

IL-JEONG PARK*, BASUDEV SWAIN*, DAE-WEON KIM*, GEON-HONG KIM*,
DEOK-HYUN HAN*, HANG-CHUL JUNG*#

PREPARATION OF NICKEL NANOPARTICLES USING NICKEL RAFFINATE SEPARATED BY SOLVENT EXTRACTION FROM THE SPENT FeCl_3 ETCHING SOLUTION

FeCl_3 bearing etching solution is mainly used for etching of metals used in shadow masks, PCBs and so on. Due course of Invar alloy etching process the FeCl_3 bearing etching solution get contaminated with Ni^{2+} which affect adversely the etching efficiency. Hence, FeCl_3 bearing etching solution discarded after several cycle of operation causes an environmental and economic problem. To address both the issues the etching solution was purified through solvent extraction and remained Ni^{2+} recovered by wet chemical reduction using hydrazine. For optimum Fe^{3+} extraction efficiency, various extraction parameter were optimized and size and morphology of the recovered pure Ni powder was analyzed. The reported process is a simple process to purify and recover Ni from industry etching solution.

Keywords: Nickel, Recycling, Solvent extraction, Chemical reduction

1. Introduction

Because of strong oxidizing power of FeCl_3 bearing etching solution is mainly used for etching various metals including iron, copper, aluminum, nickel, etc. [1]. As the etching progresses, the etching efficiency decreases due to various heavy metal ions contamination made it unsuitable for use. As result, the FeCl_3 etching solution is discharged into the waste liquid, which is an environmental and economic problem. The solvent extraction process can purify selectively the target metal, hence, solvent extraction process has been applied for address the issue. Varieties of extractants such as acidic, chelate oximes, and basic extractants have been employed by different investigators [2-6].

Ni is used as an electrode material in MLCCs. For the downsizing of MLCCs and achieving a high capacitance, the thickness of Ni-based electrode layer reduces to the sub-micron scale, and it is required that Ni powders have a small size and narrow size distribution. Generally, the nickel powder is manufactured by the reduction of metal ions in an aqueous or organic solution. The chemical reduction method has been studied intensively, which relates to superior capabilities and simple procedure for controlling the composition, size, and shape of nickel powders [7,8].

To address both the issues recovery and reuse of metals from etching waste can be feasible solution. In this study we have selectively extracted Fe^{3+} by solvent extraction from solution and Ni^{2+} was recovered from Fe^{3+} extracted etching. From FeCl_3 etching waste solution Fe^{3+} extraction was optimized by varying by the pH, the ratio of organic phase to aqueous phase (O/A ratio),

temperature, stirring speed and solvent extraction type. In order to obtain optimum conditions, the correlation between the major process parameters was studied through the optimization experiment. Followed by nickel powder was synthesized from nickel bearing waste etching solution obtained after solvent extraction by wet chemical reduction using hydrazine. The morphology, size and size distribution of obtained Ni particles were analyzed by XRD, PSA, SEM, and TEM.

2. Experimental

In this study, we have used the etching waste solution from the nickel-base alloy etching process and the constituents are shown in Table 1. A new organophosphorus acid-based solvent (KMC-P) was used as a solvent for extracting nickel, and kerosene (DAEJUNG, CP) as a diluent was added to the organic solvent to prepare an organic phase. In the solvent extraction (SX) process, the ratio of organic to aqueous phase was varied and the mixture was shaken in a 250 mL separatory funnel for 10 min. Followed by the separated aqueous phase was analyzed and the extraction efficiency of the solution was calculated by mass balance. The effects of the concentration of extractant, pH, organic/aqueous ratio (O/A ratio) and shaking rate were investigated. From stripped solution, the nickel powder was recovered by wet chemical reduction from aqueous solution using N_2H_4 acting as the reductant. An appropriate amount of N_2H_4 was slowly added to the solution with continuous stirring at 70°C . In the end,

* INSTITUTE FOR ADVANCED ENGINEERING (IAE), YONGIN, SOUTH KOREA

Corresponding author: hcjung@iae.re.kr

the solution was centrifuged and washed with de-ionized water then absolute ethanol. Followed by the nickel powder were dried in an oven at 80°C for 12 h. The crystal structure of the nickel powder was analyzed by XRD (SHIMADZU, XRD-6100). PSA (Microtrac, S3500), SEM (FEI, Nova NanoSEM 200) and TEM (JEOL, JEM-ARM200F) were used to analyze the size and morphology of the powders.

TABLE 1

Component of etching waste solution from the nickel-base alloy etching process

| Analysis item | Unit | Result |
|-------------------|-------------------|--------|
| FeCl ₃ | % | 37.16 |
| NiCl ₂ | % | 2.61 |
| Specific gravity | kg/m ³ | 1.465 |

3. Results and Discussion

3.1. Optimization of solvent extraction process

Table 2 shows the DOE using the Box-Behnken type, and the Fe³⁺ extraction and stripping efficiencies at various condition therein. From the obtained data, the extraction efficiency exceeding 90%, and its interaction between the major factors in the stripping efficiency was analyzed. It was confirmed that the stripping efficiency was determined by changing the pH depending on the concentration of solvent, the concentration of HCl in the aqueous solution, and the O/A ratio, which are factors influencing the pH during the stripping process. Fig. 1 shows the contour plot for the stripping efficiency when the solvent concentration was 26~36 wt %, the O/A ratio was 4~7, feed HCl concentration was 0-8 mL. Fig. 2 shows the optimization results for the stripping efficiency according to DOE. The maximum stripping efficiency was 69.7 % and the reliability was more

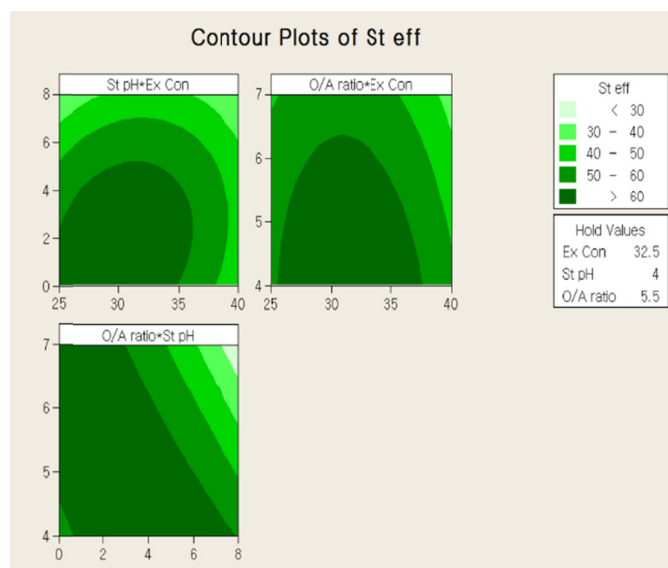


Fig. 1. Contour Plots of Stripping efficiency

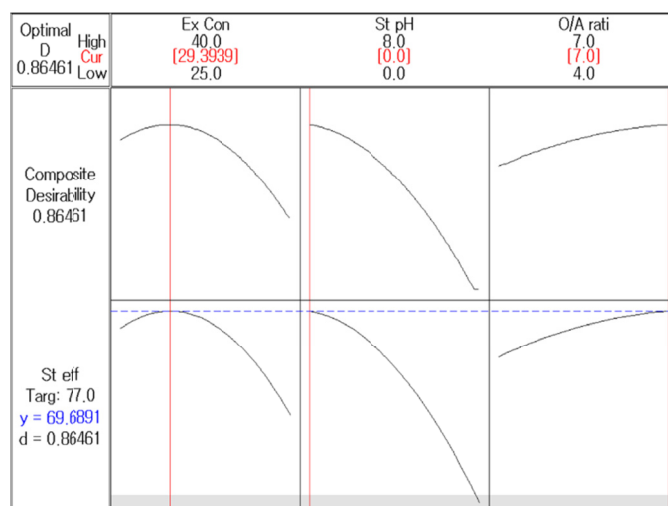


Fig. 2. Optimization conditions of stripping efficiency

TABLE 2

Experiment conditions and Results of DOE for solvent extraction process

| Run order | KMC-P Concentration (wt %) | Feed HCl (mL) | O/A Volume Ratio | Extraction Efficiency (%) | Stripping Efficiency (%) |
|-----------|----------------------------|---------------|------------------|---------------------------|--------------------------|
| 1 | 32.5 | 0 | 4 | 99.57 | 55.47 |
| 2 | 32.5 | 8 | 4 | 99.58 | 55.33 |
| 3 | 32.5 | 4 | 5.5 | 99.57 | 50.85 |
| 4 | 25 | 4 | 7 | 99.56 | 38.73 |
| 5 | 40 | 8 | 5.5 | 99.57 | 23.98 |
| 6 | 25 | 4 | 4 | 92.75 | 54.28 |
| 7 | 25 | 0 | 5.5 | 98.33 | 66.12 |
| 8 | 32.5 | 8 | 7 | 99.57 | 23.98 |
| 9 | 32.5 | 4 | 5.5 | 98.3 | 63.92 |
| 10 | 40 | 0 | 5.5 | 99.79 | 33.43 |
| 11 | 40 | 4 | 7 | 95.02 | 39.59 |
| 12 | 32.5 | 0 | 7 | 96.23 | 71.53 |
| 13 | 32.5 | 4 | 5.5 | 98.26 | 76.76 |
| 14 | 25 | 8 | 5.5 | 99.56 | 38.73 |
| 15 | 40 | 4 | 4 | 99.15 | 61.67 |

than 86 % when the concentration of the solvent was 29.4 wt % and HCl was not added and the O/A ratio was 7. However, this is an optimization result of the stripping efficiency, and it is necessary to adjust the conditions in consideration of the precipitation reaction of Fe^{3+} by forming an emulsion in the organic phase and the aqueous phase when the pH is increased.

3.2. Preparation of nickel powders

Ni powder was prepared from the etching waste solution of the nickel-base alloy etching process followed by impurities removed through a solvent extraction process. To the purified etching waste solution of the nickel-base alloy etching process, a large amount of N_2H_4 was added to reduce the Ni^{2+} from the solution as Ni powder. When a large amount of N_2H_4 was added to solution to increasing the rate of reduction of nickel. Fig. 3 shows the XRD pattern of the Ni powder. The three characteristic peaks for nickel $2\theta = 44.45, 51.71$ and 76.41° , corresponding to (111), (200) and (220), respectively, were observed, indicating that the resulting powders are face-centered cubic nickel.

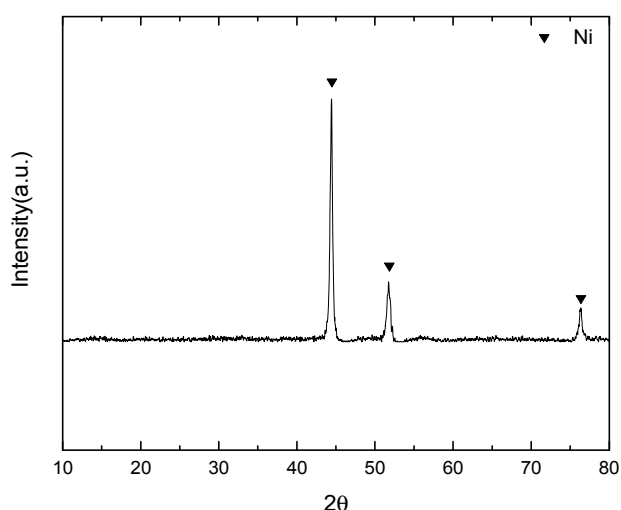


Fig. 3. XRD patterns of Ni powder synthesized by chemical reduction

Fig. 4 shows the PSA results of Ni prepared by wet chemical reduction with a large amount of N_2H_4 . The average particle size of nickel powder was about $0.9 \mu\text{m}$. The particle size distribution tended to decrease sharply at more than $1 \mu\text{m}$, which is considered to be the result of the agglomeration of fine particles. Fig. 5 shows the morphology and particle size of nickel powders produced by the chemical reduction method. It was confirmed that spherical Ni particles having a uniform size of about 150 nm were synthesized. As the amount of reducing agent is increased, the reduction reaction proceeds rapidly, and the formation of $\text{Ni}(\text{OH})_2$, which is an unreacted material, is inhibited. As a result, Ni production becomes more active and the particle size of Ni becomes smaller [10].

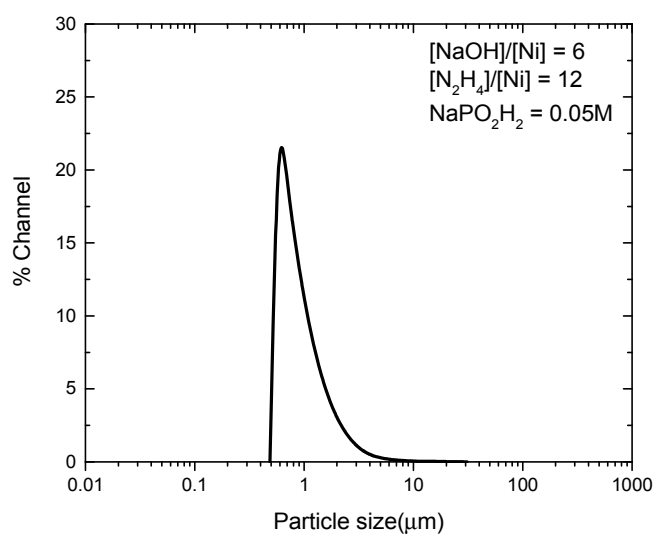


Fig. 4. Particle size distribution of Ni powders

4. Conclusions

In this study, the iron and nickel from the waste etching solution were separated by solvent extraction, and wet chemical reduction, respectively. At optimum condition, the stripping ef-

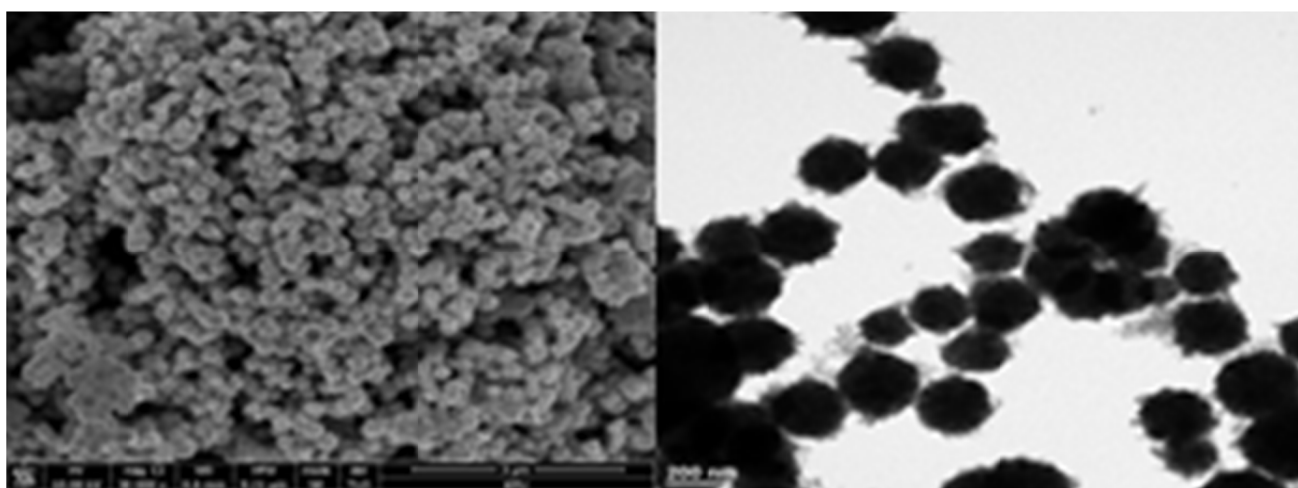


Fig. 5. SEM(Left) and TEM(Right) images of Ni powders

efficiency in the solvent extraction process was 69.7%. An excess of N_2H_4 relative to Ni was resulted in spherical uniform particles with an average particle size of about 150 nm.

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