Anodic Reaction of Arsenopyrite in Ammoniacal Solution

FANG Zhao-heng (　　　)   YU Jing-kai (　　　)

(Institute of Chemical Metallurgy   Chinese Academy of Sciences   Beijing l00080, China)

Abstract: Anodic dissolution of arsenopyrite in ammonical solution has been investigated by electrochemical methods. The process is an irreversible reaction with formation of a ferric oxidized film and is retarded by the film. The process rate is controlled by the electrochemical reaction on the electrode surface in the lower temperature range, or alternatively by the diffusion through the film in the higher temperature range. The overall reaction has 14 electron transferred and can be expressed by

$$FeAsS + 11H_2O = Fe(OH)_3 + SO_4^{2-} + HAsO_4^{2-} + 18H^+ + 14e^-,$$

and the reaction involves two steps: (1) $FeAsS + 7H_2O = Fe(OH)_3 + HAsO_4^{2-} + S^0 + 10H^+ + 8e^-$,

(2) $S^0 + 4H_2O = SO_4^{2-} + 8H^+ + 6e^-$.
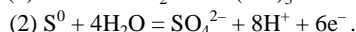
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1 INTRODUCTION

Arsenopyrite is the most common sulfide mineral in arsenic refractory gold ores. The ore refractoriness mainly results from dissemination of fine grained gold in arsenopyrite and other sulphide minerals. Oxidation of sulfides by either pyro-metallurgical or hydrometallurgical tech-niques to render these ores amenable to the standard cyanidation is therefore universally effective in gold extraction. A newly developed pretreating technology for arsenopyrite-type ores is oxygenated leaching in ammoniacal solution. A study on anodic dissolution of FeAsS will help to realize the leaching process and to improve the technology.

Several researches have been devoted to the electrochemical oxidation of FeAsS in alkaline or acidic solutions. It was reported[1,2] that the oxidation of FeAsS is retarded by a film consisting of ferric hydroxide and elemental sulfur on the electrode surface in alkaline solution with pH>7. Sanchez et al.[2] suggested that the oxidation of FeAsS in alkaline solutions occurs in two steps: elemental sulfur and arsenite are formed in the first step and they are then oxidized to sulfate and arsenate in the second step. They also found that elemental sulfur covers the surface of FeAsS at potentials about 0.5 V (SHE) in an acidic solution with pH=1.0, and that formation of $H_2AsO_3^-$ is corresponding to the main peak[3].   Wang et al. [4] pointed out that initial oxidation of FeAsS formed ferric hydroxide in alkaline solutions. Lin et al.[5] indicated that the apparent activation energy for arsenopyrite oxidation in chloride solutions is 42 kJ/mol, and transfer of electrons through the sulfur film is the rate-controlling step at 0.8 V (SHE). However, no mechanism of FeAsS oxidation in ammoniacal solution has been reported so far. In this work the anodic reaction of FeAsS in ammoniacal solution is investigated using several electrochemical techniques. The dissolution behavior, oxidation kinetics and reaction of arsenopyrite are determined.

2   EXPERIMENTAL

Arsenopyrite electrodes were prepared from high quality and homogeneous mineral specimens and cast in suitable epoxy resin. The working area of the electrode was exposed by grinding and polishing, and these operations were repeated before every experimental run. The chemical analysis of the arsenopyrite sample showed that the contents of Fe, As, S were 34.34%, 43.36%, 18.01% respectively and congruent with the theoretic stoichiometric composition of FeAsS, while other metal values, such as Ni, Cu, Co, Sb and Ag, were not observed.

Conventional electrochemical techniques (potential sweep, potential step, coulometry) and three-electrode glass cell were employed.   The reference electrode in all electrochemical experiments was a saturated calomel electrode. The effective potential is quoted with respect to the standard hydrogen electrode (SHE), assuming the potential of SCE is 0.245 V against the SHE.

3   RESULTS AND DISCUSSION

3.1   Thermodynamics of the Fe–As–S–H_2O System

The Eh–pH diagram for the Fe–As–S–H_2O system for 1 mol/L dissolved species is presented in Fig.1. These diagrams were generated employing the HSC CHEMISTRY software. The metastable sulfur, acted as the thermodynamically favorable species, is included in the diagram because the oxidation of sulfur to sulfate proceeds with a negligible rate in the potential range covered by the voltammograms. In addition, oxidation of sulfide to sulfate generally requires high overpotential and occurs at significant rate only at the potentials with sulfur being also a product. On the other hand, the hydrated iron oxide is included in the diagrams, since they are more likely to be formed than anhydrous oxides under the experimental conditions.
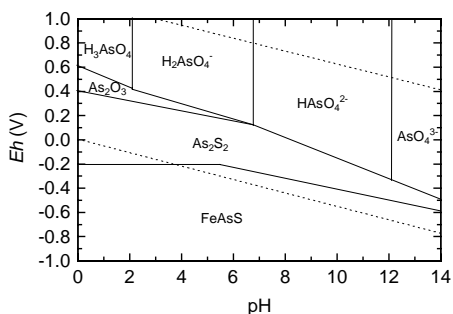

Fig.1 (a) Eh–pH diagram for As in the
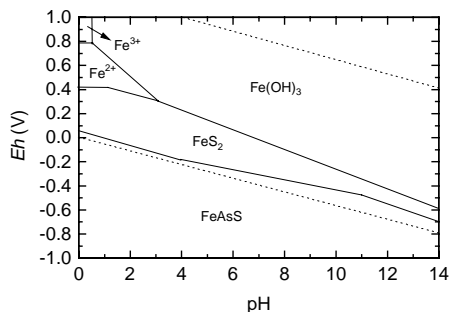Fe–As–S–H_2O system

Fig.1 (b) Eh–pH diagram for Fe in the
Fe–As–S–H_2O system

3.2   Potential Sweep

The study on current–voltage behavior of FeAsS was carried out in 5% ammoniacal solution. Measurements of the rest potential (U_r) of FeAsS electrode in both ammonia and alkaline solutions (pH=11.0) are listed in Table 1. It can be seen that the U_r in ammoniacal solution is lower than that in alkaline medium and decreased with the increase of temperature, indicating oxidation of FeAsS in ammonia solution is favorable.

Table 1 Measurement of U_r in ammonia and alkaline solutions at various temperatures (mV)

T (°C)	25	45	65	85
In 47.5 g/L HN$_3$ solution	90	65	32	20
In 4 g/L NaOH solution	163	120	90	85

Voltammograms from the potential sweep, starting from the rest potential, for a stationary electrode of FeAsS in 5% ammoniacal solution at pH=11 are shown in Fig.2. It can be seen that a current peak appears at the potential of 0.25 V with a sweep rate of 20 mV/s. Experiments of various sweep rates show that the potential of the peak is linearly increased with higher sweep rate. This suggests that the reaction corresponding to the peak is irreversible.

In the case of solution seriously agitated with a magnetic stirrer at the bottom of the cell, no effect on the voltammograms was observed as compared with the stagnant solution. It confirms that there is no soluble species produced at high potential in the process[5].
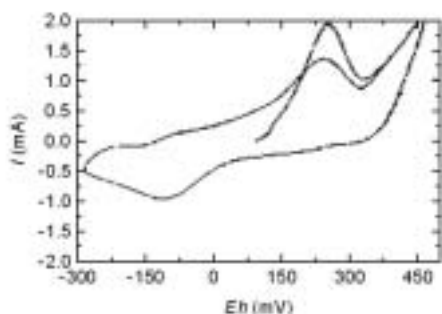

Fig.2 Voltammograms for FeAsS electrode
in ammoniacal solution at pH=11
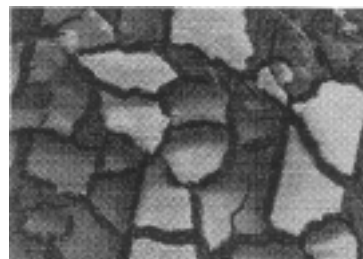

— 100 μm

Fig.3 SEM microgram of FeAsS electrode
surface oxidized at 0.25 V

It was observed that a film was formed on the electrode surface during anodic sweeping. SEM microgram of the surface oxidized at 0.25 V for 2 h is shown in Fig.3. The film is loose and porous, and characterized with irregular crevices, so that it retards anodic oxidation in certain degree but does not completely stop the reaction. The X–EDAS analysis gives that the film consists only of sulfur and iron. It seems that the solid products of oxidation reaction at this potential will hence be elemental sulfur and iron hydroxide. Unfortunately, this film could not be characterized in mineralogy and by chemical compositions in detail, because it is very thin and difficult to be sampled for analysis.

The peak current varies with temperature, as shown in Fig.4. The current increases with the temperature in the range from 298 to 323 K and when higher than 338 K, and it does not change
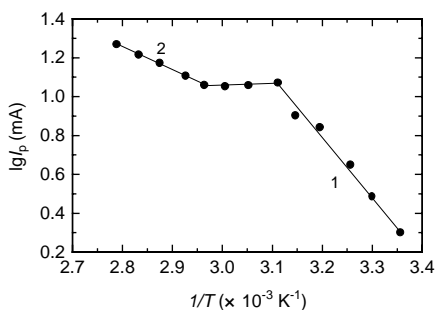

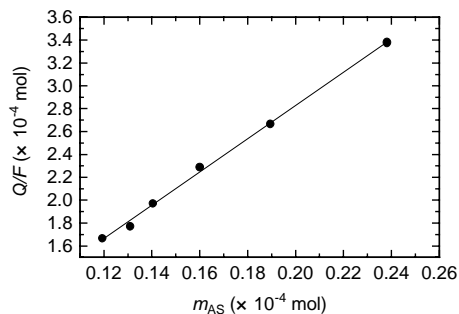Fig.4 Arrhenius diagram for peak currents

Fig.5 Plot of Q/F vs. m_{As} dissolved in solution

between 323 and 278 K. It seems that the rate processes in the high and low temperature ranges are different. From the Arrhenius diagram of the peak current the apparent activation energy of reactions is calculated as 54 and 23 kJ/mol respectively, which indicates that the rate controlling step is chemical reaction in the lower temperature range and diffusion in the higher range.

3.3　Potential Step

In potential step experiments, a potential jump was applied to the electrode in order to exert quickly the final potential from an initial value with no Faradic current. Before the step, the concentration of the electrochemically active species on the electrode surface is zero, and this guarantees that the current is Faradic immediately after the potential is jumped.

In fact, the potential jump to the electrode needs a very short time due to the limitation of the experimental equipment and the presence of changing current for the electrode capacitance. The Faradic current at t(time)=0 was usually calculated from the linear correlation of I (measured current) vs. $t^{1/2}$ for a Faradic process. Based on the Faradic current measurements at different potentials, from potential step experiments, an anodic Tafel plot of FeAsS electrode was obtained. The Tafel slop was calculated as 476 mV, much higher than the typical value for a single electron transfer reaction. This suggests that some resistance exists for the electrochemical process on the electrode surface, where is in agreement with the results mentioned in Section 3.1.

From the Faradic current measured at various temperatures, a linear correlation was observed between the logarithmic current at t=0 ($I_{t=0}$) and the reciprocal of temperature ($1/T$). The calculated apparent activation energy for the reaction is 48 kJ/mol, very close to the value (42 kJ/mol) resulting from peak current measurements in chloride solution[5].

3.4　Coulometry

At the constant potential of 0.6 V coulometric measurements were carried out. The anodic dissolution took place in a period ranging from 6 to 12 h. The As content in solution was measured by ICP. A linear plot of Q/F against arsenic moles in solution (Fig.5) gives a slop of 13.9, this suggesting what the stoichiometric number of electrons transferred in the overall reaction is 14. The overall reaction can be represented as

$$FeAsS + 11H_2O = Fe(OH)_3 + HAsO_4^{2-} + SO_4^{2-} + 18H^+ + 14e^- . \tag{1}$$
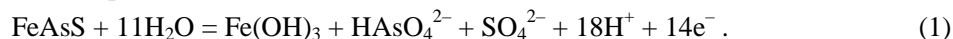
Similarly, the coulometric measurement at 0.25 V gave a value of 10.9. This indicates that the reaction mechanism at the peak potential differs from that at a higher potential. It is most possible to form elemental sulfur as a product, and the overall reaction at this potential can be represented as

$$FeAsS + 7H_2O = Fe(OH)_3 + HAsO_4^{2-} + S^0 + 10H^+ + 8e^- . \tag{2}$$
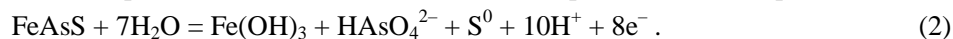
It is also possible that a parallel reaction of forming sulfate occurs because the measured transfer electron number is larger than 8.

3.5　Reaction Mechanism

The anodic dissolution of arsenopyrite in ammonia solutions is a quite complex process. The electron number transferred in the overall reaction is 14, and the reaction is represented as Eq.(1).

This anodic process includes at least two consecutive steps of reactions. The first step is the oxidation of sulfide to elemental sulfur and the formation of arsenate[Eq.(2)]. The second is the

oxidation of sulfur to sulfate at higher potentials, i.e.,

$$S^0 + 4H_2O = SO_4^{2-} + 8H^+ + 6e^- .\tag{3}$$

The main peak corresponded to the first step reaction. This result agrees with published report[2] except that no arsenite formed in the first step in ammonia solution. As mentioned in section 3.2, comparing the voltammograms from stagnant and agitated, it was found that no dissolved product species, which will be oxidized at a higher potential, was detected in the first step.

The value of the apparent activation energy of 48 kJ/mol, calculated from the initial Faradic process, suggests that electrochemical reaction, rather than transfer of reactive or produced species, is the rate controlling step during the starting period of the anodic process. However, there has different rate process for the overall anodic dissolution of arsenopyrite due to the growth of surface film and rise of temperature. With the increase of reaction temperature the rate-controlling step of the dissolution process is different, judged from different apparent activation energy calculated from the Arrhenius diagram of peak current measurements under various temperatures. In higher temperature range the process rate is controlled by the diffusion of product species through the surface film.

4　SUMMARY

The anodic dissolution of arsenopyrite in ammonia solutions has been investigated with electrochemical techniques, and the results are summarized as follows:

(1) The dissolution process in ammonia solution starts at a lower potential than that in alkaline solutions at the same pH value, and is irreversible. A ferric hydroxide film is formed during the anodic process and further dissolution reaction is thus retarded.

(2) The reaction rate of the initial anodic dissolution is controlled by electrochemical reaction. The apparent activation energy of the reaction is 48 kJ/mol. In a higher temperature range, the apparent activation energy of the overall process is 23 kJ/mol and the rate is controlled by the diffusion of produced species.

(3) Stiochiometric determinations with coulometric technique show that the electron transfer number involved in the overall reaction is 14 at 0.6 V or higher potential. The overall reaction is represented by Eq.(1).

(4) The anodic dissolution of arsenopyrite in ammoniacal solution proceeds by the two-step mechanism as expressed by Eq.(2) and Eq.(3).

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