

Formation of cobalt sulfide layers on polyamide 6 by sorption–diffusion method using solutions of dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$

N. Petraškauskienė*,

R. Stokienė,

S. Žalėnienė,

V. Janickis

*Department of Inorganic Chemistry,
Kaunas University of Technology,
Radvilėnų Rd. 19,
LT-50254 Kaunas, Lithuania*

The processes of obtaining layers of cobalt sulfides Co_xS_y by the sorption–diffusion method on polyamide 6 (PA) using solutions of dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$, as precursors of sulfur are studied. The concentration of sorbed sulfur (from ~ 50 to $\sim 300 \mu\text{mol} \cdot \text{cm}^{-3}$) increases with the increase of the duration of treatment (up to 6 h) and temperature ($20\text{--}40^\circ\text{C}$) of precursor solution. Cobalt sulfide layers are formed on the surface of polyamide after the treatment of sulfurized polymer with Co(II) salt solution. The concentration of cobalt in the layer increases with the increase of initial sulfurization duration and a different concentration of cobalt ($24\text{--}28 \mu\text{mol} \cdot \text{cm}^{-3}$) in PA at each temperature is reached. XRD spectra of polyamide films treated for different time with solutions of dodecathionic acid and then with Co(II) salt solution confirmed the formation of cobalt sulfide layers on the surface of polyamide: five phases of cobalt sulfides – CoS , Co_3S_4 , Co_6S_5 , Co_9S_8 and CoS_2 were found in the films on the polyamide surface. The morphology of modified films characterised by SEM and AFM showed a spongy structure formed by the network of plate-like crystallites.

Key words: polyamide, dodecathionic acid, cobalt sulfide, layers, composition

INTRODUCTION

Thin films of oxides and sulfides of 3d metals are of actual interest from both the fundamental and technological points of view, given their use as catalytic [1], photovoltaic [2] and magnetic layers [3]. Due to the novel optical and electric properties, metal chalcogenide thin films have been used in optical and optoelectronic devices, such as solar energy absorbers, solar cells and photo detectors [4–6].

Limited studies on cobalt sulfide (Co_xS) thin films have been reported in the literature: by chemical bath deposition [7], by modified chemical bath deposition (MCBD) [8] (cobalt sulfide thin films were deposited on glass substrates using cobalt dichloride (CoCl_2) and sodium sulfide (Na_2S) aqueous solutions). Structural properties of the films were studied by X-ray diffraction and scanning electron microscopy [8].

Cobalt sulfide thin films on glass and fused-silica substrates have been prepared [9] by low-pressure CVD (chemical vapour deposition) using tris(diethyldithiocarbamate)cobalt(III), $\text{Co}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$, complex compound as a precursor.

In study [10], high capacitance at a high charge–discharge current density of 50 mA/cm^2 for a new type of electrochemical supercapacitor cobalt sulfide has been studied.

CoS_x was prepared by a very simple chemical precipitation method from Na_2S and $\text{Co}(\text{CH}_3\text{COO})_2$. It was shown [10] that CoS_x has excellent electrochemical capacitance at large charge–discharge current density.

In report [11], synthesis of CoS thin films on a glass substrate by a modified liquid phase chemical growth process is described. The growth solution consisted of CoSO_4 , ammonia and thiourea. Surface morphology showed a network of randomly oriented elongated grains threaded into each other.

In study [12], the hollow cobalt sulfide (CoS) hexagonal nanosheets (HNSs) from $\text{Co}(\text{NO}_3)_2$ and thioacetamide in the presence of poly(vinylpyrrolidone) (PVP) at 100°C under alkaline condition have been prepared. Chinese scientists [13] studied cathodic electrodeposition of highly porous cobalt sulfide counter electrodes for dye-synthesized solar cells. Different sweep cycle (charge capacity) had a great impact on the morphology and electrocatalytic activity of CoS films.

During the last decades we have extensively studied formation of electrically conductive copper sulfide (Co_xS_y) layers on the surface of polymers using a sorption–diffusion method. This new way of formation of metals chalcogenide layers on dielectric surfaces was found about 20 years ago [14–17]. It was attractive from a technological point of view because only two solutions have to be used.

* Corresponding author. E-mail: neringa.petrasauskiene@ktu.lt

In studies [16, 17], the layers of copper sulfide on PA were obtained for the first time by a sorption–diffusion method elaborated by us [18, 19]. The method consists of 2 stages. In the first stage – sulfurization of the polymer – PA films are treated with the solution of lower potassium polythionates ($K_2S_nO_6$, $n = 3-5$) or higher polythionic acid ($H_2S_nO_6$, $n = 12-33$), the molecules of which contain chains of divalent sulfur atoms, $-O_3S-S_{n-2}-SO_3^-$. In the second stage, the sulfurized polymer is treated with a solution of Cu(II/I) salts and thin layers of semiconductive and electrically conductive copper sulfides form on the surface of polymer [19].

The aim of the present work was to study the formation, chemical and phase composition of Co_xS_y layers on PA, formed by the sorption–diffusion method using solutions of dodecathionic acid, $H_2S_{12}O_6$.

EXPERIMENTAL

PA 6 (Tecamid 6, density 1.13 g/cm^3 , $500 \mu\text{m}$ thick) films used in this work were purchased from Ensinger Company, Germany. Prior to the experiments, to remove the remainder of the monomer, pieces of the film $15 \times 70 \text{ mm}$ in size had been boiled in distilled water for 2 h. Then they were dried with filter paper and kept in a desiccator over $CaCl_2$ for 24 h.

PA films were sulfurized in a thermostatic vessel up to 6 h at a temperature of $20-40 \text{ }^\circ\text{C}$ using a continually stirred $0.002 \text{ mol} \cdot \text{dm}^{-3}$ solution of $H_2S_{12}O_6$ prepared by the method given in [20]. At certain time intervals, the PA film samples were removed from $H_2S_{12}O_6$ solution, rinsed with distilled water, dried with filtration paper, left over $CaCl_2$ for 24 h and then used in further experiments and analysis.

Sulfur concentrations (C_s) in PA film samples were determined potentiometrically [21]. Firstly, a sample of a sulfurized PA film was treated under heating with $10-15 \text{ ml}$ of $10 \text{ mol} \cdot \text{dm}^{-3}$ KOH and diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used for the potentiometric titration of the solution obtained in KOH with $0.05 \text{ mol} \cdot \text{dm}^{-3}$ solution of iodine under stirring. For the potentiometric measurements, a pH-meter – pH-673 M millivoltmeter was used.

For the formation of Co_xS_y films the samples of sulfurized PA were treated with cobalt(II) ammonia complex solution at $78 \text{ }^\circ\text{C}$ which was prepared by mixing 340 volume parts of $0.16 \text{ mol} \cdot \text{dm}^{-3}$ $CoSO_4 \cdot 7H_2O$ solution with 100 volume parts of 25% NH_3 solution. The reductor – hydroxylamine sulfate ($(NH_2OH)_2 \cdot H_2SO_4 - 0.12 \text{ mol} \cdot \text{dm}^{-3}$) was added to obtain more stable solution [15].

The concentration of cobalt in a PA sample was determined using a Varian spectra-20 plus atomic absorption spectrometer [22: wavelength $\lambda = 240.7 \text{ nm}$, diffractive gap 2.0 nm , electrodeless discharge lamp, air-acetylene flame. For the standard conditions described above, the sensitivity of Co is $0.05-15 \mu\text{g} \cdot \text{cm}^{-3}$ for 1% absorption.

The phase composition of cobalt sulfide containing layers formed on PA was investigated by X-ray diffraction employ-

ing techniques with a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-K α radiation source ($\lambda = 1.54178 \text{ \AA}$) under a voltage of 30 kV and a current of 30 mA. The XRD patterns were recorded with a step of 0.05° from $2\theta = 30^\circ$ to 70° . X-ray diffractograms of PA samples with layers containing Co_xS_y were treated using Search Match, ConvX, Xfit and Excel programs to eliminate PA maxima.

The morphology of the surface of cobalt sulfide layers and the quantitative microscopy of the roughness of layers formed on the PA surface were studied with a scanning probe microscope Nanosurf EasyScan2 (AFM) and a scanning electron microscope (SEM, Raith e-LiNe). The characteristics of the atomic force microscope are the following: maximum scan range $110 \mu\text{m}$, maximum Z $22 \mu\text{m}$, drive resolution Z 0.34 nm , drive resolution XY 1.4 nm . The scanning electron microscope has the following characteristics: magnification $20-1\,000\,000$, detectors are secondary electrons and backscattered electrons, diameter of electron beam at 1 kV is 4 nm .

RESULTS AND DISCUSSION

The nature of sulfur-containing particles sorbed by a PA film earlier was studied by means of IR and UV absorption spectra of the polymer thin ($70 \mu\text{m}$ thick) films treated in a dodecathionic acid solution [23]. It was shown that the dodecathionate anions, $S_{12}O_6^{2-}$, are sorbed–diffused into PA films if they are treated with the water solution ($0.002 \text{ mol} \cdot \text{dm}^{-3}$, $20-50 \text{ }^\circ\text{C}$) of dodecathionic acid.

The study of the kinetics of sorption–diffusion of sulfur from the solution of dodecathionic acid into the PA film used in the present work showed (Fig. 1) that the concentration of sulfur in the samples ($C_s, \mu\text{mol} \cdot \text{cm}^{-3}$) during exposure in the solution of $H_2S_{12}O_6$ at $20, 30$ and $40 \text{ }^\circ\text{C}$ increased continuously with time.

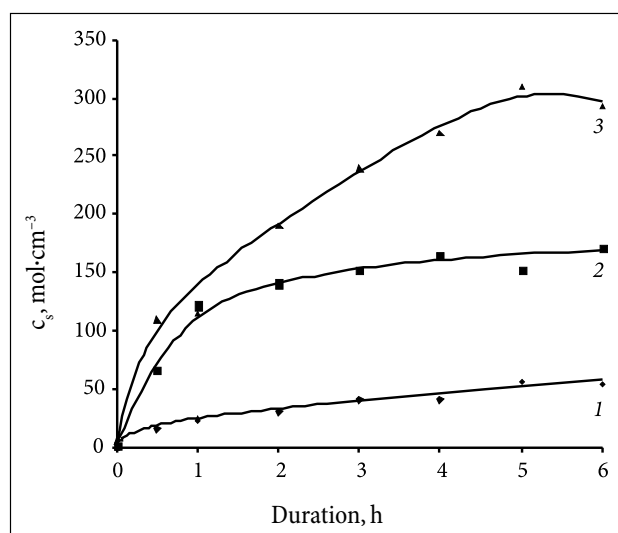


Fig. 1. Change of the S concentration in PA with time during its treatment with the $H_2S_{12}O_6$ solution at different temperature. The temperature, $^\circ\text{C}$: 1 – 20, 2 – 30, 3 – 40

These results show also that a higher sulfur concentration was obtained at a higher temperature.

The obtained results provided the conditions for the formation of the layers of cobalt sulfide, Co_xS_y , on the surface of the PA.

In order to form cobalt sulfide layers on the surface of sulfurized PA films, they were treated with the Co(II) salt solution. It was found that the concentration of cobalt in the sulfurized PA increased with the time of PA sulfurization in the $\text{H}_2\text{S}_{12}\text{O}_6$ solution, and a different concentration of cobalt in PA at each temperature is reached (Fig. 2).

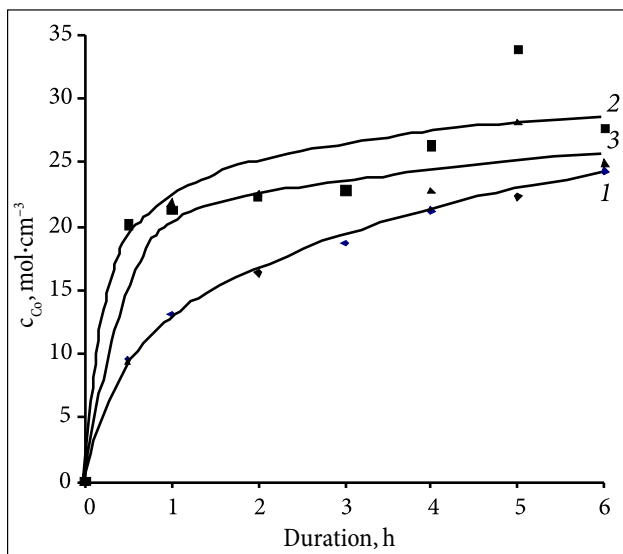


Fig. 2. Dependence of the concentration of cobalt in the PA film on its initial sulfurization duration at different temperatures. The temperature (°C) of sulfurization: 1 – 20, 2 – 30, 3 – 40

The general tendency is that the value of C_{Co} increases with the increase in temperature of the $\text{H}_2\text{S}_{12}\text{O}_6$ solution from 20 to 40 °C. That is completely understandable since with a higher concentration of sulfur sorbed–diffused into the PA a larger amount of cobalt ions may be involved in reaction with the sulfur species.

The results of XRD confirmed the formation of cobalt sulfide layers on the surface of PA. The phase composition of the layer changed depending on the conditions of initial treatment in $\text{H}_2\text{S}_{12}\text{O}_6$ solution. Figure 3 shows the XRD spectrum of PA samples sulfurized at different temperatures in the solutions of $\text{H}_2\text{S}_{12}\text{O}_6$ solution of different temperatures and different periods of time. All the main reflection peaks in Fig. 4 can be indexed as CoS (JCPDS Card 19-366), Co_3S_4 (JCPDS Card 42-1448) and Co_9S_8 (JCPDS Card 73-1442).

The morphology of films characterised by SEM (Fig. 4) shows a spongy structure formed by the network of plate-like crystallites. SEM photographs showed that the deposition density and size of the sorbed Co_xS_y particles on the PA 6 surface grew and depended on duration of the sulfurizing process.

The studies of Co_xS_y layer surface morphology by AFM have shown that depending on the duration and temperature of initial PA sulfurization in $\text{H}_2\text{S}_{12}\text{O}_6$ solution the formation of cobalt sulfide layers proceeds unevenly, in the form of islands which later grow into larger agglomerates. The surface of the layer formed is relatively uneven and rather rough (Fig. 5).

Crystallite height depends on the time of sulfurization (Fig. 5). When the polymer was chalcogenized 2 h at the temperature of 30 °C in $\text{H}_2\text{S}_{12}\text{O}_6$ solution, the height of the

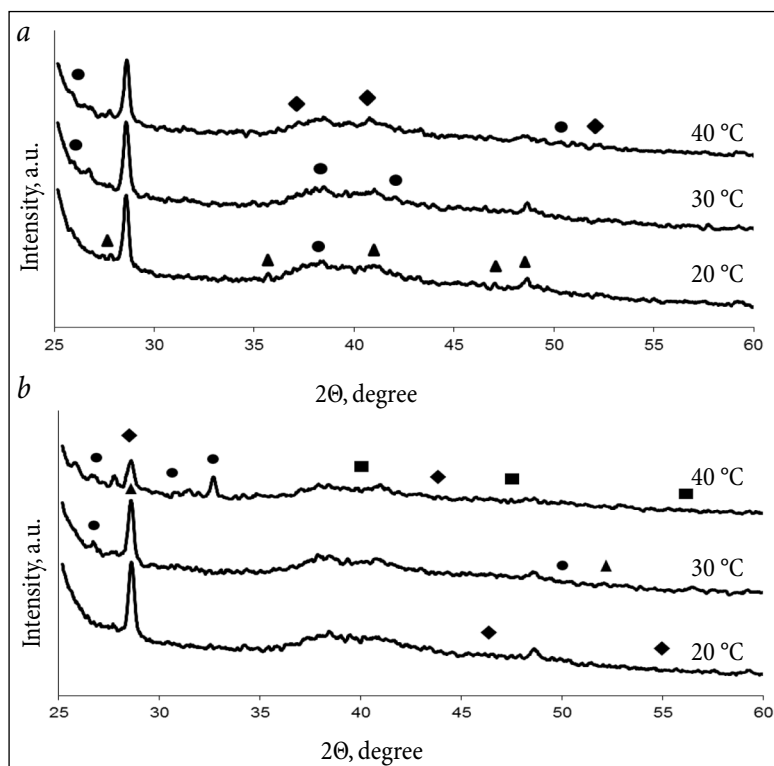


Fig. 3. XRD pattern of cobalt sulfide layers on PA. PA was sulfurized in $\text{H}_2\text{S}_{12}\text{O}_6$ solution and then treated with Co(II) solution. \blacktriangle CoS, \bullet Co_3S_4 , \blacklozenge Co_9S_8 , \blacksquare Co_6S_5 . Sulfurization time, h: a – 2, b – 4

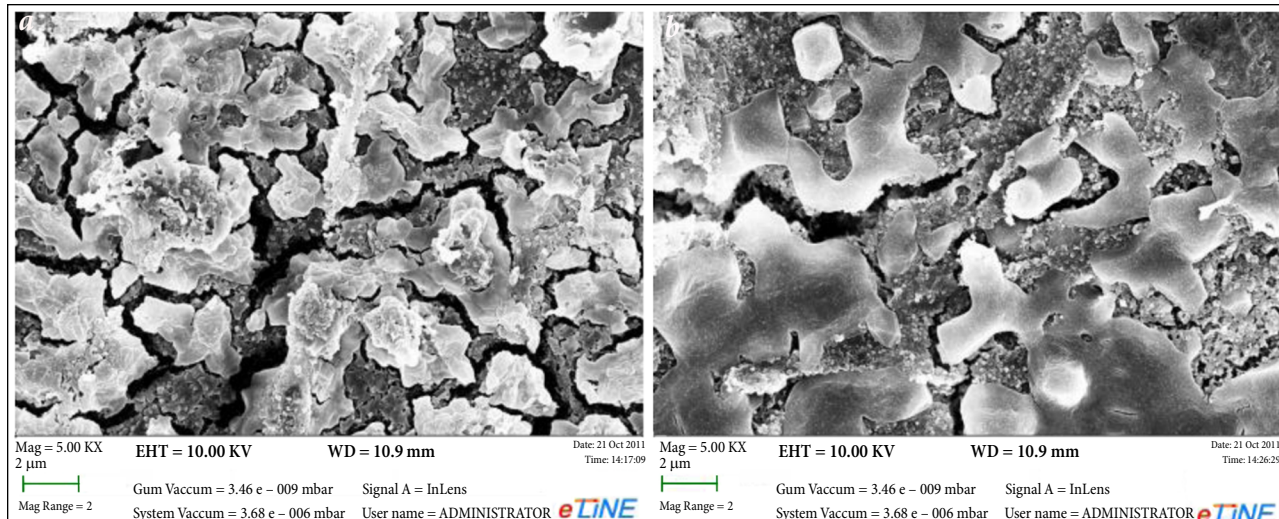


Fig. 4. SEM images of the Co_xS_y layers formed on the PA surface. PA was sulfurized at the temperature of 30 °C in $\text{H}_2\text{S}_{12}\text{O}_6$ solution and then treated with Co(II) solution. Sulfurization time, h: *a* – 2; *b* – 4

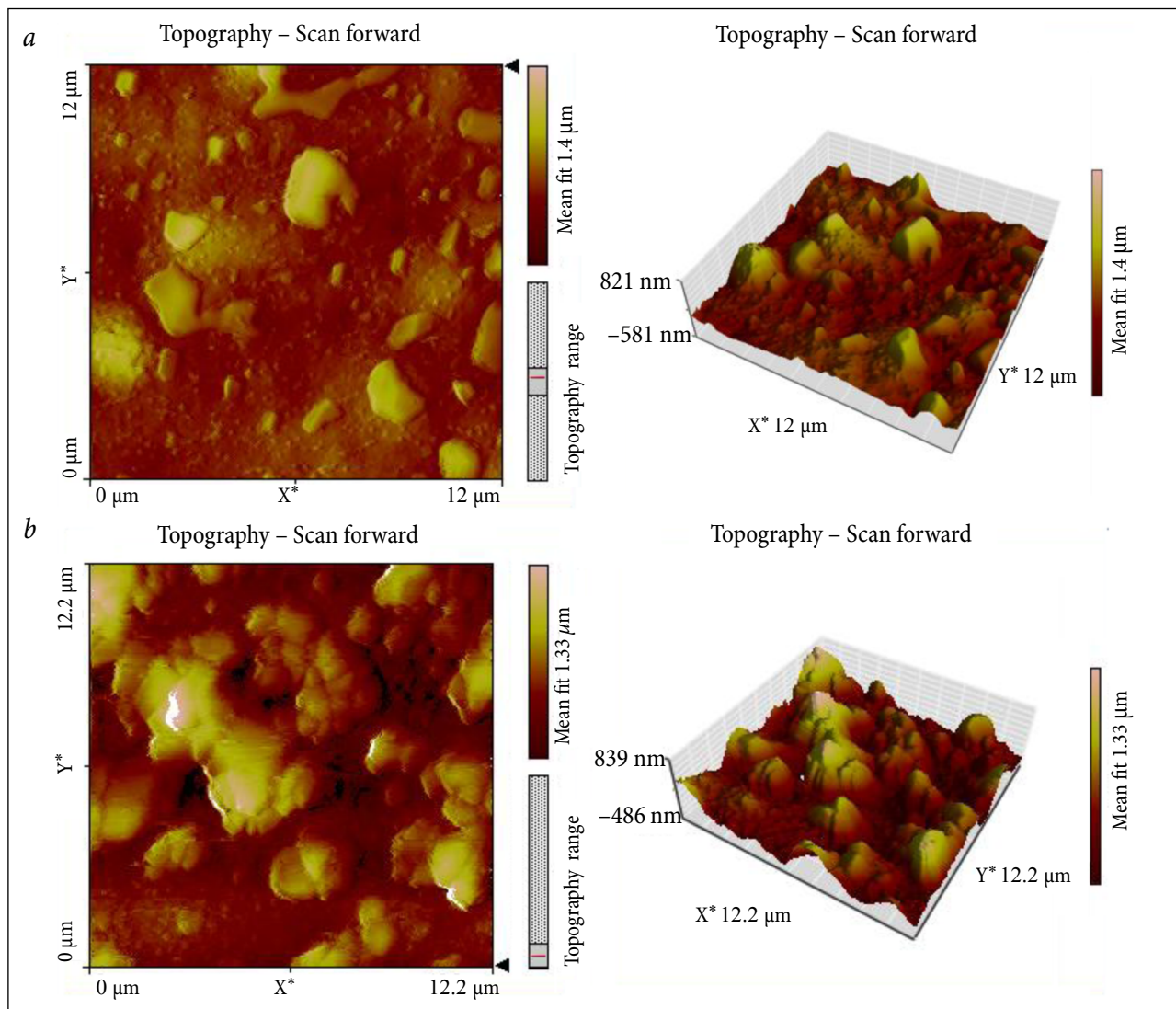


Fig. 5. AFM images of Co_xS_y layers formed on the PA surface: 2D views of lateral forces microscopy (*b*) and 3D topography views (*c*). PA was sulfurized at the temperature of 30 °C in $\text{H}_2\text{S}_{12}\text{O}_6$ solution and then treated with Co(II) solution. Sulfurization time, h: *a* – 2; *b* – 4

crystallites reaches 821 nm (Fig. 5a). On prolongation of sulfurization to 4.0 h, the height of crystallites increases only slightly – to 839 nm (Fig. 5b).

Thus, with increasing the sulfurization time from 2 to 4 h the height of crystallites changes. The reason may be the differences in the phase composition of Co_xS_y layers obtained at a different time. This was shown in our previous study of the X-ray diffraction of Co_xS_y layers formed on the PA film surface (Fig. 3).

CONCLUSIONS

1. The layers of cobalt sulfide, Co_xS_y , forms in the surface of the polyamide 6 film when the polymer is sulfurised in dodecathionic acid solution and later treated with a solution of Co(II) salt: the anionic particles $\text{S}_{12}\text{O}_6^{2-}$ containing sulfur atoms of low oxidation state react with the cobalt(II) ions.

2. The conditions of polymer sulfurization determine the concentration of cobalt and the composition of the sulfide layer: the concentration of cobalt in the polyamide 6 film increases with the increase of duration and temperature of the polymer sulfurization.

3. Changing the conditions of PA sulfurization leads to the formation of cobalt sulfide layers of different composition. The morphology of films characterised by SEM and AFM showed a spongy structure formed by the network of plate-like crystallites; the formation of cobalt sulfide layers proceeds unevenly, in the form of islands which later grow into larger agglomerates. The surface of the layer is relatively uneven and rather rough.

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KOBALTO SULFIDINIŲ SLUOKSNIŲ POLIAMIDO PAVIRŠIUJE SUDARYMAS SORBCINIŲ-DIFUZINIŲ METODU NAUDOJANT DODEKATIONATO RŪGŠTĮ $\text{H}_2\text{S}_{12}\text{O}_6$

Santrauka

Darbe tirtas kobalto sulfidinių sluoksnių (Co_xS_y) sudarymas poliamido paviršiuje sorbciniu-difuziniu metodu naudojant dodekationato rūgšties ($\text{H}_2\text{S}_{12}\text{O}_6$) tirpalus kaip sieros šaltinį. Sorbuotos sieros koncentracija didėja ($50\text{--}300\ \mu\text{mol} \cdot \text{cm}^{-3}$) ilginant sierinimo trukmę (iki 6 h) ir keliant dodekationato rūgšties tirpalo temperatūrą ($20\text{--}40\ ^\circ\text{C}$). Kobalto sulfidiniai sluoksniai poliamido paviršiuje gaunami veikiant įsierintą polimerą kobalto(II) druskos tirpalu. Kobalto koncentracija ($24\text{--}28\ \mu\text{mol} \cdot \text{cm}^{-3}$) gautuose sluoksniuose kinta ilginant sierinimo trukmę ir keičiant dodekationato rūgšties tirpalo temperatūrą. Gautų Co_xS_y sluoksnių sudėtis tirta rentgeno spindulių difrakcijos (XRD) metodu. Sluoksnių sudėtis priklauso nuo polimero apdoravimo $\text{H}_2\text{S}_{12}\text{O}_6$ rūgšties tirpalu trukmės ir koncentracijos. Nustatytos penkios kobalto sulfidų fazės: CoS , Co_3S_4 , Co_6S_5 , Co_9S_8 ir CoS_2 .

Skenuojančios elektroninės mikroskopijos (SEM) ir atominės jėgos mikroskopijos (AJM) metodai parodė akytą sluoksnių struktūrą.