Preparation of highly dispersed core–shell $\alpha''$-Fe$_{16}$N$_2$/SiO$_2$ particles using hydroxyapatite as a sintering prevention layer

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Highly dispersed core–shell $\alpha''$-Fe$_{16}$N$_2$/SiO$_2$ particles were prepared using hydroxyapatite (HAp) as the sintering prevention layer. HAp was effective as anti-sintering agent, and could be dissolved by solutions with wide pH range. The $\alpha''$-Fe$_{16}$N$_2$ phase was formed by reduction and nitridation, in spite of the presence of SiO$_2$ and HAp. HAp was effective to prevent the sintering of the core–shell $\alpha''$-Fe$_{16}$N$_2$/SiO$_2$ particles from the elimination of the surface Si–OH of silica shell layer. The HAp was successfully removed using the citric acid without the degeneration of the SiO$_2$ shell layer and $\alpha''$-Fe$_{16}$N$_2$ core particles.

Key-words : Hydroxyapatite, Iron nitride, Nanoparticle, Dispersion, Nitriding

1. Introduction

Magnetic nanoparticles have attracted much attention in both fields of hard and soft magnetic materials.1–3 These nano-materials are interested in various application as high-frequency magnetic devices, drug delivery systems, recording media, and magnets. Nanoparticles are synthesized by various approaches such as chemical synthesis, hydrothermal synthesis, thermal decomposition, microemulsion, spray pyrolysis and so on. Some materials need after annealing for appearance of objective performance. That annealing include reduction of oxides to metallic materials, gas reaction for formation of nitride or carbide, phase transformation to the ordered structure. In high-temperature annealing process, nanoparticles agglomerate and sinter.

Some approaches are applied to prevent agglomeration and sintering. One is the formation of anti-sintering layer on the surface of nanoparticles. Oxides such as SiO$_2$, Al$_2$O$_3$, MgO are prepared by chemical or physical coating method in the form of core/shell nanoparticles. These oxides have an effect to prevent agglomeration and sintering. However, shell layers are partially sintered depending on the condition.

Calcium phosphates can be synthesized at room temperature without a particular reagent. Therefore, the original nanoparticles are not received the damage during the preparation of calcium phosphate. Also, that reaction can progress in the solution which the nanoparticles dispersed and the products keep the dispersiveness of original nanoparticles.4 Among the calcium phosphate, the hydroxyapatite is stable at high temperature and the as-prepared form do not shrink or crush. These facts are important for the compression of the sintering between nanoparticles during the heat-treatment. High-dispersed nanoparticles are obtained by the removal of the calcium phosphate. The calcium phosphate can be dissolved in gentle conditions, the nanoparticles after heat-treatment are not received the serious damage.

Iron nitride, $\alpha''$-Fe$_{16}$N$_2$ had attracted to the attention for permanent magnets, spintronic devices, magnetic recording because of their giant magnetic moment as an alternative to rare-earth free material.5,6 Kim and Takahashi reported that the films of this phase bore a much larger magnetization than $\alpha$-Fe.7 Since then, many researchers study that materials by the method such as molecular beam epitaxy, sputtering, ion implantation. $\alpha''$-Fe$_{16}$N$_2$ powders also prepared by some researchers. Typically, the $\alpha''$-Fe$_{16}$N$_2$ powders are prepared by two step synthesis. Firstly, the oxide powders are reduced to metal Fe in H$_2$ stream. Then, the metal Fe are converted to Fe nitride in NH$_3$. The nitriding process is need to performed at low temperature for long time because, the $\alpha''$-Fe$_{16}$N$_2$ is metastable phase and easily decomposed.

The core–shell structure of $\alpha''$-Fe$_{16}$N$_2$/SiO$_2$/metal oxide are also prepared. SiO$_2$, Al$_2$O$_3$, Y$_2$O$_3$, etc. are used as the shell layers. The oxide coated iron oxide particles are used as starting material. The shell oxide materials are effective to prevent the sintering of magnetic core nanoparticles during the annealing. However, the long-term heat treatment can cause the agglomeration by reaction between shell layers.

In our previous study,8 the hydroxyapatite was used as sintering prevention layer. The highly dispersed $\alpha''$-Fe$_{16}$N$_2$ particles were obtained by removal of hydroxyapatite. In this study, the $\alpha''$-Fe$_{16}$N$_2$/SiO$_2$/shell core–shell particles are prepared using hydroxyapatite as sintering prevention layer.

2. Experimental

The spherical hematite nanoparticles with a diameter of about 50 nm were starting materials. The synthesis condition was referred to that reported.4 The SiO$_2$ shell layers were prepared by hydrolysis of tetraethoxysilane on the hematite particles.9 The Fe$_2$O$_3$ or core–shell Fe$_2$O$_3$/SiO$_2$ particles were dispersed in the distilled water. The calcium nitrate tetrahydrate and diammonium hydrogen phosphate were dissolved in the distilled water, respectively. The calcium nitrate tetrahydrate solution was added to the suspension and the pH of the suspension was adjusted at 9 by adding ammonium hydroxide. Then, the diammonium hydrogen phosphate solution was slowly dropped into the suspension with keeping the pH of the suspension adjusted at 9. The molar ratio of Ca/P was 5/3. For the preparation of hydroxyapatite (HAp), the suspension was stirred for 20 h. The HAp coated particles were collected by centrifugation and washed using water and ethanol to remove unreacted material, and then dried.
The HA-p coated core–shell particles were reduced with hydrogen gas at 400–500°C for 4 h, and then nitrided with ammonia gas at 130–150°C for 24 h. For the reference, the HA-p without Fe₂O₃/SiO₂ particles were also treated with same condition. The two kind of solutions were prepared to dissolve the HA-p. The ethylene diamine tetraacetate (EDTA) was dissolved in the distilled water and adjusted pH at 9 by adding the NaOH. Another one was the citric acid solution with the pH of about 2. The HA-p was dissolved using these solution, and then the α′-Fe₁₆N₂/SiO₂ core–shell particles were collected by centrifugation and washed some times. In the case of the particles which was easily oxidized, the procedure was conducted in the nitrogen atmosphere. The nanoparticles were dried in vacuum or dry nitrogen.

3. Results and discussion

Firstly, the core–shell α′-Fe₁₆N₂/SiO₂ particles were synthesized without HA-p. Figure 1 shows the FT-IR spectra of core–shell nanoparticle before and after nitriding. In Fig. 1, the absorption band due to the vibration of Fe–O at 600 cm⁻¹ was disappeared after nitriding because the core iron oxide was converted to iron nitride. The absorption band due to the vibration of Si–O–Si at 1100 cm⁻¹ (asymmetric stretching), 800 cm⁻¹ (symmetric stretching), and 460 cm⁻¹ (bending) were absorbed in the spectra of core–shell nanoparticles before and after nitriding. These results indicated that the basic structure of SiO₂ shell layer was maintained even after nitriding. However, the intensity of the absorption band at 950 cm⁻¹ ascribed for the surface Si–OH stretching vibration decreased after the nitriding. It was considered that the elimination of the surface Si–OH of silica shell layer was occurred and the new Si–O–Si bond was formed between the core–shell nanoparticles during heat-treatment. This caused the agglomeration of nanoparticles. Figure 2 shows the TEM image of core–shell α′-Fe₁₆N₂/SiO₂ particles. In the TEM image, the dark and right regions of particles were core α′-Fe₁₆N₂ particle and shell SiO₂ layer, respectively. The agglomeration of nanoparticles was observed. From these results, the sintering prevention layer was need to obtain the high dispersed core–shell nanoparticles.

We selected calcium phosphate based material as sintering prevention layer because of the thermal stability. At first, calcium phosphates were synthesized without nanoparticles for the investigation of stability of calcium phosphates. When the pH of solution was not controlled, dicalcium phosphate dihydrate [CaH(PO₄)·2H₂O, DCPD] was formed. When the pH of solution was adjusted to 9, HA-p [Ca₁₀(PO₄)₆(OH)₂] was formed. For the investigation of the thermal stability, these samples were annealed at 400–600°C. Figures 3 and 4 shows FT-IR spectra of the as-prepared calcium phosphate and annealed ones. DCPD changed to calcium polyphosphate (Ca₃P₂O₇, CPP) even at 400°C. In contrast, HA-p did not change at 600°C. Moreover, HA-p was stable during annealing in hydrogen or ammonia gases. If crystalline phase change during heat-treatment, the shapes of products were destroyed, and it is difficult to compress the sintering between core nanoparticles. Also, the gases released from calcium phosphate is considered to affect the reaction of the core nanoparticles. Therefore, HA-p is useful material to suppress the sintering and not prohibit the reaction of nanoparticles.

Fig. 1. FT-IR spectra of Fe₂O₃/SiO₂ core–shell nanoparticles (a) before and (b) after nitriding.

Fig. 2. TEM image of Fe₁₆N₂/SiO₂ core–shell nanoparticles prepared by nitriding of Fe₂O₃/SiO₂ core–shell nanoparticles without HA-p.

Fig. 3. FT-IR spectra of CaH(PO₄)·2H₂O (DCPD) (a) as-prepared and annealed at (b) 400, (c) 500, (d) 600°C.

Fig. 4. FT-IR spectra of HA-p (a) as-prepared and (b) annealed at 600°C.
The solubility of calcium phosphate after annealing was investigated using some acids. Although strong acids such as HCl were needed to dissolve CPP, HAp dissolved even in weak acid such as citric acid or acetic acid. Calcium phosphate have low solubility in alkali solution. EDTA chelate Ca ion and increase the solubility of calcium phosphate in alkali solution. HAp dissolved in EDTA solution at pH value of 7–12. Figure 5 shows change of pH value of solution during dissolution of HAp in citric acid (2 g/100 ml, initial pH of 2.1) and EDTA solution (1 g/100 ml, initial pH of 9 adjusted by NaOH). The pH values of these solutions were constant after 10 min and the solutions became clear. From these results, it is possible to remove HAp in the solutions at various pH value. This fact indicates that the damages to the nanoparticles during process could be suppressed by the select of processing solutions, and HAp can be used for various nanoparticles as anti-sintering agent.

The preparation condition was decided based on the experimental results for the crystalline phase, reactivity with core–shell particles and solubility. The hydroxyapatite was successfully synthesized by the procedure mentioned above. The HAp coated core–shell Fe2O3/SiO2 particles were reduced and nitrided. Fe2O3 was successfully converted to α'-Fe16N2 in spite of the presence of SiO2 and HAp.

The HAp was removed from the core–shell particles by dissolving using the ethylene diamine tetaacetate solution. The HAp was successfully removed, but a part of SiO2 shell layer also dissolved. From FT-IR results, the absorption band due to the vibration of SiO2 was degenerated and the dissolution of the SiO2 layer was confirmed. Moreover, the partially dissolved SiO2 was considered to be adhered together during the treatment. Although the ethylene diamine tetaacetate solution was effective for the removal of HAp from the α'-Fe16N2/SiO2/HAp structure, that was difficult to apply for the particles containing the SiO2 shell layer.

Figure 7 shows the FT-IR profiles of the core–shell Fe2O3/SiO2 particles before and after the treatment using the citric acid solution. The absorption band due to the vibration of P–O–P at 1000–1100 and 550–600 cm⁻¹ were disappeared after the treatment by the citric acid solution. This indicated that the HAp was successfully removed. The absorption band due to the vibration of Si–O–Si was not changed from the starting Fe2O3/SiO2 particles. The citric acid solution could remove the HAp without the degeneration of the SiO2 shell layer.

Figure 8 shows the FT-IR profiles of the core–shell α'-Fe16N2/SiO2 particles before and after the treatment using the citric acid solution. The absorption band due to the vibration of P–O–P in HAp were disappeared and the HAp heat-treated with H2 and NH3 was successfully dissolved by citric acid solution. The shape of the absorption band due to the vibration of Si–O–Si were slightly changed from the row starting particles, but same as those of the core–shell α'-Fe16N2/SiO2 particles prepared without HAp. This indicated that the HAp did not affect the SiO2 shell layer during heat-treatment, and the citric acid solution could remove the HAp without the degeneration of the SiO2 shell layer.
The SiO2 shell layer protected the Fe16N2 phase during the treatment by the citric acid from the XRD results. The amount of SiO2 layer, the coercive force was close to that investigated by VSM measurement. The saturation magnetization and coercive force were almost same. On the other hand, the diameters of particles were different. From these results, it was evident that the agglomeration and sintering were prevented by using HAp.

The particle sizes measured by the dynamic light scattering (DLS) method and calculated from TEM image were shown in Table 1 for the particles prepared with and without HAp. Although the agglomerate was observed for the particles prepared without HAp, the diameters of particles calculated from TEM were almost same. On the other hand, the diameters of particles measured by DLS were different. The diameter of particles prepared without HAp was large compared to another one due to the agglomeration. From these results, it was evident that the agglomeration and sintering were prevented by using HAp.

The magnetic properties of the Fe16N2/SiO2 particles were investigated by VSM measurement. The saturation magnetization and coercive force were 105 emu/g and 2130 Oe, respectively. Although the saturation magnetization was decreased by the amount of SiO2 layer, the coercive force was close to that reported.16

Table 2 summarize the state of Fe16N2 and Fe16N2/SiO2 particles after dissolution of HAp using HCl, citric acid and EDTA solutions. This results that the dispersed nanoparticles could be obtained by using the suitable process solution.

4. Conclusion

Highly dispersed core–shell α′-Fe16N2/SiO2 particles were prepared using HAp as the sintering prevention layer. The α′-Fe16N2 phase was formed in spite of the presence of SiO2 and HAp. HAp did not change during heat-treatment and could be removed by acid and alkaline solutions. HAp was effective to prevent the aggregation of the core–shell α′-Fe16N2/SiO2 particles originating in the elimination of the surface Si–OH of silica shell layer. HAp was effective as anti-sintering agent, and could be dissolved by solutions with wide pH range. This method could be used for various nanoparticles by the selection of process solution depending on the kinds of nanoparticles.

Reference

1) S. Singamaneni, V. N. Bliznyuk, C. Binek and E. Y. Tsymbal, J. Mater. Chem., 21, 16819–16845 (2011).
2) T. Xie, L. Xu and C. Liu, Powder Technol., 232, 87–92 (2012).
3) T. An, J. Chen, X. Nie, G. Li, H. Zhang, X. Liu and H. Zhao, ACS Appl. Mater. Interfaces, 4, 5988–5996 (2012).
4) H. Teymourian, A. Salimi and S. Khezrian, Biosens. Bioelectron., 49, 1–8 (2013).
5) B. Zhang, Y. Du, P. Zhang, H. Zhao, L. Kang, X. Han and P. Xu, J. Appl. Polym. Sci., 130, 1909–1916 (2013).
6) N. A. Frey, S. Peng, K. Cheng and S. Sun, Chem. Soc. Rev., 38, 2532–2542 (2009).
7) S. Dembski, M. Milde, M. Dyba, S. Schweizer, C. Gellermann and T. Klockenbring, Langmuir, 27, 14025–14032 (2011).
8) T. K. Kim and M. Takahashi, Appl. Phys. Lett., 20, 492–494 (1972).
9) K. Yamanaka, Y. Onuma, S. Ymashita, Y. Masubuchi, T. Takeda and S. Kikkawa, J. Solid State Chem., 183, 2236–2241 (2010).
10) M. Komuro, Y. Koizono, M. Hanazono and Y. Sugita, J. Appl. Phys., 67, 5126–5130 (1990).
11) M. Takahashi, H. Shojo and H. Takahashi, Appl. Phys. Lett., 20, 492–494 (1990).
12) H. Takahashi, K. Mitsuoka, M. Komuro and Y. Sugita, J. Appl. Phys., 73, 6060–6062 (1993).
13) M. Takahashi, Y. Takahashi, K. Sunaga and H. Shojo, J. Magn. Magn. Mater., 239, 479–483 (2002).
14) H. Shojo, H. Nashi, K. Eguchi and M. Takahashi, J. Magn. Magn. Mater., 162, 202–210 (1996).
15) T. Ogawa, Y. Ogata, R. Gallage, N. Kobayashi, N. Hayashi, Y. Kusano, S. Yamamoto, K. Kohara, M. Doi, M. Takano and M. Takahashi, Appl. Phys. Express, 6, 073007 (2013).
16) D. Nagai, Y. Kinemuchi, K. Suzuki, A. Towata and M. Yasuoka, J. Solid State Chem., 225, 455–458 (2015).
17) J. Lian, X. Duan, J. Ma, P. Peng, T. Kim and W. Zheng, ACS Nano, 3, 2749–3761 (2009).
18) W. Stöber and A. Fink, J. Colloid Interf. Sci., 26, 62–69 (1968).