FeCl₃ 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 FeCl₃ 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 Fe³⁺ by solvent extraction from solution and Ni²⁺ was recovered from Fe³⁺ extracted etching. From FeCl₃ etching waste solution Fe³⁺ extraction was optimized by varying 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 N₂H₄ acting as the reductant. An appropriate amount of N₂H₄ was slowly added to the solution with continuous stirring at 70°C. In the end,
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>
<thead>
<tr>
<th>Analysis item</th>
<th>Unit</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃</td>
<td>%</td>
<td>37.16</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>%</td>
<td>2.61</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>kg/m³</td>
<td>1.465</td>
</tr>
</tbody>
</table>

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...
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 Fe³⁺ 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 N₂H₄ was added to reduce the Ni²⁺ from the solution as Ni powder. When a large amount of N₂H₄ 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 2θ = 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 N₂H₄. The average particle size of nickel powder was about 0.9 μm. The particle size distribution tended to decrease sharply at more than 1 μm, 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 Ni(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-
ficiency in the solvent extraction process was 69.7%. An excess of N$_2$H$_4$ relative to Ni was resulted in spherical uniform particles with an average particle size of about 150 nm.

Acknowledgments

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REFERENCES


