

Application of AFM and XPS in measuring thickness of surface coatings for nanostructured materials

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The high specific portion of surface states in nanostructured materials, which is comparable with the bulk one, determines their high adsorption and chemical activities. This gives rise to certain problems, for example, those, connected with the control over the surface oxidation level, thickness of the adsorption layers and functional surface coatings, which is as small as in the order of several interatomic distances. In this connection, in the present paper, a technique, based on the X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) has been proposed, to measure the thickness of oxide and other coatings on the surfaces of nanostructured materials.

The main points of the technique suggested, are as follows. XPS spectra are taken from the surfaces of thin-film materials. The spectral information covers the amount of the material of the coating, and that of the substrate. Since quantitative XPS-analysis is greatly affected by surface roughness [1,2], which is expressed in the variations of the intensity ratio between the surface coating and substrate signals, the knowledge of the surface topography is urgent. Here, AFM is of use. Assuming that the film is uniform, both, compositionally and in thickness, and being aware of the surface curvature parameters, it is possible to calculate the coating thickness. Likewise, in [3] a technique for measuring the thickness of thin oxide layers on finely dispersed metal particles, was developed.

In the process of the XPS-spectra interpretation the special features of nanostructural materials should be kept in mind. For example, grooves are formed when intercrystallite boundaries come to the outer surface [4]. The depth of the grooves is comparable with a crystallite radius. This results in a peculiar roughness of the surface which is now akin to the wavy surface of the planar cluster of tightly-packed balls. A special computer-simulated model is developed, which takes account of the roughness influence on the XPS-results. The model keeps record of the shadow effects in the process of a photoelectron emission.

Below given are the results of the investigation of the thickness variations of the oxide films, formed at the surfaces of nanocrystalline iron powders, as a function of milling time and the presence of a surfactant [5].

The XPS-spectra have been measured using an ES-2401 spectrometer with a Mg anode. The AFM-investigations have been performed with a scanning probe microscope P4-SPM-MDT, in air, in a contact mode.

Fig.1 demonstrates typical surface AFM-images of iron particles prepared by mechanochemical activation. On Fig.2 given are the diagrams of the grain size distribution, constructed according to the results of the AFM-image processing.

Fe3p surface spectra taken from the initial samples and samples after mechanochemical activation are presented on Fig.3. The spectral feature at 53 eV is assigned to the metal Fe contribution, binding energy of 55.7 eV is ascribed to Fe₂O₃, and metalorganic iron compounds are in charge of the high energy peak [6].

Fig.4 shows oxide relative intensity (I_{ox}) as a function of oxide layer thickness (d) and crystallite sizes (D). The dependences are calculated assuming a non-disrupted film which is uniform in thickness. The escape depth for the 3p-electrons of metal and oxide was taken to be equal to 15 nm [6].

Using the AFM-images to determine crystallite sizes, and the XPS-spectra to get information on the oxide spectral intensity, appending here the Fig.4 dependences, we can find the oxide film thickness. The results are presented in a table.

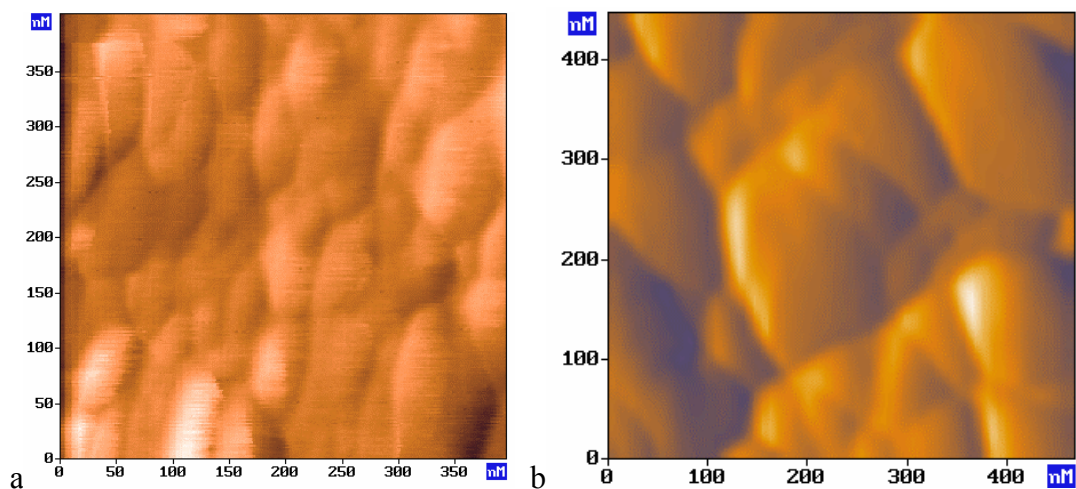


Fig.1. Typical surface images of iron particles prepared by mechanochemical activation in heptane (a) and in oleic acid (b) during 99 h

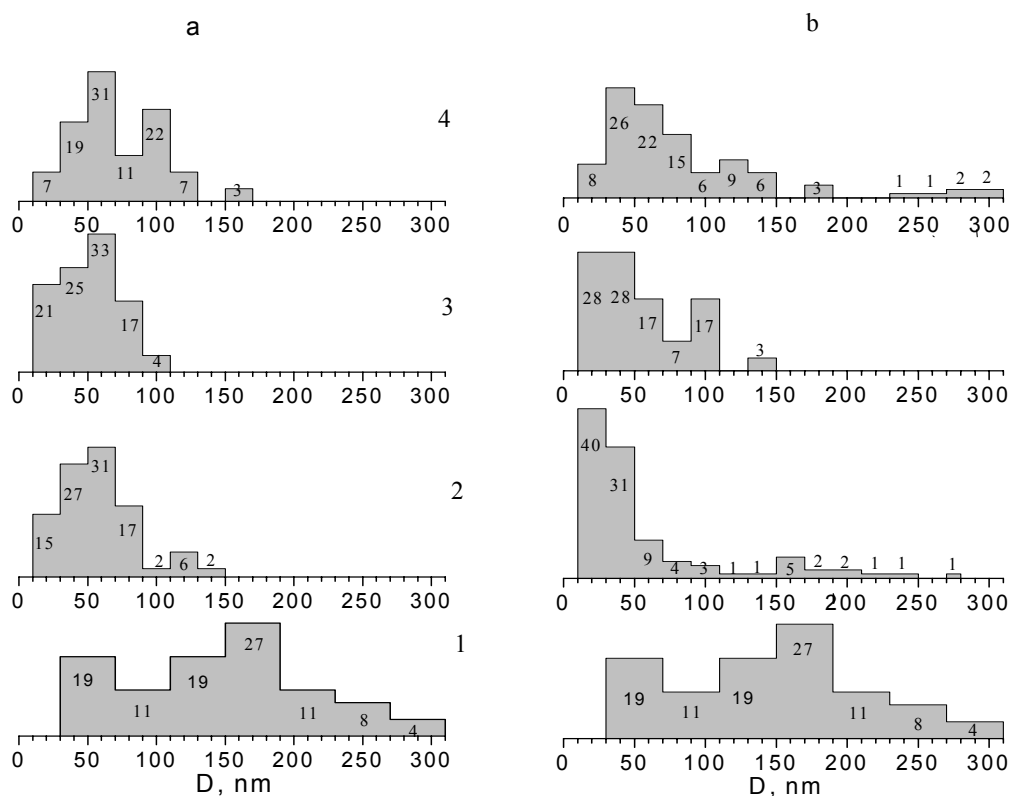


Fig.2. Diagrams of crystallite grain size distribution. a,b – milled in heptane and in oleic acid, respectively. 1 – initial iron, 2-4- 1 h, 47 h and 99 h milling, respectively.

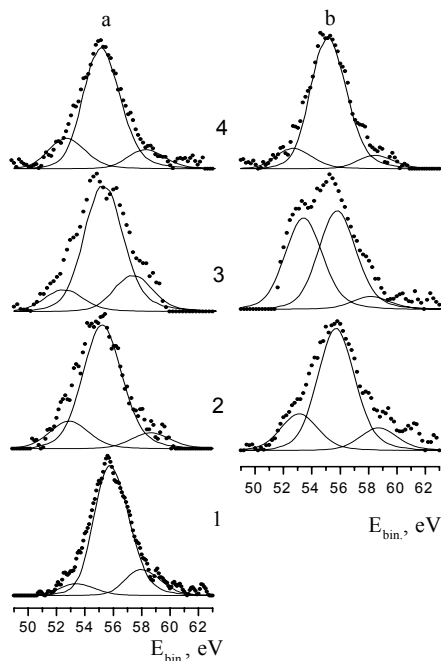


Fig.3. Fe3p-spectra
See notations on Fig.2

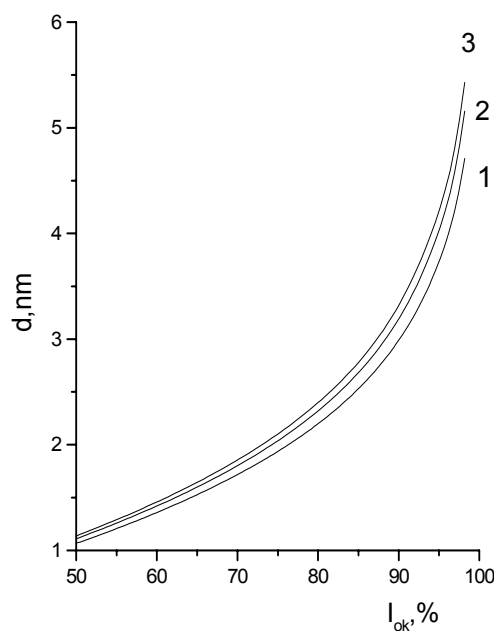


Fig.4. Oxide spectral intensity as a function of oxide layer thickness and crystallite size
1- D=20 nm, 2 – 30 nm, 3 – ≥50

	Milling in heptane			Milling in oleic acid		
	D (nm)	I _{ox} (OTH.%)	d (nm)	D (nm)	I _{ox} (OTH.%)	d (nm)
1 h	60	73	2.0	20	76	2.0
47h	60	75	2.1	30	52	1.7
99h	50	73	2.0	40	83	2.6
Initial Fe	170	90	3.4			

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