pISSN 1229-3008 eISSN 2287-6251
Progress in Superconductivity and Cryogenics
Vol.23, No.3, (2021), pp.37~40 https://doi.org/10.9714/psac.2021.23.3.037

Feasible waste liquid treatment from electroless nickel-plating by intense magnetic field of HTS bulk magnets

T. Oka[*, a], M. Furusawa[a], K. Sudo[a], L. Dadiel[a], N. Sakai[a], H. Seki[a], M. Miryala[a], M. Murakami[a], T. Nakano[b], M. Ooizumi[b], K. Yokoyama[c], and M. Tsujimura[d]

[a] *Shibaura Institute of Technology, Tokyo, Japan*
[b] *Niigata University, Niigata, Japan*
[c] *Ashikaga University, Ashikaga, Tochigi, Japan*
[d] *Aichi Giken Co. Ltd., Kariya, Aichi, Japan*

(Received 25 June 2021; revised or reviewed 23 September 2021; accepted 24 September 2021)

Abstract

Nickel (Ni) is a kind of the rare earth resources. Since Ni-containing waste is drained after several plating operations in the factories, the effective recycling technique has been expected to be introduced. An actual magnetic separation technique using HTS bulk magnet generating the strong magnetic field has succeeded in collecting the paramagnetic slurry containing Ni-sulphate coarse crystals which were fabricated from the Ni-plating waste. The Ni compound in the collected slurry was identified as $NiSO_4/6H_2O$, showing slight differences in the particle size and magnetic susceptibility between the samples attracted and not-attract to the magnetic pole. This preferential extraction suggests us a novel recycling method of Ni resource because the compound is capable of recycling back to the plating processes as a raw material.

Keywords: high temperature superconductor, bulk magnet, nickel-plating, waste liquid, magnetic separation

1. INTRODUCTION

The electroless nickel (Ni)-plating process has a significant advantage that dense and uniform coatings of Ni cover the various shapes of substrate surfaces, showing excellent mechanical and chemical tolerance. The process has been widely adopted in many factories of electronic devises, car manufacturers and others. The plating waste drained from factories have brought us some problems of environmental load. Even though the waste fluid contains Ni ions with high concentration, the waste is usually disposed of. Since Ni is one of the rare earth elements, it is necessary to recycle the resource from Ni-plating industries [1].

Fig. 1 shows an illustration of Ni-recycling plan from the electroless Ni-plating process [2-4]. The electroless Ni-plating is conducted based on the reductive reaction of Ni ions due to the oxidation of phosphorous (P) ion of hypo-phosphorous acid (H_3PO_2), depositing the metallic Ni coating on the substrate surfaces. The Ni concentration in the plating bath is adjusted to a certain value by adding $NiSO_4$ crystals as a raw material. Because the P concentration in the bath increases with increasing number of successive plating operations, the plating liquid is disposed after several repetitions until the P content exceeds a certain value.

Table shows the concentration of the ions in the waste in Fig. 1, which were estimated by ICP analysis. The waste is disposed to prevent the unusual depositions due to high-concentrated P ions. From the practical point of view, it is important to remove P to keep the plating liquid fresh and to elongate its lifetime. The P ion forms the Ni-phosphite ($NiHPO_3$) precipitate due to the catalytic Ni ion by $NiSO_4$ addition (Eq. 2) and is removed from the waste by filtering. The clear liquid can be supplied to the plating vessels again. As shown in Fig. 2a, $NiSO_4$ generates in low pH region. To extract Ni from $NiHPO_3$ slurry, $NiSO_4$ crystals are synthesized by pH controlling and heat treatments [1, 3], as shown in Eqs. (1)-(3).

$$NaH_2PO_3+NaOH \rightarrow Na_2HPO_3+H_2O \quad (1)$$
$$Na_2HPO_3+NiSO_4 \rightarrow NiHPO_3+Na_2SO_4 \quad (2)$$
$$NiHPO_3+H_2SO_4 \rightarrow NiSO_4+H_3PO_3 \quad (3)$$

The intense magnetic fields generated by the high temperature superconducting (HTS) bulk magnets (bulk magnet) can attract the weak magnetic precipitates. After forming the Ni-containing 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 bulk magnet. In this study, we tried to collect the $NiSO_4$ crystals from so-called regenerated waste through the magnetic separation technique. We aim to recycle the

TABLE
ION CONCENTRATION IN NI-PLATING WASTE [1]

Ions in waste	Concentration [ppm]
Ni ions	6,316
P ions	60,480
P (hypo-phosphoric acid) $[HPO_2]^{2-}$	9,091
P (Phosphorous acid) $[HPO_3]^{2-}$	49,904

* Corresponding author: okat@shibaura-it.ac.jp

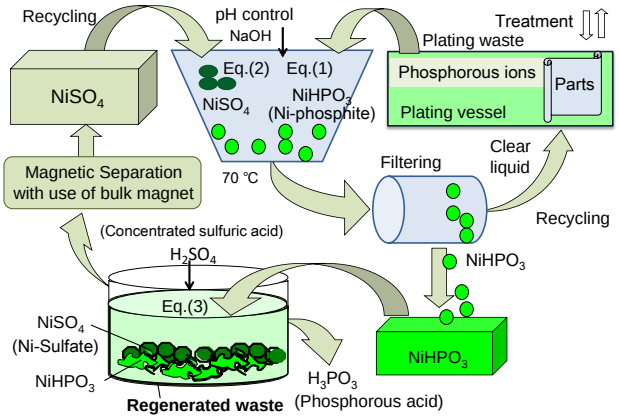

Fig. 1. Recycling process for electroless Ni-plating waste.

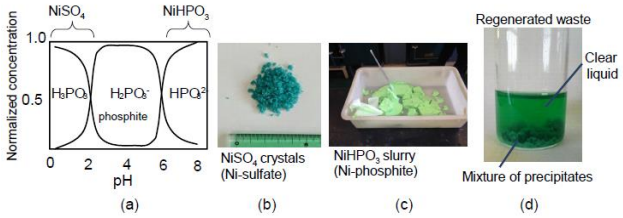

Fig. 2. pH-phase diagram to generate $NiSO_4$ [1] (a), coarse $NiSO_4$ crystals (b) generated from $NiHPO_3$ (c) in low pH region in (a), and the regenerated waste (d) to be separated, as shown in Fig. 1 and Eq. 3.

Ni resources with use of the bulk magnet, and to elongate the lifetime of Ni-plating liquid, which must reduce the amount of the plating waste and environmental loads.

2. EXPERIMENTAL METHODS

2.1. Preparation of Ni-containing precipitates

Fig. 2 shows the views of $NiSO_4$ coarse crystals derived from the saturated solution and $NiHPO_3$ fine powder after filtration in Fig. 1, and the dried mixture of regenerated waste containing both of Ni-compounds above. These precipitates of metallic compounds including ferromagnetic Ni ions are expected to be weakly magnetic. As presented in the papers elsewhere [2-4], the authors estimated the magnetic susceptibility for $NiSO_4$ and $NiHPO_3$ by SQUID magnetometer. $NiSO_4$ crystal showed the higher magnetic moment than that of $NiHPO_3$. As shown in Eq. 4, as the magnetic force F_m is proportional to the particle volume [5, 6], substantial difference should exist between large $NiSO_4$ grains and fine $NiHPO_3$ precipitates.

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

2.2. HTS bulk magnet system and its performance

Fig. 3 shows the bulk magnet system used in the experiment. The system is composed of magnetic pole containing Gd-Ba-Cu-O bulk magnet, helium compressor, vacuum pump, and temperature controller. A Gd-based

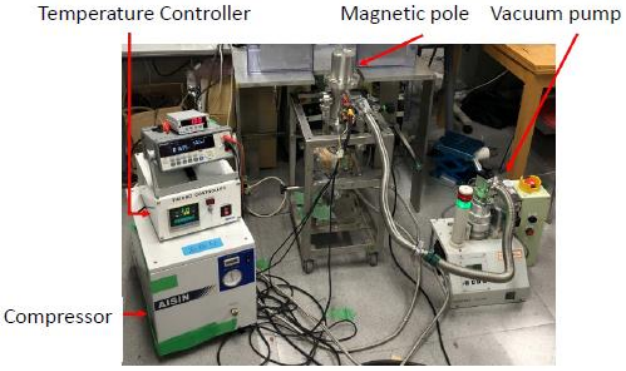

Fig. 3. Experimental setup of bulk magnet activated by pulsed field magnetization, generating 2.71T and 1.85 T at the bulk surface and at the center of pole surface, respectively.

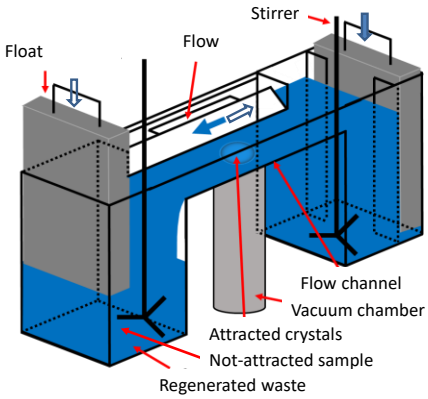

Fig. 4. A pair of containers and flow channel on the magnetic pole generating 1.41 T at the channel surface.

bulk magnet with a size of 60 mm in diameter and 15 mm in thickness were activated at 30 K by pulsed field magnetizing (PFM) method [7]. The magnetic pulses up to 4.44 T were successively applied to the bulk magnet for six times with reducing the intensity called IMRA method [8].

Finally, the trapped field reached 2.71 T and 1.85 T at the centers of bulk surface and magnetic pole surface, respectively.

2.3. Magnetic separation experiment and devices

Fig. 4 shows a schematic illustration of the magnetic separation experiment. A pair of stainless-steel containers of 6 liter are linked by a flow channel. The bulk magnet was located just under the channel. The width of the channel was designed as 100 mm so that the waste would flow in the strong magnetic field space. A couple of floats were alternately sunk into the vessel by hand to feed the waste into the channel periodically with a rate of 25 l/min. The magnetic field at the channel surface was 1.41 T. The waste containing slurry flew through the channel, and the slurry were attracted to the magnetic pole. The attracted slurry was evaluated in its crystal structure and magnetic moment by XRD (Shimazu) and the PPMS/VSM magnetometer (Quantum Design Inc., VersaLabTM), respectively. The particle sizes were estimated by ImageJ in SEM/EDX (JEOL, JSM-7100F, ImageJ).

3. RESULTS AND DISCUSSION

As shown in Fig. 5, we observed the apparent green coarse particles attracted and accumulated on the bottom of the channel after the experiment. It is sure that weakly-magnetic Ni-compound was recovered from the regenerated waste with use of our bulk magnet. After draining the fluid and slurry, we still observed an apparent "drop" of clear liquid which remained without any particles included. This means that the saturated solution is still magnetic enough to be attracted to 1.4-T magnetic pole. In other words, not only the particles including Ni compound but the solution involving Ni ions have been attracted to the magnet. The recovery of $NiSO_4$ in this manner reached 8.4 kg/day [4].

We took two kinds of samples from the attracted green particles on the channel and the slurry at the bottom of the container, as shown in Fig. 4. The results of XRD identification measurement are shown in Fig. 6. All the peaks of the diffraction patterns proved that the samples were composed of $NiSO_4$-$6H_2O$ crystal. We did not see any clear differences between these patterns. This means that major part of precipitates in the container has already finished the chemical reaction from fine $NiHPO_3$ precipitates to $NiSO_4$ coarse crystals. As P ion remains in the liquid, we observed no major peaks from P by XRD.

As shown in Fig. 7, the data of magnetic susceptibility were measured by SQUID magnetometer. The particles with 3.80 x 10^{-4} and 4.73 x 10^{-4} are classified to the paramagnetic compounds. The data for the sample attracted to the magnetic pole is a bit stronger by 24% than that of "not-attract" sample which was taken at the bottom of the container. The difference is obscure because the data were estimated in volume. One of the answers would be expected by the next topic on the particle size.

Fig. 8 shows the particle size distributions of attracted (a) and not-attracted (b) samples measured by SEM/EDX. Wide distributions of particles were observed in both results. Apparent difference between these data is that particle size distribution for the attracted crystals is wider than that of not-attract. Furthermore, the average size for attracted crystals (0.610 mm) is apparently larger by 26% than that of not-attract sample (0.485 mm). This means the magnetic pole preferentially attracted the coarser particles than fine ones, and that we would be able to separate the coarse crystal from the mixture of regenerated waste including fine and coarse $NiSO_4$ crystals with valid recovery rates.

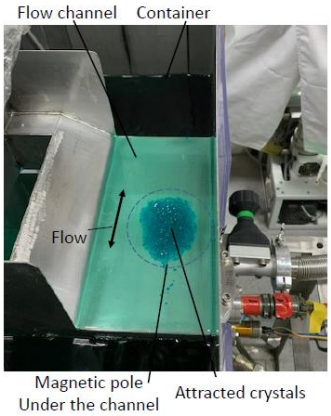

Fig. 5. Ni-containing crystals attracted on the channel.

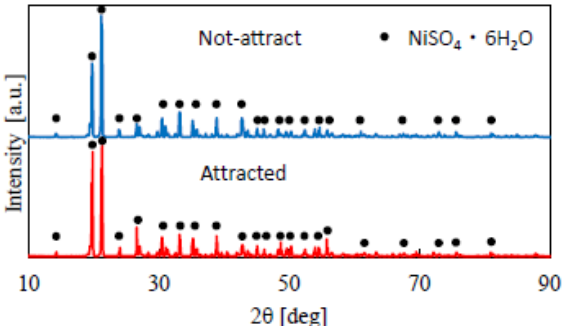

Fig. 6. XRD characterization of Ni-containing slurry after trials.

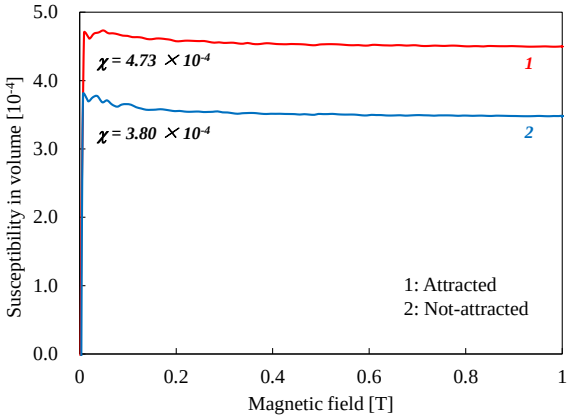

Fig. 7. Magnetic property of attracted crystals (1) and not-attracted sample in the container (2).

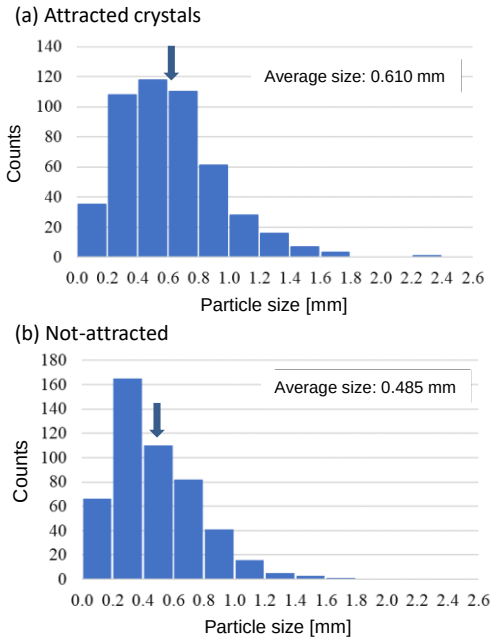

Fig. 8. Average particle sizes of attracted crystals and the not-attract sample.

4. CONCLUSION

The magnetic separation experiment for recovering Ni-including plating waste were conducted with use of single-pole bulk magnet activated by the pulsed field magnetization, which formed the intense magnetic field space up to 1.41 T at the flow channel surface. We succeeded in separating the $NiSO_4/6H_2O$ coarse crystals from the regenerated waste composed of the Ni-compound mixture. We observed slight differences in the particle size and magnetic susceptibility between the samples attracted and not-attract to the magnetic pole. This preferential extraction suggests us a novel recycling method because the compound is capable of recycling back to the plating processes as a raw material.

ACKNOWLEDGMENT

The study has been partially supported by the grants-in-aid from MEXT of Japanese government, Japan Society for the Promotion of Science, and Japan Science and Technology Agency.

REFERENCES

[1] F. Matsui, “Recycling and Circulation of Electroless Nickel Plating Bath,” *Uyemura Technical Report*, vol. 44, pp. 21-24, 1999 (in Japanese).

[2] T. Oka, H. Fukazawa, S. Fukui, J. Ogawa, T. Sato, M. Ooizumi, M. Tsujimura, and K. Yokoyama, “Collection of Ni-Bearing Material from Electroless Plating Waste by Magnetic Separation with HTS Bulk Magnet,” *Physica C*, vol. 496, pp. 58-62, 2014.

[3] T. Oka, Y. Takayanagi, S. Machida, K. Ichiju, S. Fukui, J. Ogawa, T. Sato, M. Ooizumi, M. Tsujimura, and K. Yokoyama, “Magnetic Separation for Recovering Ni-Compounds from Plating Waste with Use of HTS Bulk Magnets,” *IEEE Trans. Appl. Supercond.*, vol. 26, pp. 3700204, 2016.

[4] T. Oka, S. Sasaki, H. Sasaki, S. Fukui, J. Ogawa, T. Sato, T. Nakano, M. Ooizumi, M. Tsujimura, and K. Yokoyama, “Collecting Ni-Sulfate Compound from Electroless Plating Waste by Magnetic Separation Technique with Use of HTS Bulk Magnets,” *J. Phys.: Conf. Ser.*, vol. 1054, pp. 012047, 2018.

[5] J. Watson, “Magnetic filtration,” *J. Appl. Phys.*, vol. 44, pp. 4209-4213, 1973.

[6] T. Ohara, H. Kumakura, and H. Wada, “Magnetic separation using superconducting magnets,” *Physica C*, vol. 357- 360, pp. 1272-1280, 2001.

[7] T. Oka, “Processing and applications of bulk HTSC,” *Physica C*, vol. 463-465, pp. 7-13, 2007.

[8] Y. Yanagi, Y. Itoh, M. Yoshikawa, T. Oka, H. Ikuta, and U. Mizutani, “Pulsed field magnetization on a 36 mm diameter single-domain Sm-Ba-Cu-O bulk superconductor at 30, 35 and 77 K,” *Superconductor Sci. Tech.*, vol. 18, pp. 839-849, 2005.