Original Paper

Application of Solvent Extraction Using Synergistic Effect to Electroless Nickel Plating Waste Liquor

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Abstract

Electroless nickel plating waste liquor contains a large amount of nickel ions, but nickel ions in waste liquor have not been recovered for technical and economic reasons. If the recovery of nickel ions is effectively carried out, nickel ions could be recycled as a nickel source for electroless plating liquor. The process to recover nickel ions from electroless plating waste liquor was investigated by using a solvent extraction method.

The existence of various phosphate species and organic acids in the waste liquor causes the incomplete extraction of nickel ions with any single extractant due to the complex formation between nickel ions and them. The application of solvent extraction using a synergistic effect makes possible to separate and recover 90% or more of nickel ions in the waste liquor. The extractant mixtures of acidic extractant such as D2EHPA and PC-88A, and another extractants with electron-donating ability such as nicotinic acid dodecyl ester and iso-nicotinic acid dodecyl ester are used for this purpose.

Key words: Electroless plating, Rare metals, Nickel, Solvent extraction, Synergistic effect

1. Introduction

Electroless plating is a plating method that nickel ions are reduced on the surface of a plating object by the action of hypophosphorous acid used as a reductant in the plating liquor. Electroless plating is often used in the electronics industry, automobile industry and so on, because a uniform and thin Ni metal film can be deposited on non-conductive substances¹.

Hypophosphorous ions are oxidized to phosphorous ions as electroless plating progresses. When phosphorous ions have accumulated in the electroless plating liquor, it is impossible to reduce and plate nickel ions efficiently. Then, the plating liquor is disposed as waste solution. The total amount of waste liquor is estimated to be 130,000 ton/year². Waste liquor was previously

discarded in the sea or as landfill after a neutralization treatment. However, the discharge of waste to the sea was prohibited by the London convention in 1996. Electroless plating waste liquor is treated by precipitation methods, but valuable nickel resources in the waste liquor are not recovered. In recent years, the recycling of valuable resources has become necessary for environmental preservation and resources saving. The waste liquor contains a large amount of nickel ions and various phosphate species. It is difficult, however, to extract effectively nickel ions from the waste liquor containing various phosphate and organic species.

In this study, the separation and recovery of nickel ions from the electroless nickel plating waste liquor were investigated by the solvent extraction using synergistic effect.

2. Experimental**2.1 Extraction of Ni with single extractant**

D2EHPA, PC-88A, Cyanex272, LIX84-I, TOA, TOP and TBP were used as the extractant

Paper presented at the 7th Japan/Korea International Symposium on Materials Science and Resources Recycling, 16–17 December 2009, Kyoto, Japan
Accepted 11 July, 2010

Fig. 1 Structural formula of various pyridine compounds.

for extraction of nickel ions. The concentration of D2EHPA, PC-88A and TOP was adjusted to 0.5 mol/dm³ with kerosene, while the concentration of LIX84-I, TOA and Cyanex272 was prepared to be 19.5wt% with kerosene. TBP was used without any adjustment.

The pH of waste liquor was adjusted between 6 and 12 with NaOHaq. The same volumes, 15 cm³, of the waste liquor and the organic phase containing the extractants were introduced in a centrifuge tube equipped with a stopper, and they were centrifuged after being shaken for 15 min. The concentration of nickel ions was measured by an ICP spectrophotometer.

2.2 Extraction of Ni with extractant mixtures

Nickel ions in the electroless plating waste liquor were extracted by a solvent extraction method using a synergistic effect. D2EHPA or PC-88A was mixed with TBP, TOA, TOP, 4-ppp (4-phenylpropyl pyridine), nicotinic acid hexyl ester, nicotinic acid octyl ester, nicotinic acid dodecyl ester or isonicotinic acid dodecyl ester. Figure 1 shows various pyridine compounds used as the second extractant with electron-donating ability; (a) 4-ppp, (b) nicotinic acid hexyl ester, (c) nicotinic acid octyl ester, (d) nicotinic acid dodecyl ester and (e) isonicotinic acid dodecyl ester. The concentration of D2EHPA, PC-88A, TBP, TOA, TOP, 4-ppp, nicotinic acid hexyl ester and nicotinic acid octyl ester was adjusted to 0.5 mol/dm³ with kerosene. In the case of nicotinic acid dodecyl ester and isonicotinic acid dodecyl ester, they were diluted with toluene to the concentration of 0.5 mol/dm³. Each 15 cm³ of the waste liquor and the organic phase was mixed together in a centrifuge tube equipped with a stopper, and then both phases were separated by a centrifuge.

2.3 Solubility to acidic aqueous solution of various pyridine compounds

Nicotinic acid hexyl ester, nicotinic acid octyl ester, nicotinic acid dodecyl ester and isonicotinic

Table 1 Typical composition of electroless nickel plating bath.

Element	Content
NiSO ₄	20 g/dm ³
NaH ₂ PO ₃	25 g/dm ³
Lactic acid	25 g/dm ³
Propionic acid	3 g/dm ³
Pb	small amount
pH	4.0~5.0

acid dodecyl ester were used as the second extractant with electron-donating ability. Nicotinic acid hexyl ester and nicotinic acid octyl ester were diluted with kerosene to 0.1 mol/dm³, while toluene was used for diluting nicotinic acid dodecyl ester and isonicotinic acid dodecyl ester to 0.1 mol/dm³. The pH of aqueous phase containing nickel ions was adjusted to various values with H₂SO₄ and NaOHaq. Each 15 cm³ of the aqueous phase and organic phase was mixed in the centrifuge tube, and centrifuged after being shaken for 15 min. The concentration of organic carbon in the aqueous phase was measured by a TOC analyzer, and the solubility of the various pyridine compounds was calculated from the carbon concentration.

2.4 Stripping of Ni from extractant mixtures

Nickel ions were extracted from the electroless plating waste liquor by the extractant mixtures of D2EHPA and nicotinic acid dodecyl ester or isonicotinic acid dodecyl ester. After extraction of nickel ions, the organic phase was treated to strip nickel species with various concentrations of H₂SO₄. Each 15 cm³ of the organic phase and the stripping solution was mixed in a centrifuge tube, and then both phases were separated by a centrifuge.

3. Results and Discussion

3.1 Extraction of Ni with single extractant

Table 1 shows a typical example of the chemical composition of an electroless nickel plating bath. The plating bath contains nickel sulfate, sodium hypophosphite as the reductant, lactic acid as the complexing agent, propionic acid as the pH buffer, and a small amount of lead as the stabilizer³. The concentration of nickel ions in the plating bath is 7600 mg/dm³. This concentration decreases as the number of plating is increased. In the electroless nickel plating waste liquor, the concentration of nickel ions becomes 4700 mg/dm³.

Figure 2 shows the extraction of nickel ions with various extractants. TOA, TOP, TBP and TOA

Fig. 2 Extraction of Ni from electroless nickel plating waste.

extract nickel ions at extraction percent less than 20% in the pH range of 3.5–8. The extraction of nickel ions with D2EHPA decreases with an increase in pH. Though the extraction of nickel ions with PC-88A and Cyanex272 increases with increasing pH, the extraction of nickel ions decreases again in the pH range over 6.5 and 7, respectively. The amount of nickel ions extracted with LIX-84I increases with an increase in pH.

From the above results, it is found that nickel ions are not extracted efficiently by a single extractant. In the case of acidic extractant and chelate extractant, the extraction of nickel ions is inhibited due to the complex formation between nickel ions and various phosphate species in the waste liquor. The solvation type extractant such as TBP and TOP extracts non-charged chemical species, whereas the basic extractant such as TOA extracts anionic species. However, these chemical species do not exist in the waste liquor.

3.2 Extraction of Ni with extractant mixtures

Synergistic effect is the phenomenon that the extraction increases remarkably by using an extractant mixture compared with a single extractant⁴. For example, nickel ions have six coordination numbers. If it is assumed that four coordination sites are bound with two molecules of D2EHPA and the other two coordination sites are bound with water molecules, then nickel ions do not have enough hydrophobicity. Water molecules in the nickel complexes could be replaced by adding the second extractant having an electron-donating ability. Thus, nickel ions have enough

Fig. 3 Extraction of Ni from electroless nickel plating waste with extractant mixtures.

hydrophobicity, and the extraction of nickel ions may be promoted by using the extractant mixture.

The extractant, PC-88A or D2EHPA, is mixed with each of TOP, TOA, TBP and 4-ppp. Figure 3 shows the relationship between the extraction of nickel ions and equilibrium pH in the use of these extractant mixtures. When TOP, TOA and TBP are used as the second extractant, the extraction of nickel ions does not change compared with PC-88A and D2EHPA themselves. In the case of the extractant mixtures of D2EHPA and 4-ppp or PC-88A and 4-ppp, however, the extraction of nickel ions increases dramatically and the extraction of nickel ions reaches to 98% and 90%, respectively. From these results, it is found that pyridine compounds have a strong electron-donating ability.

Nickel ions are extracted with the extractant mixtures of D2EHPA and nicotinic acid hexyl ester, nicotinic acid octyl ester, nicotinic acid dodecyl ester or isonicotinic acid dodecyl ester. The experimental results are shown in Fig. 4 as the relationship between the extraction percent of nickel ions and pH. The extraction of nickel ions with D2EHPA alone shows only 20% or less. Nickel ions cannot be extracted at all by nicotinic acid dodecyl ester and isonicotinic acid dodecyl ester themselves. On the other hand, the extraction of nickel ions is remarkably improved by the extractant mixtures of D2EHPA and nicotinic acid alkyl esters. The extractant mixtures result in a high extraction percentage of nickel ions more than 98%.

Fig. 4 Extraction of Ni with extractant mixtures of D2EHPA and various nicotinic acids.

Nicotinic acid dodecyl ester is one of the pyridine compounds having an alkyl group bound at meta-site of a pyridine group, while the alkyl group of isonicotinic acid dodecyl ester binds to a pyridine group at para-site. When the position of the ester bond is closer to the nitrogen atom, the steric barrier occurs in the extraction of nickel ions⁵.

Extraction of nickel ions with the extractant mixture of D2EHPA and nicotinic acid dodecyl ester results in high extraction percentage of 98% or more. Nickel ions can be extracted with the extractant mixture by a single extraction operation from waste liquor without any pH adjustment.

3.3 Stripping of Ni from extractant mixtures

Nickel ions are stripped from the organic phase by inorganic acids. Pyridine compounds such as 4-ppp and nicotinic acid hexyl ester, form pyridinium salts with inorganic acid in the stripping stage of Ni. As pyridinium salts dissolve in aqueous phase to some extent, it may be difficult to use the extractant mixture repeatedly. Figure 5 shows the solubility of various pyridine compounds to acidic aqueous solution. Seventy percent of nicotinic acid hexyl ester is dissolved in the aqueous phase at pH 0, while in the case of nicotinic acid octyl ester the dissolution rate is 10% at pH 0. Nicotinic acid dodecyl ester and isonicotinic acid dodecyl ester do not dissolve in acidic aqueous solution. As nicotinic acid dodecyl ester and isonicotinic acid dodecyl ester have a long-chain alkyl group,

Fig. 5 Solubility of various nicotinic acids as a function of pH.

Fig. 6 Stripping of Ni from extractant mixtures of D2EHPA and nicotinic acid dodecyl ester or isonicotinic acid dodecyl ester.

these pyridine compounds have high hydrophobicity. Thus, these compounds do not dissolve in aqueous phase in the stripping stage of Ni.

Figure 6 shows the relationship between the stripping percentage of Ni species and H₂SO₄ concentration. The extractant mixtures used are D2EHPA and nicotinic acid dodecyl ester, or isonicotinic acid dodecyl ester. Ni species in the

organic phase is stripped by H_2SO_4 more than 0.25 mol/dm^3 . H_2SO_4 solution of 0.25 mol/dm^3 or more results in a high stripping percentage of Ni species.

4. Conclusion

The separation of nickel ions from electroless nickel plating waste liquor is difficult because nickel ions make complexes with various phosphate species and organic acid in the waste liquor. Nickel ions can be extracted and separated from the waste liquor by the extractant mixtures of D2EHPA and nicotinic acid dodecyl ester or isonicotinic acid dodecyl ester. It is possible to strip Ni species from the organic phase containing the

extractant mixtures with low concentration of H_2SO_4 .

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