Title:

Collection of Ni-Bearing Material from Electroless Plating Waste by Magnetic Separation with HTS Bulk Magnet

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Abstract

The magnetic separation experiment to collect the Ni compounds from the waste liquid of electroless plating processes was conducted in the open-gradient magnetic separation process with the high temperature superconducting bulk magnet system. The magnetic pole containing Gd-based bulk superconductors was activated to 3.45 T at 35 K in the static magnetic field of 5 T with use of a superconducting solenoid magnet. The coarse Ni-sulfate crystals were formed by adding the concentrated sulfuric acid to the Ni-phosphite precipitates which yielded from the plating waste liquid by controlling the temperature and the pH value. The open-gradient magnetic separation technique was employed to separate the Ni-sulfate crystals from the mixture of the Ni-sulfate and Ni-phosphite compounds by the difference between their magnetic properties. And we succeeded in collecting Ni-sulfate crystals preferentially to the Ni-phosphite by attracting them to the magnetic pole soon after the Ni-sulfate crystals began to grow.

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Keywords:

bulk superconductor, electroless plating, nickel compound, waste liquid, magnetic separation

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1. Introduction

Since the electroless nickel (hereafter abbreviated as Ni) plating process has an advantage that the dense Ni films uniformly covering the metal surfaces have superior anti-acid properties as well as resisting against rusting, the process has been widely utilized in numerous factories such as the electric device or car manufacturers and so on. The waste water treatments after the plating processes give rise to serious problems both on the environmental and natural resource issues. Therefore, it is necessary to establish new usable processes to collect and recycle the Ni resources.

Table 1 shows the ion concentration of Ni plating waste liquid just before its disposal treatment. The phosphorus ion concentration in the phosphorous acid is arriving at 50,000 ppm, which generates from the reductive reaction induced by hypo-phosphoric acid. When the concentration of phosphorous ions exceeds several 10 thousands ppm in the plating vessels, the liquid is to be disposed of in order to prevent unusual depositions which may happen on the work surfaces. Since the initial Ni concentration is nominally controlled to be 22,500 ppm, one sees 28% (6,316 ppm) of the Ni ions remain in the waste without using in this case. From the point of view to recycle the Ni resources, it is important to reduce the concentration of phosphorous ions to keep the plating liquid fresh and to elongate its lifetime.

The precipitates are originally expected to be magnetic when they are formed from the chemical compounds including ferromagnetic Ni ions. And the intense magnetic fields generated by the high temperature superconducting bulk magnet (hereafter abbreviated as HTS bulk magnet) would effectively attract the precipitates bearing even thin and weak magnetic property. After forming the Ni-bearing precipitates and examining the magnetic properties of the compounds, we aimed to collect them from the electroless plating processes to recycle Ni resources through the magnetic separation process with use of the HTS bulk magnet [1, 2].

2. Experimental procedure

2-1 Recycling process for Ni plating liquid

Figure 1 shows the recycling process for the plating waste. The phosphorous ions (HPO_3^{2-}) formed by the reductive reaction of Ni change to the Ni-phosphite (NiHPO_3) by adding NaOH to control the pH value at 70 °C (Eq. 1, 2). After dissolution in the concentrated sulfuric acid of 98%, the Ni-sulfate crystals precipitate, led by Eq. 3.

2-2 Characterization of Ni compounds

The data of particle size distributions of fine Ni-phosphite and coarse Ni-sulfate precipitates were measured with using the Laser Diffraction Particle Size Analyzer (Shimazu, SALD-3000S). The concentrations of Ni and P shown in Table 1 were estimated with use of the Ion Chromatograph (DIONEX, DX-100). The magnetization for the respective Ni-phosphite precipitates and Ni-sulfate crystals were measured with use of SQUID magnetometer (Quantum Design, MPMS-XL).

2-3 HTS bulk magnet system

Figure 2(a) shows a photo of HTS bulk magnet system used in the experiment, whereas Fig. 2(b) shows its magnetic field distribution measured at the surface of the magnetic pole. In the figure, N pole is expressed by the positive values. In the experiment, the bulk magnet was activated with use of superconducting solenoid-type magnet through the field cooling mode to obtain the superior magnetic field property, which reached 3.45 T in the space outside the vacuum chamber, where one can practically use [3].

2-4 Magnetic separation setup and its conditions

Figure 3 shows the schematic illustration of the experimental set up for the magnetic separation experiment. In the experiments as shown in the figure, the width of a part of the water channel was designed to be 5 mm so that the water might pass through the narrow space of strong magnetic field. The magnetic flux density remains 2.77 T at the center of the channel. The separation experiments

were operated within 30 min from the time when the crystallization reaction started in the beaker. The crystal slurry which was attracted inside the channel after the separation was investigated by dissolving each sample crystal of 1 g to the 20 ml genuine water. The concentration data of Ni and P ions in the liquid were evaluated by ICP analysis (SII, SPS1500V Plasma Spectrometer).

3. Results and discussion

3.1 Characterization of Ni compounds

Figure 4(a) shows the Ni-phosphite precipitates in the reaction bath. They were fine and uniform with the particle sizes of around 10-20 μm , and separated to the slurry and clear liquid by filtering. As shown in Table 1, after forming the Ni-phosphite precipitates, the major portion of P was included in the precipitates, which means that the phosphorous ions were almost removed from the clear liquid and changed into the Ni-phosphite precipitates. Therefore, the clear liquid is available to let it return back to the plating baths. On the other, the precipitates were dissolved in the concentrated sulfuric acid, and then the Ni-sulfate crystals are formed, as shown in Fig. 4(b), led by Eq. (3).

Figure 5 shows the reaction time dependence of the growing particle size distributions of the Ni-sulfate crystals deposited from the saturated solution of pure Ni-sulfate sample. As the reaction proceeds in the supersaturated region, the crystals grew fairly large even at the beginning of its crystallization, as shown in Fig. 5(a). The grain size evolutionally grew until it saturated to over 1 mm by 12 min, as shown in Fig. 5(b). Since the Ni-sulfate deposits from Ni-phosphite, both coexist in the solution as a mixture, as shown in Fig. 1 and Fig. 4(b).

The Ni-sulfate precipitate is the major material for the electroless plating processes, and which is available for the Ni plating operations again after certain purification treatments. However, a problem lies in the collection process of the precipitates. Since the fine crystals of Ni-sulfate are easy to dissolve again at the early time of their deposition process, it is almost impossible to collect them by any filtration methods. Therefore, the practical recycling of Ni resources does not fit for the continuing

operation in practical factories. We propose that a novel collection method for the Ni-sulfate crystals with use of intense magnetic fields generated by HTS bulk magnets which are enable to attract and collect them in the early stage of crystallization. Since the Ni-sulfate crystals are deposited in the supersaturated region of Ni concentration, and the Ni-sulfate would preferentially crystallize earlier than other compounds when it is kept in high concentration.

Figure 6 shows the result of the magnetization measurement for the respective Ni-phosphite precipitates and Ni-sulfate crystals. The magnetic properties of the precipitates are shown in Table 2. Since the value of magnetic force in volume for the Ni-sulfate large crystal is 2.5 times higher than that of Ni-phosphite fine slurry, the difference between the magnetic forces is enlarged when it is estimated for each particle. The difference between the crystal sizes results in the fairly big difference between the magnetic forces for each crystal. Therefore, it is strongly suggested to be possible to separate two kinds of crystals by using intense magnetic fields. The magnetic force in the magnetic separation technique is expressed in Eq. (4).

$$F_m = \frac{4}{3} \mu_0 \pi r_p^3 \frac{9(\chi_p - \chi_f)}{(3 + \chi_p)(3 + \chi_f)} H \cdot \text{grad}H \quad (4)$$

where r_p , χ_f and χ_p mean the radius of particles, susceptibility of liquid and particle, respectively [4].

3.2 Magnetic separation

The magnet shown in Fig. 2 is characterized as its intense and compact magnetic field generator with steep field gradient [3, 5], and is expected to suit for the application to the magnetic separation devices with strong magnetic field over 3 T and keen gradient of magnetic field of 100 T/m according to Eq. (4).

The experimental results after collecting the precipitates exhibits that the Ni-phosphite or Ni-sulfate precipitates was collected at the side wall of water channel where the magnetic field was adjacently applied and the crystals were strongly attracted to the bulk magnet like slurry. Figure 7 shows the result of ICP analysis for the separated crystals. One sees the Ni and P concentrations of three kinds of

crystals such as the pure Ni-sulfate which contains no phosphorous ions, the sample mixture of the Ni-phosphite and Ni-sulfate crystals before starting the separation, and the collected crystals after the separation. As shown in the figure, the Ni concentration of the magnetically collected crystals increases in 1,582 ppm compared with that of mixed crystal sample, while the P concentration decreases in 111 ppm. Furthermore, the result of EPMA quantitative analysis revealed that the separated crystal was composed of almost uniform Ni-sulfate compound containing only 2.37% of P. The Ni-sulfate crystals with low P content and coarser particle size than that of Ni-phosphite particles are preferentially attracted to the intense magnetic pole of HTS bulk magnet and effectively separated as shown in the results above.

Although we conducted the same investigations with use of the electromagnets which generated 1.52 T and 0.85 T, we observed no distinctive attraction phenomena to the magnetic poles less than 2 T. This means that the bulk magnet system generating the magnetic field over 3 T is essentially effective for separating such precipitates which have weak magnetic properties.

4. Conclusions

We succeeded in magnetically separating for the coarse Ni sulfate crystals which were generated from the Ni-phosphite in the waste liquid drained from the electroless Ni plating process with use of the HTS bulk magnet which yields the intense magnetic field up to 3.45 T on the magnetic pole surface. Since the crystals contain lower P and higher Ni concentration than the mixed precipitates, we can return them back to the reaction baths of the Ni-phosphite to elongate the lifetime of the plating liquids. Furthermore, it is possible to reuse the Ni-sulfate crystals in the electroless plating vessels as a raw material when it is properly refined. Thus, we clarified the possibility for recycling the Ni resource as a rare earth metal and for reducing the environmental loads of the disposal treatments for waste liquids by the magnetic separation technique with use of HTS bulk magnets.

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Figure captions

Fig. 1. Illustration of the Ni recycling process in the electroless nickel plating process, showing the fabrication of Ni-phosphite and Ni sulfate compounds.

Fig. 2. HTS bulk magnet system with GM-cooler (a) and its distribution of magnetic flux density scanned at the chamber surface (b).

Fig. 3. Experimental setup of magnetic separation (a) and distribution of magnetic flux density with a gap of 0 and 3.5 mm from the magnetic pole surface (b).

Fig. 4. Ni-phosphite precipitates formed in the reaction bath (a) and the mixture of Ni-sulfate crystal after adding the sulfuric acid to the Ni-phosphite slurry (b).

Fig. 5. Crystal size distributions of growing Ni-sulfate from Ni-phosphite slurry (a), and the time dependence of average particle sizes of Ni-sulfate crystals (b).

Fig. 6. Particle size dependence of magnetic force of Ni-sulfate and Ni-phosphite crystals measured by SQUID magnetometer, derived by Eq (4).

Fig. 7. Ni and P concentration of the mixed crystals and magnetically collected crystals in comparison with that of pure Ni-sulfate derived from the saturated solution.

Figure %

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Figure 1

(a)

(b)

Figure'

(a)

Clear liquid

NiHPO_3
precipitates

Mixture of NiHPO_3
and NiSO_4
precipitates

(b)

Figure)

Figure*

Figure 7

Table 1. Ion concentrations in nickel plating waste and clear liquid.

Ions		Waste liquid (ppm)	Clear liquid (ppm)
Ni		6,316	7,828
P		60,480	11,269
P (in hypo-phosphoric acid)	$[\text{HPO}_2]^{2-}$	9,091	10,502
P (in Phosphorous acid)	$[\text{HPO}_3]^{2-}$	49,904	766

Table 2. Characteristics of Ni-sulfate and Ni-phosphite precipitates.

Sample	Susceptibility (χ_p)	Susceptibility in volume (χ_p)	Particle Size (μm)	Magnetic Force (N)
Ni sulfate	1.66E-10	3.33E-04	575.1	1.01E-05
Ni phosphite	1.33E-11	1.31E-04	11.86	3.50E-11