

Inhibition behavior of some new mixed additives upon copper electrowinning

YU Run-lan(余润兰)^{1,2}, LIU Qing-ming(刘清明)³, QIU Guan-zhou(邱冠周)^{1,2},
FANG Zheng(方正)³, TAN Jian-xi(谭建锡)^{1,2}, YANG Peng(杨鹏)^{1,2}

1. Key Laboratory of Biometallurgy, Ministry of Education, Central South University, Changsha 410083, China;
2. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China;
3. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

Received 5 September 2007; accepted 10 December 2007

Abstract: As thiourea and sulfur-containing mixed additives contaminate cathodic copper, inhibition behavior of some new mixed additives such as gelatin+hexadecylpyridinium bromide (HDPBr), gelatin+polyethylene glycol(PEG), gelatin+polyacryl amide (PAM), gelatin+PEG+cetyl-tri-methyl ammonium bromide (CTABr) and gelatin+PAM+CTABr was investigated by cyclic voltammetry as well as cathodic polarization in order to improve the quality of cathodic copper in bio-metallurgical process. The results indicate that the inhibition performances of these additives are dependent on complex and adsorption behaviors as well as the deposit potential. For a solution of acidic copper sulphate containing 40 g/L Cu^{2+} and 180 g/L H_2SO_4 , the additive (gelatin+HDPBr) is the most efficient among the investigated additives because HDPBr with a large organic cation and π electron can adsorb on the cathodic surface to block the active sites and Br^- ion can precipitate Cu^{2+} to form Cu_2Br_2 . The additive (gelatin+PAM) also has a better inhibition performance, while the additives (gelatin+PEG), (gelatin+PEG+CTABr) and (gelatin+PAM+CTABr) are comparatively lower inhibition performance compared with the additive (gelatin+thiourea) which has been frequently used so far.

Key words: copper electrowinning; mixed additives; hexadecylpyridinium bromide; polyethylene glycol; polyacryl amide; cetyl-tri-methyl ammonium bromide

1 Introduction

Most of the copper with a purity of 4N (99.99%) is employed industrially. For copper of 5N (99.999%) or even 6N (99.999 9%), the usage can be broadened due to improvement in several physical properties, which will lead to a significant economical benefit[1–2]. For example, the sound quality of a speaker is improved when the audio pin cable or speaker cable is made of 5N or 6N copper; and the golden bonding wire for the manufacture of semiconductors can be replaced by the copper wire of this purity.

As the bacterial leaching is definitely selective to sulfide minerals in the H_2SO_4 solution with the pH value of about 2, and the extractive reagent Lix984N is of highly selective separation for copper ion, the purity of cathodic copper by the bio-hydrometallurgical process of bacterial leaching—solvent extraction—electrowinning (BioL-SX-EW) has reached about 99.9980% in China so

far[3]. If the process conditions are controlled carefully, it is considered to increase the purity of the recovered copper up to 5N or even 6N[1–4].

It is necessary for copper electrowinning or electrolytic refining to use some additives as levelling and brightening agents. Thiol or disulfide molecules and their mixed additives[5–10] have been extensively investigated. At present, the mixed additive of thiourea and gelatin is used[11–14]. As thiourea and sulfur-containing additives contaminate the cathodic deposit, the development of suitable additives substituting for thiourea is an interesting research direction to improve further the copper quality. Some non-sulfur-containing additives, such as horse-chestnut extract(HCE), mixtures of ethoxyacetic alcohol and triethyl-benzyl-ammonium chloride(IT-85)[15], poly-ethylene glycol(PEG) and chloride ion[16–18], polyacryl amide(PAM) and chloride ion[19], were developed.

In the present study, the inhibition behaviors of several new mixed additives composed of gelatin and

some substitutes of thiourea upon copper deposits from the sulphate electrolyte were investigated by cyclic voltammetry and cathodic polarization, and the additives of gelatin and thiourea used frequently in China were compared.

2 Experimental

2.1 Solution preparation

All chemical reagents are of AR grade (Changsha Chemicals Supplement Corporation, China).

A solution of acidic copper sulphate containing 40 g/L Cu^{2+} and 180 g/L H_2SO_4 was prepared by using the reagents and distilled water. The composition of the solution prepared is according to the electrodeposit solution in BioL-SX-EW process.

Several kinds of the mixed additive solutions such as gelatin+thiourea, gelatin+1-hexadecylpyridinium bromide (HDPBr), gelatin+polyethylene glycol(PEG), gelatin+polyacryl amide (PAM), gelatin+PEG+cetyl-trimethyl ammonium bromide (CTABr) and gelatin+PAM+CTABr were prepared and then added into the CuSO_4 - H_2SO_4 solution up to a definite additive concentration, respectively.

A CuSO_4 - H_2SO_4 solution containing 16 mg/L gelatin and 16 mg/L thiourea was used as the control solution.

2.2 Electrochemical experiment

The experiments were conducted in a glass cell with a three electrode system of a Cu working electrode with 2 mm in diameter, a Pt counter electrode and a saturated calomel reference electrode(SCE). The working electrode was wetly polished by abrasive paper 400[#] and 600[#], and then washed with distilled water before each run.

The cyclic voltammograms and polarization curves were recorded using Potentiostatic/Galvanostat Model 273A (EG&G PAR Company). These curves all were not ohmic drop compensation because of the neglectable ohmic drop under the conditions of the small WE-RE distance (less than 2 mm) and the small currents. All potential values in this paper are vs SCE.

3 Results and discussion

3.1 Cyclic voltammetry

Figs.1–4 show the cyclic voltammograms in the anodic and cathodic process of copper in the presence of different tested additives.

In the cathodic crystallizing process, thiourea forms two kinds of compounds, Cu_2S and $[\text{Cu}(\text{N}_2\text{H}_4\text{CS}_2)_4]_2\text{SO}_4$, in the cathodic region or on the surface of cathode directly. The formation of new Cu_2S microcrystal on cathodic surface increases the active crystal nucleus, and

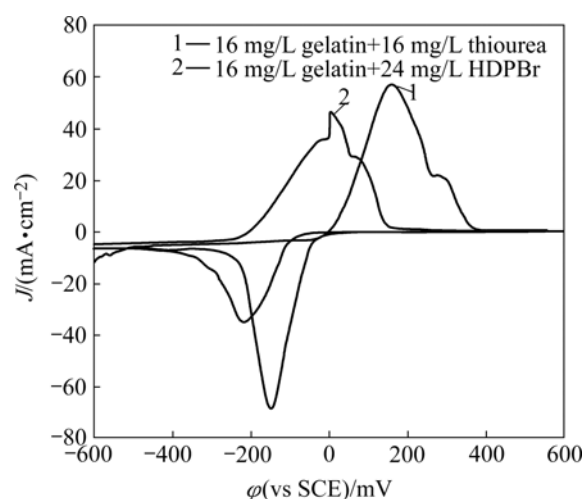


Fig.1 Cyclic voltammograms of copper electrode in acidic CuSO_4 solution containing additive of HDPBr

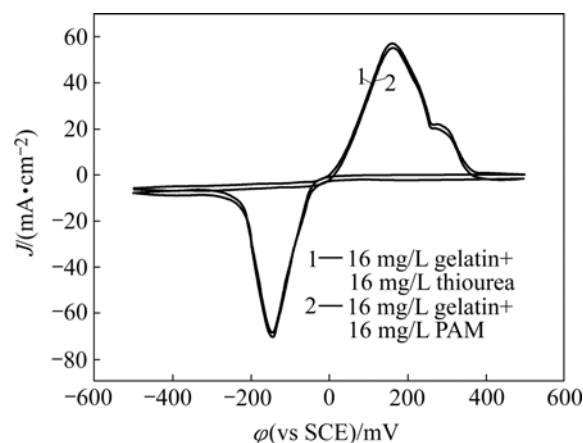


Fig.2 Cyclic voltammograms of copper electrode in acidic CuSO_4 solution containing additive of PAM

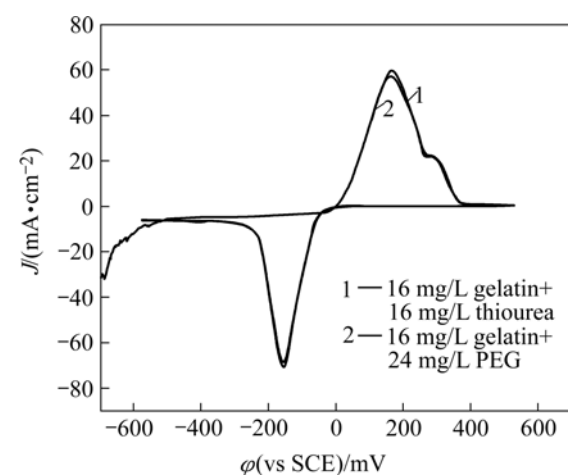


Fig.3 Cyclic voltammograms of copper electrode in acidic CuSO_4 solution containing additive of PEG

the glue film formed by a lot of complex ions $[\text{Cu}(\text{N}_2\text{H}_4\text{CS}_2)_4]^+$ around cathode increases the cathodic polarization, resulting in the reduction of the cathodic

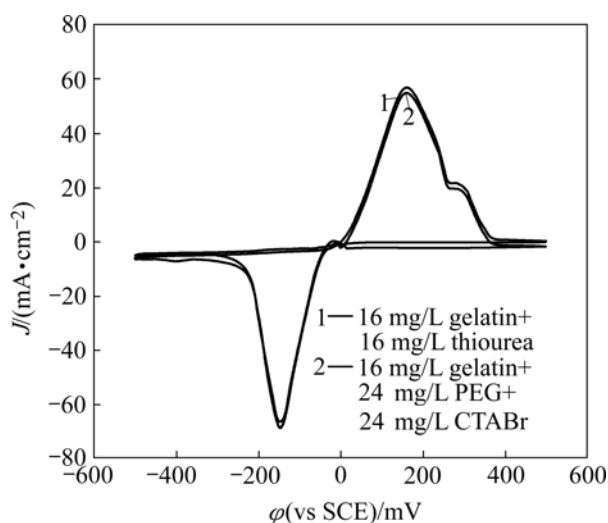


Fig.4 Cyclic voltammograms of copper electrode in acidic CuSO_4 solution containing additives of PEG and CTABr

current density. Consequently, cathode copper becomes levelling and brightening. The function of gelatin is considered glue and a complex reagent adsorbing on copper surface to reduce the growth rate of copper crystallizing due to the increase of the polarization resistance. General speaking, the complex ability with copper ions of gelatin is much weaker than that of thiourea.

For the mixed additive of gelatin and HDPBr, the cyclic voltammetrical behavior shown in Fig.1 reveals that the cathodic and anodic peaks all shift towards more negative values, and the maximum of the cathodic and anodic peaks simultaneously reduces compared with that of the mixed additive of gelatin and thiourea. The anodic peak shifts from 164 mV to 2.5 mV, and the electric current density of the peak reduces from 57.6 mA/cm^2 to 47.2 mA/cm^2 . The cathodic peak shifts from -145 mV to -218 mV , and the electric current density of the peak reduces from -68.5 mA/cm^2 to -34.6 mA/cm^2 . Specially, the reduction extent of the cathodic peak current density is more than that of the anodic peak current density. These denote that the mixed additive of gelatin and HDPBr has a stronger inhibition on the electric dissolution and crystallization than the additive of gelatin and thiourea.

HDPBr is a quaternary ammonium salt with a large organic cation, which can be adsorbed on the cathodic surface and block the active sites, and also is a polar molecule with interfacial activity which can replace adsorbed water molecules on copper surface to lower the dielectric constant on the electrode interface, and Br^- ions can be precipitant for Cu^+ to form Cu_2Br_2 , promoting inhibition.

In the cases of the mixed additives of (gelatin

+PAM), (gelatin+PEG) and (gelatin+PEG+CTABr), the cyclic voltammetrical behavior shown from Fig.2 to Fig.4 respectively are almost the same as that of the mixed additive of (gelatin+thiourea).

The structure of PAM is $\text{[CH}_2\text{CH(CONH}_2\text{)CH}_2\text{]}_n$ with some complex and flocculation action, while the structure of PEG is $\text{HOCH}_2\text{[CH}_2\text{OCH}_2\text{]}_n\text{CH}_2\text{OH}$ or $\text{H[OCH}_2\text{CH}_2\text{]}_n\text{OH}$ with strong ability of adsorbing wetting, which is dependent on its relative molecular mass. Hence, they can replace the adsorbed water molecules on copper surface, lowering the dielectric constant on the electrode interface. At the same time, PEG also has some alcohols property with some complex ability as $(\text{PEG})\text{Cu}^+$. Consequently, the additive, PEG or PAM, reveals similar inhibition characteristic to thiourea in the copper deposit. When CTABr is added into the (gelatin+PEG) additive, the cyclic voltammetrical behavior shown in Fig.4 is not obviously different from that without CTABr, as shown in Fig.3. CTABr as a cation surfactant of a quaternary ammonium salt has a stronger surface adsorption preferentially on cathode than PEG, so that the complex and adsorbing action of PEG become much weak in the presence of CTABr. Wholly speaking, the addition of CTABr does not obviously improve the inhibition behavior of the mixed additive of (gelatin+PEG).

Although both HDPBr and CTABr are strong surfactants of quaternary ammonium salt, the inhibition ability of HDPBr is much stronger than that of CTABr. The reason is that HDPBr has the complex action due to its π electron which can enter empty orbit of copper but CTABr has not.

3.2 Polarization curves

The polarization curves show a charge transfer controlled Tafel region at overpotential higher than 120 mV. The polarization corresponding to the activation of electro-crystallization process could be considered a measure of the nucleation inhibition degree.

In order to understand further the inhibition differences of the mixed additives, the Tafel curves at the sweeping rate of 10 mV/s are recorded and shown in Fig.5. The open circuit potentials basically do not vary for all of the mixed additives studied, but the cathodic currents markedly change. For the mixed additives, (gelatin+HDPBr) or (gelatin+PAM), their cathodic current is lower than that of (gelatin+thiourea), while the reverse is for (gelatin+PEG) or (gelatin+PAM+CTABr).

The polarization curves in the potential range of -220 mV to $-1\ 000 \text{ mV}$ on a copper cathode were measured to make Tafel linear region clear, as shown in Fig.6. It can be seen that there are different mechanisms

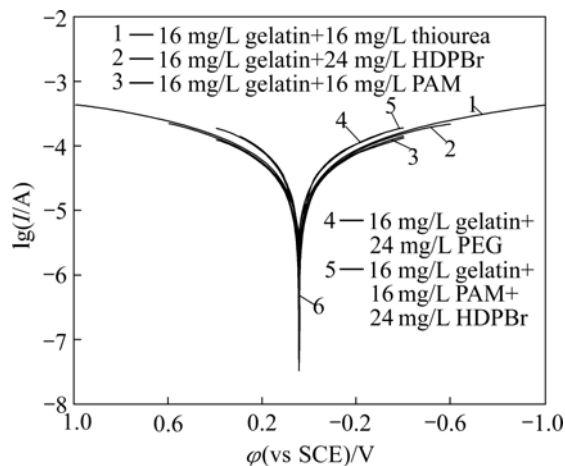


Fig.5 Tafel curves of copper electrode in acidic CuSO_4 solution with different additives

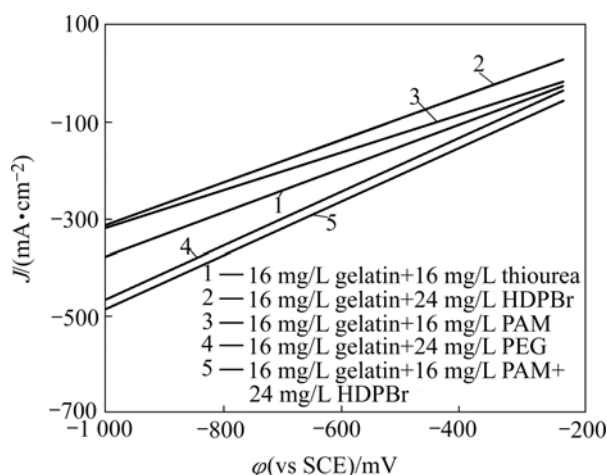


Fig.6 Polarization curves of copper electrode in acidic CuSO_4 solution with different additives

for the different mixed additives. At the same time, the mechanisms are potential-dependent in the case of same mixed additives.

In the presence of the mixed additive of (gelatin+HDPBr), the exchange current density (curve 2) is almost parallelly decreasing with the values obtained from the mixed additive of (gelatin and thiourea) (curve 1). The nucleation inhibition of the former is always stronger than that of the latter. In the presence of the mixed additive of gelatin and PAM, the exchange current density (curve 3) is also decreasing, but the curve 3 does not parallel with the curve 1 obtained from the additive of (gelatin+ thiourea) in the measured potential range.

In the presence of the mixed additives, (gelatin+PEG) or (gelatin+PAM+CTABr), their exchange current densities (curve 4 or curve 5) increase with the values obtained from the reference additives (curve 1) in the measured potential range.

When CTABr becomes a part of the additives of (gelatin+PAM), the cathodic current density becomes

higher with respect to the case without CTABr. Thereby, CTABr is not helpful for improving the inhibition performance in the cases of the mixed additives of gelatin and PAM or PEG.

4 Conclusions

1) The inhibition performance of these additives is dependent on complex and adsorption behaviors as well as the deposit potential.

2) CTABr as a surfactant of quaternary ammonium salt without complex ability will preferentially adsorb on copper surface at more negative potential and obviously reduce the inhibition of the additives such as PAM and PEG compared with thiourea.

3) For a solution containing 40 g/L Cu^{2+} as CuSO_4 and 180 g/L H_2SO_4 , the additive (gelatin+HDPBr) is the most efficient inhibitor among the investigated additives because HDPBr with a large organic cation and π electron can adsorb and complex on the cathodic surface to block the active sites and Br^- ion can precipitate Cu^+ to form Cu_2Br_2 , and the (gelatin + PAM) additive also has better inhibition performance, while the additives, (gelatin+PEG), (gelatin+PEG+CTABr) and (gelatin+PAM+CTABr) are comparatively lower as compared with the additive (gelatin+thiourea).

References

- [1] CHOI J Y, KIM D S. Production of ultrahigh purity copper using waste copper nitrate solution[J]. *Journal of Hazardous Materials*, 2003, B99: 147–158.
- [2] LIU Lin-hai, TAN Ding-sheng. Preparation methods of ultrahigh pure copper and their applications [J]. *Shanghai Nonferrous Metals*, 2004, 25(2): 60–64. (in Chinese).
- [3] YU Run-lan, QIU Guan-zhou, LIU Qing-ming. Study and discussion on technical potential of preparing ultrahigh purity cathode copper by bioleaching method in bio-metallurgy [J]. *Hunan Metallurgy*, 2006, 34(6): 3–7.(in Chinese).
- [4] WO2005JP00015, JP20040020850 [P].
- [5] STANKOVIC Z D, VUKOVIC M. The Influence of thiourea on kinetic parameters on the cathodic and anodic reaction at different metals in H_2SO_4 solution [J]. *Electrochim Acta*, 1996, 41(16): 2529–2535.
- [6] ALODAN M, SMYRL W. Effect of thiourea on copper dissolution and deposition [J]. *Electrochim Acta*, 1998, 44(1/2): 299–309.
- [7] LEUNG T Y B, KANG M, CORRY B F, GEWIRTH A A. Benzotriazole as an additive for copper electrodeposition—Influence of triazole ring substitution [J]. *Journal of the Electrochemical Society*, 2006, 153(2): C117–C120.
- [8] PASQUALE M A, BARKEY Z D P, ARVIA A J. Influence of additives on the growth velocity and morphology of branching copper electrodeposits [J]. *Journal of the Electrochemical Society*, 2000, 147(9): 3326–3337.
- [9] DOW W P, HUANG H S, YEN M Y, HUANG H C. Influence of convection-dependent adsorption of additives on microvia filling by copper electroplating [J]. *Journal of the Electrochemical Society*,

- 2005, 152(6): 425–434.
- [10] WALKER M L, RICHTER L J, MOFFAT T P. Potential dependence of competitive adsorption of PEG, Cl^- , and SPS/MPS on Cu-An in situ ellipsometric study [J]. *Journal of the Electrochemical Society*, 2007, 154(5): D277–D282.
- [11] MENG Yan-shuang, LI Jian, ZHU Zu-ze, WANG Da-jian. The influence of additives on surface quality of cathode copper [J]. *Yunan Metallurgy*, 2002, 31(5): 29–32. (in Chinese)
- [12] LU Dao-rong, LIN Jian-xin, ZHU Pei-pei. The effect of additives on the copper deposition process in the electrolysis copper system of high bismuth [J]. *Journal of Hefei University of Technology*, 1998, 21(2): 61–65. (in Chinese).
- [13] PENG Chu-feng, HE Ai-ping, LIU Ai-qing. Study on the effect cathode quality of additive on high nickel-copper electrolysis refining [J]. *Journal of Kunming University of Science and Technology*, 2002, 27(6): 36–40. (in Chinese).
- [14] ZHANG Yuan, LI Guo-cai. Research and practice of gelatin as additive of copper electrolysis [J]. *Chinese Journal of Rare Metals*, 2000, 24(1): 66–69. (in Chinese).
- [15] MURESAN L, VARVARA S, MAURIN G, DORNEANU S. The effect of some organic additives upon copper electrowinning from sulphate electrolytes [J]. *Hydrometallurgy*, 2000, 54: 161–169.
- [16] MIRKOVA L, PETKOVA N, POPOVA I, RASHKOV S. The effect of some surface active additives upon the quality of cathodic copper deposits during the electro-refining process [J]. *Hydrometallurgy*, 1994, 36: 201–213.
- [17] KEILY J J, WESR A C. Copper deposition in the presence of polyethylene glycol (I): Quartz crystal microbalance study [J]. *Journal of the Electrochemical Society*, 1998, 145(10): 3472–3476.
- [18] HASEGAWA M, OKINAKA Y, SHACHAM-DIAMAND Y, OSAKA T. Void-free trench-filling by electroless copper deposition using the combination of accelerating and inhibiting additives [J]. *Electrochemical and Solid-State Letters*, 2006, 9(8): C138–C140.
- [19] FABIAN C, RIDD M J, SHEEHAN M. Rotating cylinder electrode study of the effect of activated polyacrylamide on surface roughness of electrodeposited copper [J]. *Hydrometallurgy*, 2006, 84: 256–263.

(Edited by YUAN Sai-qian)