Collecting Ni-Sulfate Compound from Electroless Plating Waste by Magnetic Separation Technique with Use of HTS Bulk Magnets

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Abstract. The authors have developed a useful technique for extracting the Ni-sulfate compound from the “processed waste/fluid” of the electroless Ni-plating processes. After forming the fine NiHPO₃ precipitate from the waste, the coarse NiSO₄ crystals were synthesized through the reaction with the concentrated sulfuric acid. In the experiment, the open-gradient magnetic separation was employed to collect the NiSO₄ crystals from the muddy mixture composed of these compounds. The experiments were practically conducted with use of the Gd123-based HTS bulk magnets generating up to 3.99 T, which were activated by the field cooling magnetizing method operated at 35 K. Intense magnetic field emitted from the bulk magnet attracted the paramagnetic fluid and coarse NiSO₄ crystals on the bottom of the water channel, forming a giant drop of NiSO₄-saturated clear fluid and the slurry of nickel sulfate hexahydrate. This preferential collection suggests a feasible recycling process of Ni resource as a raw material in the plating processes.

1. Introduction
Since dense and hard Ni coatings uniformly cover even the complex material surfaces with its superior chemical tolerance against rusting or wearing by friction, the electroless nickel-plating process has a significant advantage, and the process has been widely used in numerous factories such as the electronic devices or car manufacturers. But, the waste water treatments after the plating processes cause the serious problems both on the environmental loads and the natural resource issues. Therefore, it is needed to establish the useful processes to collect and recycle the Ni resources as one of the rare earth metals.

We have proposed three feasible approaches in the past, such as the drain water purification which aimed to reduce the concentration of Ni and P from the drained water from factories [1]. The second trial targeted the deposition of Ni₃P which were generated by its unusual decomposition of plating fluid which contained Ni ions with high content in the waste liquid [2]. The third approach was a formation of NiSO₄ compound from the NiHPO₃ precipitate fabricated by adding the concentrated sulfuric acid to the slurry which contains Ni ions with high content [3].
Although the metallic Ni has, all we know, the ferromagnetic property, and it is easily attracted to magnets. But the fact is not well known that the chemical compound or the crystal of Ni-bearing compounds like a NiSO$_4$ crystal has weak magnetic moment and it is expected to be attracted or collected when we use extremely intense magnetic fields generated by superconducting devices. The high temperature superconducting (HTS) bulk magnets would be effectively capable of attracting these kinds of precipitates.

In the recycling process shown in Figure 1, after forming the fine NiHPO$_3$ (nickel-phosphite) precipitates by the heat treatment and pH controlling, we obtained the NiSO$_4$ crystals by adding concentrated sulfuric acid. As the mixed slurry composed of the NiSO$_4$ and NiHPO$_3$ are chemically unstable, and it is necessary to extract NiSO$_4$ crystals immediately after the deposition from the mixture.

In this study, we have tried to collect the NiSO$_4$ compounds by utilizing the slight difference between their magnetic properties from the processed waste mixture of these compounds. We aim to recycle the Ni resources through the magnetic separation processes with use of the HTS bulk magnet, and to elongate the lifetime of Ni-plating liquid, which must reduce the amount of the plating waste and resultant environmental loads.

2. Experimental procedure

2.1. Fabrication of Ni sulfate precipitates

Figure 1 shows the whole recycling process of electroless Ni-plating. The P ions formed by the reductive reaction changes Ni into the fine NiHPO$_3$ precipitates by adding NaOH at 70 °C. After the dissolution by adding the concentrated sulfuric acid, the NiSO$_4$ crystals deposit and form the mixed slurry of these compounds. NiSO$_4$ and NiHPO$_3$ crystals coexist in the sulfuric acid as a mixture.

The concentration-pH equilibrium diagram of these two compounds are shown in Figure 2 [4]. The different compounds crystalize with respect to the different regions of pH values, which precipitates on the bottom of the vessel, as shown in the figure. After the reaction, we call the mixture of NiSO$_4$ and NiHPO$_3$ crystals as “processed waste/liquid”.

Figure 3 shows a photo of largely-grown crystals generated from this reaction. Strong attractive effect is expected on these crystals, because the magnetic force is proportional to the particle size. The magnetic force is shown in Eq (1), where $V_p$, $\chi_p$ and $\chi_s$ means the volume of the particles, susceptibility of the liquid and particles, respectively [5].

![Figure 1. Recycling process of Ni-plating waste.](image1)

![Figure 2. Formation of Ni-sulfate and Ni-phosphite (a) and processed fluid from the waste (b).](image2)

![Figure 3. Crystals in the processed waste observed by the digital microscope.](image3)
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F_n = \frac{4}{3} \mu_0 V_p \frac{9(Z_p - Z_f)}{(3 + Z_p)(3 + Z_f)} H \cdot \text{grad}H
\]

The magnetic moment of the compounds and precipitates were estimated with use of SQUID magnetometer (Quantum Design, MPMS-XL).

2.2. HTS bulk magnet and its magnetic field distribution

Figure 4a shows a photo of HTS bulk magnet system used in the experiment, whereas Fig. 4b shows its magnetic field distribution measured at the surface of the magnetic pole, which indicates the most intense magnetic field of 3.99 T, emitting at the center surface of magnetic pole. The system loads a HTS Gd123-based bulk magnet with a size of 60 mm in diameter and 15 mm in thickness, which were activated at 35 K by field cooling (FC) method. The activation was operated from 6 T with use of JASTEC superconducting solenoid magnet [6, 7].

![Figure 4. HTS bulk magnet system equipped by a strong magnetic pole on the table (a), and the magnetic field distribution measured on the pole surface, which generates 3.99 T.](image)

2.3. Magnetic separation experiment

The magnetic separation experiments were conducted with respect to the NiSO₄ particles deposited from the processed fluid, where the fine NiHPO₄ slurry was dissolved by the concentrated sulfuric acid, and kept it at 58 °C under its supersaturated condition. Figure 5a and 5b show a view of the experiment

![Figure 5. A view and construction of magnetic separation experiment, showing the green slurry attracted on the pole surface generating over 3 T (a), and the schematic illustration (b).](image)
and its structure, respectively. The bulk magnet was located just under the water channel which is a path of the processed fluid. The fluid was fed from the vessel of 6 liter settled on both sides. A couple of floats are alternately sunk into the vessel to feed the fluid through the channel. The flowing processed fluid was exposed in the 3-T space the bulk magnet emits, and then, the slurry/crystals were attracted at the magnetic pole. The contents of Ni and P in the collected slurry were evaluated by ICP (SII, SPS1500V Plasma Spectrometer).

3. Results and Discussion

As shown in Figure 5a, we observed the apparent green slurry attracted on the bottom of the water channel fixed on the magnetic pole surface. A schematic illustration of the solution flow is shown in Figure 5b. The width of a part of the water channel was designed as 100 mm so that the fluid passes in the strong magnetic field. The processed fluid alternately flows between the vessels through the channel for about 1 minute. The maximum amount of collected crystal reached 29.4 g, and the amount of recovered amount corresponds to 8.4 kg a day, which inferred the feasible practical application to various actual industries.

Figure 6a shows the slurry collected on the bottom of channel. After the operation, the slurry was removed. One sees a drop of processed fluid on the bottom of the channel. Weakly magnetized paramagnetic liquid was attracted by the intense magnetic field to let the fluid form a dorm-like huge drop of solution with saturated concentration of Ni-sulfate. According to ICP analysis, we found that 85% of collected slurry were composed of NiSO₄ crystals.

![Figure 6. A view of collected slurry in the channel (a) and the processed fluid attracted on the magnet after the flowing test (b).](image)

Figure 7 shows the data of magnetic moment for the crystals of NiSO₄, NiHPO₃, and processed fluid. NiSO₄ crystal showed the highest moment. The data of processed fluid located between the rests. As magnetic moment for NiSO₄ is three times larger than that of NiHPO₃ might indicate the effective separation of NiSO₄ from the mixture.
Figure 8 shows the result of XRD for the collected slurry after the experiment. The peaks of all were identified as major nickel sulfate hexahydrate crystals and the minor tetrahydrate, which means that the major content of collected crystal should be used as a recycled raw material of plating processes.

4. Conclusion
We conducted the magnetic separation experiment on Ni-plating waste with use of the HTS bulk magnet generating 3.99 T, which was magnetically activated by field cooling method at 6 T. Intense magnetic field attracted the paramagnetic processed fluid on the bottom of the water channel, forming a giant drop of saturated fluid. The magnetic properties and the crystal structure of the collected slurry were estimated, which clarified the feasibility of separation technique. Since the crystal structure of collected NiSO₄ slurry was identified as the nickel sulfate hexahydrate, the slurry was found to be available to reuse as a raw material in the plating process after some refinement on its purity improvement.

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