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Preparation and properties of nanocrystalline Ni/graphene composite coatings deposited by electrochemical method

Grzegorz Cieślak*, Maria Trzaska

Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland
**Corresponding author: e-mail: grzegorz.cieslak@imp.edu.pl*

The paper presents results of studies of composite nickel/graphene coatings produced by electrodeposition method on a steel substrate. The method of producing composite coatings with nanocrystalline nickel matrix and dispersion phase in the form of graphene is presented. For comparative purposes, the study also includes nano-crystalline Ni coatings produced by electrochemical reduction without built-in graphene flakes. Graphene was characterized by Raman spectroscopy, transmission and scanning electron microscopes. Results of studies on the structure and morphology of Ni and Ni/graphene layers produced in a bath containing different amounts of graphene are presented. Material of the coatings was characterized by SEM, light microscopy, X-ray diffraction. The microhardness of the coatings was examined by Knoop measurements. The adhesion of the coatings with the substrate was tested using a scratchtester. The influence of graphene on the structure and properties of composite coatings deposited from a bath with different graphene contents was determined.

Keywords: Graphene, electrodeposition, composite coatings, Ni/graphene coatings.

INTRODUCTION

The dynamic development of science and technology forces research into the search for new, more functional materials. New materials are important for surface engineering treatments. Depositing thin coatings, made of functional materials, on the surface of ready-made products makes suitable modifications of their properties possible. Galvanic techniques provide important possibilities in shaping the properties of finished products by depositing coatings of different materials on their surfaces[1]. These methods also allow production of coatings made of composite materials[2–5]. By combining two or more different phases in a single composite material, it is possible to obtain new material with unique properties.

Particularly interesting approach seems to be the use of graphene as a dispersion phase for the production of composite coatings, which can be characterized by unique properties. In the literature, are given examples of the use of graphene as a dispersion phase incorporated into the metal matrix[6–12]. The results of these studies indicate that incorporating graphene into the metal matrix can have a favorable effect on properties of produced materials. Embedding graphene flakes into metal matrix increases the hardness of the coating material[6, 11, 12], improves tribological wear resistance[9–10], and also contributes to the increase of corrosion resistance of the coating materials[6–8].

The research carried out within this work is aimed on nanocrystalline coatings of nickel/graphene produced by electrocrystallization method. The aim of the study was to investigate the influence of the content of graphene flakes dispersed in the bath on the structure and selected properties of Ni/graphene composite coatings.

EXPERIMENTAL

Material

Composite coatings of Ni/graphene and Ni coatings were deposited on a carbon DC01 steel substrate (cathode). The anode was made of nickel. The deposition process was carried out in a bath containing: nickel(II) sulfate(VI) (source of Ni ions), nickel(II) chloride (to improve conductivity of the bath), boric acid (pH buffer), sodium dodecyl sulfate (surfactant), saccharin (blistering compound), hexadecyltrimethylammonium bromide (cationic surfactant). To initiate processes were also used: acetone, calcium carbonate (degreasing); sulphuric(VI) acid (digestion, activation). All chemicals were purchased from Chempur (Poland).

Deposition of Ni and Ni/graphene coatings

Composite coatings of Ni/graphene were deposited by electrocrystallization method from a bath with different amount of graphene content in the range of 0.1–1.0 g/dm^3. In order to obtain coatings of a thickness of 20 μm the electrochemical deposition of the coatings was performed within 60 minutes at the current density of 3 A/dm^2 at the bath temperature of 50°C and at pH of 4.5. Steel substrates prior to the deposition process were degreased in acetone, calcium carbonate and activated in 15% H_2SO_4 solution. In order to ensure a good dispersion of the graphene in the bath during the process, the solution was stirred with a mechanical stirrer at a speed of 100 rpm.

Characterization techniques

The topography and morphology of the produced coatings were examined by Merlin ZEISS scanning electron microscope (SEM). The characteristics of the used graphene flakes were obtained by applying transmission electron microscopy (Libra 120, ZEISS) Scanning electron microscopy with EDS detector was used to study the chemical composition of the produced composite coatings. The structure and size of the crystallites of the produced coatings were tested by X-ray diffraction (XRD) using the copper tube radiation (1.54 Å). An approximation method based on diffraction line profile analysis was used. The crystallite sizes were determined by using the Scherrer's relation[13]:

$$\beta_k = K\lambda / D_{hkl}\cos\theta_{hkl} \quad (1)$$

where: β_k – reflex width dependent on crystallite size [rad],
K – Scherrer constant being close to unity,
λ – wavelength of X-rays [Å],
D_{hkl} – the average dimension of crystallites in the direction perpendicular to the plane (hkl),

θ_{hkl} – angle of reflection [deg].

Based on the above relationship, the crystallite size was calculated for the two most intense reflections from the <111> and <200> planes.

Microhardness measurements of the coating material were made by the Knoop method using WILSON-HARDNESS T1202 micro-hardness gauge (BUEHLER) at 10 g load (HK0.01) at cross-sections perpendicular to the coatings surfaces. The test of adhesions of the produced coatings to the steel substrate was carried out by using CSEM Revetest scratching device with incremental progressive loading of 0–100 N at 60 s and a speed of 10 mm/min. The damage images of the coating material after the scratch test was captured using the VHX5000 (Keyence) digital microscope.

RESULTS AND DISCUSSION

To produce the composite coatings was used graphene manufactured by Cheaptubes (USA), in the form of flakes with a particle size of 20–100 nm and specific area > 750 m^2/g[14]. The characteristics of the used graphene flakes were obtained by applying Transmission electron microscopy (Libra 120, ZEISS) (Fig. 1b) and scanning electron microscopy (Fig. 1a) as well as Raman spectroscopy (Fig. 2)

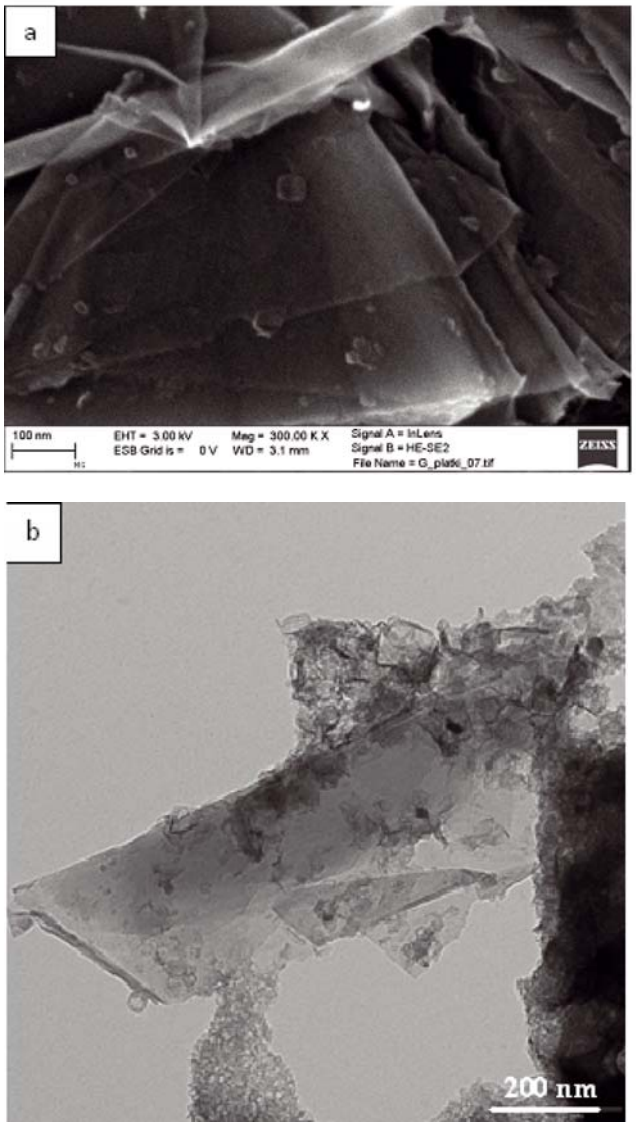

Figure 1. SEM (a) and TEM (b) images of graphene flakes

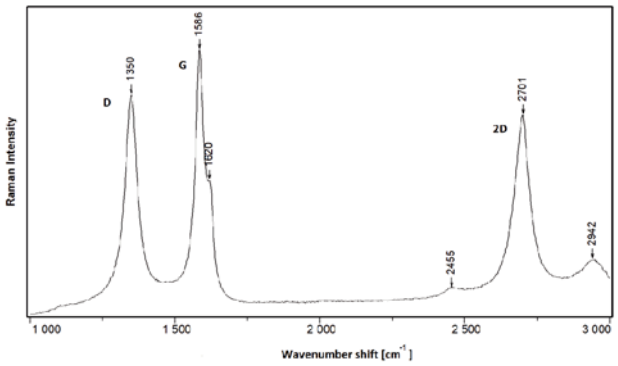

Figure 2. Raman spectrum of graphene flakes

Studies by SEM, TEM and Raman spectroscopies showed that the used graphene was in the form of multi-layered flakes of various shapes and sizes. The results of investigations demonstrated that the Raman spectrum has characteristic D (1350 cm^{-1}), G (1580 cm^{-1}), and the 2D (2700 cm^{-1}) peaks for graphene[15]. Band D is related to the occurrence of defects. The high intensity of this peak is affected by defects arising from the edges of the applied graphene flakes. The intensity of the G and 2D peaks and the ratio of these intensities as well as the increase in the 2D peak indicate on the use of the multiple layers of graphene flakes[16].

The images of the morphology and topography of the surface of the produced nickel coating without built-in graphene and the XRD pattern are shown in Figure 3.

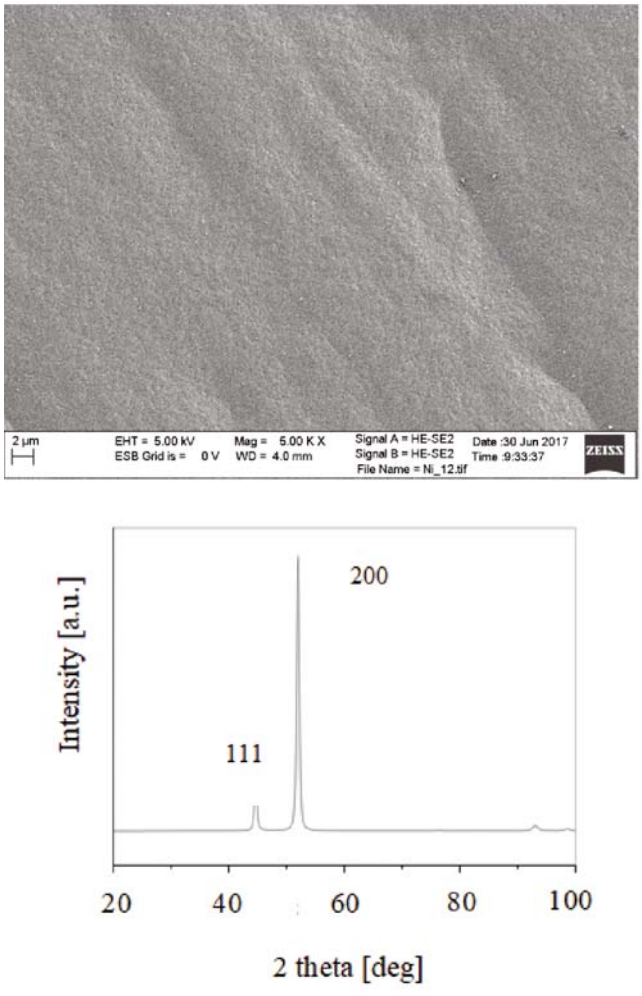

Figure 3. Images of surface and diffraction pattern of the Ni coating

The produced Ni coating is characterized by a smooth and glossy surface. The designated diffractogram of the material of the coating test shows its crystalline structure. The varied intensity of the diffraction peaks shows the strong texture of material coatings exhibiting the preferred crystallite growth <200>.

The images of the surface of Ni/graphene coatings produced in baths containing different amounts of graphene flakes are shown in Figure 4.

During deposition of the composite coatings, the graphene particles are deposited simultaneously with a growing layer of nickel. It has to be emphasized that the mechanism of co-deposition of the metal matrix with dispersion phase during the electroplating process of composite coatings was investigated in many works[17–19]. However, in this work, pre-activated graphene flakes were activated by a cationic surfactant. This treatment was intended to give graphene flakes positive electrical charges, which in the electrodeposition process ensure their attractions by the cathode and by electrophoresis incorporating them into the deposited coating. The concentration of graphene flakes in the bath, the current density and the speed as well as the method of mixing the bath are considered as parameters determining the quality of deposited Ni/graphene composite coatings. Mixing the bath during the process facilitates the transport of graphene flakes to the cathode surface where they are incorporated into the nickel matrix.

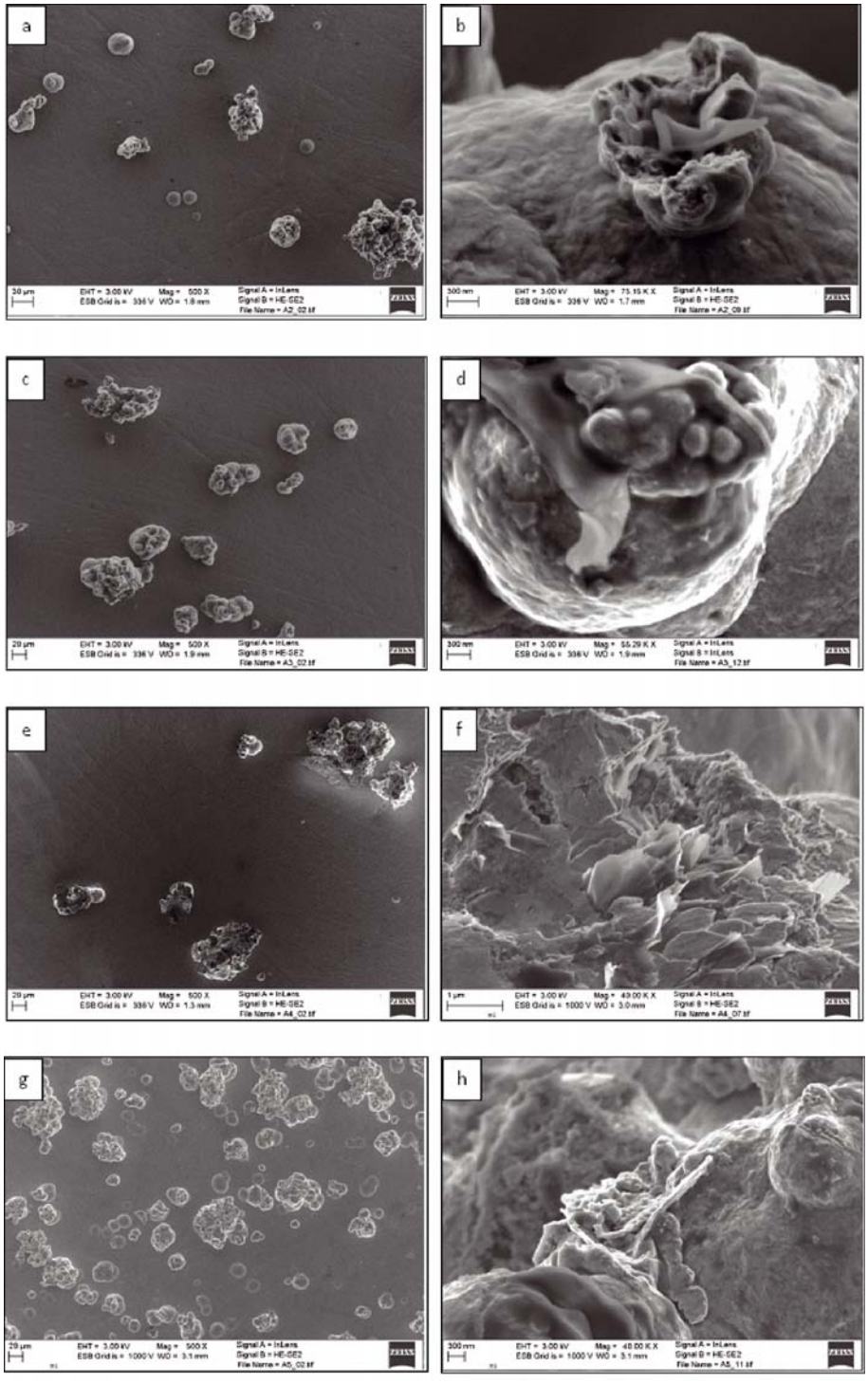

Figure 4. Surfaces of Ni/graphene composite coatings on different rows samples with different amount of graphene are presented in g/dm^3: a, b): 0.1; c, d): 0.2; e, f): 0.5; g, h): 1.0; on the left column (a, c, e, g) low magnification images, on the right column (b, d, f, h) high magnification images

Ni/graphene coatings are characterized by a high degree of surface development, and incompletely built-up flakes of graphene can be seen. The formation of such extensive structure on the surface of the coatings is the result of the tendency of the graphene flakes to form conglomerates and of the good conductivity of the graphene[20]. As a result of electric current transfer, the nickel deposits directly on the flakes leading to the development of the surface of the produced composite Ni/graphene coatings. The results of the EDS analysis of the chemical composition of the material of Ni/graphene composite coatings produced in a bath with the content of 0.5 g/dm^3 graphene flakes are shown in Figure 5.

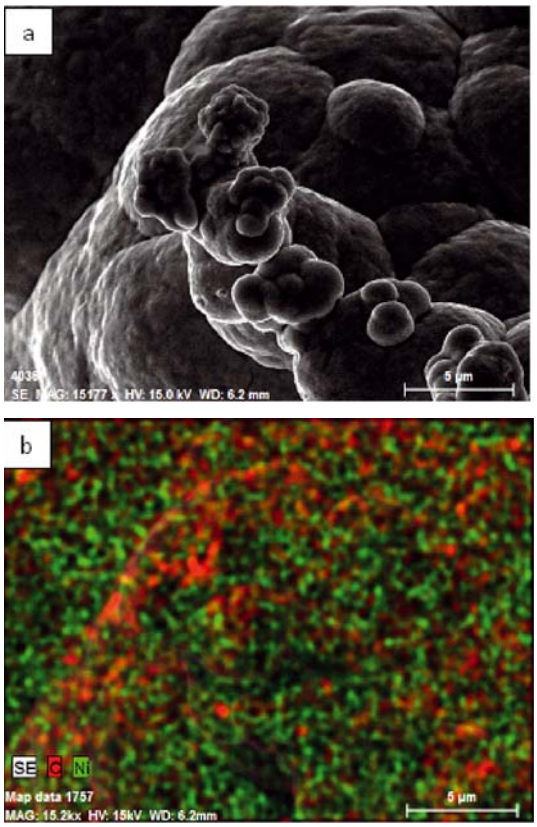

Figure 5. EDS analysis of chemical composition of Ni/graphene coating material (0.5 g/dm^3), a) surface of the coating; b) map of the elements (red – C, green - Ni)

The chemical composition map of the Ni/graphene (0.5 g/dm^3) surface area clearly shows the carbon and nickel content in the deposited coating. The carbon is visible in the places where graphene flakes are built. The percentages indicate the presence of 22% atomic carbon, the rest being nickel 76% and oxygen at 2% at. The results of the XRD analysis of Ni/graphene composite material deposited from the bath with a graphene content of 0.2 g/dm^3 and 1.0 g/dm^3 are shown in Figure 6.

The material of the Ni/graphene composite coatings is similar to the Ni coatings, but it is characterized by the strong textures of the coating material with a preferential growth direction of crystallites <200>.

Based on Scherrer's relationship, the size of the nickel crystallites in Ni and Ni/graphene coatings for crystallite growth <111> and <200> are summarized in Table 1.

The produced coatings of Ni and Ni/graphene are characterized by a polycrystalline structure with nanometric size of crystallites. Increasing the content of graphene in the bath results in a reduction in the crystallite size with

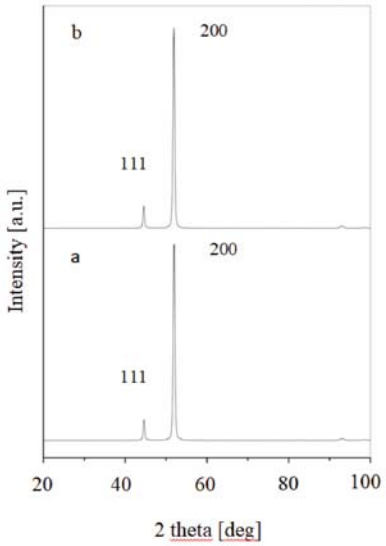

Figure 6. Diffraction pattern of Ni/graphene composite coatings: a) 0.2 g/dm^3; b) 1.0 g/dm^3

Table 1. Crystallite size of Ni coating and Ni/graphene composite coatings

Coating	Crystallite size	
	<111>	<200>
Ni	19.7	29.2
Ni/graphene (0.2)	22.5	28.9
Ni/graphene (1.0)	22.2	25.8

a preferential direction of their growth <200> in the Ni/graphene composite coatings. It follows that the incorporation of graphene into the nickel matrix contributes to the fragmentation of the structure of the produced coatings. The degree of fragmentation of the structure of the material affects its properties. The results of the microhardness measurements of the material of Ni and Ni/graphene composite coatings are shown in Figure 7.

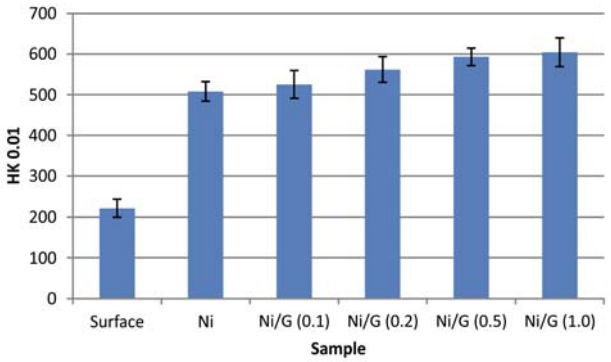

Figure 7. Microhardness of substrate material, Ni coating and Ni/G composite coatings

Microhardness tests have shown that the Ni/graphene composite material has a higher hardness compared to Ni and it increases with the degree of fragmentation of the matrix material. In the paper[7], the authors explain the increase in the hardness of Ni/graphene coatings by the fragmentation of the matrix material. As a result of the incorporation of graphene flakes, the growth of nickel crystals is blocked, resulting in the formation of smaller grain structures and a greater share of grain boundaries leading to the increase of hardness. The results of the performed study do not allow us to assess of the influence of built-in

graphene flakes on the microhardness of the Ni/graphene composite coating material. One of the criteria for assessing the quality of coatings is their connection with the substrate material. The scratch-test method was used to evaluate the strength of the adhesion of coatings to the substrate and the micromechanical properties of the coating material. Increasing indenter load during scratch-test due to the friction between the indentor and the coating causes an increase of the elastic and plastic deformation of the coating material. Changing such parameters as normal force, frictional force, friction coefficient, acoustic emission along the cracks during the scratch test of the studied coatings, and sketch images are shown in Figure 8.

Values of recorded frictional forces (approximately 50 N) and coefficient of friction (0.5) during scratch-test are similar for all tested coatings. Increasing indenter

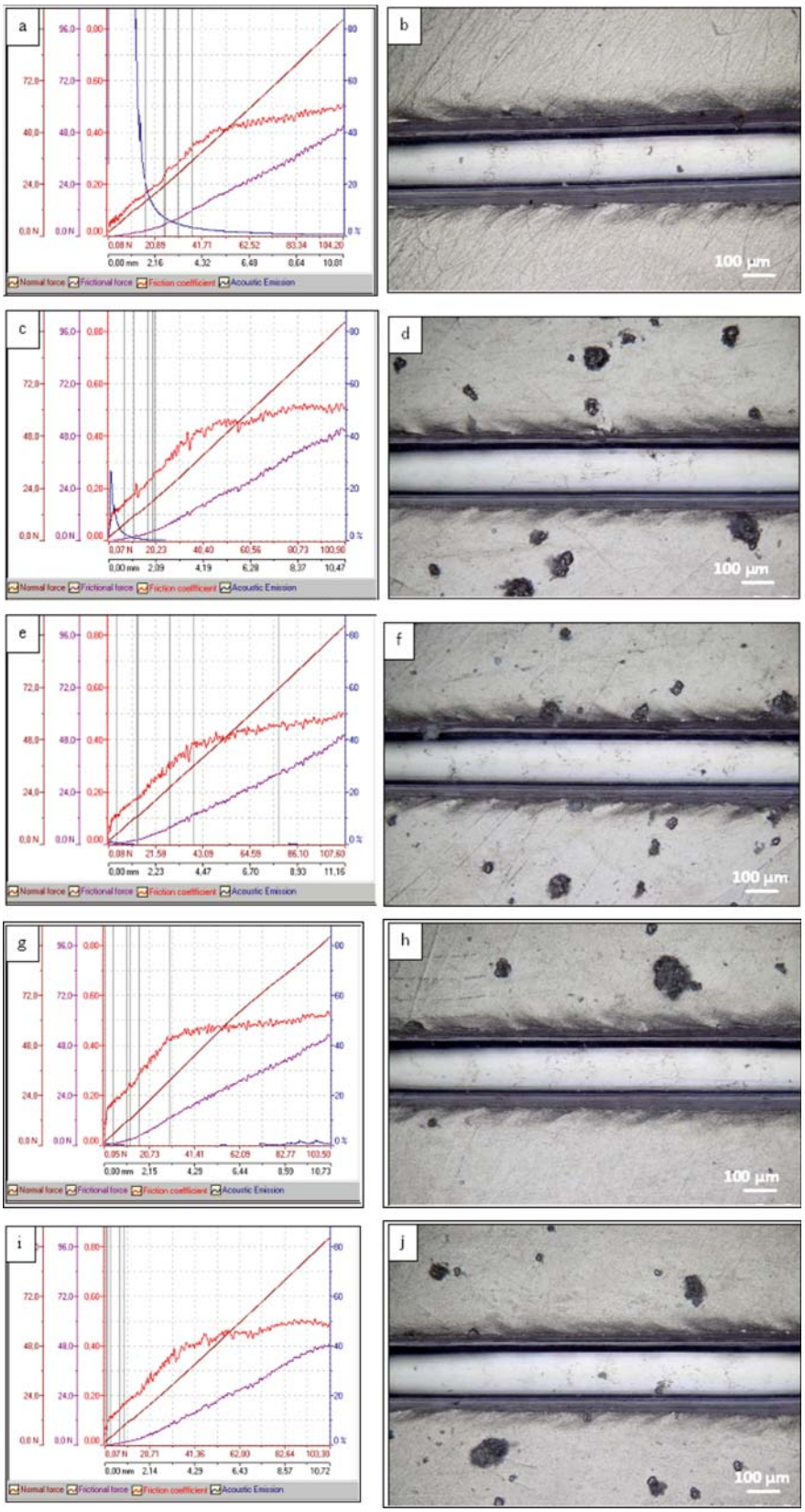

Figure 8. Diagram showing change of parameters during scratch-test process and image of scratch of the coatings: a, b) Ni; c, d) 0.1 g/dm^3; e, f) 0.2 g/dm^3; g, h) 0.5 g/dm^3; i, j) 1.0 g/dm^3

load (0–100 N) during the scratch test results in high compressive stresses and tensile stresses behind the indenter, which results in an increasing of the elastic and plastic deformation of the coatings material[21]. On the surface images of the coatings after the scratch-test, plastic deformation of the material can be observed, in the form of piles on the edges of the scratch and small cohesive fractures. There were no adhesion cracks and delaminations of the tested coatings from the substrate material.

CONCLUSION

The conducted studies have shown that electrocrysatllization method allows to deposit of nanocrystalline Ni/graphene composite surface coatings. The incorporation of graphene particles into the nickel matrix affects of the crystallites size of the crystalline nickel material of the matrix and consequently affects the hardness of the material of the produced composite coatings. Increasing the concentration of graphene in the bath increases the degree of fragmentation of the nickel matrix structure. The tendency for agglomeration of graphene flakes and the good electrical conductivity of the graphene contribute to the significant development of the surface of the produced composite Ni/graphene coatings. Composite coatings of Ni/graphene produced by electrochemical method are characterized by high fracture cracking and good adhesion to the steel substrate. Ni/graphene composite coatings can be used to coat metallic elements to improve their mechanical properties.

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