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APPLIED ELECTROCHEMISTRY  
AND CORROSION PROTECTION OF METALS

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## Anodic Dissolution of Nickel Sulfide in Acidic Cu(II) Electrolytes

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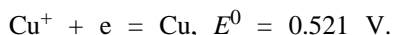
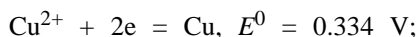
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**Abstract**—The effect of ligands on the anodic dissolution of NiS in copper-containing acidic electrolytes was studied.

Hydrometallurgical processing of non-ferrous metals is being actively developed at modern enterprises [1, 2]. It is known [3] that copper ions present in pressure leaching solutions have a significant catalytic effect on nickel sulfide dissolution. However, simultaneous presence of copper and sulfate ions results in passivation of the sulfide surface and, consequently, exerts an adverse effect on the process parameters.

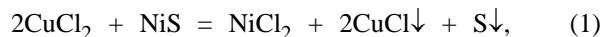
The aim of this work was to study the effects of electrolyte anion composition and depassivating additions to sulfate electrolytes on the electrochemical behavior of nickel sulfide in copper-containing electrolytes. The origin of the catalytic action of copper ions is not fully understood. Pure copper is considered to be able to deposit at a sulfide surface [3] to form microgalvanic couples, which increase the anodic potential at certain parts of the surface. At the same time,  $\text{Cu}^{2+}$  ions in acid solutions can act as an additional oxidizing agent [4] capable of oxidizing sulfur in sulfides to the elemental form.



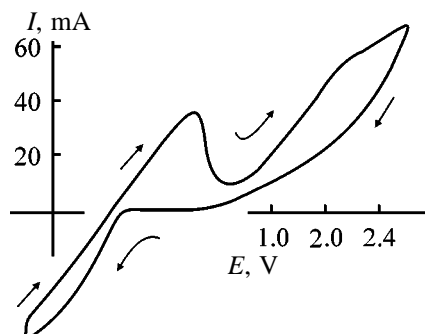
It is copper which is likely to hinder further oxidation of elemental sulfur to sulfate ions, which is extremely convenient, as sulfide sulfur is removed from the process in the elemental form. We used  $\beta$ -NiS with a nickel content of 50 at. % as a subject of the study, because, according to [5], in the course of the oxidative dissolution of nickel sulfides  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_7\text{S}_6$ , which occurs by the electrochemical mechanism [6], the surface is gradually enriched in a sulfide with a higher Ni content, up to NiS [7].

Nickel sulfide NiS (50 at. %) was synthesized by the known procedure [8] from equimolar amounts of cathodic NO-grade nickel and analytically pure grade sulfur in an evacuated quartz ampule. The working electrode was made from a nickel sulfide sample soldered to a copper holder. Its idle surface was insulated with a nitro lacquer. Before experiments the NiS surface under study (area  $1 \text{ cm}^2$ ) was smoothed with emery paper no. 0 and washed with alcohol and distilled water. Experiments with fluorine-containing electrolytes were carried out in a fluoroplastic cell with a temperature-controlled water jacket. In the other cases a YaES-2 glass cell (glass electrode cell) temperature-controlled with a UTU 2/77 thermostat was used. Electrochemical experiments were carried out on a PI-50-1.1 potentiostat equipped with a PDP4-002 plane-table recorder. We used a three-electrode cell with nickel sulfide under study as a working electrode, a platinum auxiliary electrode, and a saturated silver chloride reference electrode (electrode potentials are given vs. normal hydrogen electrode). Electrolytes were prepared from chemically pure, ultrapure, and analytically pure grade reagents.

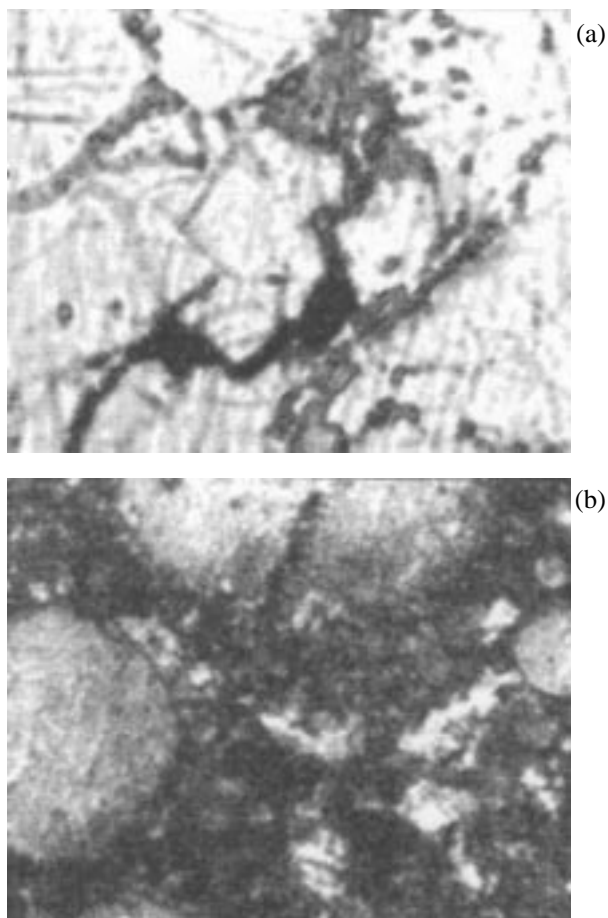
The following processes of oxidative dissolution of nickel sulfide in copper chloride and copper sulfate solutions were studied.



The processes have both advantages and drawbacks: process (1) involves high concentrations of chlorides hampering further electrolyte treatment, and process (2) requires high temperatures and pressures and also involves passivation of the NiS surface due to  $\text{Cu}_2\text{S}$  deposition. The accelerating effect of copper



**Fig. 1.** Cyclic voltammogram of NiS in 0.5 M CuSO<sub>4</sub> at 90±0.5°C: (*I*) current and (*E*) potential; the same for Figs. 3–5. Rate of potential scanning 100 mV s<sup>-1</sup>; the same for Figs. 4 and 5.



**Fig. 2.** Photomicrographs of NiS etched for 2 min at a potential of 1 V in (a) 0.5 M CuSO<sub>4</sub> at 20°C and (b) 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub> + 200 g l<sup>-1</sup> KBr at 90°C. Magnification: (a) 800 and (b) 10.

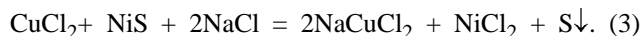
activators on the anodic dissolution of NiS is due to the possibility of removing insoluble copper products from the nickel sulfide surface owing to the formation of copper(I) complex ions under certain conditions [9].

Sulfate ions do not form complexes with copper(I) ions under common conditions [9]; therefore, the steady-state currents of NiS dissolution are insignificant. As chloride ions form sufficiently stable complexes with Cu(I) ions, copper contained in a Cu<sub>2</sub>S passivating film can partially pass into solution in the form of [CuCl<sub>2</sub>]<sup>-</sup> ions, which is observed in the experiments. An increase in the concentration of chloride ions (addition of NaCl) can result in a rise of the NiS dissolution currents.

The cyclic voltammogram (CVA) obtained on NiS in 0.5 M CuSO<sub>4</sub> (pH 2.2) at 90°C is shown in Fig. 1. The anodic peak in the forward branch seems to be due to the dissolution of both NiS and copper deposited in the course of cathodic polarization.

The electroetching of an NiS sample in 0.5 M CuSO<sub>4</sub> for 2 min at a potential of 1 V results in the formation of a new phase on the nickel sulfide surface. A photomicrograph of the etched part is shown in Fig. 2a. The light-colored phase is the starting nickel sulfide. The composition of the dark-colored phase is (mol %) S 54.6–52.8 and Ni 45.4–47.3. This phase probably corresponds to Ni<sub>3</sub>S<sub>4</sub> in the Ni–S phase diagram [10].

Anodic dissolution of NiS in CuCl<sub>2</sub> occurs according to Eq. (1), whereas in excess NaCl it is described by the equation



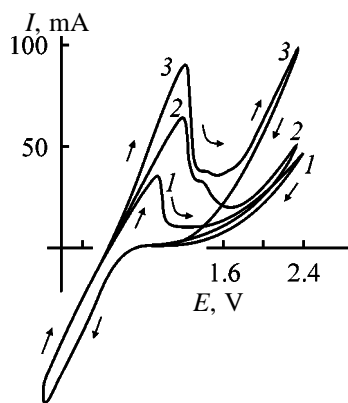
The behavior of NiS in 0.5 M CuCl<sub>2</sub> at various rates of potential scanning is shown in Fig. 3. As known [11], in the case of diffusion control the peak current (*I*<sub>p</sub>) is proportional to *V*<sub>s</sub><sup>1/2</sup> (*V*<sub>s</sub> is the rate of potential scanning). The peak current *I*<sub>p</sub> and passivation current *I*<sub>pas</sub> as functions of potential sweep rate are given below:

<i>V</i> <sub>r</sub> , mV s <sup>-1</sup>	<i>I</i> <sub>p</sub> , mA	<i>I</i> <sub>pas</sub> , mA
10	32	10
100	65	20
200	91	37

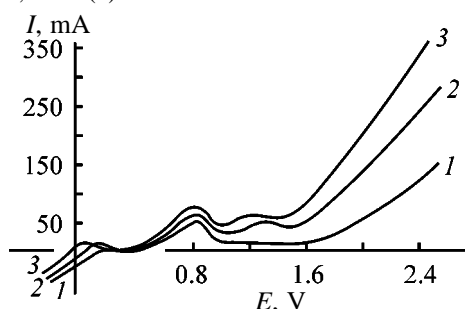
Applying the linear regression approach to these data, we obtained the formula

$$I_p = 14.3 + 5.3 V_s^{1/2}. \quad (4)$$

The effect of NaCl addition in amounts of 50–200 g l<sup>-1</sup> to 0.5 M CuCl<sub>2</sub> on the forward branches of CVA is shown in Fig. 4. The anodic peak observed in the region of 0.1 V is shifted to the cathodic region,



**Fig. 3.** Cyclic voltammogram of NiS in 0.5 M  $\text{CuCl}_2$  at  $90 \pm 0.5^\circ\text{C}$ . Potential scanning rate ( $\text{mV s}^{-1}$ ): (1) 10, (2) 100, and (3) 200.

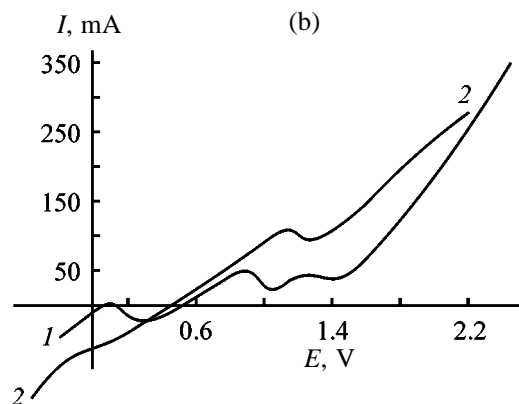
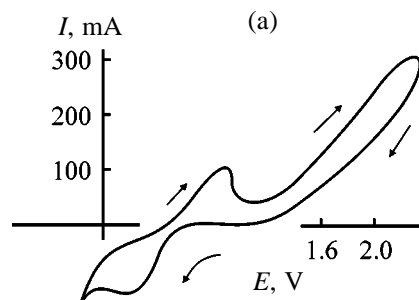


**Fig. 4.** Voltammograms of NiS in 0.5 M  $\text{CuCl}_2$  with NaCl additions at  $90 \pm 0.5^\circ\text{C}$ . NaCl ( $\text{g l}^{-1}$ ): (1) 50, (2) 100, and (3) 200.

whereas the peak current in the region of 0.8 V increases by 30–40% as the concentration of chloride ions increases. A significant increase (from 10 to 70 mA) of the current corresponding to the passivation plateau points to partial dissolution of the passivation film due to formation of  $[\text{CuCl}_2]^-$  [12, 13].

The cyclic voltammetric curves of NiS dissolution in 0.5 M  $\text{Cu}(\text{NO}_3)_2$  solution and in 0.5 M  $\text{Cu}(\text{NO}_3)_2$  solution with addition of  $200 \text{ g l}^{-1}$  KBr are shown in Figs. 5a and 5b, respectively.

Comparison of the anodic branches of the NiS CVAs in 0.5 M  $\text{Cu}(\text{NO}_3)_2$  with addition of  $200 \text{ g l}^{-1}$  KBr and NaCl (Fig. 5b) showed that in the case of chlorides (curve 1) dissolution of the passivating film (convex section) occurs in the potential range 1.1–1.4 V, and in the case of nitrates (curve 2) it occurs at 2–3 times greater passivation currents. Furthermore, the passivating film is displaced from the electrode surface by molten sulfur (Fig. 2b). At high anode potentials in the nitrate–bromide system the passivating film is absent from the electrode surface, and only the bright golden NiS surface and molten sulfur are observed. The passivating surface film is formed at low anode potentials (0.6–0.8 V) and is dissolved as



**Fig. 5.** Voltammograms of NiS (a) in 0.5 M  $\text{Cu}(\text{NO}_3)_2$  at  $90 \pm 0.5^\circ\text{C}$  and (b) in (1) 0.5 M  $\text{CuCl}_2 + 200 \text{ g l}^{-1}$  NaCl and (2) 0.5 M  $\text{Cu}(\text{NO}_3)_2 + 200 \text{ g l}^{-1}$  KBr.

the potential is increased to 1.0–1.2 V. In the course of the dissolution molten sulfur is formed (light circular parts), which tightly adheres to the sulfide surface and gradually displaces the passivating film. With  $10 \text{ g l}^{-1}$  of KBr added to  $\text{Cu}(\text{NO}_3)_2$ , the rates of NiS dissolution are greater than in the case of addition of  $200 \text{ g l}^{-1}$  NaCl to  $\text{CuCl}_2$ . Therefore, KBr additions are more efficient and more suitable for further processing of nickel-containing solutions.

## CONCLUSIONS

(1) Anions capable of complex formation with both Cu(II) and Cu(I) ions accelerate anodic dissolution of NiS in copper-containing electrolytes.

(2) The rates of anodic dissolution are the highest in the nitrate–bromide system, as the  $\text{Cu}_2\text{S}$  film formed at low potentials is dissolved by copper bromide complexes and thus is completely displaced by molten sulfur formed on the NiS surface.

(3) A new surface phase, probably  $\text{Ni}_3\text{S}_4$ , is initially formed upon anodic dissolution of NiS in  $\text{CuSO}_4$ .

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## REFERENCES

1. Sinel'shchikova, N.V. and Makarova, S.N., *Gidrometallurgiya medi i nikelya* (Hydrometallurgy of Copper and Nickel), Moscow: Tsvetmetinformatsiya, 1976.
2. *Tsvetnaya metallurgiya Finlyandii* (Non-Ferrous Metallurgy of Finland), Moscow: Tsvetmetinformatsiya, 1971.
3. Borbat, V.F. and Voronov, A.B., *Avtoklavnaya tekhnologiya pererabotki nikel'-pirrotinovykh kontsentratsiy* (Autoclave Processing of Nickel-Pyrrhotine Concentrates), Moscow: Metallurgiya, 1980.
4. Lilich, L.S. and Khripun, M.K., *Rastvory v neorganicheskoi khimii* (Solutions in Inorganic Chemistry), Leningrad: Leningr. Gos. Univ., 1984.
5. Muravchik, B.L. and Kipnis, A.Ya., *Zh. Prikl. Khim.*, 1982, vol. 55, no. 12, pp. 2650–2654.
6. *Gidrometallurgiya: Sbornik perevodov* (Hydrometallurgy: Coll. of Translations), Laskorin, B.N., Ed., Moscow: Metallurgiya, 1978.
7. Belyakov, E.A. and Kasikov, A.G., *Zh. Prikl. Khim.*, 1983, vol. 56, no. 6, pp. 1257–1261.
8. *Handbuch der präparativen anorganischen Chemie*, Brauer, G., Huber, F., et al., Eds., Stuttgart: Ferdinand Enke, 1978.
9. *Kratkii spravochnik po khimii* (Concise Handbook on Chemistry), Goronovskii, I.T., Nazarenko, Yu.P., and Nekryach, E.F., Eds., Kiev: Naukova Dumka, 1987.
10. Elliott, R. P., *Constitution of Binary Alloys*, New York: McGraw-Hill, 1965.
11. *Organic Electrochemistry. An Introduction and a Guide*, Baizer, M.M. and Lund, H., Eds., New York: Marcel Dekker, 1983.
12. Chernobaev, I.P. and Kasatkin, L.A., *Zh. Prikl. Khim.*, 1975, vol. 48, no. 2, pp. 345–349.
13. Dzhusulov, E.A., Pozin, M.Yu., and Tikhonov, K.I., *Zh. Prikl. Khim.*, 1979, vol. 52, no. 8, pp. 1692–1696.