Magnetic Cu–Ni (core–shell) nanoparticles in a one-pot reaction under microwave irradiation†

Tomohisa Yamauchi, a Yasunori Tsukahara, a Takao Sakata, b Hirotaro Mori, b Takeshi Yanagida, c Tomoji Kawai c and Yuji Wada c ad

Received (in Beijing, China) 13th October 2009, Accepted 28th November 2009
First published as an Advance Article on the web 9th January 2010
DOI: 10.1039/b9nr00302a

We successfully prepared face-centered cubic (fcc) Cu–Ni (core–shell) nanoparticles by intramolecular reduction of formate complexes of Cu$^{2+}$ and Ni$^{2+}$ with long-chain amine ligands in a one-pot reaction within an extremely short time realized only under microwave irradiation. Observation by an HAADF-STEM technique showed that the nanostructure in one particle consisted of a Ni-rich shell and a Cu-rich core. Cu$_4$Ni$_6$ nanoparticles with an average size of 11.7 nm were comprised of a Cu core with a diameter of ca. 6.0 nm, a Ni shell ca. 1.6 nm thick and a 0.9 nm thick interlayer of mixed Cu–Ni alloy between the Cu core and the Ni shell. Both the oxidation characteristics and the magnetic properties were dramatically affected by the molar ratios of Cu : Ni in the Cu–Ni nanoparticles. The magnetization of Cu$_3$Ni$_7$ and Cu$_4$Ni$_6$, comprised of a diamagnetic Cu-rich core, ferromagnetic Ni-rich shell and antiferromagnetic NiO-rich layer on the particle surface showed an exchange bias (209 and 143 Oe, respectively).

Introduction

Nanoparticles of ferromagnetic metals, such as Fe, Co, and Ni, are used in catalysts, permanent magnets, magnetic fluids and magnetic recording media. The physical and chemical properties of nanoparticle depend on their size and shape. Currently, novel bimetallic nanoparticles with chemical and physical properties superior to those of monometallic nanoparticles have attracted theoretical and practical interest. Among these novel bimetallic materials, Cu–Ni nanoparticles have been widely used as catalysts, hyperthermic magnetic fluids, electrode materials in solid oxide fuel cells, in multilayer ceramic capacitors (MLCC), and as condenser tubing in marine applications. Cu–Ni alloy nanoparticles are used in place of monometallic Ni or Cu due to their chemical stability and mechanical properties.

Generally speaking, three main types of mixing patterns for Cu–Ni alloy nanoparticles can be identified such as mixed Cu–Ni alloy, subcluster segregated alloy and core–shell segregated alloy. In the case of the mixed Cu–Ni alloy, Cu and Ni atoms are randomly dispersed without any order through the entire particle as a solid solution. The core–shell segregated alloy consists of a shell of either Cu or Ni atoms surrounding a core of the other. In this paper, the mixed Cu–Ni alloy is described as the Cu–Ni alloy for short.

The Cu–Ni system is especially noted for complete liquid and solid solubility, because of the small lattice size mismatch between Cu and Ni (3.62 Å and 3.54 Å, respectively) and the small positive enthalpies of solution for Cu in Ni and Ni in Cu. Cu–Ni alloy nanoparticles have been synthesized in both physical and chemical processing methods, as described below. For further improvements of physical and chemical properties, the preparation of Cu–Ni nanoparticles with core–shell structures still remains a significant challenge.

In physical processing methods alloy nanoparticles have been synthesized using mechanical alloying and by laser ablating targets prepared by cold-pressing powder mixtures of Cu and Ni under high temperatures (above 1273 K) and long processing times. At high temperatures, Cu–Ni alloy nanoparticles with Cu surface enrichment were obtained because Cu atoms have not only a large rate of diffusion in Ni but also a surface energy ($\sigma(111) = 69.5 \text{kJ mol}^{-1}$) that is lower than that of Ni ($80 \text{kJ mol}^{-1}$). These Cu–Ni alloy nanoparticles with Cu surface enrichment are easily oxidized in air. In order to suppress the oxidation of Cu components, a new method for the preparation of Cu–Ni nanoparticles with a Ni-rich shell is highly desirable.

Even in the chemical processing methods at lower temperatures—as with the physical processing methods—only the alloy nanoparticles were obtained. Each reduction (Cu$^{2+}$ or Ni$^{2+}$) has a unique redox potential (Ni$^{2+} + 2e^- \rightleftharpoons \text{Ni}, -0.257 \text{V}$; Cu$^{2+} + 2e^- \rightleftharpoons \text{Cu}, 0.342 \text{V}$) and a unique reduction temperature. Cu–Ni nanoparticles are more likely to be produced through the following heterogeneous nucleation process due to the difference in those reduction temperatures. At first, Cu nanoparticles are...
produced at lower temperatures and then heterogeneous nucleation of Ni particles on the surface boundaries of Cu nanoparticles occurs much more often than homogeneous nucleation of the independent Ni particles. Therefore, Cu–Ni nanoparticles with Ni surface enrichment are more likely to be produced with the liquid-phase methods at lower temperatures. However, in previous reports using several liquid-phase methods, such as electrochemical deposition, sol–gel methods, various chemical reduction methods, polyl methods, and hydrothermal reactions, the relatively homogeneous Cu–Ni alloy was obtained even at lower temperatures because of the long reaction times. Ferrando et al. speculated that this mixed alloying could be attributed to low-temperature surface melting and appreciable Ni/Cu diffusion. The authors concluded that this speculation as to the cause of alloying was correct. Therefore, an extremely short reaction time was required for the suppression of the surface diffusion of Cu atoms and the preparation of Cu–Ni nanoparticles with Ni surface enrichment.

Here we propose that the suppression of the surface diffusion of Cu atoms could be achieved by shortening the reaction time to obtain Cu–Ni (core–shell) nanoparticles. A microwave-assisted method for the present study was chosen for the following reasons. Reactants are directly and quickly heated under microwave irradiation through the interaction of the oscillating electric and magnetic fields with the substances and then a reaction solution is heated uniformly in a vessel. Therefore, nucleus growth throughout the entire reaction vessel is simultaneous and homogeneous, and particles with a narrow size distribution can be obtained within a short time. Recently, monodispersed Ag, Cu and Ag core–Cu shell nanoparticles with a narrow size distribution were prepared within a short time using a microwave-assisted method. Rapid heating and a short reaction time under microwave irradiation would be effective for the suppression of the surface diffusion of Cu atoms to obtain the monodispersed Cu–Ni (core–shell) nanoparticles.

Monodispersed Ni nanoparticles were rapidly prepared via the intramolecular reduction of Ni$^{2+}$ in a formate complex with long-chain amine ligands at 463 K under microwave irradiation. Ligation of the long-chain amine lowered the reaction temperatures by decreasing the energy barrier required for nickel formate complexes rather than for their neat formate salts. The size of the obtained particles was controlled through the use of various long-chain amine ligands. During the intramolecular reduction of formate complexes, the formate ion acts as a reducing agent for a metal ion and ultimately decomposes to hydrogen and carbon dioxide according to the following reactions.

$$2 \text{HCOO}^- \rightarrow 2 \text{CO}_2 + \text{H}_2 + 2\text{e}^-$$

$$\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M}^0 \quad (\text{M} = \text{Cu or Ni})$$

This intramolecular reduction of copper and nickel formate complexes was selected to prepare Cu–Ni (core–shell) nanoparticles with an extremely short time under microwave irradiation.

Furthermore, novel Cu–Ni nanoparticles with core–shell structures have attracted interest in their catalytic activities, chemical and physical properties, such as oxidation characteristics and magnetic properties. Zhang et al. reported that monodispersed Cu–Ni nanoparticles with a Cu-rich core and Ni-rich region were prepared by a one-pot thermolysis approach in oleylamine/1-octadecene, using metal acetylacetonatos as precursors. The obtained Cu–Ni nanoparticles, especially with the composition of Cu$_{0.3}$Ni$_{0.7}$ had high catalytic activities in the hydrolysis of NaBH$_4$ to generate H$_2$. Konno et al. reported that Co and Ni nanoparticles with an oxide layer on the particle surface showed exchange anisotropy. This phenomenon was explained by an exchange anisotropy interaction at the interface between the ferromagnetic (FM) region of the metal particles and the layers of antiferromagnetic (AFM) metal oxide on the particle surface. The surface of Cu–Ni nanoparticles is easily oxidized in air. The physical properties of small nanoparticles, such as conductivity and magnetic properties, should be influenced by oxide layers on the particle surface. Detailed investigations of both a nanostructure and its oxidation characteristics are absolutely imperative for the evaluation of the performance of nanometre-sized Cu–Ni particles.

The combination of both microwave method and intramolecular reduction of formate complexes of Cu$^{2+}$ and Ni$^{2+}$ enabled preparation of monodispersed Cu–Ni (core–shell) nanoparticles. The composition of the Cu–Ni nanoparticles was readily controlled by changing the molar ratio of both ions used in the synthesis. Both the oxidation characteristics of the particle surface and the magnetic properties of Cu, Ni and Cu–Ni nanoparticles were examined. The effects of the metal-oxide layers on both the coercivity and hysteresis loop shift are discussed.

### Experimental

#### Materials

Nickel(II) formate dihydrate and 1-octanol were purchased from Kishida Chemical Co., Ltd. Copper(II) formate tetrahydrate and 1-octylamine were purchased from Wako Pure Chemical Industries Co., Ltd. Oleylamine ((Z)-9-octadecenylamine) was purchased from Aldrich Co., Ltd. These reagents were used as supplied.

#### Preparation of Cu and Ni precursors

The precursors, copper(II) or nickel(II) formate complexes with oleylamine ligands, were synthesized as described in our previous work. The Cu precursor was synthesized by stirring a mixture of copper(II) formate tetrahydrate (2.4 mmol) and oleylamine (12.0 mmol) at room temperature for 20 min. In the case of the Ni precursor, nickel(II) formate dihydrate (3.6 mmol) and oleylamine (18 mmol) were mixed and then heated at 393 K for 10 min. The reaction solution changed from a greenish suspension to a deep-green homogeneous solution. After allowing the nickel precursor solution to return to room temperature, the color of the solution changed to turquoise.

#### Preparation of Cu–Ni nanoparticles

Microwave heating was carried out by use of a multi-mode 2.45-GHz microwave apparatus operated at 1.25 kW (Micro Denshi...
Preparation of Cu and Ni nanoparticles

Cu or Ni precursors prepared from their formate salt (5 mmol) and oleylamine (50 mmol) were added to 1-octanol (60 ml). Each solution was heated at a rate of 40 K min$^{-1}$ under microwave irradiation and allowed to stand at either 433 K [Cu] or 463 K [Ni] for 10 min under bubbling nitrogen gas. Cu and Ni nanoparticles were obtained (denoted as Cu$_n$Ni$_m$). The temperature profiles of the reaction plotted against time and microwave (MW) power are shown in Fig. S1 of the ESI.$^\dagger$ Cu–Ni nanoparticles prepared using other molar ratios, i.e., [Cu]/[Ni] = 3 : 7, 5 : 5 and 8 : 2 (denoted as Cu$_3$Ni$_7$, Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$), were obtained under the same reaction conditions.

Identification of the structure of Cu–Ni nanoparticles

The crystal phase and metallic composition of the obtained powder were determined by the powder X-ray diffraction (PXRD) and TEM-EDS analyses. The XRD pattern of the Cu$_3$Ni$_7$ nanoparticle sample is shown in Fig. 1. The 2θ angles of the characteristic reflections corresponding to the (111) and (200) planes of bulk fcc metals are 43.30, 50.43$^\circ$ (Cu) and 44.4, 51.8$^\circ$ (Ni) according to JCPDS file 4-0836 (Cu) and 4-0850 (Ni), respectively. The XRD reflection spectrum of Cu$_3$Ni$_7$ was observed as the same fcc pattern as those of bulk fcc Cu and Ni. The two peaks of the (111) and (200) planes were observed at 2θ = 43.76 and 50.84$^\circ$, respectively. The 2θ angles of these planes of Cu$_3$Ni$_7$ were larger than those of bulk fcc Cu and smaller than those of bulk fcc Ni. The XRD reflection spectra of Cu$_3$Ni$_7$, Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$ were observed as the same fcc pattern as that of Cu$_3$Ni$_7$. The reflections corresponding to the (111) planes of Cu$_3$Ni$_7$, Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$ observed at 44.06, 43.55 and 43.51, respectively, were shifted to smaller angles as the Ni content of the Cu–Ni nanoparticles increased. The EDS spectrum of Cu$_3$Ni$_7$ is shown in Fig. S5 of the ESI.$^\dagger$ Only Ni and Cu peaks were detected in the spectrum, with the exception of Mo peaks, due to the TEM Mo grid supporting the sample. The compositions determined by the EDS spectra of all types of nanoparticles are listed in Table 1. The compositions of the Cu–Ni nanoparticles were coincident with the molar ratios [Cu$^{2+}$]:[Ni$^{2+}$] used for the synthesis.

Results

The size and morphology of the Cu–Ni nanoparticles were characterized using a transmission electron microscope (TEM) operated at 200 kV with a Hitachi H-800 (Hitachi High-Technologies Co.). The solution was dropped onto a carbon film coated with a copper grid, and the grid was dried under vacuum. The compositions of the Cu$_3$Ni$_7$, Cu$_5$Ni$_5$, Cu$_8$Ni$_2$ and Cu$_3$Ni$_7$ nanoparticles were determined using an energy dispersive X-ray spectrometer (EDS) of EMAX-7000Q type attached to the TEM. Samples were placed on a holey carbon film supported on a molybdenum grid. The crystal phases of the powders were analyzed using a MultiFlex (Rigaku Co.) with a Cu K$\alpha$ radiation source in the range of the 2θ Bragg angles = 20–120$^\circ$ at 40 kV and 40 mA. The melting temperatures of the samples and the amount of surface modifying agent on the surface of the nanoparticles were determined by thermogravimetric and differential thermal analyses (TG-DTA), respectively, using a Thermo plus EVO/TG-DTA (Rigaku Co.). TG-DTA was performed at a heating rate of 20 °C min$^{-1}$ in a nitrogen atmosphere at a flow rate of 800 mL min$^{-1}$. The oxidation characteristics of Cu, Ni and Cu–Ni nanoparticles were characterized using X-ray photoelectron spectroscopy (XPS) with an Mg K$\alpha$ radiation source operated at 12 kV and 20 mA with a JPS-9010MC spectrometer (JASCO Co.). Magnetic susceptibility data were obtained in applied fields ranging between –50 and 30 kOe using a SQUID susceptometer (MPMS-SS, Quantum Design Co.).
the bulk well-mixed Cu–Ni alloy. The contents of the long-chain amine (oleylamine) in all samples were calculated based on the weight-loss, and are listed in Table 1. In the case of Cu4Ni6 nanoparticles, one molecule of oleylamine occupied the surface of one particle (Cu4Ni6) in the area of 17.3 nm². (The method for estimation is described in Appendix 1 of the ESI†).

The TEM images and particle size distributions of the Cu4Ni6 nanoparticle samples are shown in Fig. 2, respectively. The obtained nanoparticles were oblate spheroid in shape with an eccentricity of 0.91. Major and minor axes were 11.7 nm (standard deviation σ = 1.4 nm) and 4.9 nm (σ = 0.5 nm), as determined from the TEM images of Fig. 2(a) and 2(b), respectively. The particle sizes of the obtained nanoparticles are listed in Table 1. The selected area electron diffraction (SAED) pattern obtained from the entire region in Fig. 2(a) is shown in the inset of Fig. 2(a). The SAED pattern showed the fcc ring pattern of (111), (200), (220), and (311) planes. While the lattice spacing estimated from the pattern [2.000 Å (111)] was close to those of fcc Cu, Ni or Cu–Ni alloys (Cu; 2.087 Å (111), Ni; 2.035 Å (111)), the value of the lattice spacings estimated by a conventional TEM at 200 keV had a margin of error to some degree. Therefore, it was difficult to clearly specify the metallic constituents from the samples of Cu, Ni and Cu–Ni alloys by SAED analysis. Another fcc ring pattern was observed as blurry. This pattern of the (111) (*) and (220) (**) planes is shown in the inset of Fig. 2(a). The lattice spacing estimated from this pattern was coincident with those of the metal oxides (NiO, CuO or Cu2O). Identification of the metal oxide was difficult using the ring pattern of this blurry ring because both fcc NiO, CuO and Cu2O had a similar lattice spacing.28 These results clearly indicate that monodispersed Cu–Ni nanoparticles containing a small amount of metal oxides were obtained.

The Cu–Ni nanoparticles prepared under bubbling nitrogen gas by our method could undergo oxidation, when exposed to air at room temperature in both processes of washing and preparing the samples for the measurements such as XRD, TEM and XPS, respectively. The progress of the oxidation in air at various temperatures was examined by XRD measurement. The XRD reflection spectra of the Cu4Ni6 nanoparticle sample stored at 423 and 523 K for 1 h under an air atmosphere are shown in Figs. S8(a) and (b), respectively. In both spectra, the characteristic reflections corresponding to the (111) and (220) planes of fcc metal oxides (NiO and CuO) were observed at around 2θ = 37.2° and 62.5°, respectively. The intensities of these reflections were increased with the rise in the temperature. On the other hand, the intensities of these reflections observed for the sample right after the isolation were negligible (Fig. 1). This result indicated that the Cu–Ni nanoparticles prepared by our method were not easily oxidized at room temperature. Furthermore, the XRD pattern of a Cu4Ni6 nanoparticle sample stored for one year at room temperature under an air atmosphere [Fig. S8(c)] was unchanged from that of the same sample right after the isolation. The above results led to a conclusion that the oxidation rate of the Cu–Ni nanoparticles at room temperature was extremely slow even under air. The TEM measurements with resolution in nano region should have revealed the local presence of the metal oxides in a small amount in the Cu–Ni nanoparticle samples.

The concentrations of both Cu and Ni atoms in one particle were characterized using a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) operated at 200 kV with a Hitachi HD-2700. A HAADF-STEM image of Cu4Ni6 is shown in Fig. 3(a). The particle size determined from the image agree well with those from the TEM image in Fig. 2(a). Each elemental map of Cu and Ni in the area shown in Fig. 3(a) was obtained using the EDS attached to the HAADF-STEM, shown in Fig. 3(b) (Cu) and 3(c) (Ni), respectively. Cu atoms were frequently seen in the center of the particles in the image. In contrast, the distribution of Ni atoms became concentrated at the region close to the surface of the particles. The distributions between Cu and Ni atoms in a single particle are shown in Fig. 3(d). This data was obtained by measuring a single isolated particle in a different area from the measurement field shown in Fig. 3(a), which was polluted by contaminants after mapping the elements demonstrated in Fig. 3(b) and 3(c).

The Royal Society of Chemistry 2010

Table 1  Particle sizes, metal compositions, and surface-modifying agent contents of Cu–Ni nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particles size/nm</th>
<th>Cu/mol (%)</th>
<th>Ni/mol (%)</th>
<th>Weight loss/ wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu4Ni6</td>
<td>14.6 ± 1.4</td>
<td>31.5</td>
<td>68.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Cu3Ni7</td>
<td>11.7 ± 1.4</td>
<td>39.3</td>
<td>60.7</td>
<td>10.0</td>
</tr>
<tr>
<td>Cu5Ni5</td>
<td>12.9 ± 1.5</td>
<td>55.5</td>
<td>44.5</td>
<td>17.3</td>
</tr>
<tr>
<td>Cu4Ni6</td>
<td>21.4 ± 3.2</td>
<td>80.3</td>
<td>19.7</td>
<td>11.2</td>
</tr>
</tbody>
</table>

a Lengths of major axes are listed. b Metal compositions were calculated based on the Ni Kα and Cu Kα intensities in the EDS spectra. c Surface-modifying agent contents were derived from TG measurements.
The scan profiles shown in Fig. 3(d) were collected by point analyses along the cross-section line on a single isolated particle using EDS. For that purpose, an electron beam with 200 kV accelerating voltage was focused down to a spot with a diameter about 0.1 nm on the specimen. Cu–Ni nanoparticles (Cu$_4$Ni$_6$) were comprised of a Cu core with a diameter of ca. 6.0 nm surrounded by a Ni shell, ca. 2 nm thick. These results indicated that Ni shells were overgrown on Cu cores. However, the obtained nanoparticles were not simply separated as a Cu core/Ni shell region. In the region defined as the Ni shell, the layer at a depth of ca. 1.6 nm from the outermost the shell consisted chiefly of Ni atoms. The layers at depths of 1.6 nm and 2.5 nm from the outermost shell were comprised of mixed Cu–Ni alloy—in a region where the intensities of Ni atoms were larger than those of Cu atoms. Therefore, the nanostructure was identified as a Ni-rich shell and Cu-rich core, as depicted in Fig. 5(a).

**Oxidation characteristics of Cu–Ni nanoparticles (XPS)**

The oxidation characteristics of the Cu–Ni nanoparticles prepared using different molar ratios of Cu : Ni were compared using XPS. The depth profiles measured between 0.1–0.5 nm from the nanoparticle surface were obtained using an ion (Ar$^+$) sputtering technique. These surface layers at depths of between 0.1 nm and 0.5 nm were involved in the Ni-rich shell, depicted in Fig. 5(a). Therefore, the results of the depth profiles showed the oxidation state in the Ni-rich shell. Ni 2p$_{3/2}$, Cu L$_3$M$_4.5$M$_4.5$, Auger, and Cu 2p$_{3/2}$ electron spectra are shown in Fig. 4 and Fig. S9 respectively. As shown in Fig. 4(a), the binding energies (B.E.) of Ni 2p$_{3/2}$ and NiO 2p$_{3/2}$ were 851 and 853 eV, respectively. In the Cu Auger spectra [Fig. 4(f)], CuO and Cu$_2$O had the same binding energies (336 eV), which were different for Cu (334 eV). In the Cu 2p$_{3/2}$ spectra (Fig. S9), Cu and Cu$_2$O had the same binding energies (931.5 eV), which were different for CuO (932.5 eV). Therefore, each oxidation characteristic of Ni and Cu components was examined by comparing the intensities of NiO with those of Ni in the Ni 2p$_{3/2}$ spectra and the intensities of mixed CuO/Cu$_2$O with those of Cu in the Cu Auger spectra. The depth profiles of Cu$_3$Ni$_7$ and Cu$_4$Ni$_6$ showed that NiO and CuO/Cu$_2$O were present only in negligible amounts at a depth of 0.5 nm. In contrast, the depth profiles of Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$ revealed the existence of NiO and CuO/Cu$_2$O even at a depth of 0.5 nm. Therefore, the abundance ratios of the metal oxides (NiO and CuO/Cu$_2$O) relative to the corresponding metals increased as the Ni content of the Cu–Ni nanoparticles decreased.

Table 2 shows the relative intensities of metal oxides (NiO and CuO/Cu$_2$O) for the corresponding metals (Ni and Cu) measured at a surface depth of 0.1 nm to 0.5 nm for each type of the nanoparticles. The relative intensities of the metal oxides were highly dependent on Ni content (atm%). When the Ni content was greater than 50 atm%, i.e., Cu$_3$Ni$_7$ and Cu$_4$Ni$_6$, the layer at a surface depth of 0.1 nm mostly consisted of Ni, Cu and NiO, while at depths greater than 0.5 nm only Ni and Cu atoms were present. On the other hand, when the Ni content was less than 50 atm%, i.e., Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$, the layer at a surface depth of 0.1 nm was mostly comprised of NiO and CuO/Cu$_2$O, and that at a depth of 0.5 nm consisted of a mixture of Ni, Cu, NiO, and...
CuO/Cu2O. These results indicate that the Cu3Ni7 and Cu4Ni6 nanoparticles were partially covered with a ca. 0.5 nm thick metal oxide layer, which mainly consisted of NiO. The nanostructure for Cu4Ni6 determined by both HAADF-STEM and XPS

Fig. 4 XPS spectra of Ni-1 (a), Cu-2 (f), Cu3Ni7 (b, g), Cu4Ni6 (c, h), Cu5Ni5 (d, i) and Cu8Ni2 (e, j). Figures (x, y) show Ni 2p3/2 electron spectra and Cu L3M4,5M4,5 Auger electron spectra, respectively.

Fig. 5 The nanostructures of Cu4Ni6 determined by HAADF-STEM (a) and XPS analyses (b), respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth/nm</th>
<th>I_Ni</th>
<th>I_NiO</th>
<th>I_Cu</th>
<th>I_CuO/Cu2O</th>
<th>I_NiO/I</th>
<th>I_CuO/Cu2O/I_Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1</td>
<td>0.1</td>
<td>820</td>
<td>585</td>
<td>—</td>
<td>—</td>
<td>0.71</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2700</td>
<td>350</td>
<td>—</td>
<td>—</td>
<td>0.13</td>
<td>—</td>
</tr>
<tr>
<td>Cu3Ni7</td>
<td>0.1</td>
<td>421</td>
<td>622</td>
<td>128</td>
<td>28</td>
<td>1.48</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1550</td>
<td>400</td>
<td>232</td>
<td>55</td>
<td>0.26</td>
<td>0.24</td>
</tr>
<tr>
<td>Cu4Ni6</td>
<td>0.1</td>
<td>496</td>
<td>575</td>
<td>237</td>
<td>86</td>
<td>1.16</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2050</td>
<td>350</td>
<td>420</td>
<td>120</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>Cu5Ni5</td>
<td>0.1</td>
<td>230</td>
<td>380</td>
<td>60</td>
<td>148</td>
<td>1.65</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>435</td>
<td>215</td>
<td>178</td>
<td>169</td>
<td>0.49</td>
<td>0.95</td>
</tr>
<tr>
<td>Cu8Ni2</td>
<td>0.1</td>
<td>88</td>
<td>255</td>
<td>215</td>
<td>427</td>
<td>2.90</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>340</td>
<td>300</td>
<td>530</td>
<td>524</td>
<td>0.88</td>
<td>0.99</td>
</tr>
</tbody>
</table>

CuO/Cu2O. These results indicate that the Cu3Ni7 and Cu4Ni6 nanoparticles were partially covered with a ca. 0.5 nm thick metal oxide layer, which mainly consisted of NiO. The nanostructure for Cu4Ni6 determined by both HAADF-STEM and XPS
analyses are depicted in Fig. 5(b). The nanoparticles with a lower Ni content, i.e., Cu$_3$Ni$_7$ and Cu$_8$Ni$_2$, were covered with an oxide layer more than 0.5 nm thick, which consisted of mixed oxide Cu–O–Ni.

The HRTEM image of Cu$_3$Ni$_6$ in Fig. 6 shows the lattice spacing on the surface of the nanoparticles. The image in Fig. 6(b) shows two lattice spacings of 0.243 and 0.207 nm, which were similar to those of the (111) and (200) planes of fcc NiO, respectively. The oxide layers were of low thickness and had different directions in planes. These results indicate that Cu$_3$Ni$_6$ nanoparticles were covered with squamiform NiO layers, as depicted in Fig. 6(c).

**Magnetic properties**

The magnetic properties of the Cu–Ni nanoparticles were measured using a SQUID susceptometer. All samples were measured as a powder. Fig. 7 shows a plot of magnetization versus applied fields for the Cu–Ni nanoparticles in zero-field cooling (ZFC) at 5 K. The saturation magnetization ($\sigma_s$), coercivity ($H_c$) and exchange bias ($H_{eb}$) of Cu–Ni nanoparticles prepared using different molar ratios of Cu : Ni are listed in Table 3. The saturation magnetizations of Cu$_3$Ni$_7$, Cu$_4$Ni$_6$, and Cu$_5$Ni$_5$ with average particle sizes between 12–15 nm decreased as the Ni content decreased. The magnetization of Cu$_3$Ni$_7$ and Cu$_4$Ni$_6$ showed stronger ferromagnetic properties than Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$. Hysteresis loops were measured at 5 K after completion of both ZFC and field cooling (FC) processes. In the FC process, the sample was cooled from 300 K to 5 K in a magnetic field, $H$, of 1 T. Fig. 8 shows the ZFC and FC loops obtained for Cu$_3$Ni$_7$. At 5 K, an asymmetric magnetic hysteresis loop and a deviation between the ZFC and FC magnetizations, which are commonly referred to as an exchange bias field ($H_{eb}$), were observed. The $H_{eb}$ ($=|H_{ZFC}^C + H_{FC}^C|/2$) was calculated to be 209 Oe, which was indicative of an exchange bias effect. Under the condition of ZFC, the $H_c$ ($=|H_{ZFC}^C - H_{FC}^C|^2/2$) was 638 Oe, indicating a random effect.

**Discussion**

**Mechanism of Cu–Ni (core–shell) nanoparticle production**

1. The formation of the Cu–Ni (core–shell) nanoparticles. Cu$^{2+}$ is reduced at a lower temperature than Ni$^{2+}$ because of its more positive redox potential. In the case of thermal decomposition using their neat formate salts, Cu$^{2+}$ and Ni$^{2+}$ were reduced at 493 and 520 K, respectively (see Fig. S10). In the synthesis of both Cu-I and Ni-I using our method, Cu and Ni nanoparticles were obtained at 433 and 463 K, respectively. Ligation of the long-chain amine lowers the reaction temperatures by decreasing the energy barrier required for intramolecular reduction of metal ions in copper or nickel formate complexes rather than that for their neat formate salts.
Therefore, in the one-pot reaction of Cu–Ni (core–shell) nanoparticles, Cu\(^{2+}\) in a formate complex with oleylamine is readily reduced to Cu\(^0\) at around 433 K, while Ni\(^{2+}\) is reduced at around 463 K. We discuss the formation mechanism of Cu–Ni (core–shell) nanoparticles on the basis of their reduction temperatures, through the following heterogeneous nucleation process. At first, Cu nanoparticles are produced at around 433 K. A nucleus of Ni on the surface of Cu nanoparticles is produced at around 463 K. Ni shells overgrow on Cu cores prior to the growth of the Cu nanoparticles, and then Cu–Ni (core–shell) nanoparticles are produced. Finally, the oxide layer on the surface of the nanoparticles is formed when they are exposed to air atmosphere in the washing process.

2. The alloy formation in the core–shell structure of Cu–Ni nanoparticles. With the liquid-phase methods, Cu–Ni nanoparticles with core–shell structure are produced through the heterogeneous nucleation process and then the alloy formation proceeds through the diffusion of Cu or Ni atoms into Ni shell or Cu core regions. This solid solubility of Cu and Ni atoms in one particle depends on the reaction temperatures and times. Even if Cu–Ni nanoparticles are prepared under different reaction conditions—temperature, time, the precursors and solvents—the obtained nanoparticles should have the inhomogeneous concentration distribution of Cu and Ni atoms in one particle. Bonet et al. reported on the preparation of Cu–Ni alloy nanoparticles by the reduction of the mixtures of copper and nickel carbonate in a polyol process at 413 K for 39 h or at 463 K for 4 h.\(^{18}\) Li et al. prepared the alloy nanoparticles by the reduction of a mixture of CuSO\(_4\) and NiSO\(_4\) with hydrazine in a hydrothermal process in an autoclave at 423 K for 3 h.\(^{21}\) They used XRD and SAED analyses to identify the obtained particles as alloys. However, these analyses are not adequate for the precise structural determination of one particle. In the present study, we prepared Cu–Ni (core–shell) nanoparticles at 463 K for 10 min using a microwave-assisted method and precisely determined the concentrations of both Cu and Ni atoms in one particle. Observation by an HAADF-STEM technique showed that the nanostructure in one particle consisted of a Ni-rich shell and a Cu-rich core, in which the interlayer of mixed Cu–Ni alloy between the Cu core and the Ni shell existed. Cu diffused into the shell layers during the formation of the Ni shell, even in our method, but the surface diffusion of Cu atoms could be suppressed through extreme shortening of the reaction time under microwave irradiation to obtain Cu–Ni (core–shell) nanoparticles in a high yield.

Effect of the oxide layers of the Cu–Ni nanoparticles on the coercivities and hysteresis loop shifts

Bulk Cu–Ni alloys are known to be completely solid solutions. The density of states for Ni, Cu and Cu–Ni alloys are as follows. Ni metal (valence electrons: 10) has 0.6 electrons in the 4s band, and 5 and 4.4 electrons in the 3d\(^1\) and 3d\(^3\) bands, respectively, with a hole of 0.6 electrons in the 3d\(^1\) band. Therefore, Ni metal has both a spontaneous magnetization of 0.6 \(\mu_B\) (\(\mu_B\):Bohr magneton) and ferromagnetic (FM) properties. Cu metal (valence electrons: 11), which has 10 electrons in the 3d band and one in the 4s band, shows diamagnetism. The Slater–Pauling curve shows that the magnetic properties of bulk Cu–Ni alloys decrease as the Cu content increases because the 0.6-electron hole in the 3d band of Ni is filled by the 4s electron of Cu.\(^{30}\) With the composition of the bulk Cu\(_{1.75}\)Ni\(_{6.25}\) alloy, the ferromagnetic property disappears. In the case of the obtained Cu–Ni (core–shell) nanoparticles prepared in our method, the saturation magnetizations of Cu\(_3\)Ni\(_7\) had weak saturation magnetization compared to that of Cu\(_4\)Ni\(_6\), but remained FM (ferromagnetic) property in contrasted with the bulk Cu\(_{1.75}\)Ni\(_{6.25}\) alloy. This result indicates that some of the FM Ni components remained in the nanoparticles.

The effects of an oxide layer on the particle surface on hysteresis loop shift were examined. Cu and CuO have diamagnetic (DM) properties, and Ni and NiO have FM and antiferromagnetic (AFM) properties, respectively. XPS analyses of the FM Cu–Ni (core–shell) nanoparticles (Cu\(_3\)Ni\(_7\) and Cu\(_4\)Ni\(_6\)) showed that the 0.5 nm thick outer layer of the nanoparticles consisted of a NiO-rich layer. Furthermore, HAADF-STEM analysis of Cu\(_4\)Ni\(_6\) showed that these nanoparticles were comprised of a Cu-rich core with a diameter of ca. 6.0 nm, and were surrounded by a Ni-rich shell with a ca. 2.5-nm thick. These results indicated that the obtained particles had three magnetic layers—a DM Cu-rich core, a FM Ni-rich shell and an AFM NiO-rich layer on the surface. Therefore, exchange bias fields (\(H_{eb}\)) were observed as a result of exchange coupling between three magnetic layers (DM/FM/AFM). A magnetic curve for Ni-2 with the average particle size of 20.6 nm is shown in Fig. S11. The magnetic curve for sample Ni-2 showed no \(H_{eb}\), which was understandable considering the relationship between the weak AFM of the very thin NiO layer and the strong FM of the Ni core compared with Cu\(_3\)Ni\(_7\) and Cu\(_4\)Ni\(_6\).

Conclusion

In summary, we succeeded in the rapid preparation of monodispersed Cu–Ni (core–shell) nanoparticles by intramolecular reduction of formate complexes of Cu\(^{2+}\) and Ni\(^{2+}\) with long-chain amine ligands in a one-pot reaction under microwave irradiation. The composition of the Cu–Ni nanoparticles could be easily controlled by changing the molar ratios of Cu : Ni used for the synthesis. The sizes of the resulting Cu–Ni nanoparticles were...
14.6 nm (Cu2Ni5), 11.7 nm (Cu2Ni5), 12.9 nm (Cu2Ni5) and 21.9 nm (Cu2Ni5). The nanoparticles prepared using our method had different concentrations of both Cu and Ni atoms in the core and shell regions within a single particle. Observation by the HAADF-STEM technique showed the nanostructure was comprised of a Ni-rich shell and a Cu-rich core. Cu–Ni nanoparticles (Cu2Ni5) were comprised of a Cu core with a diameter of ca. 6.0 nm, a Ni shell with a ca. 1.6 nm thick and an interlayer of mixed Cu–Ni alloy 0.9 nm thick between the Cu core and the Ni shell. Both the oxidation characteristics and the magnetic properties were dramatically affected by the molar ratios of Cu : Ni in the Cu–Ni nanoparticles. The magnetization of Cu–Ni nanoparticles showed exchange bias with three different magnetic properties: DM (Cu-rich core), FM (Ni-rich shell) and AFM (NiO-rich layer on the particle surface).

Acknowledgements
This work supported financially by Nippon Steel Chemical Co., Ltd, Japan and Iwatanashi International Co., Ltd, Japan.

References