Corrosive electrochemistry of jamesonite by cyclic voltammetry

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Abstract: The corrosive electrochemistry of jamesonite was studied by cyclic voltammetry. Every peak in voltammograms was identified through thermodynamic calculation. The results show an irreversible electrode process by the strong adsorption of oxidation elemental sulfur on jamesonite. A deficient-metal and sulfur-rich compound is formed under the potential of 80 mV at pH 6.86. The passive action by elemental sulfur occurs from 80 to 470 mV and $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_4^{2-}$ are produced at potential over 470 mV. The anodic peak producing $\text{SO}_4^{2-}$ is inhibited due to the deposition of $\text{PbSO}_4$ at higher potential in $\text{Na}_2\text{SO}_4$ solution. The corrosive action of jamesonite becomes strong and the redox characterization similar to $\text{PbS}$, $\text{FeS}$ and $\text{Sb}_2\text{S}_3$ appears at pH 9.18.

Key words: jamesonite; corrosive electrochemistry; voltammetry

1 INTRODUCTION

It is very important for the potential-controlled flotation to study the electrochemical behavior on a sulfide mineral so as to understand the probable oxidized productions on the mineral surface. So far, there are two kinds of views about the flotation mechanisms and the oxidation of sulfide minerals. One is that sulfide is oxidized into elemental sulfur at certain potential, generally supported by the voltammetric studies1-4. The other is that a deficient-metal and sulfur-rich compound is formed, in general, supported by X-ray photo electron spectrum (XPS) investigation5-8. Some scholars thought that treating a XPS sample in a vacuum may result in losing volatile sulfur. In addition to this, XPS can only provide the information about the elemental distribution, and cannot establish the exact molecular identity of the surface species inferred from the binding energy shifts of the elements comprising the bulk molecule9-10. Recently, two kinds of views tend to harmony, namely, the deficient-metal and sulfur-rich compound is only formed in the early period of oxidation and the sulfide can further be oxidized into $\text{S}$, $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_4^{2-}$ under certain conditions4,11.

Jamesonite is a complicated sulfide with multimetals, which is one of mainly valuable mineral of Sn-Pb-Zn deposite in Dachang of Guangxi Province. There are few studies on the flotation electrochemistry of jamesonite due to its brittle and poor conductivity. Its electrochemical mechanism has not been reported so far. Therefore, the corrosive electrochemistry of jamesonite was studied using a carbon paste electrode(CPE)12 by voltammetry and thermodynamic calculations in this paper.

2 EXPERIMENTAL

Working electrode was a kind of carbon paste electrode that consisted of 80% (mass fraction) jamesonite particles with size of less than 0.15 mm, 10% graphite powder and 10% paraffin. The diameter of its working face exposed to the solution was 15 mm (area about 1 cm$^2$). 0.1mol/L $\text{KNO}_3$ solution was used as a supporting electrolyte. All reagents were analytically pure and prepared by distilled water. The graphite powder was spectrum grade.

A conventional three-electrode cell was used, a platinum piece was served as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All of the potential values in this paper were calibrated vs SHE (standard hydrogen electrode). The temperature was maintained at 25°C. After each measurement, the working electrode surface was gently polished on the abrasive papers of different types, and then washed by distilled water. Experimental device was the Potentiostat/Galvanostat Model 273A from EG&G PAR company and M270 soft system was employed for measuring cyclic voltammograms.
3 RESULTS AND DISCUSSION

3.1 Stable formation of oxidized products in jamesonite/solution system

It would be reasonable to assume that the concentration of an ion is $1 \times 10^{-6}$ mol/L in an electrode/solution system. So if $c(\text{Fe}^{2+})$ is assumed to be $1 \times 10^{-6}$ mol/L, then $c(\text{Pb}^{2+})$ will be $4 \times 10^{-6}$ mol/L and $c(\text{HSbO}_2(\text{aq}))$ will be $6 \times 10^{-6}$ mol/L in terms of stoichiometric coefficient of jamesonite. Some thermodynamic calculations are as follows:

$$\text{Sb}^{3+} + \text{H}_2\text{O} = \text{SbO}^+ + 2\text{H}^+, \quad \text{pH} = -1.527, \Delta G^0 = -17.42 \text{ kJ/mol}, K = 1.133$$

$$\text{SbO}^+ + \text{H}_2\text{O} = \text{HSbO}_2 + \text{H}^+, \quad \text{pH} = 0.998, \Delta G^0 = 5.06 \text{ kJ/mol}, K = 0.129$$

$$\text{Pb(OH)}_2 = \text{Pb}^{2+} + 2\text{OH}^-, \quad K_w = 2 \times 10^{-16}$$

$$\text{HSbO}_2 = \text{Fe}^{2+} + 2\text{OH}^-, \quad K_w = 2 \times 10^{-15}$$

$$\text{Fe(OH)}_3 = \text{Fe}^{2+} + 3\text{OH}^-, \quad E_h = 1.223$$

Considering their ion-product, $\Delta G^0$, $K$ (equilibrium constant) and $E_h$ (condition potential), the most stable species are $\text{HSbO}_2(\text{aq})$ and $\text{Pb}^{2+}$ in the solution of pH 6.86, according to Eqns. (1)-(4). When $c(\text{Fe}^{2+})$ is $1 \times 10^{-6}$ mol/L, $\text{Fe}^{2+}$ cannot be oxidized into $\text{Fe(OH)}_3$ until pH $\geq 7.94$, and $\text{Fe}^{2+}$ is the stable specy in the solution, known from the Eqns. (5) and (6). But $\text{HSbO}_2(\text{aq})$, $\text{Pb(OH)}_2$, and $\text{Fe(OH)}_3$ are the stable species at pH $> 9.18$, respectively.

3.2 Corrosive products of jamesonite under different potential conditions

It was reported that the oxidized products of a sulfide are probably deficient-metal compound, $S^0$, $S_2O_6^{2-}$ or $SO_4^{2-}$ at a certain potential. The voltamogram for jamesonite is shown in Fig. 1. It can be seen that there are obvious 4 anodic peaks at the first cycle voltammetry in Fig. 1. The peak currents of $ap_1$, $ap_3$ and $ap_5$ constantly increase with increasing the cycle number, but the peak heights of $ap_2$ and $ap_4$ decrease at the second cycle and then keep constant even by multi-cycle according to the experimental appearances. It is assumed that $ap_5$ peak corresponds to the reaction of forming the deficient-metal and sulfur-rich compound, whereas $ap_3$ is related to the reaction in which the deficient-metal sulfide is further oxidized into elemental sulfur. As described below, the $E_h$ values in Eqns. (7) and (8) are unanimous with the peak potential in Fig. 1.