Study of the Mechanism for Forming a Passivating Layer under Electrochemical Oxidation of Copper (I) Sulfide

O V Nechvoglod and S M Pikalov

Institute of Metallurgy, Ural Branch of the Russian Academy of Science, 101, Amundsen st., Yekaterinburg, 620016, Russia

E-mail: nechvoglodon@mail.ru

Abstract. In this study the patterns of anodic oxidation of copper (I) sulfide were considered. It was shown that during the crystallization of copper sulfide, the formation of both the chalcosine (Cu$_2$S) phase and the jarleite (Cu$_{31}$S$_{16}$) phase is possible, which is characterized by a deficiency of copper in the crystal lattice and deviation from the stoichiometric composition. The electrochemical oxidation of the sample in a solution of sulfuric acid was carried out. During oxidation, intermediate non-stoichiometric sulfides (Cu$_{1.74}$S, Cu$_{1.8}$S) were formed in the following sequence: Cu$_2$S → Cu$_{1.81}$S → Cu$_{1.74}$S → Cu$_{1.6}$S → CuS → S + Cu$^{2+}$. The process was accompanied by the transition of copper cations into solution. As elemental sulfur and copper sulfides accumulated on the reaction surface of the sample and, as a result, the rate of electrochemical oxidation decreased due to the difficulty of the product removal and the reagent supply to the reaction zone.

1. Introduction

Sulfide ores are the main raw material for the production of metallic copper [1–3]. Recently, hydrometallurgical technologies have been more widely used for their processing [4–8]. Existing leaching methods include the use of various reagents - oxidizing agents (including bioleaching) [9–11], high pressure (autoclaves) [12] and electric current [13–16]. Due to the fact that electrochemical processes are becoming more widespread in copper metallurgy, the relevance of research in this area is increasing. Of particular interest is the anodic dissolution of sulfide copper materials with the transfer of copper into solution, and elemental sulfur - into sludge [17]. A new alternative direction is the electrolysis of granular materials, in particular, sulfide copper, nickel and copper-nickel intermediates [18, 19]. For the physicochemical substantiation of the electrolysis technology of sulfide copper-containing materials, it is of interest to study the patterns of anodic oxidation of copper (I) sulfide.

Under the influence of an electric current, in a solution of sulfuric acid, Cu$_2$S is oxidized with the transition of sulfide sulfur (S$^2-$) to the elemental state (S$^0$) [20], and monovalent copper (Cu$^+$) to divalent (Cu$^{2+}$) one. The process has a stepwise mechanism and is accompanied by the formation of intermediate sparingly-soluble copper sulfides [20–22]. Copper cations pass into the solution and insoluble products – sulfides and elemental sulfur – accumulate on the reaction surface of the sample forming a sulfur-sulfide layer. This layer prevents product withdrawal and reagent supply to the reaction zone, causing diffusion limitations. A decrease in the rate of removal of copper cations from the anodic oxidation zone into the electrolyte volume leads to a decrease in the oxidation rate of the initial sample. The passivating layer (film) has a porous structure due to the removal of copper cations into the electrolyte volume, which ensures the further occurrence of electrochemical processes at the Cu$_2$S/film interface. The rate of electrochemical oxidation of
copper (I) sulfide is determined by the dissolution of the passivating layer and the diffusion of reagents and reaction products through it. The formation of a passivating layer occurs due to the phase transformations of Cu₂S under the influence of an electric current. As a result of the electrochemical oxidation of sulfide sulfur, CuS is formed through the series of transformations of sulfides of non-stoichiometric compositions.

The purpose of this study is to study the process of formation of a passivating layer and its structure formed on the surface of copper (I) sulfide as a result of electrochemical oxidation in a solution of sulfuric acid, as well as to study the sequence of phase transformations of copper (I) sulfide under the influence of an electric current.

2. Experimental
For research, a copper (I) sulfide sample was synthesized and its anodic oxidation was carried out to form a sulfur sulfide layer. The synthesis of copper sulfide was carried out by fusing copper (99.99% Cu) with sulfur in an electric resistance furnace at a temperature of 1250 °C in a reducing atmosphere. The melt was drawn into a quartz tube and cooled in air. The resulting rod of copper sulfide was pressed into the fluoroplastic. The working surface area on which the passivation layer was subsequently formed was 1 cm². A stainless steel rod was used as a cathode. The electrolyte was a solution of sulfuric acid with a concentration of 100 g/dm³ H₂SO₄ with a volume of 30 ml. The obtained copper sulfide anode was subjected to electrochemical oxidation for 15 minutes at a current density of 1000 A/m² in the current stabilization mode.

The initial sample and products of electrochemical oxidation were analyzed by various methods. X-ray diffraction method was applied to determine phase compositions of the initial copper (I) sulfide sample and the layer of its electrochemical oxidation products using a XRD-7000C diffractometer (Shimadzu Corporation, Japan). Processing of the results of XRD was performed on the basis of diffraction data from The International Centre for Diffraction Data (ICDD). The quantitative phase compositions were determined by the method of local scanning analysis using a scanning electron microscope-microanalysis system JSM-5900LV, equipped with a wave dispersive microanalyzer system INCA Energy 250 (Japan).

3. Results and Discussion
According to chemical analysis, the initial copper (I) sulfide sample contains, %: 77.4 – Cu and 22.6 – S. According to the XRD data (Figure 1, a), it is a non-stoichiometric solid solution of copper and sulfur with a predominant monoclinic structure (sp.gr. P2₁/n (14)) close in composition to copper sulfide Cu₃₁S₁₆ (jarlite). The sample contains a phase of metallic copper which is confirmed by metallographic analysis. Crystallization of the metal phase leads to the formation of a sulfide phase with a copper deficiency – Cu₃₁S₁₆, which explains the deviation from the stoichiometric composition. Also, a stoichiometric Cu₂S phase is present in the sample.

As a result of the electrochemical oxidation of copper (I) sulfide, a layer of sparingly soluble products is formed. Under conditions of anodic polarization [20–22], the oxidation of copper sulfide proceeds through a series of intermediate sulfide compounds according to the total reactions:

\[ \text{Cu}_2\text{S} - \text{e}^- = \text{CuS} + \text{Cu}^{2+}, \]  

\[ \text{CuS} - 2\text{e}^- = \text{Cu}^{2+} + \text{S}^0 \]  

According to the data presented in [20–22], under the influence of an electric current, copper (I) sulfide can decompose into copper and copper (II) sulfide:

\[ \text{Cu}_2\text{S} = \text{Cu} + \text{CuS}. \]
product layer had a dense uniform structure formed by fine particles of Cu₅S₆ sulfides of 4-6 microns in size.

![XRD patterns](image)

**Figure 1.** A) XRD pattern of the initial sample of copper sulfide; b) XRD pattern after electrochemical oxidation.

Table 1 Chemical composition at the sensing points (according to Figure 1).

| №  | Content, at.% | Phase      |
|----|---------------|------------|
|    | S            | Cu         |              |
| 1  | 37.6         | 61.5       | Cu₅S₆        |
| 2  | 36.8         | 61.9       | Cu₅S₆        |
| 3  | 11.7         | 88.1       | Cu-CuS       |
| 4  | 30.0         | 69.9       | Cu-CuS       |
| 5  | 38.9         | 60.4       | Cu₅S₆        |

According to the XRD data, the responses characteristic of elemental sulfur have been identified. However, they have a low intensity, which can be explained by sulfur amorphousness, an insignificant
amount and dispersion of particles. The film formed comprises an inner sublayer with a dense uniform structure and an outer layer with dense homogeneous and loose inhomogeneous areas. The electrochemical oxidation of copper (I) sulfide (Cu$_2$S, Cu$_{31}$S$_{16}$) in a sulfuric acid electrolyte proceeds, at the first stage, with the formation of non-stoichiometric Cu$_{1.81}$S, Cu$_{1.74}$S, Cu$_{1.6}$S up to CuS. At the second stage, CuS is oxidized to elemental sulfur. The process is accompanied by the transfer of copper cations into the solution. In the interaction of copper cations with a sulfate electrolyte in the presence of oxygen released at the anode, the formation of oxide-sulfate inclusions of the mCuO - nCuSO$_4$ type is possible.

The sequence of phase transformations of the test sample of copper (I) sulfide can be represented in a general form as follows: Cu$_2$S (Cu$_{31}$S$_{16}$) → Cu$_{1.81}$S → Cu$_{1.74}$S → Cu$_{1.6}$S → CuS → S + Cu$^{2+}$.

Figure 2. A layer of copper sulfides formed on the surface of a Cu$_2$S sample after electrochemical oxidation.

The decomposition mechanism of copper (I) sulfide by reaction (3) explains the formation of areas of metallic copper on the surface of the electrodes.

In this study, the mechanism of electrochemical oxidation of copper (I) sulfide has been validated. The data on the chemical and phase composition of sparingly soluble products have been specified and expanded. The sequence of phase transformations has been considered.

4. Conclusion

1. The electrochemical dissolution of copper (I) sulfide proceeds with the formation of a film of insoluble products due to the oxidation of sulfide sulfur to copper sulfide and sulfur in an elemental state. As oxidation progresses, intermediate non-stoichiometric sulfides are formed.
2. The sequence of phase transformations of copper (I) sulfide can be represented in a general form as follows: Cu$_2$S (Cu$_{31}$S$_{16}$) → Cu$_{1.81}$S → Cu$_{1.74}$S → Cu$_{1.6}$S → CuS → S + Cu$^{2+}$.

References

[1] Moskalyk R R and Alfantazi A M 2003 Miner. Eng. 16 893
[2] Pedersen K B, Jensen P E, Ottosen L M, Evensen A, Christensen G N and Frantzen M 2017 Miner. Eng. 107 100
[3] Wang M, Chen W and Li X 2015 Resour. Conserv. Recy. A 105 36
[4] Dreisinger D 2006 Hydrometallurgy 83 10
[5] Mizoguchi T and Habashi F 1981 Int. J. Miner. Process 8 177
[6] Letowski F, Kołodziej B, Czernecki M, Jedrczak A and Adamski Z 1979 Hydrometallurgy 4 169
[7] Xu B, Zhong H, and Jiang T 2011 Miner. Eng. 24 1082
[8] Hyvarinen O and Hamalainen M 2005 Hydrometallurgy 77 61
[9] Dreisinger D 2006 Hydrometallurgy 83 10
[10] Sheng-hua Y, Ai-xiang W and Guan-zhou Q 2008 Trans. Nonferrous Met. Soc. China 18 707
[11] Wu A X, Xi Y, Yang B H, Chen X S and Jiang H C 2007 Acta Metall. Sin. (Engl. Lett.) 20 117
[12] Jin B, Yang X and Shen Q 2009 Hydrometallurgy 96(1) 57
[13] Abd El Haleem S M and Din Abd El Aal E E 2007Alloys Compd. J. 432(1) 205
[14] Kartal L and Timur S 2018 Trans. Nonferrous Met. Soc. China 28 2143
Acknowledgements
The reported study was funded by RFBR and Sverdlovsk Region, project number 20-48-660020.