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Corrosive electrochemistry of jamesonite①

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Abstract: The corrosive electrochemistry of jamesonite ($Pb_4FeSb_6S_{14}$) was studied by the electrochemical methods of cyclic voltammetry, polarization, and AC impedance. The electrochemical processes of jamesonite were controlled by the corrosive reactions, growth of the metal-deficient and sulfur-riched layer, passivation and breakdown of elemental sulfur film on the electrode surface. The corrosive potential(φ_{corr}) moves negatively, its corrosive current increases, and hydroxyl action becomes stronger with the rising pH value. The charge transfer resistance increases and the capacitance decreases due to the gradual growth of the metal-deficient and sulfur-riched layer on the mineral surface from -378 to 122 mV (vs SHE). Element sulfur layer is formed at the potential of 122 mV. The charge transfer resistance increases and its capacitance rises slowly due to the gradual breakdown of sulfur film at voltage from 222 mV to 422 mV. $S_2O_3^{2-}$ and SO_4^{2-} ions occur when the electrode potential is over 422 mV. Under basic condition, the hydrophobic hydroxyl precipitate occurs on jamesonite surface, so that its collectorless floatability is poor. Under the condition of pH 6.86, it can be deduced that the potential range of collectorless floatability of jamesonite is from 22 to 422 mV due to the passive action of the hydrophilic sulfur on jamesonite surface, and its optimum range of floatable potential is between 122 and 322 mV.

Key words: jamesonite; electrochemistry; potential-controlled flotation

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1 INTRODUCTION

The electrochemical reactions on the surface of sulfide minerals, which decides whether the surface of sulfide minerals are of hydrophobicity or hydrophilicity, may be adjusted and controlled by potential. It is gradually developed as a new potential-controlled flotation technology which is one of the important direction in mineral processing field in the new century[1].

Surface chemistry and reactivity of minerals such as FeS_2, PbS, ZnS, $CuFeS_2$, and so on, have been studied by using a variety of electrochemical and spectroscopic methods[2-11]. Jamesonite ($Pb_4FeSb_6S_{14}$) is a very useful and complex sulfide mineral with multiple metallic ingredients in Dachang Mine. But its electrochemical mechanism has not been reported so far due to its brittleness and the poor electric conductivity. Since their surface chemistry is controlled largely by pH and redox potential across the mineral/solution interface, it is very important for controlled-potential flotation to study the electrochemical mechanisms at different potentials and pH values.

Cyclic voltammetry was extensively adopted in the investigation of flotation electrochemistry.

Recently, electrochemical AC impedance gradually became the effective method for studying the corrosive reactions, interfacial absorption and its film structure[12-16]. The interface electrochemical mechanisms of jamesonite at different pH values and potentials were first investigated by the methods of cyclic voltammetry, polarization, and impedance measurement under extensive potential and frequency conditions.

2 EXPERIMENTAL

Samples of jamesonite with high quality, which were handpicked from Dachang Mine in Guangxi province, were used in this work. Working electrode used in the experiments was a kind of carbon paste electrode consisting of 80% jamesonite with particles of less than 0.15 mm, 10% graphite powder of spectrum grade and 10% of paraffin. Its working face exposed to the solution was 15 mm in diameter, about 1 cm^2, and other faces were cov-

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ered by epoxy resin. 0.1 mol/L KNO_3 solution was used as a supported electrolyte. All used solutions in experiments were prepared from analytical reagents and distilled water.

A conventional three-electrode cell was used in experiments. A piece of platinum was severed as the counter electrode, with Ag/AgCl electrode as the reference electrode, but all potentials in the paper were calibrated vs SHE. The reference electrode was located in a Luggin capillary which was just placed above the surface of the working electrode. In order to renew the working face, the working electrode surface was gently polished by different types of abrasive papers step by step into smooth face, then washed by distilled water during every measurement. The Potentiostat/Galvanostat Model 273A from EG&PAR Company was employed. Polarization curves, cyclic voltammograms and electrochemical impedance spectra (EIS) with the amplitude of 5 mV from 10^5 to 5×10^{-3} Hz were measured by M352 soft system, M270 soft system and M398 soft system, respectively.

3 RESULTS AND DISCUSSION

3.1 Discussion of polarization measurement

Fig. 1 is the polarization curves for jamesonite electrode in 0.1 mol/L KNO_3 at different pH values. Their Tafel parameters are showed in Table 1, given by the computer' PARcal. Obviously, its corrosive potentials (φ_{corr}) move towards negatively, and the corrosive action strengthens and its oxidization speed increases with the rising pH values due to its corrosive current density (J_{corr}) increase with the enhancement of pH values. The anodic slope (b_a) increases among all experimental pH values. This indicates that hydroxyl precipitate inhibits anodic reaction. The cathodic slope (b_c) increases between pH 7 and 10.4, and reaches the maximum at pH 10.4, but decreases again at pH 11.3. This reveals that hydroxyl precipitate also inhibits cathodic reaction under weak basic condition, and the dissolvent appearance of hydroxyl precipitate occurs under strong basic condition.

Table 1 Tafel parameters of jamesonite electrode in 0.1 mol/L KNO_3 solution at different pH values

pH	φ_{corr}/mV	J_{corr}/($\mu A\cdot cm^{-2}$)	b_a	b_c
7.0	85.2	0.332	0.167	0.152
9.3	55.4	1.01	0.338	0.183
10.4	35.8	1.30	0.241	0.307
11.3	−17.8	1.51	0.251	0.197

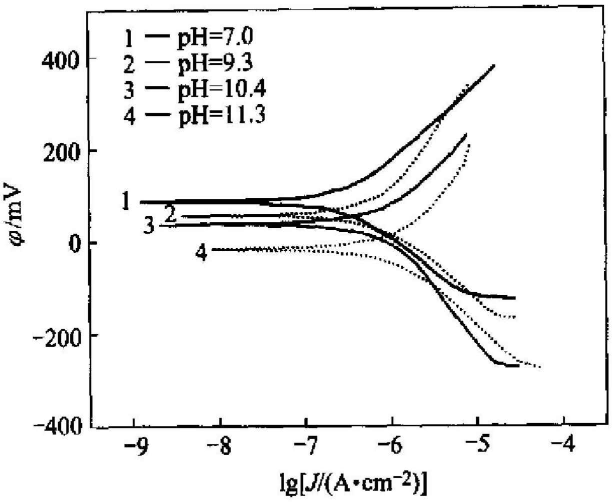

Fig. 1 Polarization curves for jamesonite electrode in 0.1 mol/L KNO_3 at different pH values

3.2 Electrochemical impedance spectrum under different potential conditions

Figs. 2−4 show the EIS of jamesonite electrode in 0.1 mol/L KNO_3 solution at pH 7 under different potential conditions. The EIS are in $x-y$ quadrant with resis-

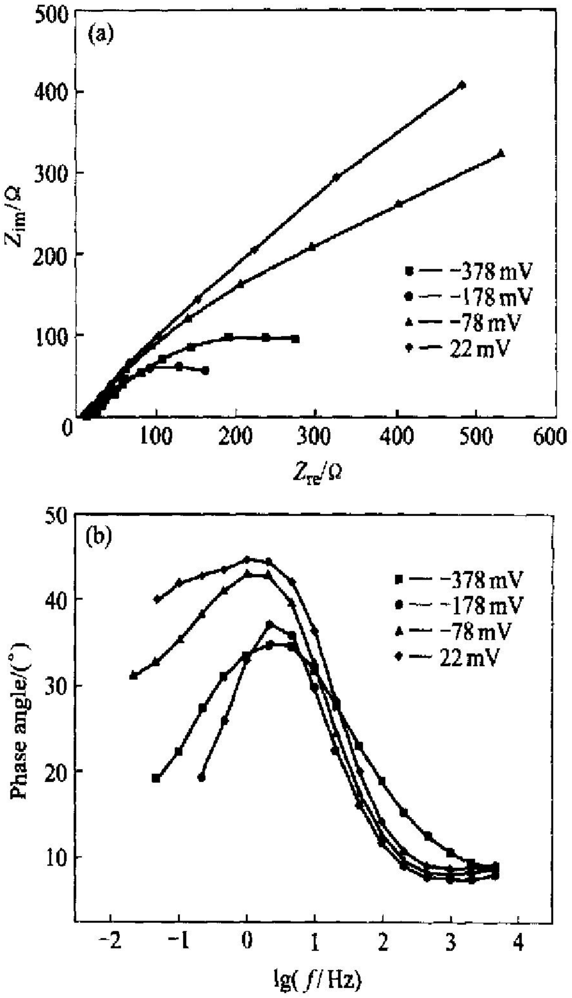

Fig. 2 EIS of jamesonite electrode in 0.1 mol/L KNO_3 solution of pH 7 from −378 mV to 22 mV
(a) —Nyquist plot; (b) —Bode plot

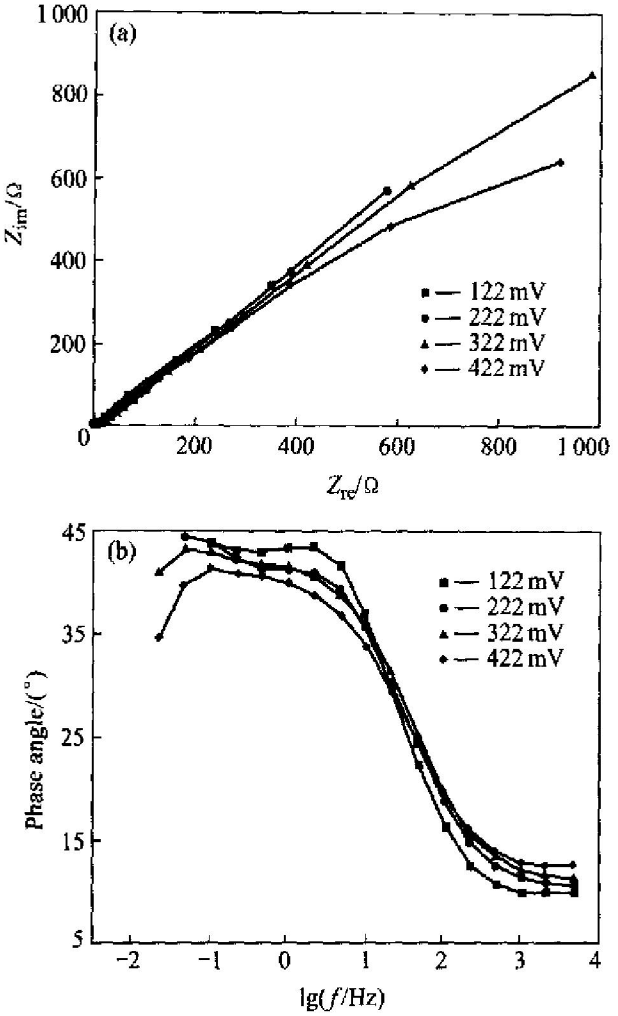

Fig. 3 EIS of jamesonite electrode in 0. 1 mol/L KNO_3 solution of pH 7 from 122 to 422 mV
(a) —Nyquist plot; (b) —Bode plot

tance (R) large than 0 and capacitance (C) large than 0, showing the electrode process of the absorbed intermediate. The equivalent circuit for the EIS is the parallel of the electrochemical resistance (R) and the absorption capacitance (C)[15-17].

It can be seen from Figs. 2 ~ 4 that all the Nyquist diagrams (a) appear single capacitive loop between -378 and 822 mV. But surface process of jamesonite electrode is controlled by quite different electrochemical process under different potential conditions[15, 16]. When the potential is between -378 and 122 mV, the charge transfer resistance (R_t) increases and its double layer capacitance decreases with the enhancement of electrode potential. Here, the growth of metal-deficient and sulfur-riched layer from anodic oxidization of jamesonite is the controlled step. Its charge transfer resistance (R_t) reaches the maximum and its double layer capacitance reach the minimum at 222 mV. When the potential is between 222 and 322 mV, the electrode process basically is in the situation of strong passivity by elemental sulfur.

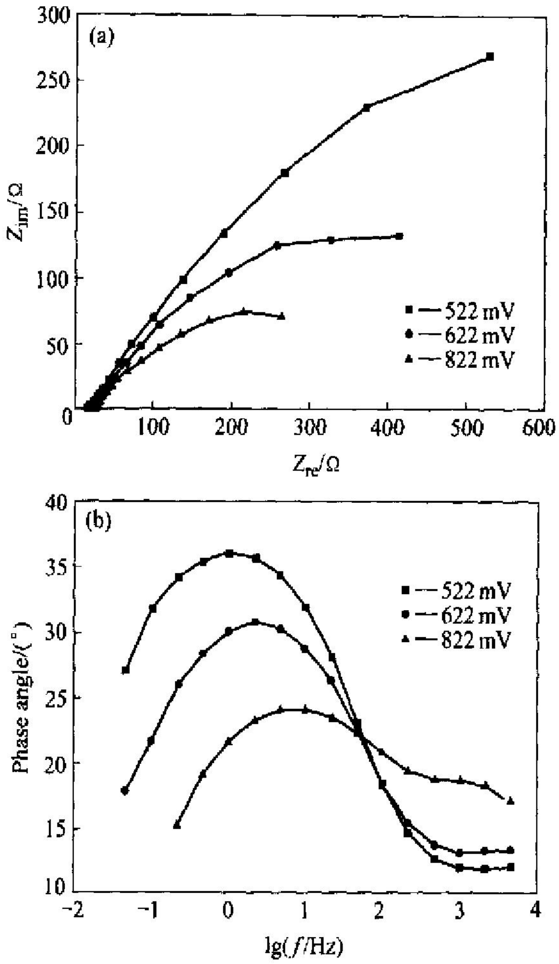

Fig. 4 EIS of jamesonite electrode in 0. 1 mol/L KNO_3 solution of pH 7 from 522 to 822 mV
(a) —Nyquist plot; (b) —Bode plot

Thereafter, the charge transfer resistance (R_t) decreases and its double layer capacitance increases again with continuous enhancement of electrode potential. Therefore, dissolution of sulfur film is the controlled step of electrode process.

Seen from Bode phase-angle plots (b), the peak of phase angle rises and becomes wide with the rising electrode potential. The passive phase-angle occurs between 22 and 422 mV as the formation of metal-deficient and sulfur-riched layer and element sulfur (S^0) adsorbed on the electrode result in the passive action. Single phase-angle appears again when the potential is larger than 422 mV, due to the complete breakdown of the passive film of sulfur. But two phase-angles exist at 822 mV. This indicates that $PbSO_4$ deposits on the electrode surface.

3. 3 Cyclic voltammograms

The oxidation products on jamesonite electrode are very complicated. If the concentrations of the ions were assumed as 10^{-6} mol/L, Fe^{2+} will be oxidized into $Fe(OH)_3$ at pH 7. 93 according to reaction (1), according to thermodynamic calculation, $HSbO_2$(aq), Pb^{2+} and

Fe^{2+} are the stable pieces existing in the solution of pH 6.86, and $HSbO_2(aq)$, $Pb(OH)_2$ and $Fe(OH)_3$ are the stable pieces existing in the solution of pH 9.18.

$$Fe(OH)_3 + e = Fe^{2+} + 3OH^- \qquad (1)$$

$$\varphi = 1.406 - 0.177pH$$

The reactions at *a*, *b*, *c*, *d* shown in Fig. 5 may be respectively as follows.

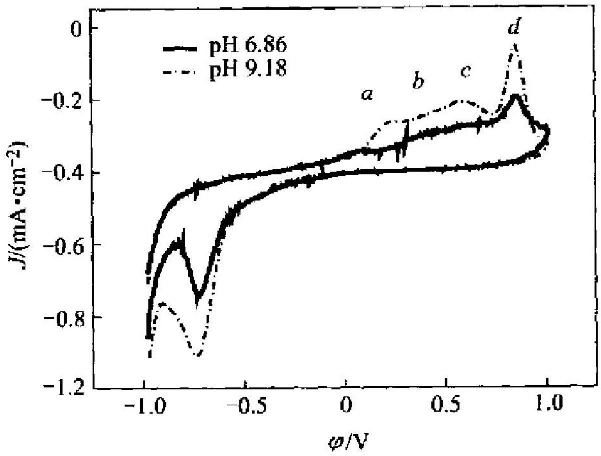

Fig. 5 Voltammograms for jamesonite electrode in 0.1 mol/L KNO_3 buffer solution at different pH values

$$6HSbO_2 + 4PbS + Fe^{2+} + 10S^0 + 20e + 18H^+ = Pb_4FeSb_6S_{14} + 12H_2O \qquad (2)$$

$$6HSbO_2 + 4Pb^{2+} + Fe^{2+} + 14S^0 + 28e + 18H^+ = Pb_4FeSb_6S_{14} + 12H_2O \qquad (3)$$

$$6HSbO_2 + 4Pb^{2+} + Fe^{2+} + 7S_2O_3^{2-} + 56e + 60H^+ = Pb_4FeSb_6S_{14} + 33H_2O \qquad (4)$$

$$6HSbO_2 + 4PbSO_4 + Fe^{2+} + 10SO_4^{2-} + 112e + 130H^+ = Pb_4FeSb_6S_{14} + 68H_2O \qquad (5)$$

Seen from Fig. 5, anodic current becomes positive at − 378 mV or so. At pH 6.86, the potential of the first oxidization peak "*a*" occurs at 61 mV. The current density almost does not change and passive appearance of sulfur film exists from 61 mV to 210 mV at pH 6.86. According to Fig. 5, the passive phase-angle exists up to 422 mV. Therefore, the peaks "*a*" and "*b*" correspond to reactions (2) and (3), respectively. Peak "*c*" represents reaction (4) due to the existing single phase-angle. Peak "*d*" represents reaction (5). Here, the adsorption of $PbSO_4$ on the electrode surface of jamesonite results in existing two phase-angles.

At pH 9.18, the similar voltammogram to those of pH 6.86 was observed. But the corrosive current density at pH 9.18 is bigger than that at pH 6.86. This is in agreement with the result shown in Fig. 1. Relative reactions are as follows.

$$6HSbO_2 + 4PbS + Fe(OH)_3 + 10S^0 + 21e + 21H^+ = Pb_4FeSb_6S_{14} + 15H_2O \qquad (6)$$

$$6HSbO_2 + 4Pb(OH)_2 + Fe(OH)_3 + 14S^0 + 29e + 29H^+ = Pb_4FeSb_6S_{14} + 23H_2O \qquad (7)$$

$$6HSbO_2 + 4Pb(OH)_2 + Fe(OH)_3 + 7S_2O_3^{2-} + 57e + 71H^+ = Pb_4FeSb_6S_{14} + 44H_2O \qquad (8)$$

$$6HSbO_2 + 4PbSO_4 + Fe(OH)_3 + 10SO_4^{2-} + 113e + 133H^+ = Pb_4FeSb_6S_{14} + 71H_2O \qquad (9)$$

4 CONCLUSIONS

1) The electrochemical behaviors of jamesonite are similar to the behaviors of the corrosion and inhibition due to producing sulfur on the electrode surface.

2) The corrosive potential(φ_{corr}) moves negatively, its corrosive current density (J_{corr}) increases, and hydroxyl action becomes strong with the rising pH value.

3) At pH 6.86, the metal-deficient and sulfur-riched layer on the mineral surface is gradually formed from − 378 mV to 122 mV. At pH 6.86, elemental sulfur film occurs at 122 mV and results in strong passive action. The passive film of sulfur on the mineral surface breaks down gradually from 222 mV to 422 mV. When the electrode potential is over 422 mV, $S_2O_3^{2-}$ and SO_4^{2-} ions occur on jamesonite surface. It can be deduced that the potential range of collectorless floatability of jamesonite is from 22 mV to 422 mV at pH 6.86, and its optimum range of floatable potential is between 122 mV and 322 mV due to the fact that the surface capacitance is lower and electrochemical resistance is bigger. But its collectorless floatability is poor due to existing the hydrophobic hydroxyl precipitate on jamesonite surface under basic condition and due to existing hydrophobic $S_2O_3^{2-}$ and SO_4^{2-} ions over the potential of 422 mV.

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