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ELECTROSORPTION OF XANTHATE ION AT THE SURFACE OF COPPER SULPHIDES OF DIFFERENT COMPOSITION - A PRELIMINARY STUDY

Several copper sulphides in the range of composition from Cu_2S to CuS were obtained and characterized by X-ray diffraction measurements and the measurements of the potential difference of the galvanic couples: $\text{Cu}_x\text{S}/\text{Cu}_{\text{aq}}^{2+}/\text{Cu}^0$. The cyclic voltammetry experiments in the solutions of potassium ethylxanthate were performed in order to reveal the differences in the reaction of electrosorption of ethylxanthate ion at the surface of different sulphides. Significant differences in the position of voltammetric maxima between chalcocite (Cu_2S) and non-stoichiometric cuprous sulphides were found.

1. Introduction

The most abundant copper mineral is chalcopyrite (Habashi, 1978). However, in Polish copper ore deposits copper appears mainly as copper sulphides. The system copper-sulphur is very complicated. In the range of compositions from Cu_2S to CuS there are four thermodynamically stable and about ten metastable phases (Potter, 1977). The differences in physical properties between copper sulphides close in composition are sometimes very small and in some cases only X-ray diffraction analysis enables the phase identification of the sample.

During last years more and more sophisticated methods of the control of the flotation process are developed. For example Outokumpu Oy

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company has developed very efficient method of the control of flotation by regulating the electrochemical potential of the flotation pulp (Heimala et al., 1985). In this method several parameters (Eh, pH, potential of several mineral electrodes) characterizing the conditions in the flotation pulp are measured and a redox potential regulating agent together with a pH regulating agent are fed into the flotation pulp, to attain the optimum conditions for the sorption of the flotation collector. Such procedure requires obviously the detailed knowledge about the potential at which the process of collector electrosorption at the mineral surface occurs.

There are many papers in the literature in which the electrosorption of xanthates at the surface of copper sulphides was investigated (Kowal and Pomianowski, 1973, O'Dell et al., 1984, Walker et al., 1984, Richardson et al., 1984, Heimala 1985). However, those works were performed either using pure, stoichiometric chalcocite or using sulphides with unknown stoichiometry and no information about the influence of sulphide stoichiometry on the course of electrosorption process may be drawn.

The Polish copper ores are undoubtedly composed mainly of non-stoichiometric cuprous sulphides with chalcocite as only one of many components. So, any information on the influence of the stoichiometric composition of copper sulphides on their surface properties and especially the electrosorption of xanthates would help in understanding the behaviour of these copper ores in flotation.

To obtain such information the series of copper sulphides of different stoichiometric composition was synthesized and their surface properties were investigated by electrochemical methods. The results of the preliminary investigation of the influence of copper sulphide composition on xanthate electrosorption are presented below.

2. Experimental

2.1. Materials and apparatus

The copper sulphides were synthesized by reacting copper and sulphur of p.a. grade purity and next melting the obtained sulphide in a quartz tube. Rod-like pieces of copper sulphides were embedded in glass tubes with an epoxy resin. The front surface of the electrode was polished on emery papers - at the back surface the electrical contact

was made with a drop of mercury. Commercial potassium ethylxanthate was crystallized several times from acetone and kept in the dessicator. The phosphate buffer (pH 8.5) was used as a base electrolyte. Typical electrochemical set-up in three electrode configuration was used in voltammetric experiments. The saturated calomel electrode (SCE) was used as a reference electrode (all potentials are quoted versus this electrode). Before experiments solutions bubbled with argon to remove oxygen. All experiments were done at the room temperature except the measurements of the potential differences of galvanic couples which were done at the temperature of 25°C. More information concerning the preparation and handling of sulphide electrodes may be found in previous papers (Nowak, 1987, Nowak and Pomianowski, 1989).

2.2. Characterization of sulphide samples

The stoichiometric composition of the samples was known from the weight of copper and sulphur taken to synthesis. The phase composition was studied by X-ray diffraction. The obtained diffraction patterns were compared with literature data (Roseboom, 1966, Potter and Evans, 1976, ASTM 23962). For each phase in the system copper-sulphur its free enthalpy of formation (ΔG) may be calculated from the measurements of the potential difference (ΔE) of the galvanic couple: $\text{Cu}_x\text{S}/\text{Cu}_{\text{aq}}^{2+}/\text{Cu}^0$ (Potter, 1977). Such measurements have been made for all samples and the obtained results, compared with the value calculated from the data given by Potter (1977), are presented in table 1.

Table 1. The characteristics of the used copper sulphide samples.

Number	Cu/S ratio	Phase composition (from X-ray)	$\Delta E/\text{mV}$ calculated	$\Delta E/\text{mV}$ measured
1	2.00	low chalcocite	0 - 137.5	90.0
2	1.97	low chalcocite + djurleite	137.5	141.6
3	1.87	djurleite + digenite	170.2*	151.3
4	1.70	digenite	170.2-165.2	157.9
5	1.34	digenite + covellite	165.2	162.8
6	1.20	digenite + covellite	165.2	164.2
7	1.00	covellite	170.1-275.9	166.0

*149.7 for djurleite + anilite, stable mixture for that composition

Digenite was found from X-ray analysis in several samples despite the fact that this compound is unstable and should decompose to anilite (Potter, 1977). On the other hand, it is known (Morimoto and Koto, 1970) that grinding anilite produces digenite which may alter the results of the X-ray analysis. Anyway anilite and digenite are very similar to each other both in the structure and in composition as well as in physical properties and they should behave in similar manner.

3. Results and discussion

In figure 1 the voltammetric curves in pure base electrolyte and in 0.001 mol/dm^3 xanthate solution for three different samples are shown. The range of potentials was chosen for each sample in such a way that only small Faradaic current flows in pure base electrolyte. Changing the potential outside of the limits of this region causes that rather large current of anodic or cathodic decomposition starts to flow. The general shape of voltammetric curves in xanthate solution is the same: the main anodic peak (A3) is preceded by one (in the case of sulphides with the lower copper content) or two (for the case of copper-rich sulphides) adsorption peaks. The products of anodic oxidation rest at the surface and are reduced in one peak (C). Restricting the anodic limit one may observe on the cathodic half-cycle the reactions reverse to A1 and A2. The positions of voltammetric peaks for the samples used and for the Cu electrode are collected in table 2.

Table 2. The potentials of voltammetric peaks for copper and copper sulphide electrodes in 0.001 mol/dm^3 EtXK. Sweep: rate 0.1 V/s .

Sample Number	A1	A2	A3	C
Cu ⁰	-770	-650	-495	-875
1	-590, -540	-500	-355	-685
2	-440	-370	-230	-525
3	-410	-340	-220	-490
4		-330	-210	-490
5		-310	-190	-485
6		-290	-180	-480
7		-280	-170	-480

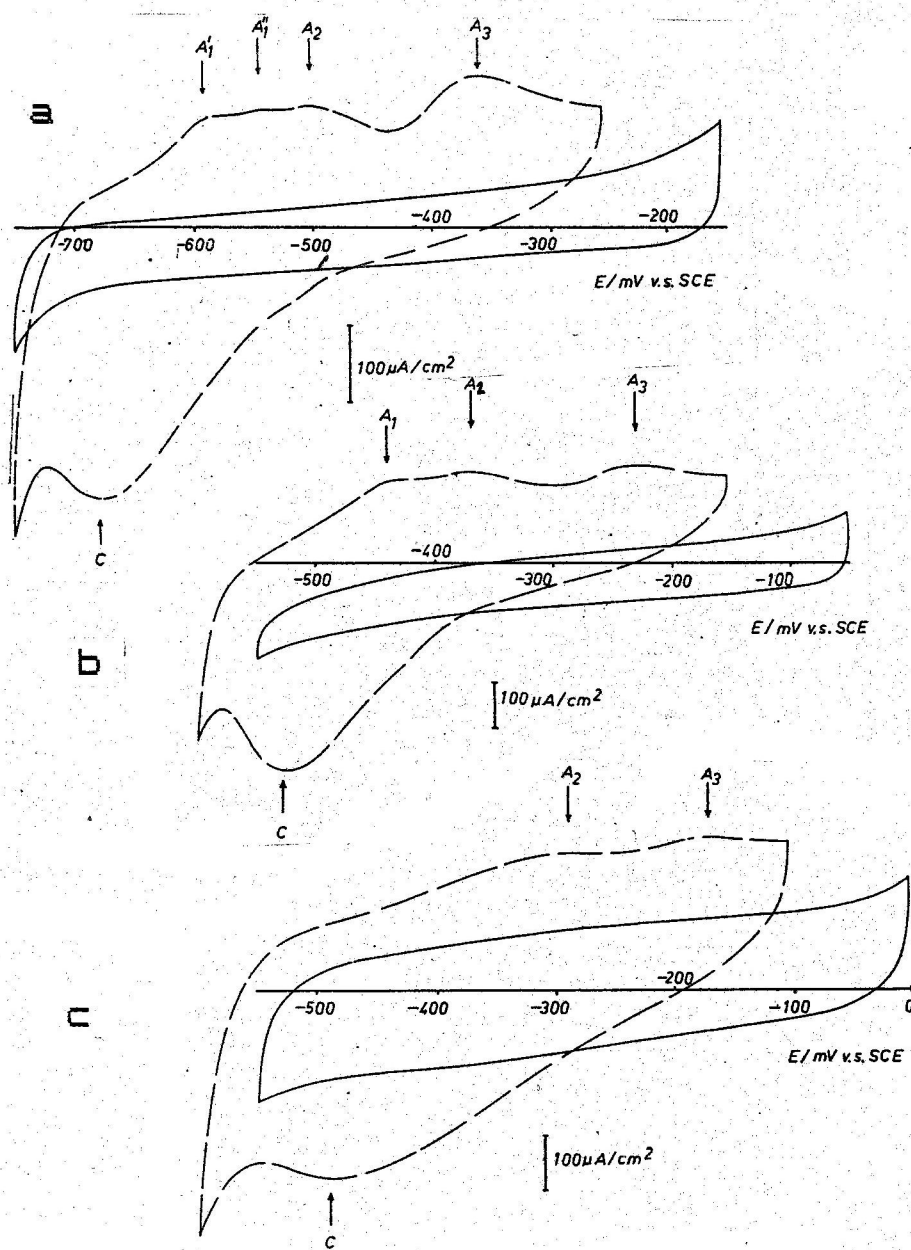


Fig. 1. The stationary voltammetric curves for copper sulphide electrodes in base electrolyte (phosphate buffer, pH=8.5) - full lines, and in base electrolyte plus 0.001 mol/dm³ potassium ethylxanthate - dashed lines. Potential sweep rate: 0.1 V/s: a- Cu_2S electrode, b- $\text{Cu}_{1.97}\text{S}$ electrode, c- CuS electrode.

Due to the complexity of the Cu-S system there is no thermodynamic description of reactions in the system: copper-sulphur-xanthate. Only lastly the Eh-pH diagrams for the system copper-sulphur-water, taking into account other than chalcocite copper sulphides, were published (Woods et al., 1987). The situation is further complicated by the fact that in potentiodynamic conditions the position of a voltammetric maximum never occurs at the potential defined by thermodynamics. So, the simplified approach was applied in the interpretation of the results. The Eh-pH diagram for the system copper-water-potassium ethylxanthate is well known (Hepel and Pomianowski, 1977). Due to the inertness of the sulphidic sulphur in copper sulphides one may treat non-stoichiometric cuprous sulphide in similar manner like an amalgam electrode, with the activity of copper lowered in comparison to pure metal. So, any redox process for a sulphide electrode should be shifted in anodic direction on potential axis in comparison to analogous process for the copper electrode. That shift should be equal to the potential difference of the galvanic couple: $\text{Cu}_x\text{S}/\text{Cu}_{\text{aq}}^{2+}/\text{Cu}^0$ (see table 1) for a two-electron process and twice as much as this difference for a one electron process.

The electrochemical reaction responsible for the A3 peak in the case of the copper electrode is undoubtedly the formation of monovalent copper xanthate. So, the shift of the A3 peak for particular sulphides should be twice as much as the potential difference for the above mentioned galvanic couple. The comparison of potential values given in both tables (1 and 2) corroborates the proposed interpretation.

So, it is very probable that despite the big differences in potentials at which the voltammetric maxima occurs the mechanism of the electrosorption reaction in the case of copper and copper sulphides is the same.

There is really a significant difference in potentials ascribed to individual voltammetric maxima between stoichiometric chalcocite and other copper sulphides. So, chalcocite is not a good model compound for investigations on improvement of the flotation process for ores containing non-stoichiometric cuprous sulphides. Significant differences might be expected also for covellite. Unfortunately, all attempts of synthesis of stoichiometric covellite were unsuccessful due to high pressure of the sulphur vapours over CuS at the melting temperature of covellite.

4. Conclusions

Synthesis of several copper sulphides were performed and the investigations of the electrosorption of xanthate ion at the surface of these sulphides were performed using cycling voltammetry method. The system copper-sulphur is very complicated and not all possible phases existing in that system were studied, however even for such limited range of investigated samples same conclusions may be drawn.

It was clearly shown, that the potential at which the processes of xanthate electrosorption occurs at the surface of individual copper sulphide depends strongly on the composition of sulphide phase, even if the mechanism of the process is the same. For non-stoichiometric cuprous sulphides that potential is shifted in anodic direction and that shift is significant even in the case of such small deviations from ideal stoichiometry as few percent. So, the stoichiometric composition is a very important factor, which may influence the behaviour of copper sulphides in flotation.

Acknowledgement

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Streszczenie

Nowak, P., Elektrosorpcja jonu ksantogenianowego na powierzchni siarczków miedzi o różnym składzie stechiometrycznym. Fizykochemiczne Problemy Mineralurgii 22: 13-20.

Przeprowadzono syntezę kilku próbek siarczków miedzi o różnym składzie stechiometrycznym w zakresie od Cu_2S do CuS . próbki scharakteryzowano metodą dyfrakcyjnej analizy rentgenowskiej oraz poprzez pomiar różnicy potencjałów ogniw: $\text{Cu}_x\text{S}/\text{Cu}_{\text{aq}}^{2+}/\text{Cu}^0$. W celu stwierdzenia różnic w przebiegu procesu elektrosorpcji na różnych próbkach wykonano pomiary metodą woltamperometrii cyklicznej w roztworach ksantogenianu. Stwierdzono znaczne różnice w położeniu maksimów na krzywych woltamperometrycznych pomiędzy chalkozynem i niestechiometrycznymi siarczkami miedziawymi.

СОДЕРЖАНИЕ

П. Новак. 1990. Электросорбция ксантогенатного иона на поверхности сульфидов меди разного состава. Физикохимические вопросы обогащения. 22: 13-20.

Несколько сульфиды меди в области составов Cu_2S - CuS были получены и характеризованные методом рентгенографической дифрактометрии а даже методом измерения напряжения гальванических элементов $\text{Cu}_x\text{S}/\text{Cu}^{2+}/\text{Cu}^0$. Для обнаружения разниц в реакции электросорбции ксантогената на сульфидах о разным составе были проведены эксперименты методом циклической вольтамперометрии в растворах ксантогената. Обнаружено значительные разницы потенциалов вольтамперометрических максимумом между халькозином и нестехиометрическими сульфидами меди.