Study on the removal of iron impurities in methanesulfonic acid tin plating bath

Hou-li LIU, jian-jun CHEN* and hong-liang PAN

School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai 200237, China
jjchen@ecust.edu.cn

Abstract. This thesis investigated the the influence of sodium sulfite as reducing agent on the recovery rate of tin ion. The approach is that HZ016 type cation exchange resin was used to adsorb Sn²⁺ and Fe²⁺ in electroplated tin solution first. After adsorption, the resin was removed by sulfuric acid, which was added with NaOH to adjust pH value to form precipitation and separate tin. X-ray diffraction (XRD) and energy spectru (EDS) method were used to analyze the composition of the precipitates adjusted by pH. The results show that when the mass ratio of resin to bath is 1:2, the adsorption efficiency of resin reaches 98.3% and 97.1% respectively, and the elution efficiency of tin and iron reaches 95.1% and 94% respectively when the mass ratio of resin to eluent sulfuric acid is 1:4. Sodium sulfite was added to increase the efficiency of tin recovery by 8.1%. EDS and XRD atlas showed that after pH regulation, the main composition of the filtration precipitation was the hydroxides of tin.

1. Introduction

Tin is a silver white metal. It has many advantages such as corrosion resistance, innocuity, easy-soldering, softness and good ductility. Tin plating is resistant to organic acids, and has almost no effect with sulfur and sulfide. What’s more, it also has good corrosion resistance [1]. Tinplate is made of cold rolled sheet metal coated with metal tin on both sides. It has excellent weldability, ductility, softness, corrosion resistance and anti-tarnishing, which is widely applied in food packaging, electronic devices and other industries [2, 3].

At present, the sulfuric acid tin plating process, mainly the ferostan tin plating process is widely adopted both home and abroad [4]. Tin methanesulfonic acid has been widely used because of its wider current density, less sediment and more environmental advantages [5]. Since the first introduction of methanesulfonic acid unit by Meishan Iron and Steel Plant in 2009, the environmental friendly tin plating process of methanesulfonic acid has been developed rapidly in recent years. And almost all new production lines adopt this process [6].

Due to its production in high speed, tin plating can bring a certain amount of iron ions produced in the pretreatment process such as pickling and so on. In addition, the iron impurity will also be introduced into the plating strip and equipment. The accumulation of iron impurities in the plate will cause the roughness of the coating surface, the non meticulous crystallization and the decrease of corrosion resistance of the tin plating [7]. The presence of iron ions causes the oxidation of Sn(II) to Sn(IV), resulting in the turbidity of the plating bath and the increase in the amount of tin mud [8].
At present, the removal methods of iron ions in tin plating are mainly chemical precipitation, redox, ion exchange resin, selective adsorption, crystallization and so on. There are a lot of reports for the removal of ferrous ion in phenol sulfonate tin plating solution [9-11]. But the methyl sulfonic acid tin plating bath and method of removing iron ion of tin recovery have not been reported yet. This paper adopts the method of using cation exchange resin adsorption in liquid iron, tin plating and other metal cations by selective electroless tin ion in the eluent recycling resin, investigating the effect of adding sodium sulfite as a reducing agent in the eluent on the recovery of tin, with the help of XRD and EDS on chemical precipitation.

2. Experiment

2.1 Experiment material
The HZ016 hydrogen type strong acid cation exchange resin provided by Shanghai Hua Zhen Technology Co., Ltd. is used to remove metal cations from tin plating solution. The physical and chemical parameters are shown in Table 1:

| Parameters                                  | Value          |
|---------------------------------------------|----------------|
| frame                                       | styrene        |
| Functional groups                           | -SO3-          |
| Form in factory                             | Na+            |
| Moist content (%)                           | 35~45          |
| Total mass exchange capacity (mol/g)         | ≥4.2           |
| Volume total exchange capacity (mol/ml)      | ≥2.0           |
| Moist apparent density (g/ml)               | 0.80~0.87      |
| Wet true density (g/ml)                     | 1.25~1.35      |
| Granularity range (mm)                      | 0.315~1.25≥95% |

Resin pretreatment: dry resin is soaked in hot water at 60~70 °C for 30min. After filtering the hot water, it is soaked with 4~5% hydrochloric acid about 2 times of resin volume for four hours. Then filtrating the acid solution, deionized water is added, with rinse the resin to the effluent until it is neutral. After filtration, it is encapsulated for experimental use.

2.2 Experimental Device and Method Introduction
The experiment was carried out in the self-made iron tin plating solution test device, which adopts PLC automatic control, resin adsorption and elution by "dual-use equipment" manner, namely two series adsorption resin column and third resin elution. Through the setup of different flow velocity and time, the device can adjust the adsorption elution solution with sulfuric acid the amount. After the setup of the corresponding parameters, the system can be automatically operated in cycle. The experimental device is shown in Figure 1. The ion exchange resin column was pretreated and resin was adsorbed. The plating solution was injected into the ion exchange column at a certain speed, and the same rate was achieved by sulfuric acid washing and resin adsorption. By using the solubility product of tin and iron ion hydroxide, NaOH regulated the pH value of the eluent, so that tin ion first precipitated in the form of Sn(OH)2, and the precipitated filtrate precipitated to recover tin. By adding different amounts of Na2SO3 in the eluent as a reductant to verify the effect on the recovery of tin ions, the composition of XRD and EDS was analyzed after pH adjusted filtration.
2.3 Laboratory Reagents and Instruments
Methyl sulfonate electroplating tin solution is provided by a steel mill. Sodium hydroxide and sodium sulfite are commercially available.

MIK-PH6.0 industrial online acidity meter, Hangzhou Micco Sensor Technology Co. Ltd; JA5001 electronic balance, Shanghai Puchun Measuring Instrument Co. Ltd; 2XZ-0.25 straight rotary vane vacuum pump, Shanghai Kangjia Vacuum Pump Co. Ltd; Phg-9070a electric thermostatic drying oven, Shanghai Jinghong Experimental Equipment Co. Ltd; Falion 60S energy spectrometer (EDS), EDAX, Inc.; D8 Focus X-ray diffractometer (XRD), Bruker Corporation; Varian 710-es full spectrum direct reading plasma emission spectrometer (ICP), Agilent Technologies.

3. Results and Discussion
3.1 Plating Solution Adsorption - eluting Experiment
Each resin column is preloaded with each resin column, which is preloaded with 5kg resin. The mass ratio of the resin to the plating bath is 1:2, at the speed of 2BV/L in adsorption, with the operation time 1 hour. After the adsorption, the bath was emptied to facilitate the elution of the resin. The resin elution was washed with 2mol/L sulfuric acid, and the mass ratio of the resin to the elution of sulfuric acid was selected as 1:4. After sampling 250 times of the dilution of the original plating solution, the adsorbent effluent and the eluent outflow solution, respectively, the determination of tin and iron ion mass concentration was tested[12,13]. The results are shown in Table 2.

|                  | Original Liquid | Adsorption Liquid | Eluent |
|------------------|-----------------|-------------------|--------|
| Sn (g/L)         | 14              | 0.24              | 6.54   |
| Fe (g/L)         | 11.5            | 0.33              | 5.25   |

It can be known from the adsorption- eluting experiment that: the resin can better adsorb tin and iron ions in the choice of resin plating liquid mass ratio of 1:2, and by calculation, the efficiency of resin adsorption tin was 98.3%, the efficiency of iron adsorption was 97.1%, the efficiency of tin
elution was 95.1%, the efficiency of iron elution was 94%, and the resin preferentially adsorbed tin ions in the plating solution.

3.2 Effect of sodium sulfite on the recovery of tin

Due to the difference of solubility product of Sn2+ and Fe2+, the NaOH solution of mass fraction of 30% was used for pH adjustment of the sulfuric acid effluent after resin elution, so that tin first precipitated, and the experimental pH value was chosen 3.8. After taking 800ml volume of the sulfuric acid eluent and dividing them into four groups, with 200ml each group. Sample 1 is without adding Na2SO3, Sample 2, 3 and 4 were added with 0.1g, 0.3g and 0.5g Na2SO3 respectively to do comparative experiments. The pH adjustment completed the filtration of precipitate components, and the filtration solution sampling dilution was used to detect the quality of tin and iron ions. The results were shown in Table 3.

Table 3. Mass concentration of tin and iron ions in the filtrate after pH adjustment

|       | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|-------|----------|----------|----------|----------|
| Sn (g/L) | 0.56     | 0.43     | 0.21     | 0.3      |
| Fe (g/L) | 2.93     | 3.22     | 3.35     | 3.15     |

The separation efficiency of tin and iron ions in the pH effluent can be calculated by the next formula:

\[ \eta = \frac{V(C_0 - C)}{V_0C_0} \times 100\% \]  (1)

In the formula: \( C_0 \) and \( C \) respectively on behalf of tin and iron mass concentration before and after pH adjustment (g/L); \( V_0 \) and \( V \) respectively on behalf of the volume of solution before and after pH adjustment (L).

The results showed that when Na2SO3 was added into the eluent as the reducing agent, it could enhance the recovery rate of tin ion. The recovery of 0.3g Na2SO3 tin ion in 200ml sulfuric acid eluent reached the highest, 95.2%, while the recovery rate of tin ion without adding reducing agent was 87.1%. Under the same conditions, the eluent with Na2SO3 can increase the recovery efficiency of tin ion by 8.1%, which can provide data support and theoretical basis for the removal of iron ions in tin plating liquid in industrial production.

3.3 Analysis of precipitation composition

After the pH adjustment was completed, the precipitation was filtered and the deionized water was cleaned, leaving the effect of Na2SO3 on the test. After the cleaning, the precipitation was put into the dryness box. At the temperature of 60 ℃, it was dried for 3 hours and the sample was tested by SEM and EDS in turn. EDS test results are shown in Table 4:

Table 4. Energy spectrum analysis of pH adjustment filtration

|       | N (Wt%) | O (Wt%) | S (Wt%) | Sn (Wt%) |
|-------|---------|---------|---------|----------|
| Sample 1 | 1.61    | 26.88   | 0.63    | 70.88    |
| Sample 2 | 2.05    | 26.11   | 1.62    | 70.22    |
| Sample 3 | 0       | 20.17   | 2.68    | 77.15    |
| Sample 4 | 3.04    | 19.56   | 3.29    | 74.11    |
Figure 2. Add different amount of sodium sulfite precipitation SEM picture

Through the energy spectrum analysis, when 0.3g Na₂SO₃ was added, the content of tin was the highest, while the content of tin ion in the filtrate was the lowest, indicating that Na₂SO₃ as a reducing agent can improve the recovery efficiency of tin ion in pH adjustment process.

In order to further determine the precipitating components, after drying, sample 1 was filtered and precipitated for XRD detection to identify the main components. The results were analyzed by MDI Jade software, and the results were shown in figure 3:

Figure 3. X-ray diffraction pattern of pH-adjusted precipitation

According to the MDI Jade software analysis, the best fit for the standard peak position is tin hydroxide, which indicates that the major component of the precipitate is tin hydroxide.

4. Conclusion

HZ016 resin can better adsorption-eluting tin and iron ions in methanesulfonic acid tin plating solution, when the mass ratio of resin to plating solution is 1:2, the resin adsorption efficiency of tin
and iron reaches 98.3% and 97.1%; The mass ratio of resin to 2mol / L sulfuric acid was 1: 4, and the elution efficiencies of tin and iron were 95.1% and 94%. Sodium hydroxide adjusted eluent pH to 3.8, and the addition of sodium sulfite in the eluent as a reducing agent can improve the tin ion recovery efficiency of 8.1%, the energy spectrum and X-ray diffraction showed that the precipitated composition is tin hydroxides.

5. Acknowledgement
This research was financially supported by the Natural Science Foundation of China (51105143, 51675182).

References
[1] Hao Jian-jun and An Cheng-qiang 2007 J. Journal of Bohai University. 28(4) 297-300
[2] Bengoa L N,Tuckart W R and Zabala N 2015 J. Journal of Materials Engineering & Performance. 24(6) 1-8
[3] Blunden S and Wallace T 2003 J. Food & Chemical Toxicology An International Journal Published for the British Industrial Biological Research Association. 41(12) 1651-62
[4] Jin Xu- fang, Zhao Peng- fei, WU Xiao-Bing and MA Ya-li 2013 J. Steel Rolling. 30(3) 41-42
[5] Nozaki T, Yuuki K and Hamahara K 2007 J. Jfe Technical Report. 9 76-79
[6] BO Wei 2014 J. Baosteel Technology. 6 32-35.
[7] WANG Zhi-deng, WANG Ming-hao, WANG Xi-yu and LI Ning 2015 J. Electroplating and finishing. 34(20) 1139-44
[8] Hahn D, Dreibigacker U. Method for removing ferrous ions from acidic tinning electrolytes and tinning electrolyte recovery plant for iron using the same: US, US5891343[P]. 1999.
[9] WANG Xiao-wei, CAO Li-xin, YU Yuan-chun and ZHANG Jing-shuang 2008 J. Electroplating & Pollution Control. 28(1) 17-19
[10] KONG Mei-ling, HUANG Dan-lan and RAO Ze-hua 2014 J. Materials Protection. 47(5) 54-56
[11] LIU Jun-mei, WANG Hai-hua and LI Lu 2015 J. Electroplating and finishing. 34(15) 856-59
[12] CHEN Qian, WU Xi, HOU Xian-deng and XU Kai-lai 2015 J. Spectroscopy and Spectral Analysis. 9 2393-96
[13] WANG Xiao-qiang, HOU Xiao-lei and YANG Hui-ling 2011 J. Rock and Mineral Analysis. 30(5) 576-79