ANDRZEJ KOWAL

UDC:620.193.197:621.794.44=20

Application of STM and AFM techniques for the investigation of corrosion processes and materials protection

The Scanning Tunneling Microscope (STM) uses the quantum tunneling effect to determine the distance between the probe and the surface. A very sharp metal tip is brought close (0.5 – 1 nm) to the sample and a small potential difference is applied between them. Resulting tunneling current depends exponentially on the distance. When the tip is scanned line by line above the sample, the topography of the surface can be determined. STM is a technique that allows the investigation of electrically conducting surfaces. In Atomic Force Microscopy (AFM) the topography is mapped out by measuring the mechanical force exerted on the tip due to the tip - surface interaction. AFM has the capability to determine the surface structure of conducting and insulating materials. Both techniques can be used in a vacuum, in air and in liquids.

Digital monitoring of surface topography makes it possible to estimate the surface roughness by means of the two parameters: R_q (denoted also as RMS) and R_a (mean roughness) defined below.

R_q – is the standard deviation of the Z values (height) within the given area and is calculated as :

$$R_q = \sqrt{\frac{\Sigma (Z_i - Z_{ave})^2}{N}}$$

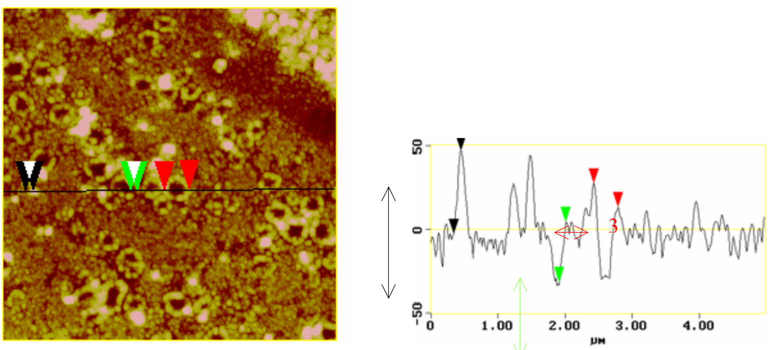
where Z_{ave} is the average of the Z values within the given area, Z_i is the current Z value, and N is the number of points within the given area. This value is not corrected for tilt of the data; therefore, plane fitting or flattening the data will change this value.

R_a – is the mean value of the surface relative to the center plane and is calculated using:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_y} \int_0^{L_x} |f(x,y)| dxdy$$

where f(x,y) is the surface relative to the center plane and L_x and L_y are the dimensions of the surface.

The ability of AFM and STM to probe surface topography at high resolution offers great advantages in the study of corrosion. Thus, for example we used these microscopes to investigate the corrosion of nickel (Fig.1 and 3) and zirconium layers (Fig.2) deposited on iron.



a b

Fig.1 - AFM image (5000x5000x200 nm) of corroded Ni layer deposited on iron (a).Section analysis (b) shows the height profile along the line chosen on Fig.1a.Roughness analysis: R_q (RMS) =13.3 nm, R_a (mean roughness) =9,1 nm.

Adresa autora Adresa autora: Andrzej Kowal Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Ul. Niezapominajek 8, 30 239 Cracow, Poland

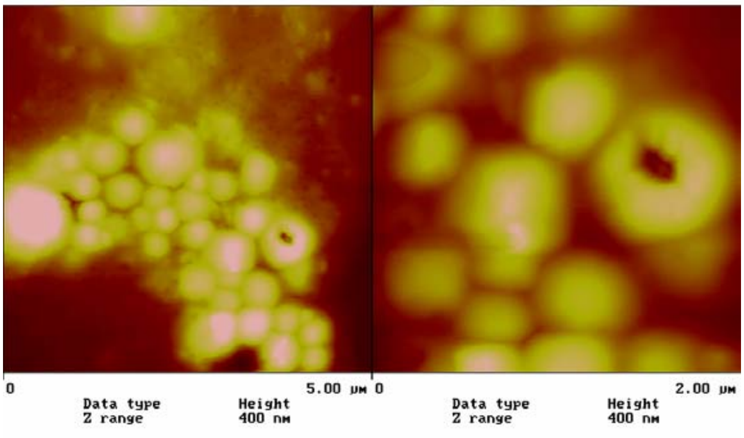


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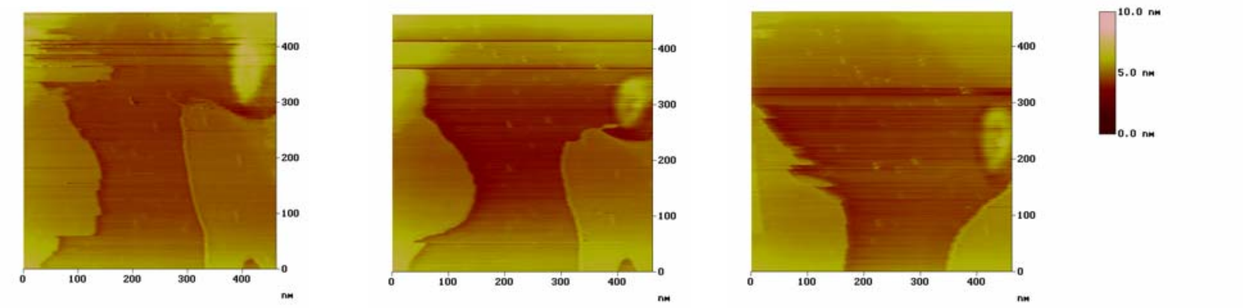
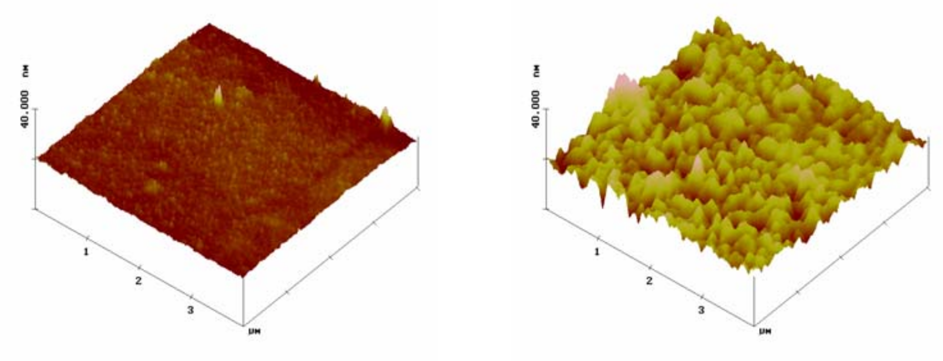
Fig.2 Corrosion of zirconium layer deposited on iron. AFM images of the same region; scan range (a) 5000 nm and (b) 2000 nm. Roughness analysis: R_q=72,7 nm, R_a=58,8 nm for (a) and R_q=47,8 nm , R_a=38,2 nm for (b).



a b c

Fig. 3 - In –situ STM observation of the dissolution of the Ni layer in 0.01 M H_2SO_4. Series of constant-current in-situ STM images of Ni electrode recorded at constant potential 1,1 V and tunneling current 5nA. (a) – fresh electrodeposited Ni electrode, (b) and (c) – after 5 and 10 min, respectively.

AFM, as a non-destructive and non-invasive direct observation technique, can be used in the study of historic stained glasses. Along the years the stained glasses have suffered deep alternations which started on their surfaces due to the interaction with the environment (see Fig.4).



a b

Fig. 4 - The long-term atmospheric corrosion of stained glass.

AFM images (4000x4000x40nm) show: (a) freshly prepared sample, (b) after being submitted to ageing for 20 years. Roughness analysis: R_q=0,48 nm, R_a=0,36 nm for (a) and R_q=1,94 nm, R_a=1,49 nm for (b).

One of the methods of materials protection again corrosion is the formation of polymer layer on the surface exposed to the corrosive medium. Exemplary AFM images are given in Fig. 5 and 6.

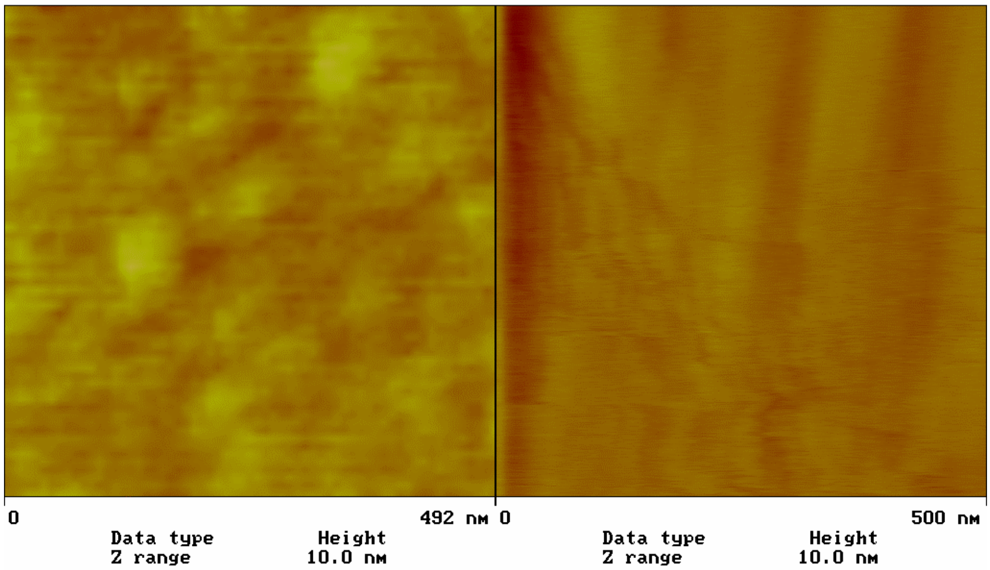
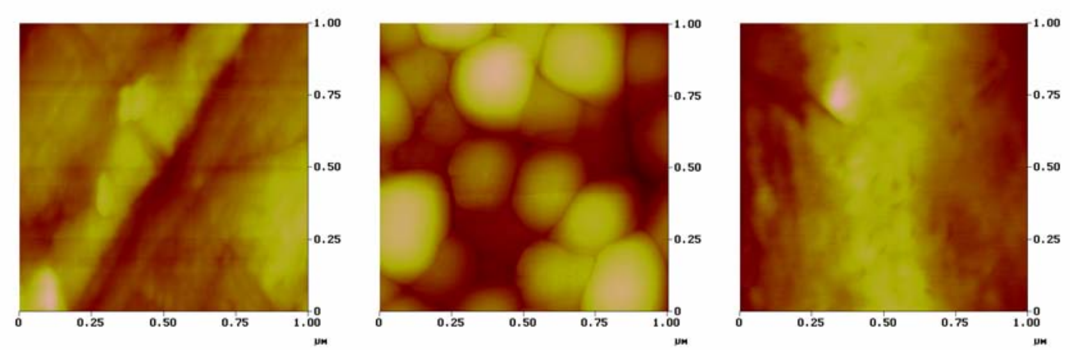


Fig.5 AFM image of (a) fresh glass surface, (b) glass surface coated with thin polymer layer . Roughness analysis: Rq=0,48 nm, Ra=0,36 nm for (a) and Rq=0,24 nm, Ra=0,17 nm for (b).



a (1000x1000x50 nm) b (1000x1000x100 nm) c (1000x1000x30 nm)

Fig. 6 - The formation of protective layer of PTFE on the metal surface: (a) aluminium surface, (b) aluminium surface coated with the grains of PTFE copolymer, (c) the resulting surface after heating at 400°C.

Summing up, it can be concluded that Scanning Tunneling Microscopy and Atomic Force Microscopy have become extremely valuable techniques for nano- scale investigations of corrosion processes and materials protection.