

Removal and Recovery of Nickel Ion from Wastewater of Electroless Plating by Reduction Crystallization

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Abstract—Wastewater treatment after electroless nickel plating runs has been known to be difficult and this has been a subject of worldwide concern. Discarding wastewater of electroless nickel plating into sea was prohibited under the London Dumping Treaty since 1996. We have studied on recovering nickel from wastewater by reduction crystallization. In this study, the characteristics of nickel ion removal and recovery were investigated in the process of reduction crystallization using a laboratory scale batch crystallizer (500 ml), in order to propose a new process for wastewater treatment from nickel plating. In the reduction crystallization, which can use hypophosphite ion as a reducing agent for nickel ion in the wastewater, nickel ion could be recovered as a form of nickel metal by seeding nickel powder having large specific surface area.

Key words: Electroless Plating, Reduction Crystallization, Nickel Powder, Reducing Agent

INTRODUCTION

In recent years, electroless plating has played an important role in industry and has been widely used. In particular, the application of electroless nickel plating for corrosion resistance of functional articles has received considerable attention [Hayashi et al., 1994].

Nickel metal is deposited by chemical reduction in the electroless nickel plating process; therefore, nickel ion and hypophosphite ion decrease as the reaction proceeds. In this method, nickel sulfate and sodium hypophosphite are normally added in the plating bath to supply these ions. However, in spite of accurate management in the bath, as time and metal-turn-over increase, it is unavoidable that sodium phosphite and sodium sulfate are accumulated, to lower the quality of deposited film. Therefore, the repeatedly used plating bath needs to be disposed of [Kanbe, 1992].

Wastewater treatment has been known to be difficult after electroless nickel plating runs; this has been a subject of worldwide concern. Discarding wastewater of electroless nickel plating into the sea has been prohibited under the London Dumping Treaty since 1996, and regulations as to such chemicals and industrial wastes have tended to be reinforced [Atarashi, 1995].

Many research groups have proposed and developed the treatment technology for electroless plating wastewater. For example, with the aim of removal and recovery of nickel ion, nickel oxalate can be recovered after oxalic acid is added in the wastewater. After that, wastewater in which calcium hydroxide is added is baked in a kiln. In this case, a process by which calcium phosphite and sodium sulfate could be recovered has been proposed [Izawa et al., 1995, 1996]. The purpose of this work was to treat the mother liquor harmlessly, but there have also been problems in that the organic compounds of the complexing agent and additives need to be treated, and that phosphorous concentration of the treated mother liquor has

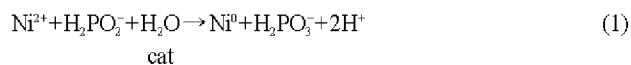
exceeded the regulation standard value [Hoshino et al., 1997].

Environmental crystallization (environmentally used crystallization) has been proposed from the standpoint of such as wastewater treatment. There is a need for treating contaminants in wastewater efficiently and economically, and for designing a new environmental restoration process. One valuable process is to remove and recover ions as a form of stable solids, such as crystals [Hirasawa, 1999].

This idea could be applied to heavy metal recovery. In this paper, reduction crystallization is investigated for recovering nickel ion from electroless nickel plating wastewater, with seeding nickel powder having a large specific surface area, by using reduction crystallization that can use hypophosphite ion as a reducing agent for nickel ion in the wastewater [Horikawa et al., 1999]. Preliminary experiments for reduction crystallization were performed, to make sure of the efficiency of nickel ion recovery and to propose a new process.

1. Reaction Mechanism

Various explanations have been proposed for the deposited reaction in an electroless nickel plating bath. The principal reaction formulas by using hypophosphite ion as a reducing agent are shown in Eqs. (1) and (2) [Kanbe, 1984].



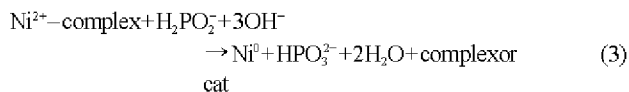
In Eq. (1), deposited nickel metal catalyzes itself and accelerates the plating reaction continuously. On the other hand, as shown in Eq. (2), decomposing itself without effectively utilizing hypophosphite ion as a reducing agent performs an undesirable reaction, that is, the hydrolysis in Eq. (2) greatly consumes the reducing agent.

The pH is very important for regulating the reaction, higher pH increases reducing power of hypophosphite ion. However, higher pH causes hypophosphite ion to decompose itself early and pre-

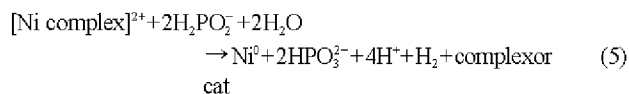
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cedes the hydrolysis in Eq. (2). In addition, the decrease in pH lowers the reducing power of hypophosphite ion by forming hydrogen ion in the bath as accelerating the plating reaction of Eq. (1). In the practical nickel plating process, the degree of nickel reduction was reported to be approximately 30% in the operation, to obtain adequate thin film of nickel; and control of pH was also thought to be important, considering the reaction equation [Tashiro, 1999]. On the other hand, the two reactions are also considered to occur by alkaline side [Kanbe, 1986].



The overall chemical reaction for electroless nickel deposition with sodium hypophosphite can be written as Eq. (5) [Mallory et al., 1985].



Eqs. (3), (4) and (5) show similarly that the nickel complex is in equilibrium with free nickel ions (which are reduced to Ni^0) and complexor. Therefore, a process has been needed to crystallize with maintaining reduction efficiency while pH is adjusted during the operation.

The reducing agent in the bath is oxidized on the metal surface with catalytic activity in the electroless plating process. Then metal ion can be reduced and film plating can be performed. Furthermore, the addition of plating material is needed to accelerate the plating reaction. Hence, a surface, which causes the reducing agent to oxidize, is required and metallizing non-conductors should be used for the plating material [Hayashi et al., 1994]. When the plating material as the reaction medium is dipped and suspended in the bath, the plating reaction in Eq. (1) can occur on the material surface, and then nickel metal is deposited with nucleation and crystal growth.

The objective of the present study is removal and recovery of nickel ion from the wastewater of electroless nickel plating by utilizing the above reaction in the bath, and we propose reduction crystallization as a new method. We discussed the reduction crystallization process to remove and recover nickel ion by adjusting pH by using nickel powder for plating material as seed crystals. This process has the advantage that metallizing non-conductors is not necessary. A schematic diagram of the reduction crystallization method is shown in Fig. 1.

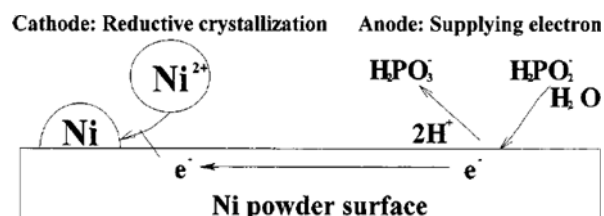


Fig. 1. Schematic figure of the reductive crystallization method.

Table 1. The composition of wastewater

| | |
|---------------------------|-------|
| PO_4^{3-} (mg/L) | 15500 |
| PO_3^{3-} (mg/L) | 40000 |
| SO_4^{2-} (mg/L) | 11700 |
| Na^+ (mg/L) | 18800 |
| NH_4^+ (mg/L) | 1600 |
| Specific gravity | 1.09 |
| pH | 5.1 |

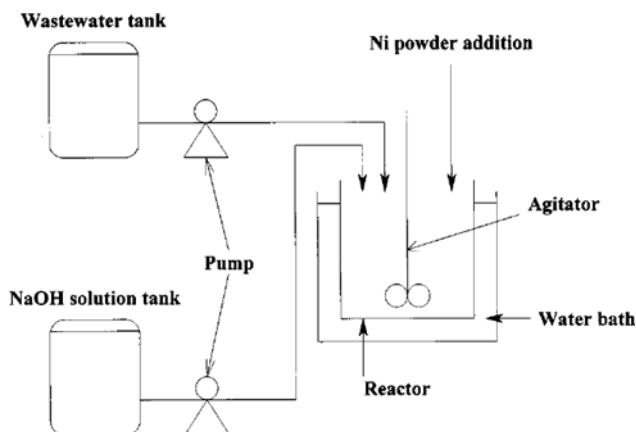


Fig. 2. Experimental apparatus.

EXPERIMENTAL PROCEDURES

1. Composition of Wastewater

A plating bath is normally used several times, accompanied by supplying nickel sulfate and sodium hypophosphite. Then the used plating bath becomes wastewater, because both nickel sulfate and sodium phosphite accumulate after a nickel plating operation. The composition of wastewater is shown in Table 1. The composition of the used plating bath is complicated, since pH regulator, buffer, complexing agent, stabilizer and brightener are included.

2. Experimental Method

The experimental apparatus is shown in Fig. 2. First, 250 ml of the wastewater was fed into a 500 ml beaker and 40 ml of 25% sodium hydroxide solution (1st Stage pH adjustment) was added to the wastewater, to adjust pH. Then nickel powder was added, accompanied by mixing and heating of the solution. Reduction crystallization proceeded under constant pH 8.0 with 10 ml of 25% sodium hydroxide solution addition (2nd Stage pH adjustment) and temperature 353 K. After the determined crystallization time, the mixed suspension was drawn out, to obtain nickel after vacuum filtration.

At first, experiments were performed to obtain the optimum conditions for pH adjustment. The conditions for experiments were as follows: nickel powder suspension density: 0.13, 0.65 and 1.30 volume %, respectively, to wastewater; holding time in the first and second pH adjustments: 0.5 hr and 1.0 hr. The experimental conditions are shown in Table 2. Residual nickel ion concentration was measured by ICP emission spectrometry to compare residual nickel ion concentration of the first pH adjustment with that of the second pH adjustment.

Table 2. The experimental conditions

| Ni powder suspension density | 0.13% | 0.65% | 1.30% |
|---|--------|--------|-------|
| Holding time in the 1st and 2nd pH adjustment | 0.5 hr | 1.0 hr | |

Table 3. Residual concentration of nickel ion after the first and second pH adjustment (mg/L)

| Ni powder suspension density | 0.13% | 0.65% | 1.30% |
|---|--------|------------|-----------|
| Holding time in the 1st and 2nd pH adjustment | 0.5 hr | 5.4 (212) | 9.9 (146) |
| | 1.0 hr | 7.8 (172) | 3.8 (128) |
| | | 10.2 (135) | 6.6 (120) |

Batch experiments were repeated ten times by using produced nickel powder under the optimum conditions obtained in the above experiments. Then scanning electron microscopy was used for observing the nickel powder crystals recovered by vacuum filtration to ascertain the reduction crystallization efficiency of repeated batch experiments.

RESULTS AND DISCUSSION

1. Effect of Suspension Density and Method of pH Adjustment on Nickel Ion Recovery Efficiency

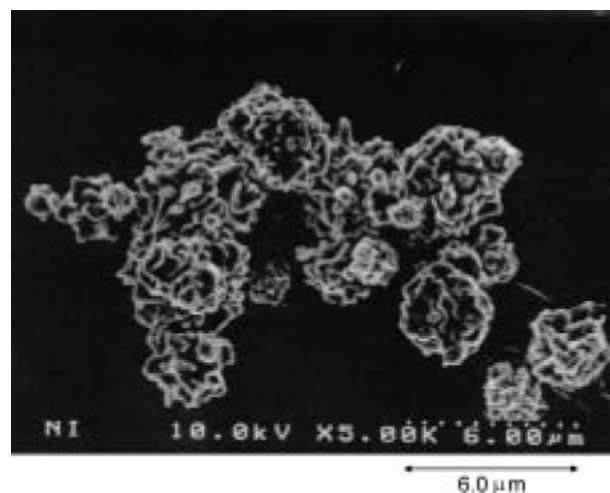
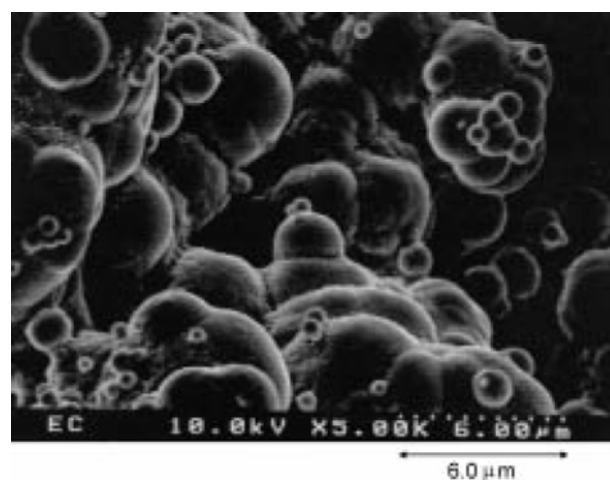
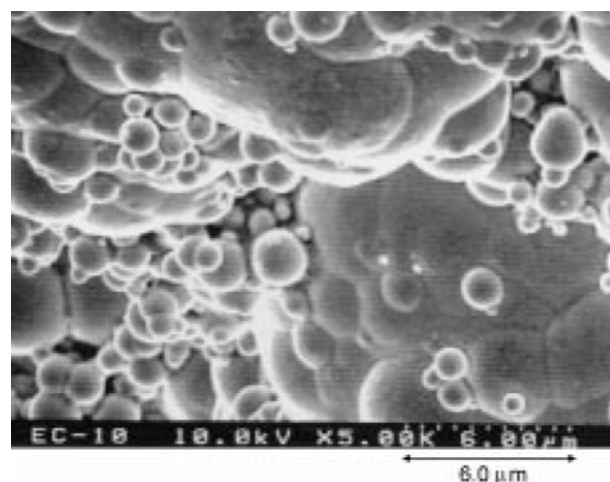
Table 3 shows the residual concentration of nickel ion after the one batch reductive crystallization. The value in parentheses expresses the results obtained after the first pH adjustment. Recovery efficiency was over 99.7% in each experimental run, by changing suspension density and holding time in the first and second pH adjustment processes. But the recovery efficiency after the second pH adjustment was better than that after the first pH adjustment. This fact suggested that pH was decreased by producing H^+ in the process of the reaction of Eq. (1) in the holding time after the first pH adjustment, which leads to suppression of the reduction of nickel ion. The crystallization of nickel metal was also accelerated by the second pH adjustment during the reaction, to control the reaction of Eq. (2).

Considering reduction crystallization of nickel ion from the wastewater, the two main reactions proceeded simultaneously, and so the effect of pH must be studied by a quantitative understanding of reaction engineering. But organic impurities were contained in the wastewater, and therefore model analysis was difficult.

Nickel ion recovery efficiency has been sufficiently obtained even if nickel powder is less suspended and the reaction time is short. Considering practical operation, the optimum conditions were determined that nickel powder suspension density was 0.13% and the holding time in the first and second pH adjustments was 0.5 hr. Batch experiments were repeated ten times by recovering nickel powder under above conditions to ascertain the reduction crystallization efficiency in the case of repeated runs.

2. Effect of Repeated Use of Produced Nickel Metal as Seeds on Recovery Efficiency

Figs. 3, 4 and 5 show SEM photos of the seed nickel, and one produced after the 4th and 10th batch experimental runs. The nickel produced was observed to grow with regeneration of the crystal surface, and also newly produced nickel fines were there. The re-

**Fig. 3. Seed nickel powder.****Fig. 4. After the 4th batch experimental runs.****Fig. 5. After the 10th batch experimental runs.**

lationship between residual concentration of nickel and number of repeated runs is shown in Fig. 6. The residual concentration of nickel in the mother liquor decreased as batch experiments were re-

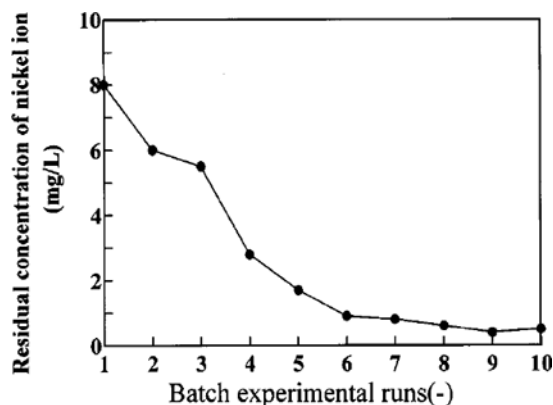


Fig. 6. Relationship between batch experimental runs and residual concentration of nickel ion.

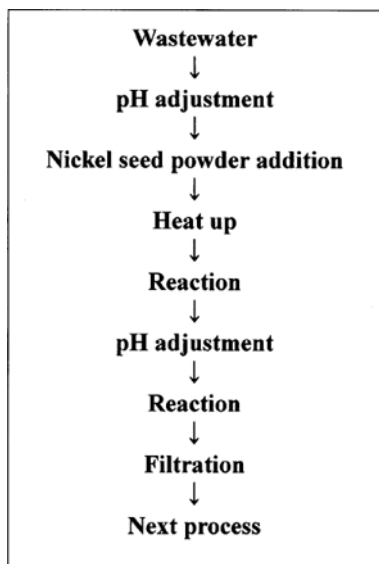


Fig. 7. Proposal for a new process.

peated. It was recognized that repeatedly using recovery nickel powder would have no effect on nickel ion recovery, but make the residual concentration lower. However, these results were obtained under the same suspension density, but newly produced fines contributed to the increase in surface area of nickel metal as shown in SEM observation. It was recognized that newly produced nickel accelerated reduction reaction on the surface.

PROPOSAL FOR A NEW PROCESS

By the result obtained above, a new process to remove and recover nickel ion from the wastewater of electroless nickel plating

is proposed in Fig. 7. Nickel ion from the wastewater could be removed and recovered as a form of nickel metal by the reduction crystallization based on this process arrangement.

CONCLUSION

By laboratory scale batch experiments, over 99.7% nickel ion was removed and recovered by reduction crystallization with seeds added and two stage pH adjustment. The amount of seeds in the crystallizer and the second pH adjustment could decrease the residual concentration of nickel ion. Produced nickel metal also could be used as seed for reduction crystallization. A new process for removing and recovering nickel ion as a form of metal was proposed.

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