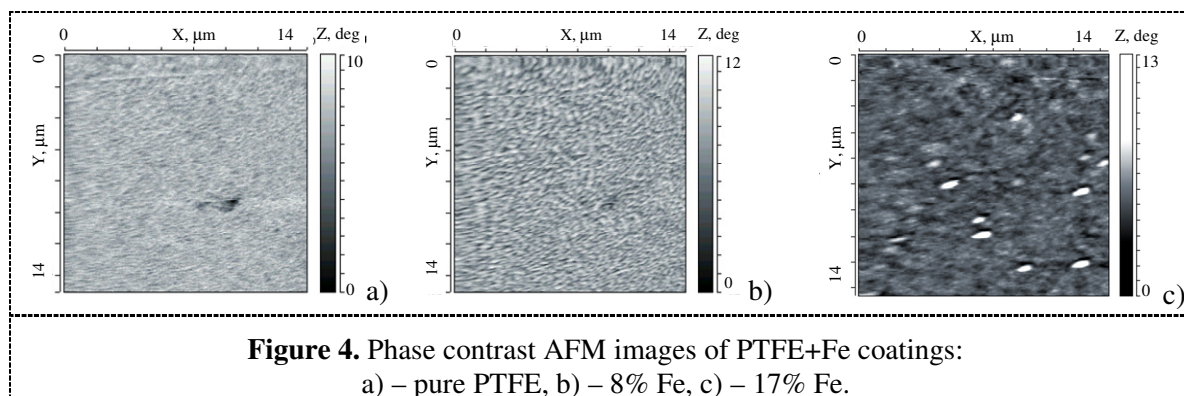
The structure of metal (iron) containing PTFE nanocomposite coatings can be considered as polymer matrix and uniformly distributed metal particles of 100-200 nm size. These coatings become continuous with effective thickness higher than 3 nm. This fact can be related to the influence of metal particles onto adsorption and polymerization processes. Well-ordered areas of polymer near the metal particles can be observed on the phase contrast AFM images after surface etching in glow discharge plasma (figure 3). The size of ordered polymer areas around the metal particles is about 200-300 nm for PTFE-Fe coating.



Morphology of the coating surface depends greatly on the metal concentration (filling factor). Roughness of the surface increases with the increasing of filling factor and typical dimensions of the metallic particle vary as well (figure 4).

Fractal analysis of topography AFM images shows a nonmonotonic character of the fractal dimension. The fractal dimensions have a maximum at 8% of metal-organic compound concentration. The analysis of phase contrast AFM images indicates the formation of compact cluster structures with

lower fractal dimension while the concentration of metal particles is increased. It is connected with volume structuring processes as a result of metal nanoparticles coalescence.



IR spectra of copper contained PTFE coating (20% Cu) have several low intensity absorption bands at $1750 \div 1400 \text{ cm}^{-1}$ which indicate the forming of copper-organic chemical compounds.

We have also observed the increase of order sensitive bands at 516 and 640 cm^{-1} and amorphous sensitive bands at 720 cm^{-1} in IR spectra of copper contained PTFE coatings deposited at additional plasma activation condition. The variations of IR spectra indicate the chemical interaction between the electron beam dispersion products of PTFE and copper. Copper particles may be the centres of polymer phase structuring.

Table Variation of relative optical density of IR absorption bands of the pristine PTFE and the PTFE coatings. Reference band is 1150 cm^{-1} .

Specimen	Wavenumber, cm^{-1}					
	516	625	638	720	740	516/740
Pristine PTFE	1.236	0.075	0.173	0.013	0.003	465.89
PTFE	0.320	0.045	0.112	0.032	0.003	100.76
PTFE*	0.329	0.048	0.121	0.032	0.011	30.26
PTFE+20%Cu	0.332	0.047	0.106	0.030	0.002	137.33
PTFE+20%Cu*	0.350	0.052	0.131	0.038	0.007	46.99

* deposited in additional activation conditions.

4. Conclusion

Thin nanocomposite polymer coatings (PU+PTFE, PTFE+Fe, PTFE+Cu) have a developed morphology. The structure of coatings depends greatly on deposition parameters and conditions. Additional activation of dispersion products by glow discharge leads to the formation of more continuous coatings with excellent tribological properties.

References

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