Study of copper sulfide layers on a polyamide film formed by the use of higher polythionic acids

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Cu_xS layers on polyamide obtained by a sorption-diffusion method have been studied. These layers are formed when ions of higher polythionates and sulfur sorbed into polyamide react with a solution of Cu(I–II) salt. By potentiometric studies it has been determined that x varies in the interval $1 < x < 2$ in electrically conductive or semiconductive copper sulfide layers. The composition of the Cu_xS layer changes more significantly during the first 30 days in the direction of x decreasing. X-ray diffraction studies of the Cu_xS layers revealed six phases: with $x = 2$ (chalcocite), $x = 1.9375$ (djurleite), $x = 1.75$ (anilite), $x = 1.12$ (yarrowite), $x = 1.06$ (talnakhite), and $x = 1$ (covellite). The phase composition of the Cu_xS layer depends on the period of keeping in Cu(I–II) salt solution and on the sulfur concentration in the polyamide.

Key words: *polyamide; polythionic acid; sulfurisation; layer of copper sulfide*

1. Introduction

Semiconductive and electrically conductive composites have been widely studied and used in various fields of modern technology. Polyamides (PAs) with layers of copper sulfides belong to this group of composites. These modified polymers may be used as conductive substrates for the deposition of metal [1–3], as semiconductors [1, 4], gas sensors functioning at temperatures tending to room temperature [5, 6], as polarizers of infrared radiation [7] or solar absorber coatings [8].

Copper sulfide films are formed mainly in two ways: by treating a polymer containing an absorbed sulfurisation agent with a solution of a metal salt or by the sulfurisation of metal compounds absorbed in a polymer. Various solutions can serve as agents for the sulfurisation of polymers, e.g. sodium polysulfide (Na_2S_n, $n = 4.8$) aqueous solutions [9], polythionic acid ($H_2S_nO_6$, $n = 9$–45) aqueous solutions [10]. Hydrophobic polymers adsorb elemental sulfur from Na_2S_n [11] or $H_2S_nO_6$ [10] solu-

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tions. Hydrophilic and semi-hydrophilic polymers, including PA are capable of absorbing ions of various electrolytes from aqueous solutions [12]. Therefore, PA absorbs polysulfide ions from sodium polysulfide solution [13] and polythionate ions from polythionic acid solution [14]. Unfortunately, a solution of polysulfide is highly alkaline at high concentrations (about 2 mol/dm^3), therefore this agent is suitable only for the sulfurisation of alkali–resistant polymers.

In this study, layers of copper sulfide on PA were obtained by the sorption −diffusion method developed by us [15], using 2 mmol/dm^3 solutions of polythionic acids. Copper sulfide layers on PA are formed via heterogeneous chemical reactions [16]:

$$S_nO_6^{2-} + 2Cu^+ + 2H_2O \rightarrow Cu_2S + (n-3)S + 2H_2SO_4 \tag{1}$$

$$2xCu^+ + 1/8S_8 \rightarrow Cu_xS + xCu^{2+} \tag{2}$$
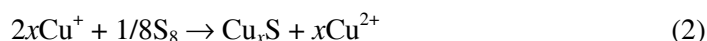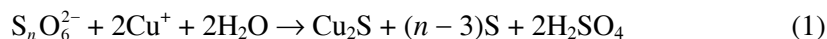
Molecules of elemental sulfur in PA are formed [14] as a result of the known decomposition [17] of higher polythionic acids:

$$H_2S_nO_6 \rightarrow H_2S_{n-x}O_6 + xS \tag{3}$$

The rate of decomposition at elevated temperatures is significantly higher than at room temperature.

In the first stage of the process, the ions of higher polythionates diffuse into PA when it is kept in a solution of higher polythionic acid ($H_2S_nO_6$, $n = 9$–45) [14, 16]. In the second stage, sulfurised PA is treated with a solution of Cu(II) sulfate containing hydroquinone as the reducing agent [15, 16].

The usefulness of composites obtained by modifying polymers with layers of copper sulfide is determined by their electrical properties, which vary significantly even when the chemical composition is only slightly changed [9, 18]. The electrical resistance itself increases over 6 times when the value of x in Cu_xS is increased from 1 to 2 [19]. Therefore, electrical measurements enable preliminary information about the composition of the layer to be obtained. The composition can be more precisely determined by X-ray diffraction studies.

The aim of the present work was to study the phase composition of copper sulfide in PA formed by the sorption-diffusion method, using highly sulfurised $H_2S_nO_6$ ($n = 21$–33), on the basis of potentiometric measurements and X-ray diffraction analysis.

2. Experimental

The layers of copper sulfide were deposited on a PA PK-4 (specification TY 6-05 -1775-76) film 70 μm thick. Samples 15×70 mm^2 in size were used. The samples were boiled before sulfurisation in distilled water for 2 h in order to remove the remainder

of the monomer. Then they were dried using filter paper and subsequently over $CaCl_2$ for 24 h [14].

PA samples were exposed to a solution of polythionic acid. The average number of sulfur atoms n in a molecule of $H_2S_nO_6$ was established by the methods described in Ref. [20]. PA was treated in a thermostatic vessel, using a continually stirred $H_2S_nO_6$ solution. Polythionate ions, $-O_3S-S_n^{2-}-SO_3^-$, i.e. the anionic particles containing the chains of divalent sulfur atoms [21], were incorporated into PA. Then the samples were removed, rinsed with distilled water, dried over $CaCl_2$, analyzed, and then used in further experiments.

Samples of sulfurised PA were treated with the solution of a mixture of univalent and divalent copper salts (Cu(I–II) salt, containing 0.34 mol/dm^3 of Cu(II) salt and 0.06 mol/dm^3 of Cu(I) salt) prepared from crystalline $CuSO_4·5H_2O$ and hydroquinone [16, 22]. Then they were rinsed with distilled water and dried over $CaCl_2$. The amount of sulfur in PA samples was determined by the amount of iodine used for the complete oxidation of polythionates diffused into PA [23]. The amount of copper in PA samples was determined by AAS [24].

The electrode potentials of PA films with Cu_xS layers were measured in the acidic solution of cupric sulfate by a universal EB-74 ionometer.

The phase composition of copper sulfide layers was investigated by X-ray diffraction using a DRON-6 diffractometer (CuK$_\alpha$ radiation). X-ray diffractograms of PA samples with layers of Cu_xS were analysed using the programs "Search Match", "ConvX", "Xfit", and "Microsoft Excel" to eliminate the maxima of PA.

3. Results and discussion

In our previous study [16], we found that the physical properties of PA films with deposited layers of Cu_xS, for instance their electrical conductivity, are determined by the concentration of sorbed sulfur in PA and by the treatment conditions of sulfurised PA in the solution of Cu(I–II) salt. Cu_xS is a p-type semiconductor, having hole conductivity. The most conductive sulfide layer is the one with the composition close to CuS [25]. CuS is distinguished among the binary (1:1) metal sulfides due to its mixed-valency and unique structure, which contains both monosulfides and disulfides. In CuS, the formal charge [26] of Cu is +1 and the average charge of S is –1. The Cu^{2+} ion is a relatively strong oxidizer, capable of oxidizing sulfide to a disulfide ion. During this process, the one missing d-electron (hole) of the d^9 configuration is transferred to the sulfur. Therefore, Cu is essentially monovalent in copper sulfides. In CuS, the electron deficiency (holes) in S is partially relieved by the formation of S–S bonds (for two-thirds of the S atoms) and partially delocalized through the p-band of S, which gives a formalism of $(Cu^+)_3(S_2^{2-})(S^-)$ or $(Cu^+)_3(S_2^-)(S^{2-})$. Thus, CuS exhibits an ideal metallic behaviour [27].

We have established [16] that at lower sorbed sulfur concentrations in PA, thin copper sulfide layers of low electrical conductance are formed. When the sulfur con-

centration is sufficient and the period of interaction with copper salt is rather short, more conductive layers are obtained, since their composition (according to the data of chemical analysis) differs significantly from that of Cu_2S. After keeping such sulfurised films in a solution of copper salt for a long time, copper ions diffusing into the sulfide layer change not only its thickness, but also its stoichiometric composition [16]. Simultaneously, these ions fill the vacancies in the copper lattice and increase the x value. The composition of layers approaches that of Cu_2S, and its conductivity decreases. Thus, having measured resistance, one can determine the surface layer composition. The approximate composition of copper sulfide layers can be estimated according to their electrode potentials. The aqueous electrochemical method is ideal for studying phase equilibria of binary sulfides, since stable and metastable assemblies can be differentiated and phase fields accurately delineated [28]. It is known [28] that the composition of copper sulfides can be estimated according to their electrode potentials in acidic $CuSO_4$ solution when the following reversible reaction takes place [29]:

$$Cu_xS \leftrightarrow Cu_{x-y}S + yCu^{2+} + 2ye \tag{4}$$

It has been pointed out that the potentials are practically independent of the composition of the electrolyte. The electrode potential was measured in the electrochemical cell $Cu|aq. CuSO_4 + H_2SO_4|Cu_xS$ [28].

When the value of x in copper sulfides increases, the electrode potential against copper over the temperature range of 0–105 °C decreases from 280 mV to 0 mV. The potential for low chalcocite was 0–125 mV, djurleite – 125–145 mV, anilite – 145–165 mV, covellite – 165–280 mV, sulfur – ≥ 280 mV [28]. The results of experiments [16, 30] show that the sulfide layer composition continued to change after 30 days following its formation.

Copper and sulfur form five solid phases stable at room temperature, two of which are stoichiometric, i.e. CuS (covellite) and Cu_2S (chalcocite), while the remaining three are non-stoichiometric: $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite) and $Cu_{1.95}S$ (djurleite). Copper and sulfur form also a number of mixed phases [31]. At 27 °C, the stable phases are CuS, $Cu_{1.75}S$, $Cu_{1.95}S$ and Cu_2S [32]. In the present study, all the measured potential values were less than 280 mV and greater than 0 mV. Consequently, by depositing the sulfide layers using the method of the sorption-diffusion, copper sulfide (Cu_xS) layers with x varying in the interval $1 < x < 2$ were obtained.

The potentials of Cu_xS layers on PA were measured 1 hour and 1, 10, 30, and 60 days after its formation. The results obtained show that the potentials of these layers are higher when PA is sulfurised in a solution of polythionic acid $H_2S_nO_6$ with a higher value of n for a longer time [14, 16] and at higher temperatures. Under these conditions, the polymer structure [30] undergoes the most intensive amorphization, resulting in more favorable conditions for the diffusion of sulfur compounds. In our opinion, there is a possibility of chemisorption of polythionic acids. In aquatic, neutral, and slightly acidic medium, polycaproamide functional groups (–COOH and –NH$_2$) are ionized, i.e. contain protonated amino ($-NH_3^+$) and carboxylic (–COO$^-$)

groups [33]. A variety of new effects become important insofar as the interactions of inorganic sorbates with PA are concerned, i.e. electrostatic interaction of $S_{n-2}(SO_3)^{2-}$ with the sorbent and exchange reactions of these ions with ligands previously bound to the polymer surface or their ionized functional groups.

Ionic strength of the solution and ionic competition also affect the sorption to charged sorbent groups, especially if inorganic ions compete for binding sites. The most probable mechanism for the other interaction involves chemical bonding of the charged sorbate ions $S_{n-2}(SO_3)^{2-}$ to the surface or to some functional groups of the solid phase. A surface reaction forms other sorbed species, different from inorganic ions dissolved in the proximity of the surface. A special role must also be attributed to the interaction of copper ions (Cu^{2+}, Cu^+) with the sorbed products. Sulfur, either as a free chalcogenide ion, or covalently bound to the amido group of PA, behaves as a very effective Lewis base towards many transition metals, e.g. iron, copper, zinc and molybdenum [34]. Potentiometer readings showed a decrease in the molar ratio Cu:S; i.e. the composition of Cu_xS changes in the direction of decreasing x with the increase of c_s in the polymer sulfide layer.

The results of our research show that copper ions only slightly diffuse into boiled PA. After 30 min of treatment in a solution of copper salt, the mass of non-sulfurised PA increases by 1−3%. X−ray structural tests of PA show [30] that the acidic medium as well as PA interaction with $S_nO_6^{2-}$ ions drastically changes the crystal structure of PA. Favorable conditions for the fast and easy diffusion of copper ions into PA are formed. This is proved by Cu:S molar ratios (Table 1) calculated after having kept the PA sample in $H_2S_nO_6$ and copper salt solutions. In our opinion, the molar ratios of the amounts of copper and sulfur in PA at the beginning were twice higher due to the adsorption of copper compounds onto the surface of the formed layer. The longer PA is kept in $H_2S_nO_6$ solutions the more the structure of PA changes and more $S_nO_6^{2-}$ ions diffuse, and, consequently, diffusion of copper ions through the sulfide layer is obstructed to a greater extent.

Table 1. Molar ratios of Cu/S in layers of copper sulfide[*]

Duration of treatment[**] (min)	4	6	10	15	20	30	60
Cu:S	2.62	2.10	2.10	1.59	1.71	1.46	1.18

[*]The duration of treatment with the solution of Cu(I–II) salt was 15 min
[**]With the solution of $H_2S_{21}O_6$

The change in potential with time shows that the composition of the Cu_xS layer changes in the direction of decreasing x. This change is particularly noticeable during the first 30 days, when the surface potentials grow on average by 15 mV. The measurements of the potential after 1, 2, and 3 months show that it does not change (Fig. 1).
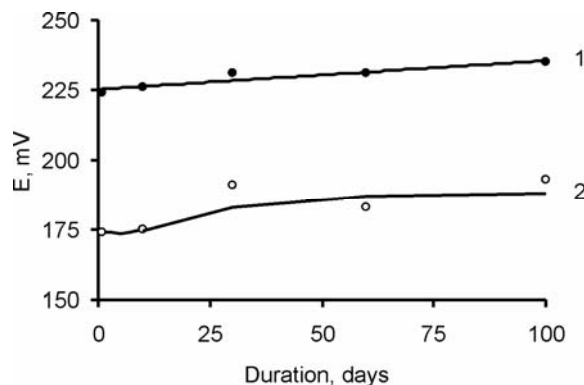
Fig. 1. The time dependences of the electrode potential of copper sulfide layers
formed on PA. PA was treated with $H_2S_nO_6$ solution
at 50 °C for 30 min. The average number of sulfur atoms
in $H_2S_nO_6$ molecules, n: 1 – 33; 2 – 23

In this case, changes in the composition of the Cu_xS layer are caused by factors other than changes in the structure of PA. A small potential of the surface of Cu_xS layer in 1 hour after its formation shows that the composition of layers aproaches $Cu_{1.75}S$. These high values of x can be attributed to the agility of copper ions, slow stirring of copper salt solution, swelling of PA in highly sulfurised $H_2S_nO_6$ solutions, and to its more activated surface. In the course of time, however, due to the interaction of the copper sulfide layer with unreacted elemental sulfur and polythionate ions remaining in the polymer, the phase composition of the outer layer changes; x decreases and the potential increases. The following solid-phase reactions proceed:

$$(x - y)Cu_xS + yS \rightarrow xCu_{x-y}S \tag{5}$$

$$(x - y)Cu_xS + yS_nO_6^{2-} \rightarrow xCu_{x-y}S + yS_{n-1}O_6^{2-} \tag{6}$$
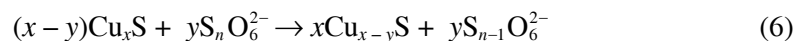
The stoichiometric composition of Cu_xS layers changes more significantly during the first 30 days (Fig. 1). Several phases of copper sulfides are metastable. Consequently, solid-state transformations take place: the metastable forms of copper sulfides may convert to the thermodynamically more stable ones. For example, after a few hours, the high digenite ($Cu_{1.805}S$) inexorably began to convert into the low digenite ($Cu_{1.765}S$), which, in turn, converts to anilite ($Cu_{1.750}S$) [28]. At 41 °C, anilite decomposes into CuS and low digenite, whereas low digenite transforms into high digenite around 82 °C [32].

The potential of the Cu_xS layer on PA depends on the time PA is kept in $H_2S_nO_6$ solution (Fig. 2). Up to 60 minutes in $H_2S_nO_6$ ($n = 33$) solution results in the prevalence of CuS with an average phase composition of $Cu_{1.75}S$. An interval of 60–120 min shows a marked increase in the potential, and the layer phase composition approaches CuS and remains almost stable. The Cu:S molar ratio, however, changes only by 0.03 after 60–120 min. Thus, after 2 hours the destruction of PA is high and the sulfide layer is

uniform enough not to obstruct the diffusion flow. This results in a Cu_xS layer possessing fewer copper-containing phases. Measurements of the potential after 30 days show that they changed more for PA soaked in $H_2S_nO_6$ solution for a shorter time (Fig. 2, curves 2 and 4). The potentials of PA soaked for longer times changed insignificantly. This proves that diffusion processes are faster in PA with a more destructed crystalline structure, due to a slighter blocking effect of the sulfide layer.
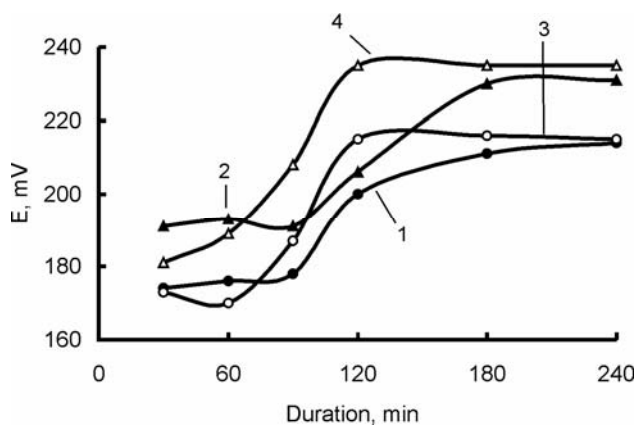

Fig. 2. The dependence of the electrode potential of copper sulfide layers
formed on PA on the duration of treatment with a solution
of $H_2S_nO_6$ at 50 °C. The average number of sulfur atoms
in $H_2S_nO_6$ molecules, *n:* 1, 2 − 21; 3, 4 − 33. The electrode potentials
were measured after: 1, 3 − 1 h; 2, 4 − 30 days

The potential of a Cu_xS layer on PA kept in $H_2S_nO_6$ for a shorter time changes in a different manner (Fig. 3).
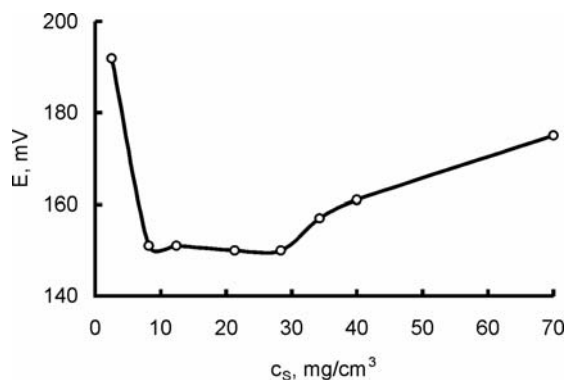

Fig. 3. The dependence of the electrode potential of copper sulfide layers
formed on PA on the sulfur concentration in the polymer.
PA samples were treated with the solution of $H_2S_{21}O_6$ at 50 °C.
The duration of treatment with a solution of Cu (I–II) salt was 15 min

During the first 8 minutes, there is a sudden drop in the potential, followed by the stabilization of a phase for about 20 min. After this, the potential of the Cu_xS layer starts to slowly increase. This indicates that the Cu_xS layer is immediately formed on the polymer surface, its uniformity being higher if PA structure is less destroyed. Further changes in potential are related to changes in the phase composition, due to slow diffusion of copper ions through the sulfide layer as well as by its reaction with sulfur compounds in the deeper layers of a polymer.

While changing the interaction time of PA with copper salt solution, the potential of Cu_xS layers changes as well (Fig. 4). It can be noted that a sulfide layer with a predominant phase close to CuS forms on the polymer surface during the first 5 minutes of interaction with copper salt solution. It has not yet "blocked" the movement of the diffusion stream, therefore it takes 5 minutes of interaction for the uniformity of the layer to start growing and the value of x to reach ~1.75. After 12−15 minutes, a sufficiently compact layer is formed, significantly slowing copper ion diffusion into the bulk of the polymer, and the phase with $x = 1.75$−1.95 becomes predominant.
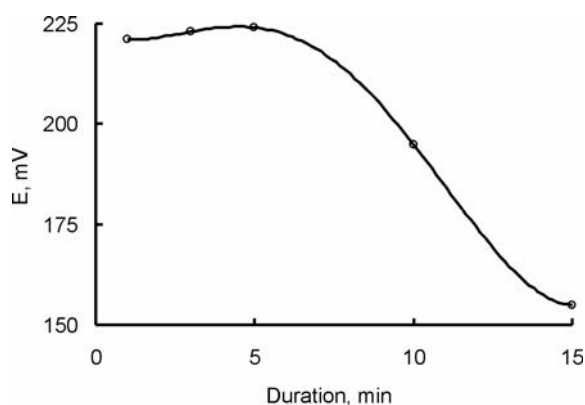

Fig. 4. The dependence of the electrode potential of copper sulfide layers formed on PA on the duration of treatment with a solution of Cu(I–II) salt at 78 °C. PA samples were treated with a solution of $H_2S_{21}O_6$ at of 50 °C. The concentration of sulfur in PA was 70.0 mg/cm^3

An increase of the temperature of $H_2S_nO_6$ solution influences the composition of Cu_xS layers slightly more at temperatures above 40 °C (Fig. 5); it does not depend significantly, however, on the number of sulfur atoms n in $H_2S_nO_6$ molecule.

Potentiometric tests of Cu_xS layers allow only a relative determination of the phase composition of the layer formed on the polymer surface. The value of potential highly depends on the number of copper ions absorbed in PA and on the degree of the polymer swelling resulting from a non-uniform sulfide layer. According to the data in [32], the potential of the $Cu_{2-x}S$ electrode in a solution of cupric salts is nearly always more positive than the potential of the Cu electrode under the same conditions, and the placement of both electrodes in the same cell containing Cu^{2+} ions should give the following reactions:

$$Cu(s) + Cu^{2+}(aq) \rightarrow 2Cu^+ \tag{7}$$

$$Cu_{2-x}S(s) + 2yCu^+ \rightarrow Cu_{2-x+y}S(s) + yCu^{2+}(aq) \tag{8}$$
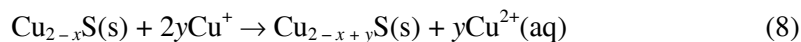
The sulfide electrode should, hence, be continuously reduced and change its composition during an experiment. Therefore, X-ray phase tests were applied to specify the data on the phase composition of the sulfide layer.
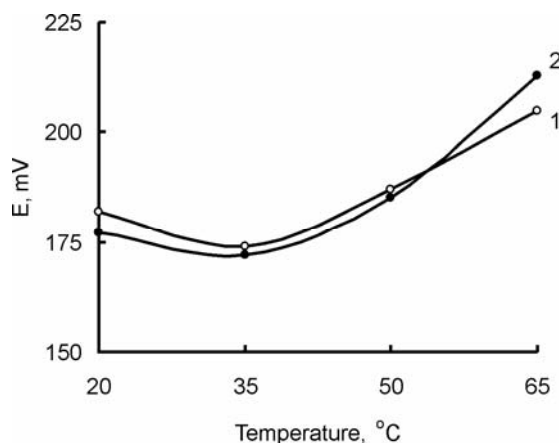

Fig. 5. The dependence of the electrode potential of copper sulfide layers
formed on PA on the temperature of the $H_2S_nO_6$ solution.
The average number of sulfur atoms in $H_2S_nO_6$ molecules, n: $1 - 21$; $2 - 27$

The phase composition of the deposited film was established by comparing its X-ray images with those of known minerals [35–37]. The chemical composition and crystal structure of the majority of Cu_xS minerals, such as chalcocite (Cu_2S), djurleite ($Cu_{1.95}S$), yarrowite ($Cu_{1.12}S$), and covellite (CuS) were investigated [38]. The crystal structure of Cu_xS depends on the chemical composition and conditions of synthesis. The composition of Cu_xS deposited by chemical methods has been scarcely investigated.

Structural studies of Cu_2S layers deposited by sorption-diffusion methods are limited by the polycrystallinity of the layers obtained, by the existence of Cu_xS phases with various compositions and structures, and by the crystallinity of the PA film itself. The intensities of its maximum at $\theta < 130°$ exceeds the intensity of copper sulfide maximum a few times. Therefore, the region of $2\theta \geq 26.0°$ was investigated in detail.

When keeping PA samples with the sorptive polythionate anions for different periods of time in copper salt solution at 78 °C, Cu_xS layers of different compositions we obtained. X-ray diffractograms of the layers showed the peaks of not one but various copper sulfide phases (Figs. 6 and 7).

The monoclinic djurleite ($Cu_{1.9375}S$) prevails (peaks at $2\theta = 33.96$, 35.30, 37.30, 38.41, 40.57, and $48.02°$) in the composition of sulfide films on PA, initially sulfurised for 4 min (Fig. 6, curve 1) in $H_2S_{21}O_6$ solution at 50 °C (the time of the sulfurised PA treatment with Cu(I–II) salt solution was 15 min, the temperature of the

Cu(I–II) salt solution was 78 °C). Phases of orthorhombic anilite ($Cu_{1.75}S$) (peaks at $2\theta = 36.30$ and $46.02°$) and chalcocite (Cu_2S) (peak at $2\theta = 49.01°$) are also present in the layers. When the time of treatment in the polythionic acid solution is prolonged to 10 min, changes in film composition occur: the intensity increases for the peaks at $2\theta = 38.41$, 40.57, and $48.02°$ of monoclinic djurleite and for the peak of orthorhombic anilite at $2\theta = 46.02°$. A new phase in the composition of the sulfide film on PA – a phase of hexagonal yarrowite ($Cu_{1.12}S$, peaks at $2\theta = 43.51$ and $47.12°$) also appears. As soon as after 15 minutes of PA treatment in a solution of $H_2S_{21}O_6$, the orthorhombic anilite phase peaks at $2\theta = 34.73$, 36.30, 42.61, 46.02, 49.59, 50.17, and $50.72°$ predominate in the composition of sulfide layers (Fig. 6, curve 3).
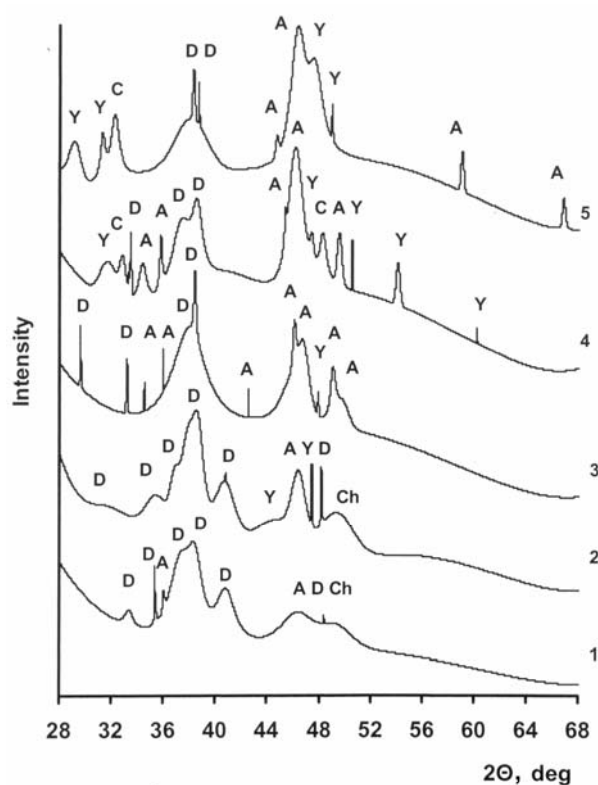

Fig. 6. X-ray diffraction patterns of layers of Cu_xS on PA (peaks of: D – djurleite, A – anilite, Ch – chalcocite, Y – yarrowite, C – covellite). PA was initially treated with a solution of $H_2S_{21}O_6$ at 50 °C for different times (τ_s, min) and subsequently with a Cu(I–II) salt solution for 15 min. The concentration of sulfur in the polymer c_s [mg/cm³]: 1 – 2.5 ($\tau_s = 4$); 2 – 21.3 ($\tau_s = 10$); 3 – 28.4 ($\tau_s = 15$); 4 – 40.0 ($\tau_s = 30$); 5 – 70.0 ($\tau_s = 60$)

After 30 minutes of initial PA sulfurisation, new peaks at $2\theta = 31.10$, 50.64, 54.15, and $60.06°$ for hexagonal yarrowite (Fig. 6, curve 4) and peaks at $2\theta = 32.82$, 44.82, and $47.47°$ for hexagonal covellite (CuS) appear in the diffractograms. When

the time of treatment in $H_2S_21O_6$ solution is further prolonged, the hexagonal yarrowite and orthorhombic anilite phases become dominating in the sulfide layers on PA.
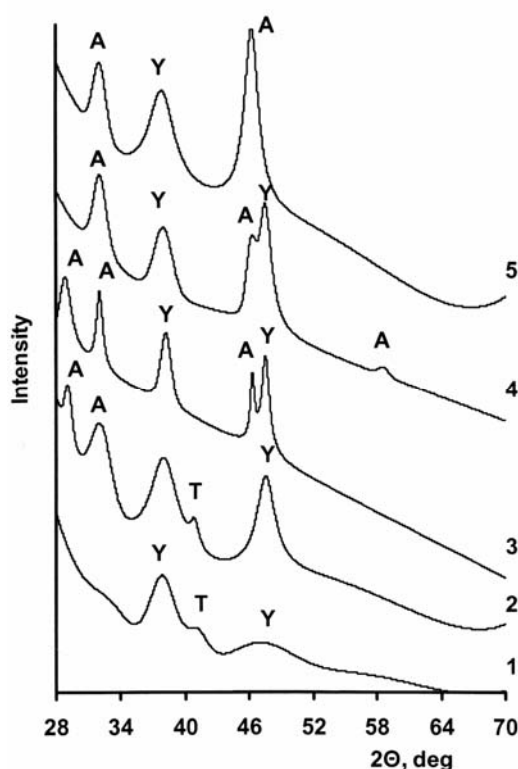

Fig. 7. X-ray diffraction patterns of layers of Cu_xS on PA (peak of: T – talnakhite, Y – yarrowite, A – anilite). The sulfur concentration in PA was 70.0 mg/cm^3. The period of treatment with a Cu(I–II) salt solution at 78 °C: 1 – 1 min; 2 – 3 min; 3 – 5 min; 4 – 10 min; 5 – 20 min

X-ray diffractograms of PA sulfurised under the same conditions ($H_2S_{21}O_6$, 50 °C, sulfur concentration in PA c_s = 70 mg/cm^3) and treated for various periods of time in the solution of Cu(I–II) salt at 78 °C are presented in Fig. 7. After 1-min treatment, peaks at 2θ = 38.4 and 47.7°, due to hexagonal yarrowite, and a negligible peak at 2θ = 40.6°, due to cubic talnakhite ($Cu_{1.06}S$), are noticeable (Fig. 7, curve 1). When the treatment time in the Cu(I–II) salt solution is prolonged (3 and 5 min), the intensities of the peaks of yarrowite increase and new peaks of orthorhombic anilite at 2θ = 29.1, 32.1, and 46.3° appear in the patterns (Fig. 7, curves 2 and 3). On further prolongation of the time of sulfurised PA treatment in Cu(I–II) salt solution (10 and 20 min), the intensities of the anilite peaks increase and those of the yarrowite peaks decrease (Fig. 7, curves 4 and 5). Consequently, when the concentration of sulfur in PA is the same and treatment time in Cu(I–II) salt solution is prolonged, the phase composition of the layer obtained becomes uniform. After 20 minutes, the anilite phase remains the

dominating phase in the sulfide layer. Hence, in the course of sulfurised PA treatment in Cu(I–II) salt solution, the phase composition of Cu_xS films changes in the direction of increasing x.

4. Conclusions

Cu_xS layers on polyamide (PA), obtained by the sorption-diffusion method using highly sulfured polythionic acids ($H_2S_nO_6$, $n = 21–33$) were studied. These layers are formed when ions of higher polythionates and sulfur sorb into polyamide and react with a solution of copper (I–II) salt. The approximate composition of copper sulfide layers on PA was determined on the basis of potentiometric measurements and X-ray diffraction analysis. It was determined by potentiometric studies that the value of x in the composition of copper sulfide layers varies in the interval $1 < x < 2$. The potential of copper sulfide layers increases with increasing sulfur concentration diffused into the polymer. Due to the interaction of the copper sulfide layer formed with unreacted elemental sulfur remaining in the polymer, the phase composition of the outer layer changes; the value of x decreases, resulting in an increase in the potential of the Cu_xS layer. The composition of Cu_xS layers changes more significantly during the first 30 days in the direction of decreasing x. By the X-ray diffraction studies it was determined that the Cu_xS layers obtained are composed of six phases, comprising monoclinic djurleite ($Cu_{1.9375}S$), orthorhombic anilite ($Cu_{1.75}S$), chalcocite (Cu_2S), cubic talnakhite ($Cu_{1.06}S$), hexagonal yarrowite ($Cu_{1.12}S$), and hexagonal covellite (CuS). The ratio between the concentrations of these phases depends on the duration of polyamide sulfurisation in a solution of polythionic acid and on the time of sulfurised polymer treatment with the copper (I–II) salt solution. Djurleite prevails in the composition of Cu_xS film if PA is sulfurised shortly (a few minutes) in a solution of $H_2S_nO_6$. When the duration of sulfurisation is prolonged, the maxima of djurleite slightly decrease and the maxima of anilite increase. On further prolongation, the phases of anilite and yarrowite become dominating. When polyamide sulfurised under the same conditions is shortly treated (few minutes) in a solution of copper(I–II) salt, the yarrowite, talnakhite, and anilite phases are detected. If treatment in the Cu(I–II) salt solution is prolonged, the formation of a sulfide phase containing more copper, namely anilite, is observed. Thus, in the course of sulfurised polyamide treatment with the solution of Cu(I–II) salt, the phase composition of Cu_xS film changes and x increases.

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