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Magnetic precipitate separation for Ni plating waste liquid using HTS bulk magnets

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ABSTRACT

The magnetic separation experiment for recycling the nickel-bearing precipitates in the waste liquid from the electroless plating processes has been practically conducted under the high gradient magnetic separation technique with use of the face-to-face HTS bulk magnet system. A couple of facing magnetic poles containing Sm123 bulk superconductors were activated through the pulsed field magnetization process to 1.86 T at 38 K and 2.00 T at 37 K, respectively. The weakly magnetized metallic precipitates of Ni crystals and Ni–P compounds deposited from the waste solution after heating it and pH controlling. The high gradient magnetic separation technique was employed with the separation channels filled with the stainless steel balls with dimension of 1 and 3 mm in diameter, which periodically moved between and out of the facing magnetic poles. The Ni-bearing precipitates were effectively attracted to the magnetized ferromagnetic balls. We have succeeded in obtaining the separation ratios over 90% under the flow rates less than 1.35 L/min.

1. Introduction

The electroless nickel plating technique is one of the most popular surface treatments on metals and resins. A large amount of wastes has been disposed from the Ni plating factories such as car manufacturers and electronic parts companies. The electroless plating liquid is composed of Ni sulfate, sodium hydro-phosphoric acid and other chemical compounds. Table 1 shows a data of the conventional waste liquid from the Ni plating process. The phosphorus ion concentrations in the waste liquid are listed as two kinds of P compounds of the pre-reacted hypo-phosphoric acid ions and post-reacted phosphorous acid ions, respectively. The concentration of P ions increases with procedure of the reduction reaction. The liquid contains the phosphorous acid ions $[H_2PO_3]^-$ with high concentration, which are generated as a by-product of the oxidation–reduction reaction of the hypo-phosphoric acid ions $[H_2PO_2]^-$. As the phosphorous acid ions with high concentration in the plating baths cause unusual depositions, the plating liquid which still contains a large amount of Ni ions are disposed after several turns of the plating treatments. And it is expected to collect and utilize the Ni metal again from the aspect of recycling natural resources. It is also possible to recycle the Ni ions as a raw material of the plating processes, if they would be derived from the waste liquid with reasonable and acceptable costs.

The melt-processed high temperature superconducting bulk magnets (hereafter abbreviated as bulk magnets) in cooperation with small-sized refrigerators are characterized as intense magnetic field generators [1–3]. A couple of the bulk magnets which are contained in each vacuum chamber are activated by the pulsed field magnetization technique (PFM), and then the magnetic poles are settled face-to-face on the frame. The PFM technique is known to be an easy and compact method to activate the bulk magnets in comparison with the field cooling method which requires large scale superconducting solenoid magnets [4]. Fujishiro et al. [5] reported that the performance of trapped magnetic fields has reached 5.2 T by applying the multi-pulse fields in the process of stepwise temperature falls.

We know a couple of magnetic separation systems. One is the high gradient magnetic separation (HGMS, [6]) and the other is the open gradient magnetic separation (OGMS, [7]). It has been reported by Oka et al. [8] that the Fe in the groundwater was effectively removed by HGMS technique with use of face-to-face HTS bulk magnets, in which the iron balls of 3 mm in diameter were installed in a water channel between the magnetic poles emitting the magnetic fields over 2 T. Fujishiro et al. [9] reported that the Fe oxide powder mixed beforehand in the water has been effectively separated by passing it through the multi-pole magnet which

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Table 1
Ion concentration in nickel plating waste liquid (ppm).

Ions	ppm	Chemical formula
Ni ions	6316	
P ions	60,480	
P (hypo-phosphoric acid)	9091	$[H_2PO_2]^-$
P (phosphorous acid)	49,904	$[H_2PO_3]^-$

contains five activated bulk magnets in a line. On the other, Oka et al. [10] clarified that HGMS technique with use of the multi-pole magnet mentioned above was useful for purification of the groundwater, too.

In the study, the ferromagnetic Ni-bearing precipitates which are decomposed from the waste liquid decomposed by the chemical reactions are collected by means of the magnetic separation technique using an intense magnetic field. We aim to show the usefulness of this system for the practical recycling of Ni resources and the environmental issues on the waste water purification.

2. Experimental

2.1. Sample preparation

Fig. 1 shows the process to form the Ni-bearing metallic precipitates from the waste liquid. We added the NaOH solution to the waste acid (pH = 4–5) to form the Ni phosphorous until the pH value reached 10.3. After heating it to 363 K, the decomposition of the liquid generated the hydrogen gas, and afterward yielded the black metallic precipitates. The reaction lasted around 20 min. As shown in Fig. 2, the precipitates in the liquid are attracted to 2 T magnetic pole which contained an activated bulk magnet. This implies that the powder is ferromagnetic and the magnetic processing must be successful for collecting the precipitates. In Table 2, the result of ICP analysis showed the concentrations of Ni and P ions in the plating waste liquid, the decomposed precipitates, and in the remaining clear liquid. Although the P ions remain thick in the waste after the plating process while the Ni ions remain thin, almost all the Ni ions have precipitated with including only 10% of P atoms. On the contrary, since the clear liquid contains no Ni ions, the Ni element in the waste is able to be magnetically separated and recycled through this disposal treatment. Fig. 3 shows the size distribution of the precipitates estimated by the Laser Diffraction Particle Size Analyzer (Shimazu, SALD3000S). Since the distribution of the Ni-bearing particles sizes is fairly narrow, it is inferred that the attractive force is expected to be uniform in the operations. As shown in Fig. 4, the results from the X-ray diffraction showed that the precipitates are composed of the metallic Ni crystals and Ni_3P compound powders. Since both of the powders are ferromagnetic, the magnetic separation technique must be effective to separate them from the decomposed waste liquid. Fig. 5 shows the distribution maps of Ni and P elements, respectively. The maps were examined by the electron probe micro-analyser EPMA-JXA8621 (manufactured by JEOL). As indicated the circles in the figure, the distributions of Ni and P elements do not always coincide with their positions, the particles of Ni and Ni–P precipitated in different particles.

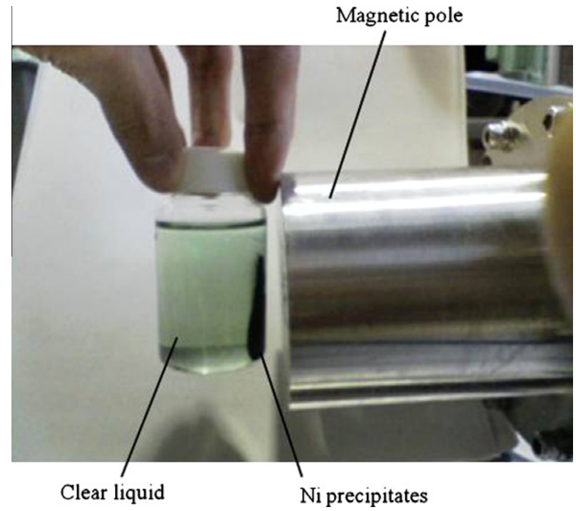

Fig. 2. Attracting phenomenon of the Ni-bearing precipitates to the magnetic pole of 2 T.

Table 2
Ni and P ion concentration (ppm).

Concentration (ppm)	Ni	P
Plating waste liquid	6316	60,480
Clear liquid	395	32,885
Precipitate	4770	584

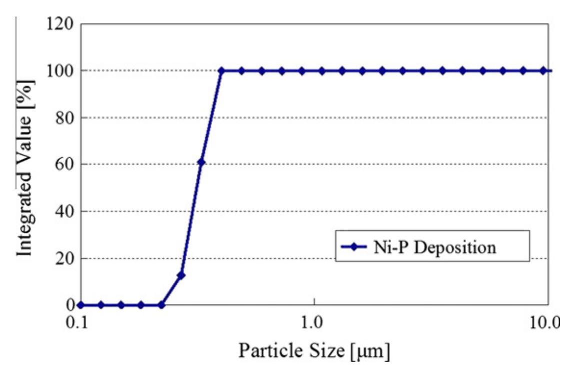

Fig. 3. Particle size distribution of the precipitates decomposed from the waste liquid.

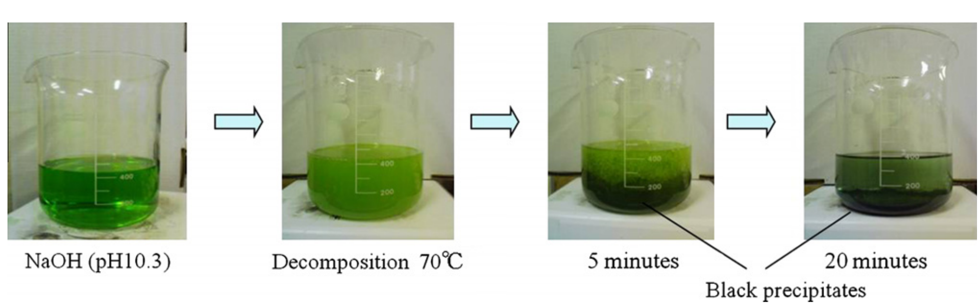

Fig. 1. Fabrication process to form the Ni-bearing metallic precipitates from the plating waste liquid.