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ANALYSIS OF THE COMPOSITION AND MORPHOLOGY OF PRODUCTS OF THE ANODIC DISSOLUTION OF Cu₂S

ANALIZA SKŁADU I MORFOLOGII PRODUKTÓW ANODOWEGO ROZTWARZANIA Cu₂S

The anodic dissolution of copper (I) sulphide in an electrolyte with a composition similar to that of refining electrolyte leads after a sometime to a potential jump. Any of the following may bring about the occurrence of the potential jump: crystallisation of $CuSO_4$ within anode pores, the appearance of copper hydroxides, the appearance of an extremely slowly dissolving CuS layer on the surface of the sulphide, or the presence of elemental sulphur which blocks the anodic reactions.

The composition and morphology of the products of the electrolysis of powder and solid anodes dissolved by applying a current with an anodic density ranging between 100 and 500 A/m^2 has been investigated. The phase composition of the surface layers of powder granules was examined by means of X-ray analysis, mass spectroscopy, and linear micro-X-ray analysis. The topography of Cu_2S granule surface before and after dissolution was observed in polarised light and also by using a scanning microscope or an atomic force microscope (AFM).

Changes were observed in the chemical and phase composition of the surface layers of powder granules. Instrumental methods were applied in order to determine the presence of copper (II) sulphide and elemental sulphur. Copper (II) sulphide (CuS) constitutes the dominant phase. Elemental sulphur is present in small quantities, difficult to detect. No traces of hydrated $CuSO_4$ or copper hydroxides were detected. Changes in phase composition are accompanied by changes in surface topography, i.e. the surface undergoes distinct development. Fractures along the boundaries of sulphide crystals appear, and they make it possible for the electrolyte to penetrate within the material.

Anodowe roztwarzanie siarczku miedzi (I), w elektrolicie o składzie zbliżonym do stosowanego w elektrorafinacji miedzi, prowadzi po pewnym czasie do wystąpienia skoku potencjału. Powodem wystąpienia skoku potencjału mogą być: krystalizacja $CuSO_4$ wewnątrz porów anody, pojawienie się na powierzchni siarczku warstewki wodorotlenków

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miedzi, warstewki roztwarzającego się bardzo wolno CuS lub obecność siarki elementarnej blokującej reakcje anodowe.

Badano skład oraz morfologię produktów elektrolizy anod proszkowych i litych roztwarzanych prądem o anodowej gęstości pomiędzy 100 a 500 A/m². Skład fazowy warstewek powierzchniowych ziaren proszku badano za pomocą analizy rentgenowskiej, spektroskopii masowej oraz mikrorentgenowskiej analizy po linii. Topografię powierzchni ziaren Cu_2S przed i po roztwarzaniu obserwowano w świetle spolaryzowanym oraz za pomocą mikroskopu scanningowego i mikroskopu sił atomowych (AFM).

Stwierdzono zmiany składu chemicznego oraz fazowego warstw powierzchniowych ziaren proszku. Metodami instrumentalnymi stwierdzono obecność siarczku miedzi (II) oraz siarkę elementarną. Siarczek miedzi (II) (CuS) stanowi fazę dominującą. Siarka elementarna występuje w niewielkich, trudnych do wykrycia ilościach. Nie stwierdzono obecności wykrystalizowanego, uwodnionego $CuSO_4$ ani wodorotlenków miedzi. Zmianom składu fazowego towarzyszą zmiany topografii powierzchni — następuje jej wyraźne rozwinięcie. Pojawiają się pęknięcia wzdłuż granic kryształów siarczku umożliwiające penetrację elektrolitu w głąb materiału.

1. Introduction

Metal sulphides have properties similar to those of semiconductors and conductors. More than 100 years ago, M a r c h e s e [1] suggested a method of anodic dissolution of copper sulphides whereby copper turns into a solution and subsequently deposits on the cathodes. Elemental sulphur remains as a slime.

The advantage of this method consists in the fact that elemental sulphur and metal are obtained through one process. Its disadvantage, however, is the constant increase in voltage during electrolysis, which is brought about by the formation of a layer of products on the anode [2]. In the case of synthetic Cu_2S, the cause of the passivation may be the formation of a layer of elemental sulphur, the surface presence of CuS (intermediate phase of the dissolution process), or the crystallisation of $CuSO_4$. As far as industrial copper sulphide is concerned, passivation may also be brought about by chemical compounds with a low solubility (e.g. $PbSO_4$ deposits) or, for example, by silver compounds that cannot be dissolved anodically.

It has been experimentally established that Cu_2S does not dissolve directly into Cu^{+2} ions and elemental sulphur. The dissolution process proceeds through a number of intermediate phases with different properties, which are characterised by decreasing copper content [3]. The dissolution of Cu_2S is frequently written down in the form of two summary reactions:

$$Cu_2S = CuS + Cu^{+2} + 2e^- \qquad (1)$$

$$CuS = Cu^{+2} + S^0 + 2e^- \qquad (2)$$

Initially, the dissolution of solid Cu_2S anodes in an industrial electrolyte under current with a density of 200 A/m² takes place within a range of low potentials (0.5—0.7 V) with respect to the saturated calomel electrode. Under this potential the

sulphur should, theoretically, be oxidised into sulphate. However in the range of temperatures typical for electrolysis (40–60°C) this process proceeds extremely slowly and consequently elemental sulphur is obtained [4]. Data obtained from the X-ray analysis [5] related to the anodic dissolution of Cu_2S shows that following the transferral of 10% of the initial copper content from the surface layers of the electrode to the solution, nearly the entire surface of the anode is digenite ($Cu_{1.8}S$). Once a further 40% of copper is dissolved, the composition of the surface layers corresponds to that of covellite (CuS). If the dissolution of this sulphide is continued, elemental sulphur is obtained. The dissolution of CuS by applying a current with a density of $150–200$ A/m^2 leads to a rapid potential jump towards electropositive potentials. This is causes by the different crystal structure of covellite [6]. Hypothesis explaining the causes of this potential jump additionally assume either the formation of a thin oxide layer [7, 8] or the presence of elemental sulphur, which may block the surface reaction [9]. The hypothesis concerning the formation of an oxide layer is highly improbable due to the reactivity of copper oxides in acid solutions.

The overpotential of the electrode may be decreased without decreasing the current intensity by increasing the reaction surface. This was achieved by grinding Cu_2S and making a powder electrode [5, 10, 11]. In the system applied by M a o et al. [5], the powder was located in the hollowed out vertical space of the graphite plate, which at the same time functioned as the current supply. The relocation of powder was prevented applying a diaphragm that covered the powder particles. The mechanism of dissolution of powder anodes assumed by these authors is analogous to the mechanism of dissolution of solid anodes (reactions (1) and (2)). The anodic current density was calculated by M a o et al. [5] with respect to the geometrical surface of the diaphragm. It is known, however, that the application of a powder anode leads to the development of the active surface of the electrode. This means that the anodic current density is low in relation to the actual powder surface. Thus, the time required to reach the moment of the potential jump increased from several minutes (solid electrodes) to several hours. The authors [5] have suggested that the potential jump observed following the dissolution of approximately 70% of copper contained in the sulphide is connected with the isolation of sulphide particles from the electrolyte by the formation of a layer of elemental sulphur. The compactness of this layer is a precondition for the isolation of sulphide granules to take place. The formation of a porous layer will only hinder the transport of copper ions. It appears that the cause of the passivation of powder granules discussed above may be analogous to the phenomenon observed during the leaching of chalcopyrite granules with Fe^{+3} ions. In this case granules are covered with a closely adhering nonporous layer of elemental sulphur and the leaching process is rapidly inhibited [12].

The coincidence of the lengthening of the passivation time with a fall in the anodic current density is well known in literature. The shortening of the passivation time, which accompanies the increase in anodic current density, is most probably connected with the rapid increase in the concentration of copper ions in the pores of

the surface layer. The rate of increase of the concentration of copper ions is directly proportional to anodic current density. If a low current density is applied, the rate of anodic dissolution of copper sulphide will be low. Thus, the rate of transport of Cu^{+2} ions is sufficiently high to prevent the crystallisation of $CuSO_4$. If a high current density is applied, the rate of dissolution will be so great, that Cu^{+2} ions transport will fall behind the rate of the anodic reaction. This will bring about an increase in the concentration of Cu^{+2} ions; the solubility limit of $CuSO_4$ will be exceeded. It will crystallise in pores and the transport of ions will be blocked, leading to the passivation of the anode.

When the anodic current density falls, the time necessary for the potential jump to occur is lengthened and the mass of copper dissolved anodically increases; this has already been shown in the previous papers [13, 14]. It appears that the application of high current densities leads to a more rapid change in the phase composition of the surface layer: CuS phase appears. When current densities are high, it dissolves extremely slowly [4]. This leads to the gradual process inhibition. During electrolysis, the surface area covered by CuS increases continuously. This is accompanied by a gradual increase in anode potential until the occurrence of the potential jump. In the case of low anodic current densities, the rate of dissolution of Cu_2S is low. It has been observed that elemental sulphur appears on the surface of granules, and this means that the dissolution of CuS also takes place under these conditions. Both sulphides undergo dissolution, though each of them at a different rate. Only when the CuS phase becomes dominant, does the process visibly slow down and a rapid increase in anode potential is observed.

The objective of the present paper consists in an attempt to identify the causes of the potential jump during dissolution of a sulphide anode. The composition and morphology of the products of electrolysis were examined applying the following methods: X-ray analysis, AFM, observation under a scanning microscope, mass spectroscopy, observation in polarised light, and linear micro-X-ray analysis.

2. Experimental

The electrolyte was made from $CuSO_4 * 5\ H_2O$ (analytical grade) (30 g/dm^3 Cu^{+2}), concentrated H_2SO_4 (analytical grade) (150 g/dm^3), and distilled water. Concentrations of copper ions in the solution were determined using the iodometric method.

Copper (I) sulphide was synthesised by roasting the copper powder and elemental sulphur (analytical grade) in a graphite crucible. Because of the oxidation of S to SO_2, the copper powder and sulphur were mixed with 25% excess sulphur in relation to the stoichiometry of the sulphide (Cu_2S). The mixture thus obtained was introduced by batches into the crucible, which had previously been heated to a temperature of 1250°C. The sulphide underwent synthesis and melting. The crucible was subsequently cooled in a nitrogen atmosphere, and the ingot obtained

cleaned of melting loss. Chemical composition of the synthetic sulphide has been determined. It was established that excess copper was present in relation to the compound stoichiometry. The formula of the sulphide obtained may be written down as: $Cu_{2.16}S$.

In order to carry out experiments using solid electrode, the synthetic copper (I) sulphide was cute with a diamond saw. The anode was oriented vertically in conventional electrolysis cell. Parallel and at a distance of 30 mm from anode, two thin copper metal plates cathodes were placed. The electrolyte was pumped using a peristaltic pump in a way that electrolyte flow occurred from the anode to the cathodes.

In order to made powder electrode the synthetic copper (I) sulphide was crushed and then sifted through a sieve. Experiments were carried out using powder with granule diameters ranging from 0.6 mm to 2.5 mm. The powder was placed on a graphite plate with an area of 28.3 cm^2, which simultaneously functioned as the current supply. The plate was oriented horizontally. Above it, in parallel and at a distance of 30 mm, a thin copper metal plate cathode was placed. The electrolyte washed the powder granules as it was pumped through orifices (diameter of 0.5 mm) drilled in the graphite plate. The flow of the electrolyte was forced using a peristaltic pump in a way ensuring that it occurred from the anode to the cathode.

Luggin's capillary tube was introduced in order to measure the potential of the anode in the system (the end of each experiment was determined by the jump of anode potential — passivation). A saturated calomel electrode was used as the reference electrode. Differences in anode and reference electrode potentials were measured using a digital millivoltmeter connected to a register (printer). The temperature was maintained using a thermostat with an accuracy of $\pm 0.2°C$.

Neither relocation within the solution, nor the settlements of solid products of the electrolysis on the bottom of the electrolyser was observed. Losses in anode mass were determined applying the gravimetric method without removing the layer of oxidation products.

3. Results

The morphology and phase composition of samples taken from copper sulphide (I) anodes dissolved using a current with a density of from 100 to 500 A/m^2 in electrolyte with a composition similar to that of refining electrolyte were observed. A number of instrumental research techniques were applied.

a) X-ray analysis
Phase identification of the investigated material was carried out by the diffractional X-ray analysis using DRON 3 X-ray diffractometer and applying filtered CuKα radiation. Phase identification was done on the basis of JCPDS data. In order to avoid the presence of texture, the material of the anode in the form of powder was examined before and after dissolution.

Figure 1 shows the diffraction pattern of a powder sample made from synthetic Cu_2S. As can be seen, the material obtained is not homogeneous. The presence of two phases was established: Cu_2S and $C_{1.96}S$. The assignation of peaks to the first phase has been presented in the form of perpendicular broken lines. The heights thereof correspond to the relative intensities of peaks in accordance with the JCPDS data. Peaks from the $Cu_{1.96}S$ phase have been marked with stars. Their location partially coincides with that of peaks coming from the Cu_2S phase.
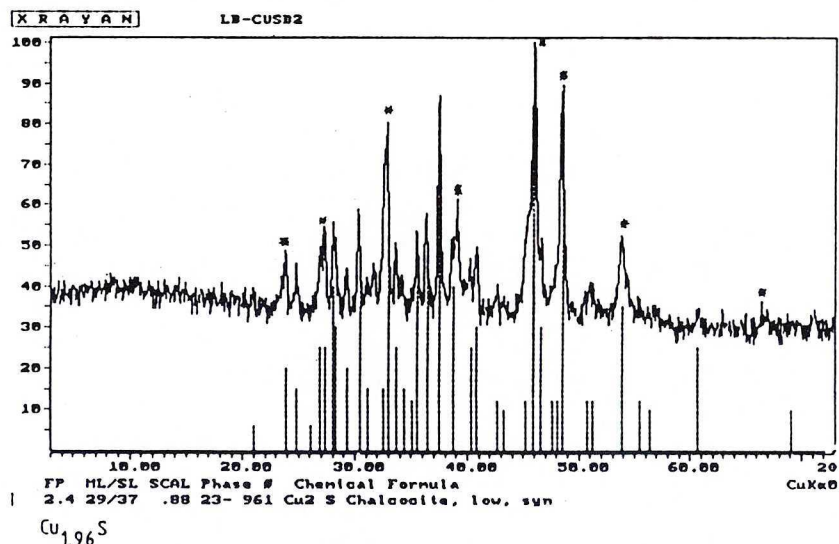
Fig. 1. X-ray diffraction pattern of Cu_2S powder before anodic dissolution

The chemical analysis of the synthetic samples shows that, with relation to the stoichiometry, the material of the anode contains excess of metallic copper. The diffraction pattern does not contain any peaks coming from the phase in a small quantity. For this reason, peaks coming from copper are not visible in the diffraction pattern.

The diffraction pattern presented in figure 2 shows the phase composition of a synthetic copper sulphide (I) sample after dissolution when a current with a density of 100 A/m^2 at a temperature of 60°C were applied. The diffraction pattern contains no peaks coming from the Cu_2S phase. Peaks coming from the $Cu_{1.8}S$ and Cu_9S_5 phases coincide with those coming from the CuS phase. No separate peaks for the $Cu_{1.8}S$ and Cu_9S_5 phases are present that permit the identification thereof. Thus, we may conclude that — within the limits of the sensitivity of the method — the entire surface of the anode is made of CuS. Furthermore, tarnishes with a colour characteristic of elemental sulphur were observed. However, these layers are too thin for any peaks from this phase to appear in the diffraction pattern.
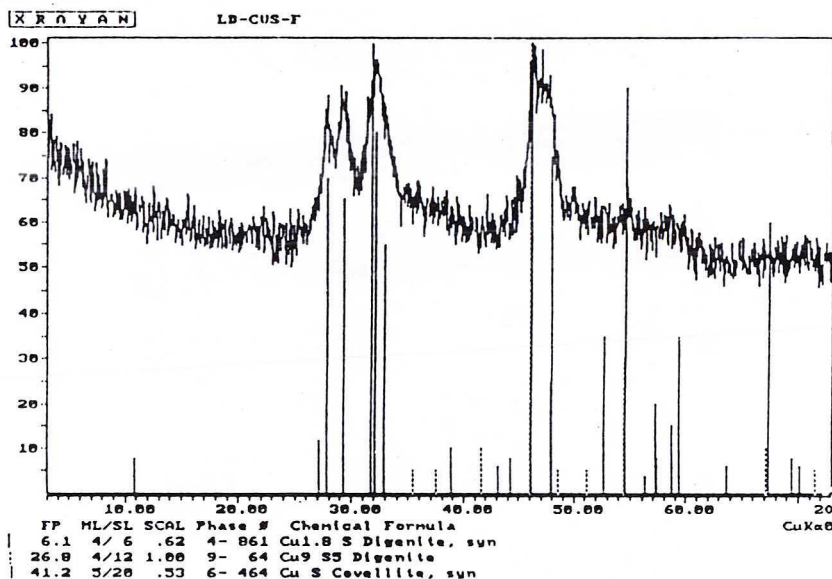
Fig. 2. X-ray diffraction pattern of Cu_2S powder after anodic dissolution, $i = 100$ A/m^2, $T = 60°C$

b) scanning analysis

The scanning analysis of solid anodes before and after anodic dissolution were performed. The objective was to trace microstructural changes in the sample material. Figure 3 shows the microstructure of synthetic Cu_2S before the process of dissolution. Crystalline structures were observed. However, there are clearly visible horizontal continuous formations with a completely different morphological structure. It is assumed that these formations were created as a result of applied method of the sample casting.

Figure 4 contains a microphotography of the synthetic Cu_2S sample after the dissolution at temperature of 60°C applying a current with an anodic density of 100 A/m^2. We can see clearly that in the course of dissolution the sample cracks, which is caused by a change in molar volume during the transition from Cu_2S to CuS. This makes it possible for the electrolyte to penetrate deeply within the material of the anode. For the most part, dissolution occurs along grain boundaries.

Local micro-X-ray analyses were carried out repeatedly at various points of grain surfaces. These results are presented in figure 5. In the case of material after anodic dissolution, the relative intensities of peaks coming from copper have clearly decreased in comparison with those recorded for the initial material. This shows that the material undergoes depletion into copper during the process. Comparing the relative intensities of peaks coming from copper and sulphur, we may conclude that the stoichiometry of the material after anodic dissolution is close to CuS.
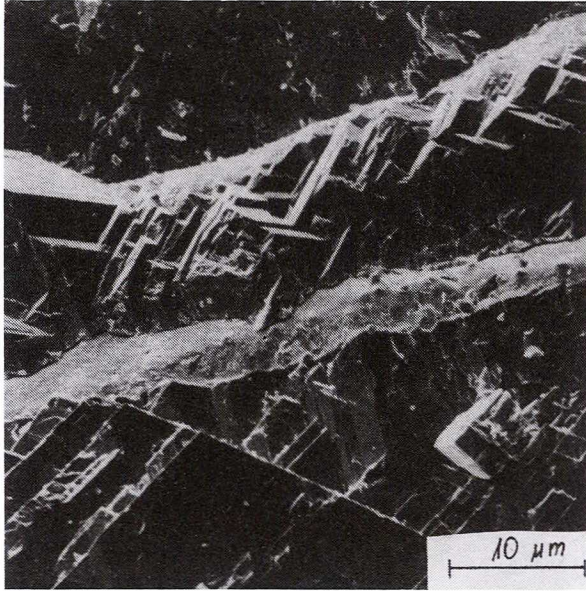
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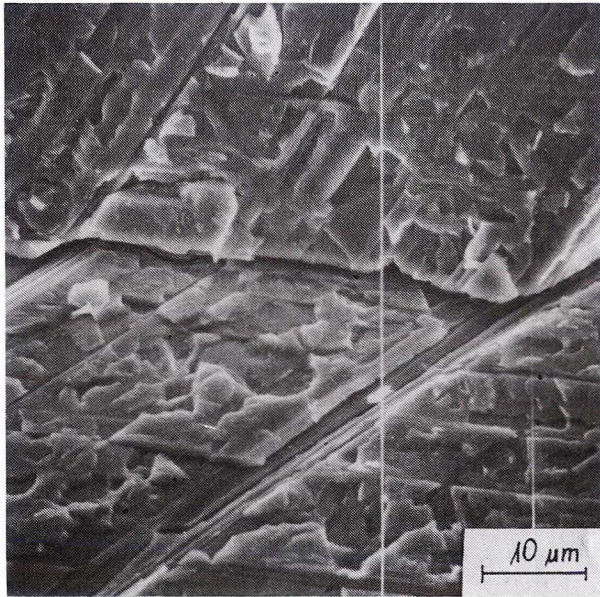Fig. 3. Microstructure of Cu_2S powder before anodic dissolution

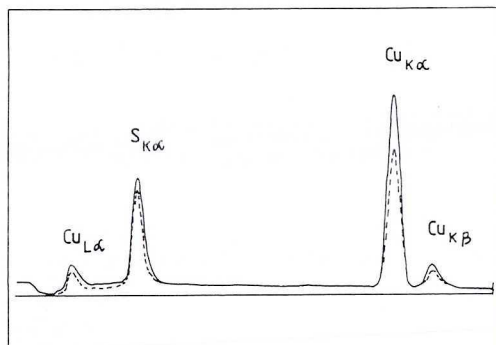

Fig. 4. Microstructure of Cu_2S powder after anodic dissolution

Fig. 5. *X*-ray microanalysis of Cu$_2$S:
———— before anodic dissolution
- - - - - - - - after anodic dissolution

c) AFM

Changes in surface topography depending on anodic current density were investigated using a Nanoscope E AFM (Atomic Force Microscope) manufactured by Digital Instruments Inc. Measurements were carried out using an Si$_3$N$_4$ tip with a force constant of 0.12 N/m. AFM microscopy is the only method known that enables researchers to image the surface topography of a sample (the microscope measures three components of the measuring point in space). However, the application of this technique makes it possible to count automatically the degree of development of a surface characterised by roughness. Since the sample image is recorded digitally, one may easily determine grain sizes, distances and cross-sections between any points on the image. Thus, it is especially suitable for the analysis of samples with a variable grain-size distribution and topography (geology and mineralogy) [15, 16].

Figure 6 shows the surface topography of fractures in cuprous sulphide samples. Figure 6a shows the surface of solid Cu$_2$S before electrolytic dissolution while figures 6b-d show sulphide surfaces after dissolution by applying current with anodic densities of 100, 300 and 500 A/m^2, respectively.

As we can see from these figures, dissolution leads to a change in the topography of the surface of the sulphide. An increase in anodic current density brings about a distinct development of the surface. As anodic current density decreases, the surface becomes smoother.

The degree of development of the surface may be characterised through roughness that is through the standard deviation σ of the average value of vertical co-ordinates of measuring points. It is defined by the following formula [17]:

$$\sigma = \sqrt{\frac{1}{N-1} \cdot \left[\sum_i \left(z_i - \bar{z} \right) \right]^2}, \tag{3}$$

where:

N — number of measuring points (262144 for each measurement),
z_i — vertical co-ordinate of the measuring point,
z — average value.

Figure 7 contains a chart presenting the dependence of surface roughness on the anodic current density applied. This dependence is linear.
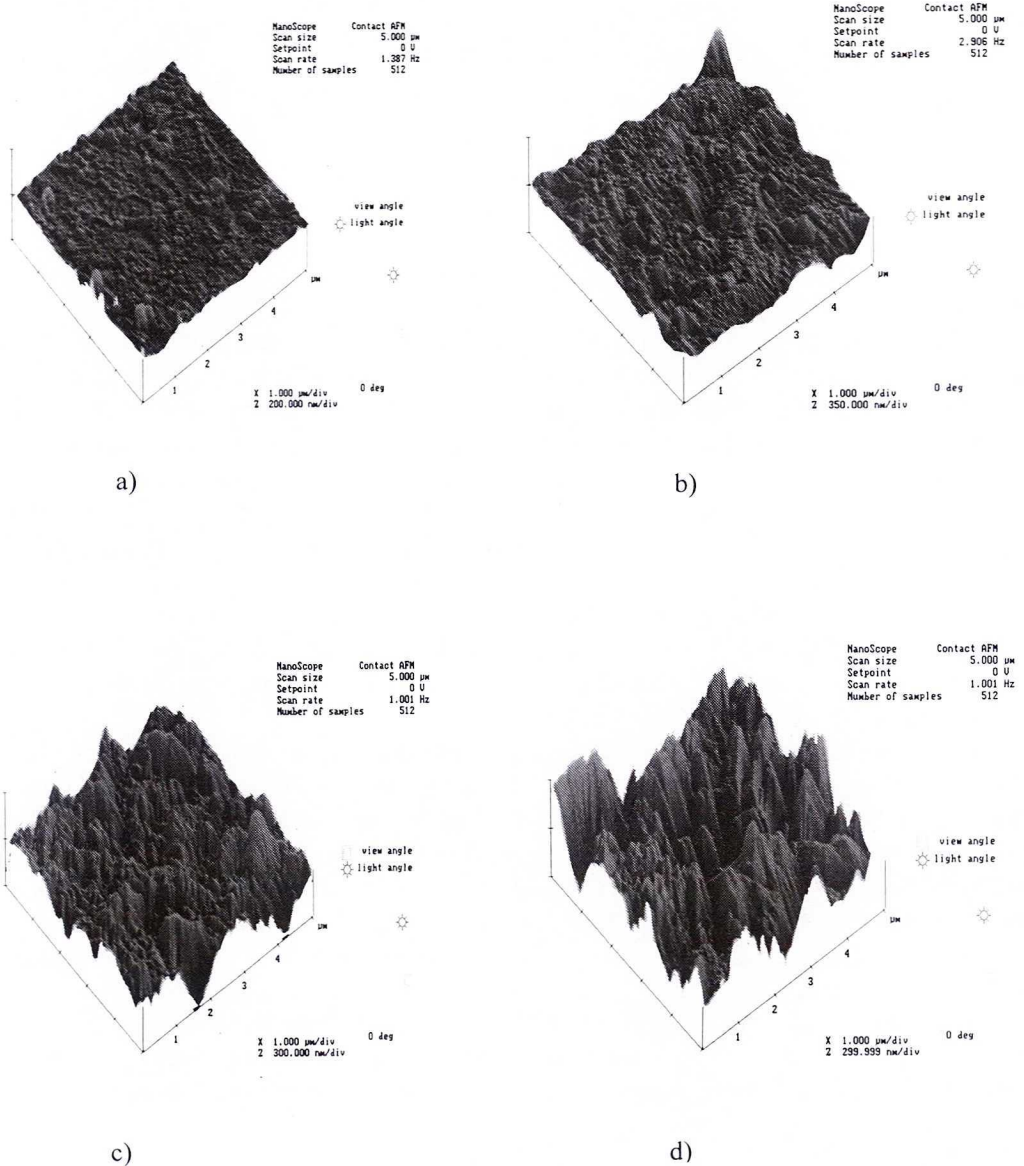

Fig. 6. The topography of Cu_2S surface: a) before anodic dissolution, b) after anodic dissolution $i = 100$ A/m², c) after anodic dissolution $i = 300$ A/m², d) after anodic dissolution $i = 500$ A/m²
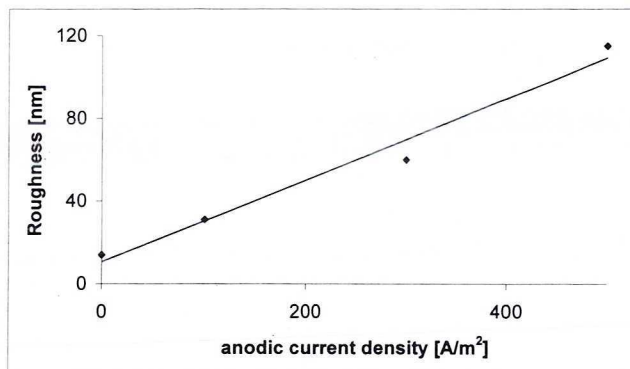
Fig. 7. The dependence of Cu_2S surface roughness on anodic current density

The electrolytic dissolution of cuprous sulphide samples leads to changes in both the phase composition and surface topography. The degree of development of the surface, characterised through roughness, increases along with anodic current density. This would be an obvious conclusion in the case of the dissolution of a homogeneous systems.

It would appear that in the heterogeneous system examined, the formation of irregularities of surface during dissolution by applying a current with a high anodic density is connected with the phase composition of the surface of the sample. During the electrically forced process, on the initial surface with a diversified phase composition ($Cu_2S + Cu_{1.96}S$) intermediate phases are successively formed that gradually undergo depletion into copper as a result of the passage of Cu^{+2} ions into the solution. Their dissolution progresses at high and comparable rates. Following the dissolution of 50% of the mass of copper, cupric sulphide (CuS) with different properties appears on the surface of the anode. At high anodic current densities, its dissolution from the surface layer is extremely slow, and this leads to increase in the potential of the electrode towards electropositive values. Depending on the phase composition of the surface, the time necessary for CuS to appear starts to differ. Rapid phase transition from Cu_2S to CuS, when applying a current with high anodic densities, leads to an inhibition of the dissolution of cuprous sulphide from deeper electrode surface layers. In effect, we witness strong surface development.

The lowering of the anodic current density leads to a slower dissolution of cuprous sulphide. Then dissolution proceeds at a uniform rate on the entire surface of the anode and, at the same time, phase transitions occur at greater depths. It would appear that the application of low anodic current densities results in the parallel and independent progression of the reaction of anodic dissolution of Cu_2S and CuS formed as a result of the dissolution of Cu_2S. The dissolution rates of both sulphides are then similar. This leads to the uniform transfer of copper ions from the entire active surface of the anode. Consequently, we observe a low surface roughness.

d) observations in polarised light

The identification of various phases on sections of grains of the sulphide anode may be conducted on the basis of photographs showing the polished surfaces of fractures in polarised light. The structure of the products of the reaction that is formed during of dissolution is revealed. Microscopic investigations were carried out using a NEOPHOT 32 optical microscope in polarised light. Observations in polarised light constituted a supplemet to X-ray phase analysis and led to a detailed analysis of the examined material, due to the characteristic colouration in polarised light of metals, non-metals, and the compounds thereof. Figure 8 contains a photograph of the section of a grain of Cu_2S powder following dissolution applying a current with a density of 100 A/m^2. As we can see the material of the anode starts to crack in the course of dissolution of the sulphide, and electrolyte penetrates within the material of the electrode. It would appear that these cracks run along grain boundaries. Inside the cracks, the material of the anode also undergoes dissolution. As a result of the process, different new phases (different colouration) are formed, the identification of which was carried out applying linear micro-X-ray analysis.
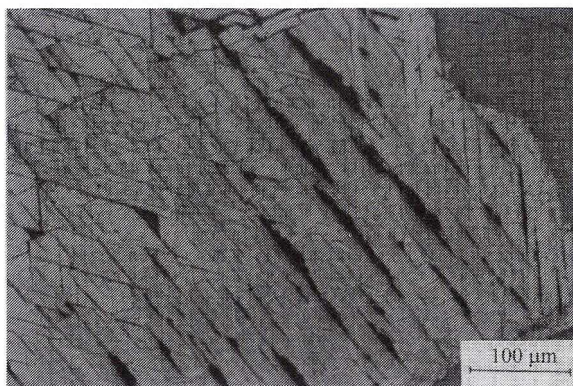

Fig. 8. Photograph taken in polarised light of the section of a Cu_2S grain following dissolution applying a current with a density of 100 A/m^2

e) mass spectroscopy

Elemental sulphur, that is a product of anodic dissolution, is present on the surface of powder grains in very small quantities. For this reason, in order to enable its identification it was necessary to select an analytical method that is characterised by high sensitivity and precision. These requirements are fulfilled by the mass spectroscopy. Figure 9 shows the dependence of the rate of sample mass decrement during system heating for three samples: initial Cu_2S, Cu_2S after anodic dissolution, and CuS of natural origin. Curves for Cu_2S samples following dissolution and for mineral CuS samples at temperature of 380°C display a very strong peak. This is connected with the thermal decomposition of CuS into Cu_2S and the emission of elemental sulphur. Such a peak is not present on the heating curve of the initial

copper sulphide (I) sample. This constitutes indirect proof of the fact that the CuS phase occurs as an intermediate stage in the process of dissolution of copper sulphide. In addition, the heating curve of Cu_2S after anodic dissolution at
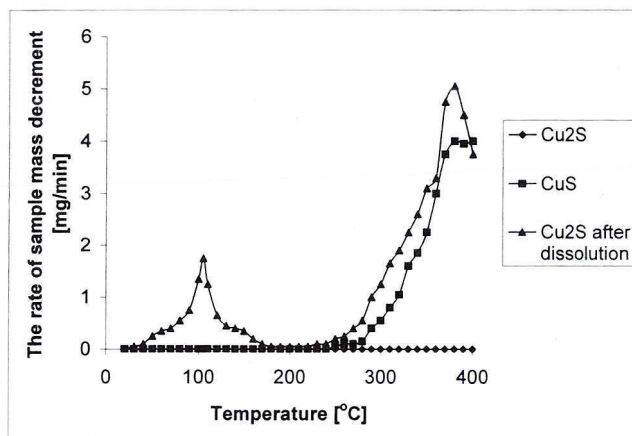

Fig. 9. The dependence of the rate of sample mass decrement on temperature

a temperature of approximately 110°C displays a strong and wide peak. At this temperature and under lowered pressure there occurs the evaporation of elemental sulphur. Most probably, it is this phenomenon that is responsible for the sample mass decrement. This is confirmed by an analysis of vapours carried out using a mass spectrometer. The detector shows peaks with relative atomic masses of 32, 64 and 96. This corresponds to the presence of S, S_2 and S_3 molecules. The peak in question would not have appeared, if elemental sulphur had not been the product of the reaction of anodic dissolution of Cu_2S.

f) linear micro-X-ray analysis

In order to identify the chemical composition of the products formed in the course of the process of electrolysis linear micro-X-ray analysis was applied. Figure 10 contains a chart presenting the relative content of sulphur and copper within one powder grain after the process of dissolution. The analysis was carried out on the surface of the polished fracture from the grain boundary to deep within the material. At a certain distance from the grain boundary (approximately 80 μm), we may observe a stable Cu and S content. This corresponds to the CuS phase. As we come nearer to the grain boundary, the content of sulphur increases visibly, while that of copper decreases minimally. This would point to the presence of a two-phase system of CuS and elemental S, and also that on the phase boundary the dissolution of CuS in accordance with the reaction (2) occurs. Elemental sulphur is formed on the surface of the sulphide. This layer is very thin and unable to cover totally the reaction surface. Thus, we confirmed results obtained using the mass spectroscopy method.
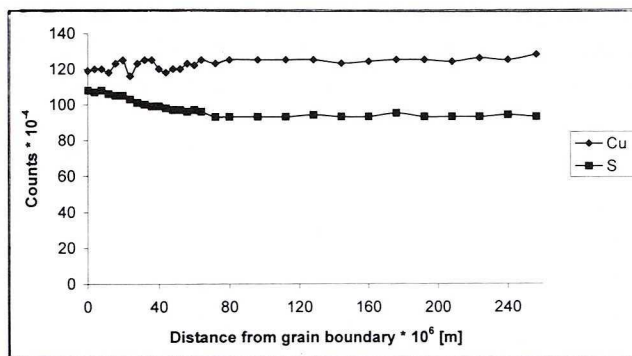
Fig. 10. Relative content of Cu and S on the section of a grain following anodic dissolution applying a current with a density of 100 A/m^2

4. Discussion

In each of the above experiments the potential jump was observed; this signified the passivation of the anode. The potential jump could have been caused by the following processes: the crystallisation of CuSO$_4$ within anode pores, the appearance of a layer of copper hydroxides or a layer of slowly dissolving CuS on the surface of the anode, or the presence of tightly adhering elemental sulphur inhibiting the anodic reactions. On the basis of conducted experiments, it would appear that the passivation is caused by CuS formation, an intermediate product of the reaction of Cu$_2$S dissolution. Under experimental conditions, CuS dissolves extremely slowly. This is evidenced by the exceedingly small mass of elemental sulphur detected on the surface of the anode upon completion of electrolysis, which — however — is insufficient to cover totally the active surface of the electrode.

No crystallised hydrated CuSO$_4$ was found on the surfaces of grains or within pores formed as a result of the process. Also no traces of copper hydroxides were detected on the surface of sulphide. Due to different mobility fo H$^+$, Cu^{+2} and SO$_4^{-2}$ in the investigated system we could expect impoverishment of hydrogen ions in electrolyte near anode. pH of Cu(OH)$_2$ precipitation (for $c_{Cu^{+2}} = 0{,}47 M$, $I_{Cu(OH)_2} = 19{,}9$) was calculated. Reaction of Cu(OH)$_2$ precipitation should appear at pH $= 3{,}9$. It seems to be unlikely that in the course of the process of electrolysis pH becomes so high. Theoretically, also CuOH could precipitate on the surface of electrode. Concentration of Cu$^+$ ions near anode surface is not known. The minimal concentration of Cu$^+$ ions for CuOH precipitation was calculated (for pH $= 0$; $I_{CuOH} = 14{,}7$). For precipitation of CuOH the concentration of Cu$^+$ ions should be 0,67 M. It appears that this is quite impossible, because Cu$^+$ ions are oxidized anodically or in reaction with oxygen dissolved in electrolyte.

The key to the obtainment of a high — nearly 100% — degree of dissolution of copper lies in defining conditions for conducting the electrolysis of sulphates that

would ensure the required rate of dissolution of covellite (CuS). It appears that this may be achieved only in one two ways. The first consists in applying very low anodic current densities (of 1 A/m^2), while the second — in using additional substances introduced into the electrolyte solution, which would assist the process of dissolution of covellite through complexing or secondary currentless reactions.

5. Conclusions

The electrolytic dissolution of sulphide anodes leads to changes in anode surface topography. In the course of dissolution the material of the anode cracks along grain boundaries and pores start to appear. As a result, the active surface of the anode undergoes development. The degree of surface development is characterised through its roughness. As the anodic current density is lowered, the surface of the electrode becomes smoother.

It would appear that the application of high anodic current densities stops the dissolution of Cu_2S upon the appearance of a layer of CuS on the surface of the electrode in connection with the consideration overpotential that accompanies the dissolution of covellite. When the anodic current density is lowered, the reaction of Cu_2S and CuS dissolution proceeds simultaneously. This is confirmed by mass spectroscopic measurements and linear micro-X-ray analysis on samples dissolved with low anodic current densities. The quantities of elemental sulphur detected were, however, very small.

It would appear that the degree of dissolution of copper from a powder anode may be increased by either radically lowering anodic current density or adding substances assisting the dissolution of sulphides to the electrolyte solution.

REFERENCES

[1] E. M a r c h e s e, patent niemiecki 22.429 (1882).

[2] F. H a b a s h i, N. T o r r e s - A c u n a, The Anodic Dissolution of Copper (I) Sulfide and the Direct Recovery of Copper and Elementar Sulfur from White Metal. Trans. AIME. **242,** 780 – 787 (1968).

[3] P. B r e n n e t, S. J a f f e r a l i, J. V a n s e v e r e n, J. V e r e c k e n, R. W i n a r d, Study of the Mechanism of Anodic Dissolution of Cu_2S. Met. Trans. **5,** 127 – 134 (1974).

[4] D. J. M c K a y, The Direct Electrorefining of Copper Matte. Journal of Metallurgy **3,** 44 – 48 (1993).

[5] M. H. M a o, E. P e t e r s, Direct Electrorefining of Cuprous Sulphide — Based Particulate Anodes. Can. Met. Q **22,** 437–446 (1983).

[6] F. K. C r u n d w e l l, The Influence of the Electronic Structure of the Solids on the Anodic Dissolution and Leaching of Semiconducting Sulphide Minerals. Hydrometallurgy 21 (1988).

[7] E. H i l l r i c h s, R. B e r t r a m, Anodic Dissolution of Copper Sulphides in Sulphuric Acid Solution I. The Anodic Dissolution of $Cu_{2-x}S$. Hydrometallurgy **11** 181 (1983).

[8] E. H i l l r i c h s, R. B e r t r a m, Anodic Dissolution of Copper Sulphides in Sulphuric Acid Solution II. The Anodic Dissolution of CuS. Hydrometallurgy **11,** 195–207 (1983).

[9] E. G h a l i, B. D a n d a p a n i, A. L e w e n s t a m, Electrodissolution of Synthetic Covellite in Hydrochloric Acid. J. Applied Electrochem **12** (1982).

[10] M. H o j o, E. P e t e r s, Direct Electrorefining of Chalcocite. Proceedings of the 5th Australian Electrochemical Conference, 345–364 August 1980.

[11] D. J. M a c K i n n o n, Fluidised Bed Anodic Dissolution of Chalcocite. Hydrometallurgy. **1,** 241–257 (1976).

[12] F. H a b a s h i, Principles of extractive metallurgy. **1.** General principles. Gordon and Breach Science Publishers Inc. 151, 1969.

[13] L. B u r z y ń s k a, P. Ż a b i ń s k i, Anodic Dissolution of copper(I) sulfide. Physicochemical Problems of Mineral Processing, XXXV Symposium, 11–28 (1998).

[14] L. B u r z y ń s k a, P. Ż a b i ń s k i, A. K o w a l, Application of AFM microscopy for surface topography analysis of copper(I) sulfide during anodic dissolution. Physicochemical Problems of Mineral Processing **42,** 215–226 (1998).

[15] D. S a r i d, Scanning Force Microscopy with Applications to Electric, Magnetic and Atomic Forces. Oxford University Press, New York 1994.

[16] D. A. B o n n e l l, Scanning Tunneling Microscopy and Spectroscopy: Theory, Techniques and Applications. VCH Publishers, Inc., New York 1993.

[17] J. A. D e R o s e, T. T h u n d a t, L. A. N a g a h a r a, S. M. L i n d s a y, Gold grown expitaxially on mica: conditions for large area flat faces. Surface Science **256,** 102 (1991).