Preparation of Nickel, Iron, and Cobalt Nanopowders via Reduction of Salts with Sodium Dissolved in Liquid Ammonia

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Abstract—Nickel, iron, and cobalt powders are prepared via reduction of salts with sodium dissolved in liquid ammonia. The low temperature of the process and the ability of liquid ammonia to stabilize dangling chemical bonds notably reduce the growth rate of metal particles and prevent their aggregation. The magnetic properties of the nanopowders are investigated.

INTRODUCTION

Nanopowders of iron-group metals possess a high saturation induction and are potentially attractive for producing magnetic fluids and composites. Dispersions of iron-group metal nanoparticles are used as engine oil additives for reclaiming worn parts of automotive and other engines directly during operation [1]. Such nanoparticles can also be used as magnetic-recording media, for manufacturing permanent magnets, in magnetic cooling systems, as magnetic sensors, in drug delivery systems, as magnetic resonance imaging contrast media, and in other applications [2].

Submicron powders of iron-group metals can be prepared via pyrolysis of appropriate volatile carbonyls. The chief drawbacks to this process are the high toxicity of carbonyl precursors and the relatively large size of the resultant particles. Nanopowders can be prepared by reducing appropriate salts with borohydrides or hypophosphates in aqueous solutions [3, 4], but the resulting metal nanoparticles are unstable to oxidation and aggregation in the solution. Moreover, the metals obtained with the use of such reductants contain significant amounts of boron or phosphorus, which are extremely difficult to remove from the precipitate. Irongroup metals can also be obtained by reducing their salts with aqueous hydrazine. The resultant metals contain no difficult-to-remove impurities, but the reduction potential of hydrazine is not very high and cannot ensure a thermodynamic supersaturation high enough for producing metal nanoparticles [5]. Thus, the development of new processes for the preparation of metal nanopowders is of great practical importance.

As shown earlier [6], one efficient way of preparing Fe nanopowders is by reducing Fe salts with Na dissolved in liquid ammonia. This process has a number of important advantages. Na solutions in liquid ammonia have a very high reduction potential and can, therefore, ensure high thermodynamic supersaturations necessary for the synthesis of nanopowders. The low temperature of the process in liquid ammonia $(-33 \text{ to } -50^{\circ}\text{C})$ and the ability of liquid ammonia to stabilize free radicals [7] substantially reduce the growth rate of metal particles, preventing aggregation of the resulting precipitate. The objective of this work was to develop a process for preparing powders of iron-group metals via reduction of appropriate chlorides with Na dissolved in liquid ammonia.

EXPERIMENTAL

Metal nanoparticles were synthesized using appropriate chlorides or sulfates, Na metal, and anhydrous liquid ammonia. The chlorides were dehydrated in a vacuum of 10² Pa at 180°C for 24 h. Liquid ammonia was prepared via condensation of predried ammonia



Fig. 1. Small-angle x-ray scan of Fe particles prepared by reducing iron(II) sulfate with sodium dissolved in liquid ammonia.



Fig. 2. Specific saturation magnetization as a function of temperature for Fe nanoparticles prepared by reducing iron(II) sulfate with sodium dissolved in liquid ammonia.



Fig. 3. Reciprocal magnetic susceptibility as a function of temperature for Fe₂O₃ prepared via oxidation of Fe nanopowder.

gas. The ammoniacal solutions and liquid ammonia were stored in glass Dewar flasks. The Na solution (0.24 M) in ammonia was prepared immediately before experiments by adding pieces of metallic Na to vigorously stirred liquid ammonia. The solution was deep blue. According to current views, sodium dissolved in ammonia is fully ionized and can be thought of as a mixture of sodium ions and solvated electrons. The latter play a central role in determining the redox and other properties of the solution.

Metal-salt suspensions were prepared by reacting the anhydrous chlorides or sulfates and liquid ammonia. The reactions between the chlorides and ammonia yielded ammines, as a rule, with the general stoichiometry $MCl_2(NH_3)_6$. The salt concentration was 0.16 M. Sodium was present in excess (5–10%) of the stoichiometric amount for the full reduction of the metal by the overall reaction $M^{2+} + 2Na \longrightarrow M + 2Na^+$. To reduce the metal, a metal ammine chloride solution (suspension) was added to the Na solution with vigorous stirring. In the course of the reaction, the solution changed color from blue (sodium dissolved in ammonia) to black (sol of Co metal). The metal powders were prepared, purified, and stored in a dry argon atmosphere.

The metal was recovered by magnetic separation or ultrafiltration. After washing with liquid ammonia and ethanol, the filtrate was transferred to a quartz cell filled with anhydrous toluene. The powders thus prepared



Fig. 4. X-ray emission spectrum (electron-beam excitation) of the Ni powder after holding in an oxygen-poor atmosphere; the oxygen content of the sample is 15-20 at %.

were characterized by x-ray diffraction (XRD), magnetic measurements, and electron microscopy.

RESULTS AND DISCUSSION

Iron powder. The synthesized Fe powder was pyrophoric: when exposed to air, it self-ignited. The combustion of the powder led to sintering of the forming oxide particles. To prevent this process, the powder was oxidized in an oxygen-poor (2–5 vol %) atmosphere for several hours. In this process, the powder changed color from black (fine-particle Fe) to yellow-brown (iron oxide).

After washing and drying, the Fe powder was examined by XRD, which showed no reflections from crystalline phases, indicating that the sample was amorphous and consisted of nanoparticles. The latter was confirmed by small-angle x-ray scattering: an x-ray scan showed a broad band centered at $2\theta = 3.5^{\circ}$, with a full width at half maximum of about 3° (Fig. 1).

It is known that small-angle x-ray scattering data can be used to evaluate the average particle size of the material and the variance of the particle size [8]. Using the procedure described by Svergun and Feigin [8], the average particle size of the powders prepared by the sodium-in-ammonia process was determined to be 2-3 nm.

Figure 2 shows magnetization versus temperature data for the Fe powder prepared by the sodium-inammonia process. The decrease in magnetization with increasing temperature is characteristic of ferromagnetic materials. The fact that σ decreases nonmonoton-

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ically can be accounted for by a superparamagnetic state of the particles. The curve in Fig. 2 shows an anomaly characteristic of a diffuse Curie transition at 970 K, which is somewhat lower than the Curie temperature of bulk Fe.

The reciprocal magnetic susceptibility χ^{-1} of the powders was measured as a function of temperature by the Faraday method in a magnetic field of 640 kA/m. The force acting on the sample in a nonuniform magnetic field was measured using a Sartorius BP 310 S electronic analytical balance. The variable temperature



Fig. 5. Magnetic hysteresis loop of the Ni powder.



Fig. 6. XRD pattern of nanoparticles prepared by reducing cobalt(II) chloride with sodium in liquid ammonia.

attachment we used enabled the temperature to be varied continuously in the range 80–1200 K, without changing the sample position. Above room temperature, susceptibility was measured in a dry argon atmosphere.

Since the Fe powder was amorphous, it was rather difficult to ascertain which iron oxide was formed on the surface of the Fe nanoparticles in the initial stages of oxidation. After heat treatment at 500°C in air, the XRD pattern of the powder showed reflections from hematite. Using temperature-dependent magnetic susceptibility measurements, we revealed the main magnetic phase transitions of α -Fe₂O₃ (Fig. 3).

At 250 K, we observed an anomaly due to an antiferromagnetic–antiferromagnetic phase transition. Above 600 K, a ferromagnetic component of magnetization appeared as a result of partial destruction of the antiferromagnetic order. Above 900 K, the powder underwent a transition to a paramagnetic state. All these transitions are characteristic of α -Fe₂O₃ [9].

Nickel powder. Ni metal was prepared by the same process as Fe. In contrast to the Fe powder, Ni was obtained in the form of aggregates about 1 μ m in size. The likely reason is that one possible intermediate in the reaction between nickel and ammonia is the relatively stable amide Ni(NH₂)₂, which has time to crystallize in the ammoniacal solution. At room temperature, this amide decomposes after ammonia evaporation. The aggregate size seems to be determined by the crystal size of Ni(NH₂)₂.

The Ni powder was also pyrophoric, but to a lesser extent than the Fe powder. Exposure to an oxygen-poor

(1–5%) atmosphere for 0.5 h suppressed the pyrophoric properties and markedly inhibited subsequent oxidation of the Ni powder. Electron probe x-ray microanalysis showed that the aggregates were covered with a stable oxide layer, which prevented the sample from further oxidation.

The x-ray emission spectrum of the Ni powder is shown in Fig. 4. After air exposure, the powder particles had a composite structure: Ni/Ni_2O_3 or $Ni/Ni(OH)_2$. This was also evidenced by XRD analysis.



Fig. 7. Magnetic hysteresis loop of the Co powder.

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Fig. 8. Specific saturation magnetization as a function of temperature for Co particles (a) 30, (b) 60, and (c) 80 nm in size.

In addition, the sample contained a small amount of nickel nitride. The diffraction peaks from all of the phases present were broadened, attesting to a small particle size. From the width of XRD peaks, the particle size was evaluated to be 30–50 nm.

Figure 5 shows the magnetic hysteresis loop of the Ni powder. The coercive field evaluated from this loop is 8–16 kA/m. This value is substantially lower than the coercive field in bulk Ni, suggesting that the shape-anisotropy and mechanical-stress contributions are very small [9].

Cobalt powder. Metallic Co was prepared by a procedure similar to that for Fe and Ni. As the Co precur-

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sor, we used $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, which was dehydrated in a vacuum of 10^2 Pa at 180°C and then reduced in the same way as the Ni precursor.

The main structural and magnetic properties of the Co powder prepared by reducing $CoCl_2$ (Figs. 6, 7) are very similar to those of the Ni powder. A noteworthy feature is that the coercive fields of both the Ni and Co powders are substantially smaller than those of bulk Ni and Co. Moreover, all of the phase transitions in the Ni and Co powders occur at lower temperatures.

The specific magnetization of Co nanoparticles was measured in the range 77–1450 K by the Faraday method in a field of 640 kA/m during both heating and

cooling. The results (Fig. 8) demonstrate that increasing the particle size from 30 to 80 nm increases the specific magnetization of the nanoparticles. During heating, the magnetization of the three samples increases sharply at ≈ 600 K. The increase in specific magnetization during the first heating to above 600 K is irreversible. Measurements during cooling and subsequent heating reveal virtually a classic $\sigma(T)$ behavior of ferromagnets. Note that the temperature of the sharp increase in specific magnetization rises slightly with decreasing nanoparticle size.

The Curie temperature of the nanoparticles studied coincides, to within the present experimental accuracy, with that of polycrystalline cobalt.

We believe that the nitrogen and hydrogen dissolved in the metal powders prepared in this study play a central role in stabilizing their amorphous state. Auger analysis shows that the amorphous powders contain up to 20 at % N. The incorporation of nitrogen seems to be the result of catalytic ammonia decomposition on the surface of nanoparticles and/or decomposition of unstable amine groups which may form as reaction intermediates in the reduction process:

$$\begin{split} \text{Na} + \text{HN}_3 &\longrightarrow \text{HN}_2^- + \text{H} + \text{Na}^+, \\ \text{Co} + \text{NH}_2 &\longrightarrow \text{Co}(\text{NH}_2)_2 &\longrightarrow \text{CoN}_x\text{H}_y + \text{H}_2 + \text{N}_2. \end{split}$$

CONCLUSIONS

The sodium-in-ammonia process described in this work offers the possibility of preparing amorphous metal nanoparticles, as exemplified by the synthesis of iron, nickel, and cobalt powders. An important point is that these metals were obtained in an amorphous state without introducing difficult-to-remove components. The small particle size of the synthesized powders is evidenced by their sedimentation stability in ammonia, the absence of diffraction peaks in their XRD patterns, and the observed small-angle x-ray scattering peak. The small particle size of the powders shows up in their magnetic properties. The chief advantage of the described process is the high reduction potential of sodium solutions in ammonia.

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