# High Purity α"-Fe<sub>16</sub>N<sub>2</sub> Particles with Tunable Sphere Structures via Spray Drying Method

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A facile and scalable method to synthesize high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> powders with tunable sphere structures is developed. This strategy combined spray drying of Fe salt particles with hydrogen reduction and subsequent ammonia nitridation to form  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phase. The solid and hollow sphere structures of precursor particles can be easily tuned by adding ethanol as a directing agent. In addition, the initial structure of Fe spheres is maintained even after phase transformation process. The resulting particles prepared by optimum condition consist of high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> with a phase fraction of 95.52 wt%, showing a coercivity of up to 1471 Oe and a magnetic energy product of up to 2.25 MGOe at room temperature.

Keywords : iron nitride, rare-earth free, permanent magnet, spray drying, hollow sphere, solid sphere

## 1. Introduction

The  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> has a great attention as a powerful rareearth-free permanent magnet due to their giant saturation magnetization ( $M_s \sim 290 \text{ emu/g}$ ) and large magnetocrystalline anisotropy ( $K_u \sim 1.0 \times 10^7 \text{ erg/cm}^3$ ) as well as its abundant amount of Fe source [1]. Thus, many researchers have interested on the fabrication method of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phase and several attempts have been successfully to develop  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phase in thin film [2] and foil [3] and powder [4-6] form. Among these fabrication methods, the fine particles of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> were mostly prepared by using iron oxide nanoparticles. Subsequent hydrogen reduction and nitridation enables the oxides to transform into  $\alpha$ -Fe and  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>. However, the iron oxide nanparticles undergo significant coarsening during the reduction, resulting in detrimental effect in the final magnetic properties [6]. The approaches such as coating shell on the oxide surface [5] and applying high pressure during the hydrogen reduction [6] were attempted and show the excellent enhancement in lowering coarsening. However, they involves complicated or costly process for  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> synthesis.

Spray drying is a simple, continuous, and scalable way to produce fine particles and widely applied in various fields such as chemical, pharmaceutical and food industries. In addition, the microstructure of the resulting particles is easily controllable by adding drying control chemical additives [7, 8] and can be maintained even after significant phase change process [9]. However, the process has not applied to the preparation of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> to the best of our knowledge.

Herein, we develop a facile and scalable method to prepare  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> by spray drying. The synthesis involves simply spray drying of Fe salt solution and hydrogen reduction followed by ammonia nitridation. It is note that the resultant powders exhibit no significant aggregations of spheres and high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phase. Our method has the potential to be generally applied to the synthesis of other magnetic powders with low cost and high purity.

#### 2. Experimental Methods

The Fe<sub>2</sub>O<sub>3</sub> with solid and hollow sphere structures were prepared by a spray drying method followed by annealing in air. In a typical synthesis, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (10 wt%) were dissolved in H<sub>2</sub>O to form a clear solution. Ethanol was added to the Fe precursor solution with 40 wt% to

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produce hollow microspheres. The resulting solution was then spray dried using a Buchi mini spray drier B-290 (the maximum spraying rate  $\sim 1.8$  L/h) at an inlet temperature of 220 °C, an aspirator rate of 100 %, a rotameter setting of 60 mm, and a pump rate of 10 % (3.0 mL/min). The spray dried Fe precursor powders were then annealed in air at 400 °C for 5 h with a temperature ramp rate of 2 °C/min. Then, the Fe<sub>2</sub>O<sub>3</sub> spheres were reduced to α-Fe under a hydrogen (H<sub>2</sub>) stream (99.999 % purity, 0.5 L/min) for 4 h under the various temperature conditions. After the reduction process the tube furnace was cooled to room temperature, the hydrogen gas in the reaction tube was purged with argon gas for 1 h, followed by ammonia (NH<sub>3</sub>) gas (99.999 % purity, 1 L/min). Nitridation was, then, carried out between 145 and 175 °C for 6 to 18 h. Finally, the samples were cooled down to room temperature in the furnace under argon (Ar) atmosphere. The composition and phase formation of synthesized magnetic powders were identified by X-ray diffractometer (XRD, Rigaku, D/MAX-2500) using Cu Ka radiation operating at 40 kV and 250 mA. Relative values of weight fraction in  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> and  $\alpha$ -Fe were calculated by XRD patterns using Rietveld refinement by JADE 9.0 (Materials Data, Inc.). The XRD patterns of each sample were obtained with a scan rate of 4°/min from 10° to 90°. Morphology of the resulting particles was observed by using field emission scanning electron microscopy (FESEM). The magnetic properties were analyzed by a vibrating sample magnetometer (VSM, LakeShore, VSM 7407) at room temperature with an



**Fig. 1.** (Color online) Schematic for the fabrication procedure of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> particles via spray drying followed by annealing in air, H<sub>2</sub> reduction and NH<sub>3</sub> nitridation.

external applied field of 15 kOe. To extract structural information and phase purity of  $Fe_{16}N_2$  powders prepared by optimized synthetic condition, we performed powder x-ray diffraction in 3D beamline of Pohang accelerator laboratory (PAL). Scan range was from 10° to 70°, and scan step was 0.05°. The wavelength of x-ray beam was set to 1.23983 Å. With the diffraction patterns, Rietveld refinement was conducted to obtain structural information and phase purity [10]. We used structural parameters of  $\alpha$ -Fe and  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> in the previous study [11].

## 3. Results and Discussion

Figure 1 illustrates the procedure to prepare  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> particles by using spray drying process combined with hydrogen (H<sub>2</sub>) reduction and ammonia (NH<sub>3</sub>) nitridation.



**Fig. 2.** SEM images of spray-dried Fe precursor particles showing (a) solid and (b) hollow structures, (c), (d) their oxidized particles after annealing in air, (e), (f) corresponding reduced powders and (g), (h) subsequently nitrogenated particles in  $NH_3$  stream, respectively.

The first step involves the spray drying of Fe precursor solution. The droplet containing Fe salt was sprayed in the hot chamber, resulting in formation of precursor powder with solid or hollow sphere structure by evaporation of the liquid in the droplets. In the second step, the resulting Fe salt powders were annealed in the air in order to form Fe oxide particles. Then, reduction of the samples in H<sub>2</sub> stream was conducted, followed by nitridation of the reduced particles with NH<sub>3</sub> gas. Finally,  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> microspheres were obtained with two different microstructures.

The morphology of the Fe salt powders prepared by spray drying is shown in Fig. 2(a) and (b). The SEM images show that the spray-dried particles consist of microspheres with sizes ranging from 500 to 2000 nm (Fig. S1). The particles have a smooth surface and exhibit little aggregation. From the broken part of a microsphere of Fig. 2(b), it is confirmed that hollow spherical structure was formed by drying ethanol-water mixture solvent. Addition of alcohol into the salt solution leads to form hollow particles since it induces rapid evaporation of liquid before the solid diffuses toward the droplet center [12]. Fig. 2(c) and (d) show post-annealed powders in the air, which surface was roughened by growth of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (Fig. S2). As shown in Fig. 2(e) and (f), the agglomeration and coarsening of nanocrystallites on the surface was occurred during reduction in a H<sub>2</sub> atmosphere. Subsequently nitrogenated particles were shown in Fig. 2(g) and (h), where no significant particle growth was observed. In addition, the spherical shape and microstructure (solid and hollow sphere) were maintained regardless of phase transformation in the second step.

For the synthesis of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> magnetic powders, the reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders was optimized. Figure 3(a) and (b) show the XRD patterns of the initial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles with solid and hollow structure and samples reduced at various temperatures for 4 h. With increasing reduction temperature,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> begins to transform into the mixture of Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe at around 300 °C in both solid and hollow particles. As the reduction temperature



**Fig. 3.** (Color online) XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe particles with (a) solid structures (S-Fe<sub>2</sub>O<sub>3</sub> and S-Fe) and (b) hollow structures (H-Fe<sub>2</sub>O<sub>3</sub> and H-Fe) under various H<sub>2</sub> reduction temperatures for 4 h, (c) H<sub>2</sub> reduced at different temperatures and subsequently nitrogenated solid particles (S-H<sub>2</sub>-temperature-NH<sub>3</sub>). (d) phase fraction (wt%) of the corresponding particles after nitridation (145 °C, 15 h).

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is raised to 320 °C, all the phase of hollow spheres transforms into  $\alpha$ -Fe while solid spheres still exhibit Fe<sub>3</sub>O<sub>4</sub> peak. Above 330 °C, only α-Fe phase was detected in both samples. To optimize the reduction temperature, NH<sub>3</sub> nitridation at 145 °C for 15 h was conducted by using α-Fe solid powders reduced at 330, 340 and 370 °C. As shown in Fig. 3(c), the main XRD peaks of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phases were detected in all the three samples. With increasing the reduction temperature, the intensities of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>{220} peak were increased as compared to  $\alpha$ "- $Fe_{16}N_2$ {202} intensities. The peak is overlapped with the one of  $\alpha$ -Fe{110} phase, which means the existence of residual  $\alpha$ -Fe phase in the powders [5]. The result corresponds to the phase fraction of Fig. 3(d). 100 % transformation into a"-Fe16N2 was occurred in the samples reduced at 330 °C. In contrast, residual α-Fe was remained in the samples reduced at relatively high temperature such as 340 °C to 370 °C after nitridation. It is speculated that high temperature induces the agglomeration and growth of nanocrystallites during reduction, which led to decrease nitiding efficiency of  $\alpha$ -Fe during nitridation. The phenomenon was analogous to what has been reported in the previous study, showing the H<sub>2</sub> reduction temperature has a significant effect on the efficiency of nitridation process [6].

In order to obtain high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>, the reduced  $\alpha$ -Fe particles were nitrided under various reaction conditions. Nitriding temperatures in a range of 145 °C-175 °C and nitriding time in a range of 6 h-18 h were investigated as shown in Fig. 4. The solid powders nitrided at 145 °C for 15 h exhibit clear XRD patterns of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> as shown in Fig. 4(a), indicating the successful synthesis of single phase  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> particles. Upon increasing the nitriding temperature above 145 °C, however, the peak



**Fig. 4.** (Color online) XRD patterns and magnetic properties (coercivity, saturation magnetization and energy product) for at different nitrading conditions for  $\alpha$ -Fe particles; (a), (c) samples prepared by different nitridation temperatrue (S-H<sub>2</sub>-NH<sub>3</sub>-temperature) for 15 h and (b), (d) samples nitrided at 145 °C for various time conditions (S-H<sub>2</sub>-NH<sub>3</sub>-time).

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intensity of  $\alpha$ -Fe{110} combined with Fe<sub>16</sub>N<sub>2</sub>{220} phase was increased in the 160 °C condition. In addition, at 175 °C nitridation, γ'-Fe<sub>4</sub>N phase was appeared as well as the broadening  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>{202} peak was occurred. Phase fraction graph (Fig. S3(a)) obtained from the XRD patterns shows the similar tendency to increase the soft magnetic phases by increasing the reaction temperature. On the basis of the results, high temperature condition is not helpful to transform  $\alpha$ -Fe into  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phase with narrow phase width. Occupying the interstitial sites of Fe with only 11.1 at.% nitrogen is required to develop the metastable phase [3]. At the elevated temperature, thus,  $\gamma$ '-Fe<sub>4</sub>N as an over-nitrided component or  $\alpha$ -Fe appeared as reported previously [13]. The corresponding magnetic properties of Fig. 4(c) exhibit the clear dependence on the nitrogenation temperature. As the nitriding temperature is increased, the magnetic properties of the resulting powders were deteriorated, which is attributed to both increase in soft magnetic phases and decrease of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>. Based on these results, 145 °C was chosen to be the best condition and used in further nitriding time optimization. Figure 4(b) show the decrease in peak intensities of  $\alpha$ -Fe{110} overlapped with  $Fe_{16}N_2$ {220} phase upon increasing the reaction time from 6 h to 15 h. Prolonged nitridation for 18 h, however, exhibit the increased intensity of  $\alpha$ -Fe{110} peak, again. To clarify the effect of nitriding time on phase formation of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>, phase fraction was



**Fig. 5.** (Color online) Rietveld refinements of the XRD pattern (obtained from 3D, PAL) for (a), (c) solid and (b), (d) hollow  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> nanoparticle samples prepared by the optimized condition (145 °C for 15 h in pure NH<sub>3</sub> flow). The top row of the Bragg markers is for the  $\alpha$ -Fe majority phase, with a second row shown for  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>.

**Table 1.** Calculated parameters for Rietveld refinement of XRD spectra for  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> spheres with solid and hollow structure prepared by the optimized conditions.

	Solid		Hollow	
_	$\alpha$ "-Fe <sub>16</sub> N <sub>2</sub>	α-Fe	$\alpha$ "-Fe <sub>16</sub> N <sub>2</sub>	α-Fe
Phase fraction (wt %)	95.52	4.48	91.21	8.79
<i>a</i> (Å)	5.7202	2.8676	5.7200	2.8675
<i>c</i> (Å)	6.2903	-	6.2894	-
Volume (Å <sup>3</sup> )	205.8298	23.5805	205.7767	23.5793
Bragg R-factor	5.11710	5.79509	7.61465	4.65648
Rf-factor	11.0269	3.64918	16.6273	5.69601
$\chi^2 = (\mathbf{R}_{wp}/\mathbf{R}_{exp})^2$	0.185		0.203	

estimated from XRD patterns as shown in Fig. S3(b). Significant amount of residual  $\alpha$ -Fe over 25 wt% was remained in the samples nitrided below 9 h whereas the 18 h reaction time led to small amount of  $\alpha$ -Fe residue. In addition, most of  $\alpha$ -Fe was transformed into  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> in 15 h nitrogenation. The magnetic properties of the resulting powders are clearly dependent on the nitridation time as shown in Fig. 4(d). As the time increase from 6 h to 15 h, the magnetic propterties improves significantly and decrease again at 18 h. The results are attributed to the change in phase fraction of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> from  $\alpha$ -Fe. This result demonstrates that the nitridation at 160 °C for 15 h is effective to obtain high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> particles.  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> particles prepared by the optimum condition possess saturation magnetization of 174 emu/g (intrinsic  $J_s \sim 176$ emu/g), coercivity of 1471 Oe and maximum energy product of 2.25 MGOe under the magnetic field 15 kOe.

To determine the phase fraction of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> with more accuracy, synchrotron based x-ray scattering experiment and corresponding Rietveld refinement analysis was conducted as shown in Fig. 5 and Table 1. The results show the samples prepared by the optimized condition consist of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> with phase fraction of 95.52 wt% in solid structure and 91.21 wt% in hollow structure. Thus, high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> phases can be produced by spray drying combined by phase transformation process.

#### 4. Conclusions

In summary, we have presented a facile method to synthesize high purity  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> powders via spray drying combined with H<sub>2</sub> reduction and NH<sub>3</sub> nitridation. The synthetic strategy has several notable features. First, metal salt powders with controllable sphere structures can be precisely produced. Second, the spherical microstructure was maintained without significant aggregation through all the process involving phase transformation. Third, the

resulting particles contain  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> with a phase fraction over 91 wt% by optimized reduction and nitridation. Thus, the strategy used in this work would pave the way for the industrial production of rare-earth free magnetic materials based on spray drying.

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