Synthesis of Ni–Cu Particles by Hydrogen Reduction in Hot-compressed Water

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Synthesis of Cu and Ni–Cu particles from their aqueous formate solution by hydrogen reduction in hot-compressed water was carried out at 673 K with a titanium alloy autoclave. Hydrogen was produced by thermal decomposition of the formates. Metal particles having an average size of around 500 nm were produced without any additives. Ni–Cu metal alloy particles having different compositions were obtained by changing Cu/Ni molar ratio in starting solutions.

Ni and Cu particles are widely used in several fields because of their catalytic, electronic, and magnetic properties.[1] In addition, Ni–Cu alloy particles have large potentials for the improvement of the properties of pure Ni and Cu particles. A variety of techniques have been used for producing several pure metal and metal alloy particles such as ball milling,[2] spray pyrolysis,[3] microemulsion,[1] and sol–gel.[4] In some methods, the controllability of particle size and composition is theoretically limited. Additionally, in the aspect of environmentally sustainable simple chemical processes there exist some difficulties such as high temperature operation above 1273 K, the use of harmful organic solvent and high concentration of reducing agent, and multistep operation.

Hot-compressed water (HCW) around critical point of water ($T_c = 647$ K and $P_c = 22.1$ MPa) has significant potentials for controlling specific solvent properties, i.e. density, dielectric constant, and ion product, with temperature and pressure.[5] For example, hot-compressed water has low dielectric constant (about 10 to 25) compared with water at room temperature (about 80), and it forms homogeneous mixture with hydrogen gas at this condition.[6] From the viewpoint of reaction solvents, the HCW has the possibility to lower the use of organic solvent and to supply homogeneous redox reaction field. In addition, the reaction rate near P_c and above T_c can be drastically controlled with temperature, pressure, and also oxidizing and reducing agents (H_2 and O_2). This means that particle size, crystal structure, composition, redox state of metals, and morphology can possibly be varied with these factors.

We have reported synthesis of Ni particles by hydrogen reduction in HCW environment from nickel acetate and iron sulfate.[7] Iron sulfate was used for producing Fe_3O_4 nuclei because Ni cannot nucleate homogeneously from a solution.[7] In the work, formic acid was used for producing hydrogen by thermal decomposition at higher temperatures[8] and Ni particles formed through the following two steps: formation of Fe_3O_4 nuclei by hydrothermal synthesis from aqueous iron sulfate solution and precipitation of Ni on the surfaces of the nuclei by hydrogen reduction from nickel acetate aqueous solution. 1,10-Phenanthroline was used as a complex for preventing hydrolysis of Ni^{2+} because hydrolysis promotes formation of $Ni(OH)_2$ and/or NiO particles at higher temperatures. Recently, we reported a simple method for Ni synthesis in HCW.[9] In the method, nickel formate was only used as a starting material and Ni particles formed through the following two steps: formation of NiO or $Ni(OH)_2$ particles from Ni^{2+} by hydrothermal synthesis and precipitation of Ni on the surface of the nuclei by hydrogen reduction.

In this work, we synthesized Cu and Ni–Cu particles from copper and nickel formates in HCW. We examined reaction time and Cu/Ni molar ratio in starting solution on the composition of the obtained alloys.

Solutions were prepared by dissolving precise amounts of $Ni(COOH)_2 \cdot 2H_2O$ (Wako Pure Chemicals, Japan) and $Cu(COOH)_2 \cdot 4H_2O$ (Wako Pure Chemicals, Japan) in distilled water. For the synthesis of Ni–Cu alloy, Cu/Ni molar ratio was changed from 0.33 to 3.00. Total concentration of metals was kept constant 0.1 mol/kg in all experiment.

Nickel formate (NF) and/or copper formate (CF) aqueous solutions were loaded into the batch reactor made of titanium alloy (Ti6Al4V) of 153 cm^3. The temperature was measured with a K-type thermocouple that was inserted into reactor. The air in the reactor was replaced with nitrogen by successive purging and then the reactor was sealed. Reactor load water density was 0.35 g/cm^3, which corresponds to about 30 MPa at a reaction temperature of 673 K. The reactor was heated by immersion into a temperature-controlled molten-salt bath. Approximately 5 min was required for the batch reactor to reach the reaction temperature. Reaction time was 3–30 min, which includes heating up time. The reactor was quenched in a water bath, which was kept at room temperature. Formic acid decomposes into hydrogen and carbon dioxide and yields of H_2 and CO_2 increase to ca. 90% at 673 K within 2 s.[8]

The crystal structures of the products were analyzed by powder X-ray diffractometry (XRD) (Rigaku, RAD-B system with monochrometer), using Cu Kα radiation. Observation of these products was performed by a scanning electron microscope (SEM) (JOEL, JSM-5400LVS). Concentrations of remaining Ni and Cu ions in the recovered aqueous solution were measured by atomic absorption spectroscopy (Shimadzu, AA-6300). Conversion of metal ion to solid product was defined as $(1 - C/C_0) \times 100$, where C and C_0 are molal concentrations of the metal species in the recovered and starting solutions, respectively.

Typical SEM images are shown in Figure 1. XRD patterns of the products from CF and NF + CF mixture are shown in Figures 2 and 3, respectively. As shown in Figure 3, two kinds of crystals are produced from NF + CF. The peak positions of the crystals are slightly shifted from pure Ni and Cu. The lattice parameter varies linearly with the amount of Cu in the lattice according to Vegard's low. The compositions of these crystals were determined with the calculated value of the cell parameter on the basis of Vegard's low. No significant difference with reaction temperature was observed. The compositions at 30 min as a function of Cu concentration in starting solution are shown in Figure 4. Conversions in all experiment were more than 98.6% and no significant dependence was observed.

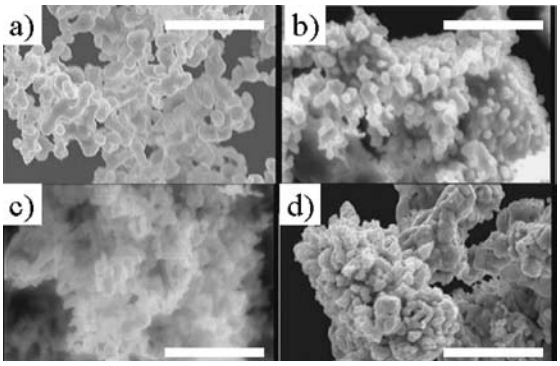

Figure 1. SEM images of metal particles for 30 min (Bar = 5 µm): a) 0.1 mol/kg NF, b) 0.75 mol/kg NF + 0.25 mol/kg CF, c) 0.5 mol/kg NF + 0.5 mol/kg CF, and d) 1.0 mol/kg CF.

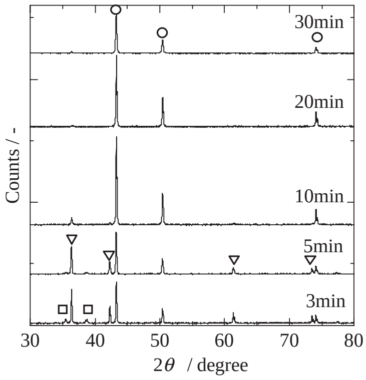

Figure 2. XRD patterns obtained from CF for 3–30 min. Circle, triangle, and square denote Cu, Cu_2O, and CuO, respectively.

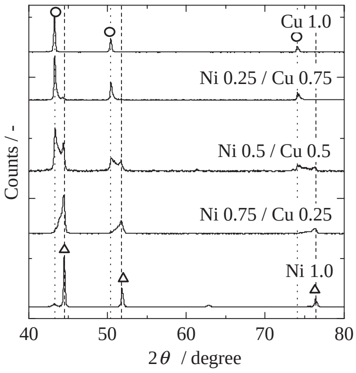

Figure 3. XRD patterns obtained from CF + NF for 30 min. Circle and triangle denote Cu and Ni, respectively.

Firstly, in the case that CF solution was used, the products for 3 min were assigned to the mixture of Cu, Cu_2O, and CuO as shown in Figure 2. With increasing reaction time, the peaks of Cu_2O and CuO disappeared and Cu crystal was detected after 20 min. As shown in Figure 1d, particles obtained for 30 min have diameters ranging from 0.3 to 1.0 µm.

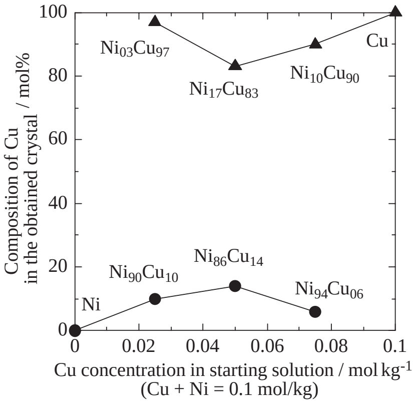

Figure 4. Cu composition in the obtained metal crystals for 30 min.

Secondary, in the case that CF and NF solution was used, both Ni-rich and Cu-rich crystals were produced as shown in Figure 3. With increasing Cu concentration in starting solution, Cu composition of Ni-rich alloy firstly increased and $Ni_{86}Cu_{14}$ particles were obtained. Further increases in the molar ratio lead to decrease the composition. In addition, Cu composition of Cu-rich alloy firstly decreased, and $Ni_{17}Cu_{83}$ particles were obtained. Further increases lead to increase the composition. No significant difference between the obtained particle sizes was observed as shown in Figure 1, and the particle have diameters ranging from 0.2 to 1.0 µm.

In conclusion, Cu and Ni–Cu alloy particles were successfully synthesized from their formates by hydrogen reduction in hot-compressed water and the composition of the alloy could be controlled by changing Cu/Ni molar ratio in starting solution.

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