Synthesis of Fine Iron–Cobalt Alloy Particles by the Co-Reduction of Precursors with Solvated Electrons in Sodium–Ammonia Solution

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Fine iron–cobalt alloy particles were synthesized by the co-reduction of their precursors with sodium in liquid ammonia. The reaction took place instantaneously because of the highly reductive solvated electrons. Very reactive, fine particles of the order of ~10 nm size were obtained. Annealing process is crucial for the magnetic properties of the products, the saturation magnetization being ranging from 29 to 238 A·m²·kg⁻¹. One spot reduction with solvated electrons and the consequent annealing treatment in the synthesis vessel has potential ability for the synthesis of a variety of metal and alloy particles.

Keywords: iron–cobalt alloy, reduction, solvated electrons, liquid ammonia

1. Introduction

The synthesis of nano-scale metal and alloy materials is of great interest in the past decades. Because of the excellent soft magnetic properties of the iron–cobalt alloy, considerable attention has been also paid for synthetic processes of nano-scale Fe–Co alloy particles. Various processes have been studied including thermal decomposition of carbonyl precursors, sonochemical method, and other chemical processes such as microemulsion method and polyol process. In chemical synthetic routes, a general pathway is the reduction of the precursor compounds, so that the exploring of reducing reagents is one of the key points in the research of the wet processes.

Alkali metal is dissolved in liquid ammonia to form metastable solutions. One of the interesting properties of the solution is that its physical properties are drastically changed by the metal concentration, resulting from the excess electrons released from the metal. At low metal concentration, the solution has characteristic blue colour arising from the electrons solvated by ammonia molecules. With increasing the metal concentration, it changes to shiny metallic colour.

Metal–ammonia solutions are strongly reductive in nature, and are used as a reducing reagent particularly in organic syntheses. With regard to its application to inorganic syntheses, only a few works have been reported, as far as the authors are aware. Zhu and Sadoway reported the preparation of some elemental (Ta, Cu) and an alloy (Nb3Al) nanoparticles synthesized by sodium–ammonia solution. Alkalides are relevant to the solvated electrons, where the alkali metal anions are produced when dissolved in non-reducible solvents. Dye proposed the alkalide route for the nanoparticle synthesis, and series of the works, including the synthesis of iron–cobalt nanoparticles, have been reported by Wagner’s group.

In the present paper, we address the applicability of solvated electron route, describing the synthesis process of fine Fe–Co particles by the co-reduction of their chloride precursors with sodium–ammonia solutions. On the basis of the magnetic properties of the bulk alloy, the composition of Fe2Co has been focused, at which the saturation magnetization shows a maximum value of 245 A·m²·kg⁻¹. The overall reaction is described as:

\[
\text{CoCl}_2 + 2\text{FeCl}_2 + 6\text{Na} = \text{CoFe}_2 + 6\text{NaCl}. \tag{1}
\]

As the synthesized particles are highly reactive and unstable in ambient atmosphere, we focus the annealing treatment of the materials.

2. Experimental Procedure

2.1 Materials

Because metal–ammonia solutions are less stable in ambient atmosphere, all the syntheses were carried out in pyrex glass vessels connected to a vacuum line (~10⁻³ mbar). All the vessels were cleaned with H₂SO₄–HNO₃ acid mixture in order to avoid the decomposition of the solution, i.e., amide formation, which is promoted by impurities on glass walls.

Ammonia, purchased from Taiyo Nissan, was liquefied and reacted with sodium metal (98%, Kanto Chem. Co., Ltd.) at −60°C until blue-coloured solution was obtained. Water impurities in ammonia can be rigorously removed by this process. The purified ammonia was then vacuum distilled into a pyrex glass storage tank containing lithium nitrate. The saturation of the salt enables the store of the liquid ammonia at ambient temperature.

2.2 Synthesis of fine Fe–Co particles

The mixture of FeCl₂ (99.9%, Kojundo Chem. Lab. Co., Ltd.) and CoCl₂ (97%, Wako Pure Chem. Co., Ltd.) powders at stoichiometric ratio, i.e., eq. (1), was introduced in a bottom of a pyrex glass synthesis vessel. Pieces of sodium metal were put in a small V-shaped vessel which was connected via glass joint to the top of the synthesis vessel. By turning the V-shaped vessel, sodium metals are dropped into the bottom of the synthesis cell. Typical composition of the solution was FeCl₂ of 382 mg, CoCl₂ of 195 mg, Na of 160 mg, and the solution volume of 10 mL. As discussed in

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the sodium composition was lower than the stoichiometric ratio given in eq. (1), typically 80% of the stoichiometry. Therefore, we focus on the characterization of reaction products rather than the product yield in the present paper.

Prior to the reduction of the salts, they were dried under vacuum at 200°C. Ammonia was introduced to the synthesis vessel through vacuum distillation, and the salts were mixed in liquid ammonia at −60°C. Sodium was then introduced from the V-shaped compartment. The colour of the solution turned to blue, and the reaction took place instantaneously. After the solvent was evaporated, the synthesized powders were taken from the cell, and washed with distilled water. The product is hereafter called as “as-made” sample. In most of the cases, however, the products were taken from the cell in an argon-filled glove bag, in which black-coloured products were washed with ethanol.

Some annealing treatments were carried out for the reaction products with an electric furnace. In some cases, the annealing was conducted in the pyrex cell prior to taking the sample in a glove bag. Detailed conditions are described in the section of results and discussion.

2.3 Characterization of the reaction products

The products were characterized by an X-ray diffractometer (Shimadzu, XRD-6100), a scanning electron microscope with an EDS analyser (JEOL, JSM-6330F and JED-2140), and a transmission electron microscope (Hitachi, H-8). The magnetic properties were examined by a vibrating sample magnetometer (Toei Kogyo, VSM-5) at room temperature at the sweep speed of 0.8 MA·m⁻¹ per 3 min.

3. Results and Discussions

3.1 Characterization of as-made product

Figure 1 shows an X-ray diffraction pattern of an as-made product sample obtained by the reduction reaction. Weak peaks of the cobalt ferrite, CoFe₂O₄, are observed in the diffractogram. A typical atomic composition of products, determined by a SEM-EDS analysis, is cobalt 9%, iron 21%, oxygen 69%, sodium 1% and chlorine of 0.2%. As chlorine and sodium are essentially removed from the product, the reduction of the precursor chlorides takes place in the treatment with sodium–ammonia solution. The as-made sample, when exposed in ambient atmosphere, results in the exothermic reaction. Thus, it is considered that the oxidation of the synthesized alloy took place during the handling of the sample, resulting in the substantial oxygen content in the product. It should be here also noted that the existence of un-reacted sodium in the synthesis cell leads to the formation of alkaline compounds during the washing treatment of the reaction product, giving rise to the formation of iron or cobalt hydroxides. Therefore, the sodium content should be less than the stoichiometric ratio. Even for the less sodium content, the atomic ratio of the product is Fe:Co ~ 2:1, implying the comparable kinetics of the reduction reaction of both the chlorides.

The morphology of the reaction products was fine powder with the particle size of ~10 nm, as shown in the SEM and TEM images (Fig. 2). The TEM image shows the existence of amorphous phase as well as crystalline, the latter of which is probably due to the XRD peaks of cobalt ferrite.

As shown in Fig. 3, an elemental mapping of the products with a scanning transmission electron microscope (STEM) suggests the co-reduction of the precursors, as both elements co-exist in the product particles without significant segregation. Thus, the result supports the comparable kinetics of the reduction of the elements, as anticipated above.

In regard to the formation mechanism of the nanoparticles, its full understanding is one of the most challenging tasks in the synthesis of nanoparticles via chemical route. Here, we refer to the work by Zubris et al., where the reaction kinetics of FeCo nanoalloy formation by thermal decomposition of carbonyl precursors was studied. The formation mechanism of nanoalloy systems is supposed to be co-transformation, co-aggregation of different metallic clusters. The reduction kinetics of each component is one of the crucial factors for the phase separation. In the present case, the reduction kinetics is presumably very fast because of the strong reductive nature of the solvated electrons, rather different from the case of carbonyl decomposition of the reaction time scale of ~10³ s. Moreover, the phase diagram of binary Fe–Co system exhibits co-solubility over the most of the compositional range. Thus, similar reaction rates and homogeneous formation of the alloy particles are expected in the reduction of divalent iron and cobalt salts. The present results support this consideration, though detailed studies, such as kinetics and high resolution TEM measurement under careful sample treatment, are desired.
3.2 Influence of the annealing treatment

As reported in literature, fine Fe–Co alloy powders are easily oxidized.\textsuperscript{2,11} We have, therefore, explored the following annealing treatments for the preparation of air-stable Fe–Co alloy particles: (1) post-anneal, where the as-made sample was annealed for 4 h under reducing atmosphere of a gas (95\%He–5\%H\textsubscript{2}) flow at 600°C, (2) low $p_{O_2}$ treatment, where the sample was exposed under the atmosphere with low oxygen partial pressure. This was achieved by the heating of Cu and Cu\textsubscript{2}O powder mixture at 150°C held in a glass container attached next to the synthesis cell, and (3) pre-anneal treatment, where sample was annealed at 400°C for 4 h in the synthesis cell after the solvent evaporation. Note that, in the last two types of treatments, the annealing was conducted in the synthesis cell and the products were, then, washed with ethanol in an argon-filled glove bag, while the sample of post-annealing treatment was exposed in ambient atmosphere before the annealing treatment.

Representative atomic composition of the annealed sample is summarized in Table 1. Obviously, the oxygen content is reduced in comparison with the as-made powder (see 3.1). Thus, the annealing treatment is effective for the reduction of the oxidized species.

Figure 4 shows the SEM images of the samples after the annealing treatments. The growth in particle size ($\sim$100 nm) of the post-annealed sample with distinct particles is obvious, while the samples treated in synthesis cell are not well-defined as that of as-made sample, and do not exhibit the significant change in particle size. As reported in literature, the annealing at high temperature results in the agglomeration and the particle growth.\textsuperscript{2,10,11}

It is anticipated that the annealing under reducing atmosphere (post-anneal) results in the reduction of the

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<th>Table 1 Typical atomic composition of the annealed samples determined with SEM-EDS analysis.</th>
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Fig. 3 STEM image (left) and the corresponding cobalt (middle) and iron (right) mapping images of as-made powder prepared by sodium–ammonia solution.

Fig. 4 SEM images of the sample after different annealing treatments: (a) annealed under He–H\textsubscript{2} atmosphere at 600°C for 4 h (post-anneal), (b) exposed under low oxygen atmosphere for 6 h (low $p_{O_2}$), (c) annealed under vacuum at 400°C for 4 h in the synthesis cell (pre-anneal).
oxides. On the other hand, the annealing under inert atmosphere or the treatment under low oxygen partial pressure in the synthesis cell can lead to the formation of protective oxide layer or the agglomeration and the particle growth, preventing the rigorous oxidation when exposed in ambient atmosphere. The XRD patterns of the annealed samples are shown in Fig. 5. The post-annealing results in the essentially full reduction of the as-made annealed samples are shown in Fig. 5. The post-annealing exposure under low oxygen partial pressure, the existence of protective oxide layer or the agglomeration and the particles. Among the examined processes, the pre-anneal treatment is a key issue for the preparation of air-stable particles. Among the examined processes, the pre-anneal treatment and pre-annealing are effective for the protection against the rigorous oxidation of the fine particles.

3.3 Magnetic property of the products

The results of the VSM measurements of the synthesized powder are shown in Fig. 6 and Table 2. Taking the values of the remanence ratio into account, all the samples have similar characteristics with an assembly of randomly oriented uniaxial particles. The as-made sample has the saturation magnetization of 29 A·m²·kg⁻¹, while the room temperature magnetization loop of the post-annealed sample exhibits highest saturation magnetization of 238 A·m²·kg⁻¹ with smallest coercivity of 11 kA·m⁻¹, comparable to the values of the bulk Fe₂Co alloy. The latter compound is, thus, representative soft-magnetic material. As for the annealing treatment in the synthetic cell, low pO₂ treatment does not improve the magnetic properties, as the hysteresis loop is comparable with that of as-made sample. On the other hand, the annealing in the synthesis cell enhanced the saturation magnetization up to 76 A·m²·kg⁻¹.

Therefore, materials with different magnetic properties can be obtained by an appropriate annealing treatment. Further optimization in the annealing process can improve the magnetic properties of the Fe–Co fine particles.

4. Conclusion

Synthesis of fine Fe–Co particles by co-reduction of precursors with sodium-ammonia solution is studied in the present work. The reduction reaction takes place instantaneously, and the chlorine of the precursors are fully removed by the treatment with sodium-ammonia solutions. Annealing treatment is a key issue for the preparation of air-stable particles. Among the examined processes, the pre-anneal process, conducted in the synthesis cell after the reduction, avoids the rigorous oxidation, as observed in the XRD pattern of the product.

In summary, synthesis with solvated electrons is a powerful method for the synthesis of fine particles. Further improvement in the annealing treatment or the process of the protective layer can achieve the synthesis of fine particles with variety of magnetic properties.

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REFERENCES