

Article

Production of Rare-Earth-Free Iron Nitride Magnets (α'' -Fe₁₆N₂)

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Abstract: To realize rare-earth-free magnets, we studied iron nitride (α'' -Fe₁₆N₂) magnets, which contain no rare-earth elements. Fe-N powder with the α'' -Fe₁₆N₂ phase has a high saturation magnetization comparable to high-performance rare-earth magnets but is not stable at temperatures over 539 K. We consolidated Fe-N powder into bulk material at low temperatures by spark plasma sintering (SPS) and spark plasma sintering with dynamic compression (SPS-DC). Fe-N magnets were successfully obtained at low temperatures of 373–573 K. The magnets produced by the SPS-DC method had a higher density than those produced by the SPS method. The density of the magnets produced by the SPS-DC method increased as the consolidation temperature increased. That produced at 373 K had a saturation magnetization of 1.07 T with a coercivity of 0.20 MA/m.

Keywords: iron nitride; spark plasma sintering; coercivity

1. Introduction

The industrial use of neodymium magnets composed of Nd₂Fe₁₄B is expanding rapidly and globally in automotive, robotic, industrial, medical, and consumer electrical applications [1–3]. The high demand for electric and hybrid vehicles is concerning owing to the shortage of rare-earth supplies, which are essential for Nd-Fe-B magnet production, being concentrated in specific countries. This concentration is driving research and development for alternative permanent magnets with less or no rare-earth elements to replace Nd-Fe-B magnets.

New rare-earth-free iron-based magnets, such as those with L1₀-FeNi and α'' -Fe₁₆N₂ phases, are considered prospective alternatives to high-performance Nd-Fe-B magnets [4,5]. The superiority of Nd-Fe-B magnets arises from the Nd₂Fe₁₄B phase, which has a large saturation magnetization, a high anisotropy constant, and a high Curie temperature [6]. Table 1 shows the intrinsic magnetic properties of the Nd₂Fe₁₄B, L1₀-FeNi, and α'' -Fe₁₆N₂ phases.

The L1₀-FeNi phase, known as tetrataenite, is found in iron meteorites [7]. It has a face-centered tetragonal structure, in which the layer of Fe atoms and the layer of Ni atoms stack alternately along the c-axis of the structure [8]. It has a high saturation magnetization similar to that of the Nd₂Fe₁₄B phase and a higher Curie temperature [9]. Although its anisotropy constant is smaller than that of the Nd₂Fe₁₄B phase, it is high enough to support a permanent magnetic material. Thus, the L1₀-FeNi phase is an ideal alternative for high-performance Nd-Fe-B magnets, but it cannot be easily obtained by conventional solidification techniques, because that found in iron meteorites forms naturally at an extremely slow cooling rate of 1 K/10⁶ years. In recent years, a new technique for producing the single L1₀-FeNi phase has been developed [10]. Named the NITE (nitrogen insertion and topotactic extraction) method, it involves the nitriding of the FeNi phase and denitriding from the resultant FeNiN phase to the L1₀-FeNi phase. L1₀-FeNi powder prepared by the NITE method has a high saturation magnetization of 139 Am²/kg with a



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coercivity of 0.14 MA/m. Further work to improve the magnetic properties of the L1₀-FeNi powder is underway [11].

Table 1. Intrinsic magnetic properties of Nd₂Fe₁₄B, L1₀-FeNi, and α'' -Fe₁₆N₂ phases.

Phase	Saturation Magnetization I_s (T)	Anisotropy Constant K_1 (MJm ^{−3})	Curie Temperature T_c (K)
Nd ₂ Fe ₁₄ B	1.6	4.5	586
L1 ₀ -FeNi	1.6	1.0	773
α'' -Fe ₁₆ N ₂	2.4	1.0	810

Among other alternatives for high-performance Nd-Fe-B magnets, the α'' -Fe₁₆N₂ phase is the most promising candidate, since it can be prepared by the nitrogenation of iron without the need of rare metals. The crystal structure of the α'' -Fe₁₆N₂ phase is the body-centered tetragonal structure, in which N occupies the interstitial sites of the body-centered cubic lattice of the α -Fe phase in an ordered manner [12]. The α'' -Fe₁₆N₂ phase has a much higher saturation magnetization than the Nd₂Fe₁₄B phase (Table 1). Although the high value was first reported in 1972 [5], it was not confirmed until 1991 [13]. Its anisotropy constant is similar to that of the L1₀-FeNi phase but is smaller than that of the Nd₂Fe₁₄B phase. Its Curie temperature is higher than that of the Nd₂Fe₁₄B phase [14]. Thus, the α'' -Fe₁₆N₂ phase is also an ideal alternative to high-performance Nd-Fe-B magnets. It cannot be easily obtained by conventional solidification techniques because it is the metastable phase. The disadvantage of the α'' -Fe₁₆N₂ phase is its low decomposition temperature, but it can be obtained by (1) nitrogenation: α -Fe phase $\rightarrow$ γ -FeN phase; (2) quenching: γ -FeN phase $\rightarrow$ α' -FeN phase; and (3) long tempering: α' -FeN phase $\rightarrow$ α'' -Fe₁₆N₂ phase [15]. However, it is not possible to obtain a pure α'' -Fe₁₆N₂ phase in this way because the solubility of N in the γ -FeN phase is less than required (12.5%). Thus, studies of the α'' -Fe₁₆N₂ phase have used various thin-film processing techniques [16–19]. α'' -Fe₁₆N₂ powders have been produced by chemical synthesis, that is, the reduction of nano-sized α -Fe₂O₃ powders followed by the nitriding of the resulting fine α -Fe powders [20,21]. α'' -Fe₁₆N₂ powder has a high saturation magnetization of 234 Am²/kg at 5 K and a magnetocrystalline anisotropy constant of 9.6×10^5 J/m³ [20]. We have recently revealed its hard magnetic properties: powder prepared by chemical synthesis has a high saturation magnetization of 168 Am²/kg with a coercivity of 0.21 MA/m [22].

Here, we aimed at producing rare-earth-free magnets of Fe-N powder with the α'' -Fe₁₆N₂ phase. Nd-Fe-B magnets have been commercially produced by the conventional sintering of green compacts of Nd-Fe-B powder at high temperatures [6]. The conventional sintering process cannot be used to produce Fe-N bulk magnets, however, because the α'' -Fe₁₆N₂ phase is metastable and decomposes into the α -Fe and γ -Fe₄N phases at high temperatures. However, a newly developed rapid sintering technique called spark plasma sintering (SPS) can consolidate powders at lower temperatures in a short period [23]. Sm-Fe-N powder, which is unstable at high temperatures, was consolidated into bulk magnets by the SPS method [24–26] and at lower consolidation temperatures by the modified SPS with dynamic compression (SPS-DC) method [27]. Here, we investigated the possibility of producing rare-earth-free magnets of Fe-N powder using the SPS and SPS-DC methods. The structures and magnetic properties of the Fe-N magnets are discussed.

2. Materials and Methods

Fe-N powder with the α'' -Fe₁₆N₂ phase (Future Materialz Co., Ltd., Tokyo, Japan) was prepared by the reduction of nano-sized α -Fe₂O₃ powder under a hydrogen atmosphere at 643–683 K for 9–12 h, followed by the nitriding of the resulting fine α -Fe powder at 408–418 K for 15 h under an ammonia atmosphere. Small amounts of the powder were poured into a carbon die and then placed in the chamber of the SPS apparatus (Plasman,

S. S. Alloy, Hiroshima, Japan). Figure 1 shows the temperature–pressure–time diagram of the Fe-N magnets produced by the SPS method. In a vacuum, the temperature of the die was increased from room temperature to the consolidating temperature of 373–573 K over 300 s and then held at that temperature for 300 s by applying a pulsed electric current. A pressure of 100 MPa was applied during heating and sintering (static pressing).

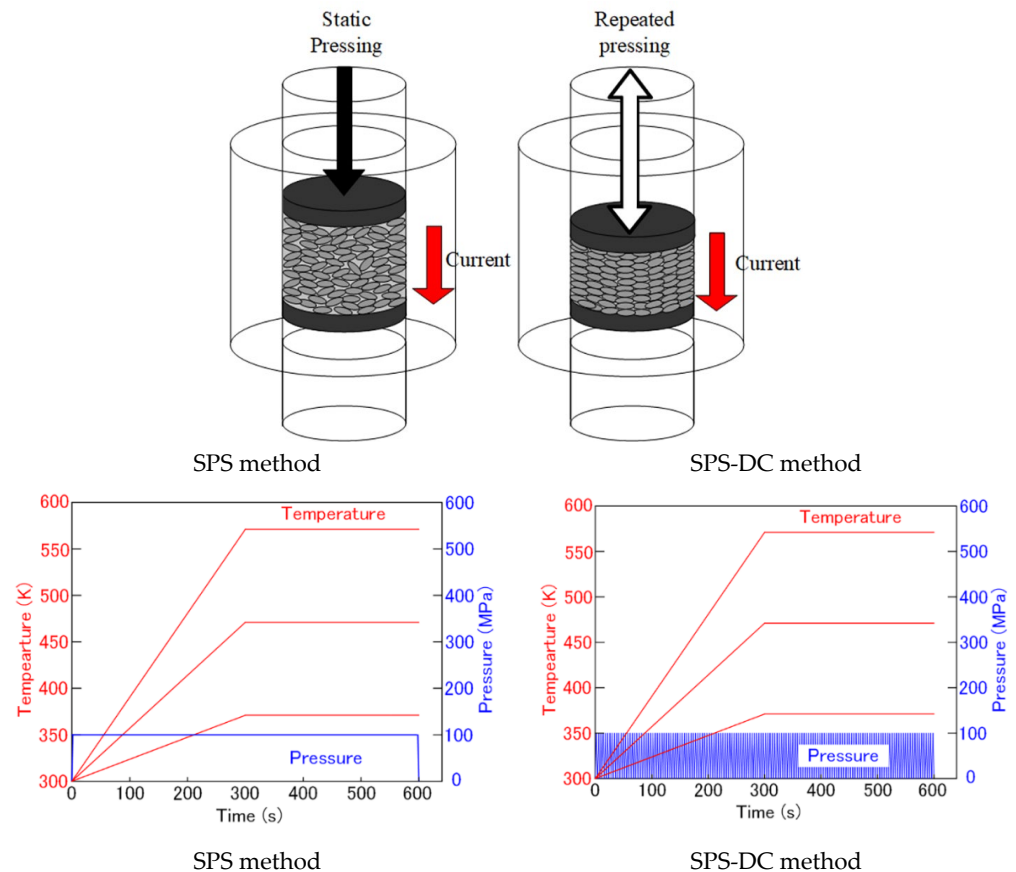


Figure 1. The temperature–pressure–time diagram of the Fe-N magnets produced by the SPS and SPS-DC methods.

In the SPS-DC method, small amounts of the powder were poured into a cemented carbide die. The temperature–pressure–time diagram of the Fe-N magnets produced by the SPS-DC method is also shown in Figure 1. In a vacuum, the temperature of the die was increased from room temperature to the consolidating temperature of 373–573 K over 300 s and then held at that temperature for 300 s by applying a pulsed electric current. A pressure of 100 MPa was cyclically applied 300–600 times to the powder during heating and sintering (repeated pressing) [28]. Bulk specimens of the Fe-N powder were taken out of the die after it had cooled to room temperature in the depressurized SPS chamber.

The densities of the magnets were measured by the Archimedes method on an electronic balance. The morphology of the specimens was examined under an optical microscope, a scanning electron microscope (SEM: JEOL, JSM-IT300LA, Tokyo, Japan), and a transmission electron microscope (TEM: JEOL, JEM-2010F, Tokyo, Japan). The crystallographic structure of the specimens was investigated by X-ray diffraction (XRD: Rigaku, MiniFlex600, Tokyo, Japan) with Cu K α radiation. The thermal stability of the specimens was investigated by differential thermal analysis (DTA, STA7300, Hitachi-hightech, Tokyo, Japan). The magnetic properties of the specimens were examined by a vibrating sample magnetometer (VSM: Riken Denshi, BHV-525RSCM, Tokyo, Japan). In the magnetic measurements, the powder was fixed in paraffin, and the magnets were cut into rod-like specimens (0.5 $\times$ 1 $\times$ 10 mm) to avoid the need to correct for demagnetization.

3. Results and Discussion

Since the Fe-N powder was prepared by chemical synthesis from the α -Fe₂O₃ powder, it may contain some residual α -Fe₂O₃ or α -Fe powder. Thus, we examined the structures of the initial Fe-N powder by XRD analysis. Figure 2 shows the results of the XRD study. In the XRD pattern of the Fe-N powder, all of the diffraction peaks corresponded with the α'' -Fe₁₆N₂ phase (body-centered tetragonal structure). No other peaks of the α -Fe or α -Fe₂O₃ phase are present, confirming that the Fe-N powder in this study consisted solely of the α'' -Fe₁₆N₂ phase.

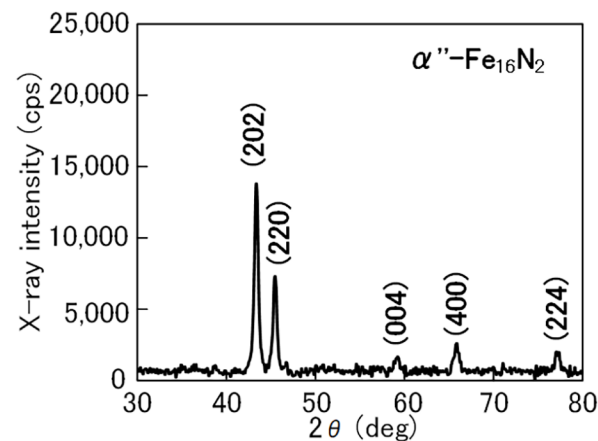


Figure 2. The XRD pattern of the Fe-N powder.

Figure 3 shows the hysteresis loop of the Fe-N powder. Fe-N powder has a high saturation magnetization of 1.53 T, comparable to that of Nd-Fe-B magnets [28]. Although the observed value is smaller than the expected value of the α'' -Fe₁₆N₂ phase (Table 1), it is comparable to the reported saturation magnetization of Fe₁₆N₂ powder prepared by Dirba et al. The difference between the theoretical and observed values is the result of the oxidation of Fe-N powder [21]. Fe-N powder has a coercivity of 0.21 MA/m, smaller than that of Nd-Fe-B magnets but larger than that of commercial Alnico magnets. This value is slightly higher than that of the α'' -Fe₁₆N₂ powder (0.18 MA/m) prepared by Dirba et al. Thus, Fe-N powder is a promising candidate for future rare-earth-free magnets.

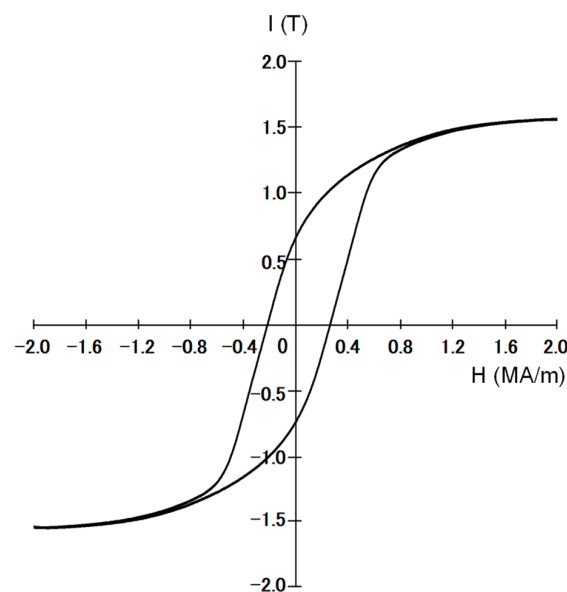


Figure 3. The hysteresis curve of the Fe-N powder.

The thermal stability of the Fe-N powder is a crucial criterion for producing bulk magnets. Thus, the thermo-magneto-gravimetric curve of the Fe-N powder was examined. The result is shown in Figure 4. In the thermo-gravimetric curve, four peaks (T_1 , T_2 , T_3 , and T_4) are observed. The summary of the thermomagnetic studies of the Fe-N powder is shown in Table 2. The T_1 peak is considered to be the decomposition temperature of the α'' -Fe₁₆N₂ phase: α'' -Fe₁₆N₂ $\rightarrow$ α -Fe + γ -Fe₄N. Its decomposition temperature was 539 K, much lower than the Curie temperature of the α'' -Fe₁₆N₂ phase (810 K) [29] but close to another reported value (523 K) [12]. The T_2 peak is considered to be the Curie temperature of the γ -Fe₄N phase [30]. The T_3 peak is considered to be the eutectoid reaction temperature (γ -Fe $\rightarrow$ α -Fe + γ -Fe₄N). The T_4 peak is considered to be the Curie temperature of the α -Fe phase. This confirms that the α'' -Fe₁₆N₂ phase decomposed into the Fe₄N and α -Fe phases at 539 K.

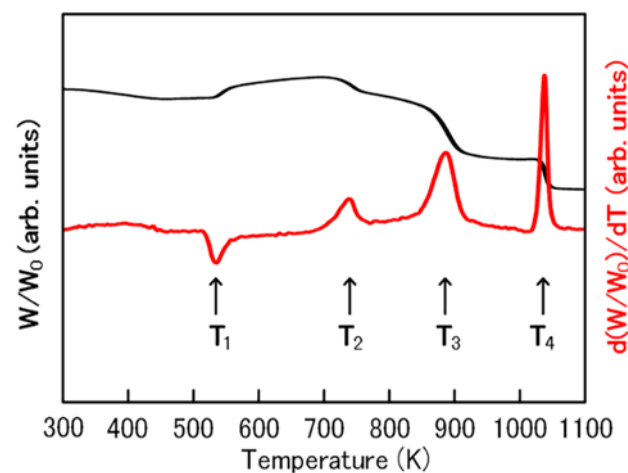


Figure 4. The thermo-gravimetric curve of the Fe-N powder.

Table 2. The summary of the thermo-gravimetric studies of the Fe-N powder.

Temperature	Phenomenon
T_1 (539 K)	Decomposition temperature (α'' -Fe ₁₆ N ₂ $\rightarrow$ α -Fe + Fe ₄ N)
T_2 (743 K)	Curie temperature (T_c of γ -Fe ₄ N phase)
T_3 (885 K)	Eutectoid reaction temperature (γ -Fe $\rightarrow$ α -Fe + γ -Fe ₄ N)
T_4 (1043 K)	Curie temperature (T_c of α -Fe phase)

Since it was found that the α'' -Fe₁₆N₂ phase in the Fe-N powder decomposed into the Fe₄N and α -Fe phases at 539 K, the Fe-N powder was consolidated by the SPS method at 373 K and 473 K (below the decomposition temperature of the α'' -Fe₁₆N₂ phase) and 573 K (just above it).

Figure 5 shows photographs of the powder and the resulting magnet. Even at a consolidation temperature as low as 373 K, the SPS method successfully produced an Fe-N magnet. The Fe-N magnets were also obtained at 473 and 573 K by the SPS method.

Although the Fe-N powders were consolidated at low sintering temperatures, the Fe-N magnets were nevertheless successfully produced, and the results from examining their densities are shown in Figure 6. The density of the magnets increased from 5.94 Mg/m³ (relative density of 79.8%) at 373 K to 6.06 Mg/m³ (81.5%) at 573 K. This suggests that higher consolidating temperatures promote the densification of Fe-N magnets by the SPS method. However, the poor thermal stability of the α'' -Fe₁₆N₂ phase prevents any further increase in temperature.

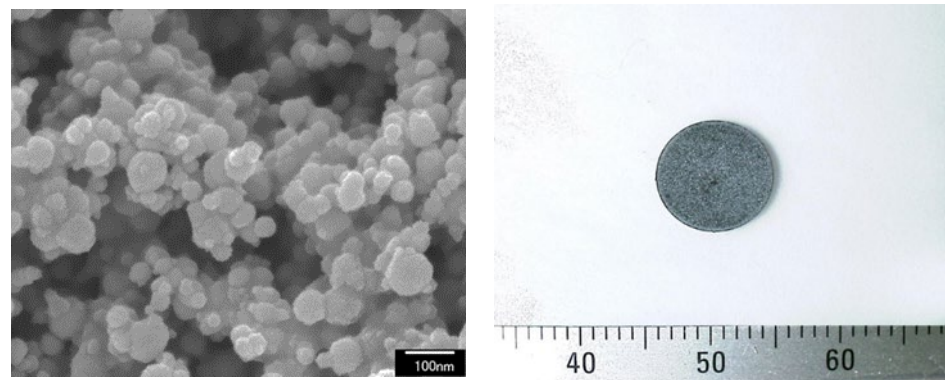


Figure 5. Photographs of the Fe-N powder (**left**) and the Fe-N magnet (**right**) produced from the Fe-N powder at 373 K by the SPS method.

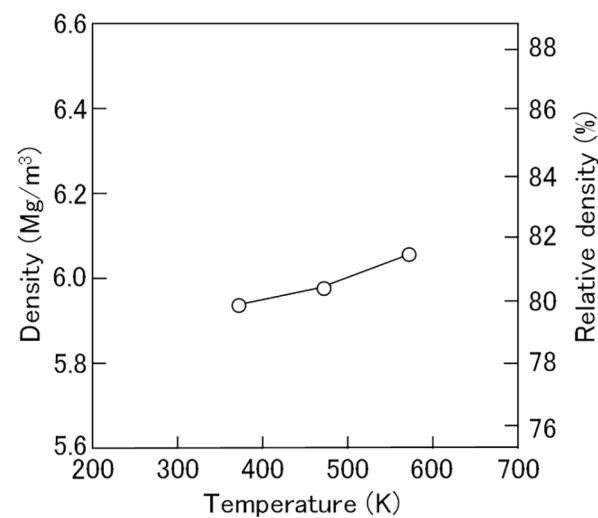


Figure 6. The dependence of the absolute density and relative density of the Fe-N magnets produced by the SPS method on the consolidation temperature.

In order to increase the density of the Fe-N magnets, the SPS-DC method was applied for the production of the Fe-N magnets. In the SPS-DC method, the density of the Fe-N magnets may be increased by repeated pressing (Figure 1). A photograph of an Fe-N magnet prepared at 373 K by the SPS-DC method is shown in Figure 7. The SPS-DC method also produced Fe-N magnets.

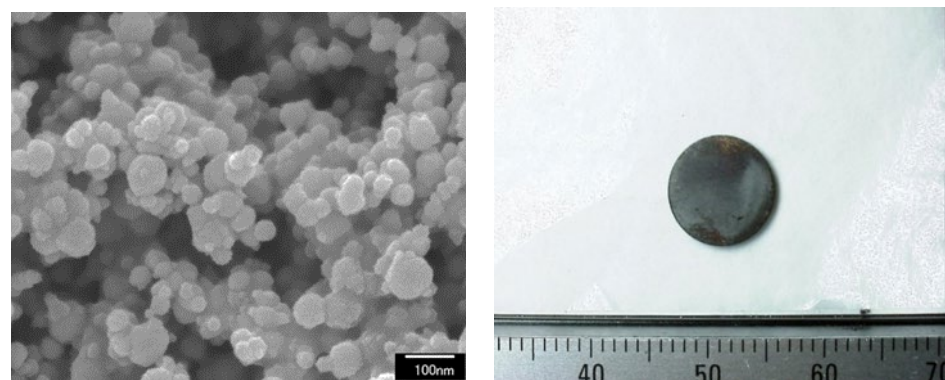


Figure 7. Photographs of the Fe-N powder (**left**) and the Fe-N magnet (**right**) produced from the Fe-N powder at 373 K by the SPS-DC method.

The densities of the Fe-N magnets produced by the SPS and SPS-DC methods are compared in Figure 8. At all consolidation temperatures, the density of the Fe-N magnet was higher in the SPS-DC method than in the SPS method and increased from 6.06 Mg/m³ (relative density of 81.5%) at 373 K to 6.12 Mg/m³ (82.3%) at 573 K. The magnets produced by the SPS-DC method had a relative density of >80% even when the powder was consolidated at as low as 373 K, as confirmed by the TEM images (Figure 9), in which the amount of Fe-N powder particles, indicative of the density, seems to increase with the consolidation temperature.

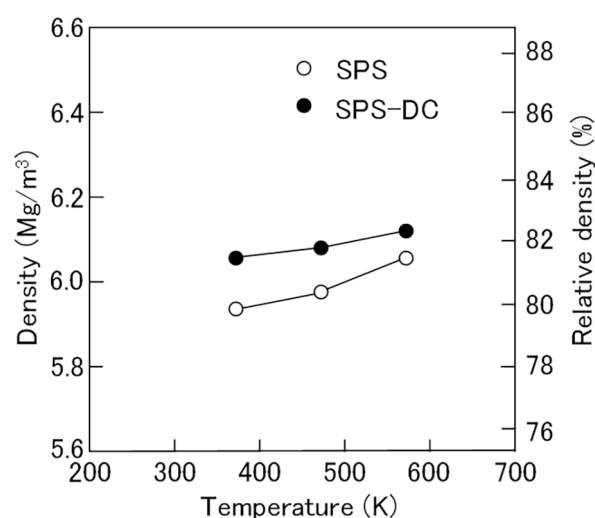


Figure 8. The dependence of the absolute density and relative density of the Fe-N magnets produced by the SPS and SPS-DC methods on the consolidation temperature.

There are two ways to perform the sintering process: solid-state sintering and liquid-phase sintering [31]. It is known that rare-earth magnets have been produced by liquid-phase sintering [32]. On the other hand, iron parts for machines are usually produced by solid-state sintering. Since no liquid phase is involved in the sintering of Fe-N powder, the sintering mechanism is solid-state sintering, in which the powder particles react with each other. In order to increase the density of the Fe-N magnet, it is necessary to add the additives that act as the liquid phase during the sintering.

We also examined the structures and magnetic properties of the magnets produced by the SPS-DC method. Figure 10 shows the XRD patterns of the Fe-N magnets produced by the SPS-DC method. In the XRD pattern of the magnet produced at 373 K, all of the diffraction peaks observed correspond with the α'' -Fe₁₆N₂ phase. The absence of the α -Fe or Fe₃O₄ phase suggests that the magnet produced at 373 K consisted of the α'' -Fe₁₆N₂ phase. The diffraction peaks of the α'' -Fe₁₆N₂ phase are seen in the XRD pattern of the magnet produced at 473 K, along with the peaks of the Fe₃O₄ phase. This suggests that the magnet produced at 473 K consisted of the α'' -Fe₁₆N₂ phase together with small amounts of the Fe₃O₄ phase. On the other hand, the peaks of the α'' -Fe₁₆N₂ phase are absent in the XRD pattern of the magnet produced at 573 K, but those of the α -Fe, Fe₄N, and Fe₃O₄ phases are present, because the consolidation temperature of 573 K was higher than the decomposition temperature of the α'' -Fe₁₆N₂ phase. Therefore, it is essential to consolidate the Fe-N powder below the decomposition temperature of the α'' -Fe₁₆N₂ phase.

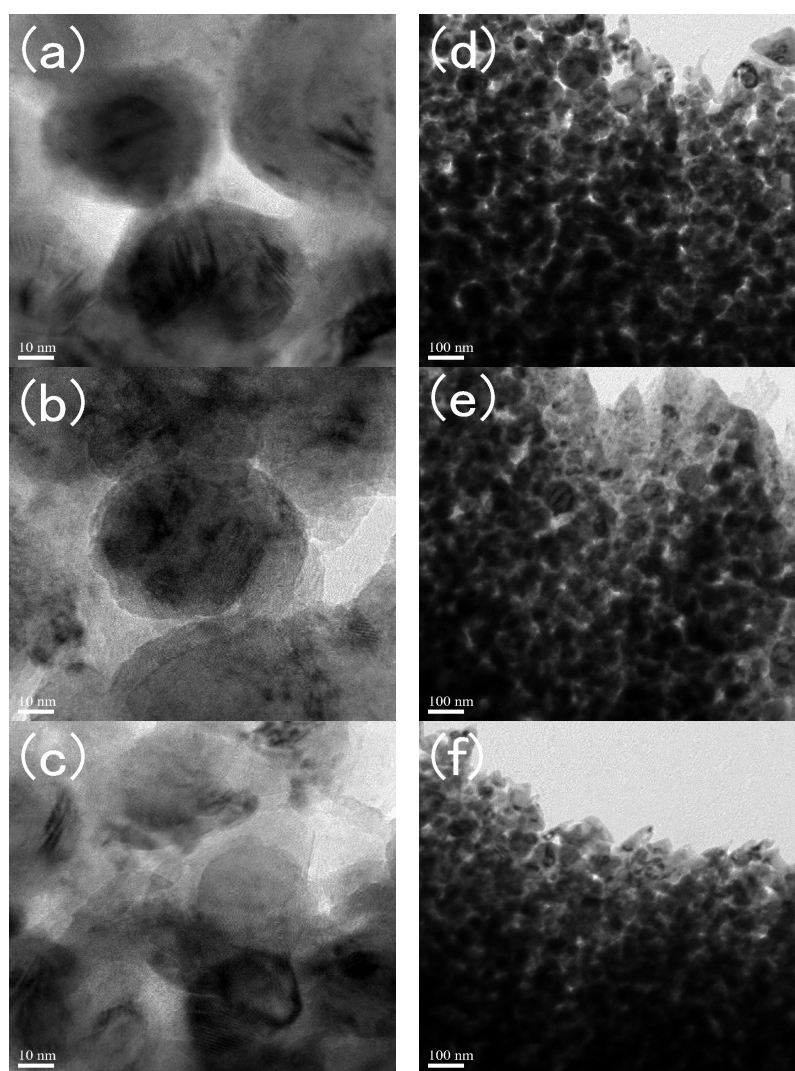


Figure 9. TEM images of the Fe-N magnets produced at (a,d) 373 K, (b,e) 473 K, and (c,f) 573 K by the SPS-DC method. The images represent the original Fe-N powder particles where the particles' surfaces melted and bonded together.

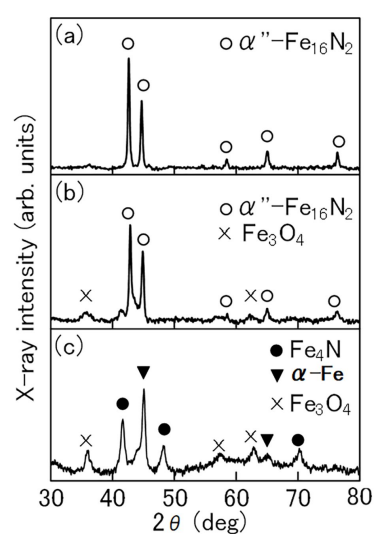


Figure 10. The XRD patterns of the Fe-N magnets produced at (a) 373 K, (b) 473 K, and (c) 573 K by the SPS-DC method.

Figure 11 shows the thermo-gravimetric curves of the Fe-N magnets produced by the SPS-DC method. These thermomagnetic curves show clear magnetic transitions (T_1 , T_2 , T_3 , and T_4): T_1 is the decomposition temperature of the α'' -Fe₁₆N₂ phase, T_2 is the Curie temperature of the γ -Fe₄N phase, T_3 is the eutectoid reaction temperature, and T_4 is the Curie temperature of the α -Fe phase. These results correspond to the thermomagnetic studies of Fe-N powders (Figure 4, Table 2). In the thermomagnetic curve of the magnets produced at 373 K and 473 K, four magnetic transitions (T_1 , T_2 , T_3 , and T_4) are observed. On the other hand, only three magnetic transitions (T_2 , T_3 , and T_4) are seen in the thermomagnetic curve of the magnet produced at 573 K. This confirms that the magnet produced at 573 K did not contain the α'' -Fe₁₆N₂ phase. Since the consolidation temperature of 573 K was higher than the decomposition temperature of the α'' -Fe₁₆N₂ phase, the α'' -Fe₁₆N₂ phase decomposed into the α -Fe and Fe₄N phases during the consolidation.

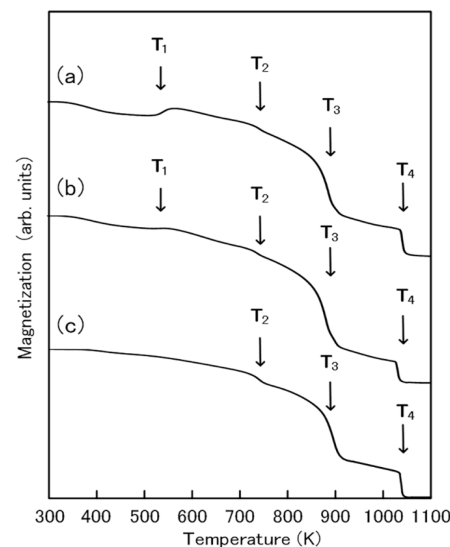


Figure 11. Thermo-gravimetric curves of the Fe-N magnets produced at (a) 373 K, (b) 473 K, and (c) 573 K by the SPS-DC method.

Figure 12 shows the hysteresis loops of the Fe-N magnets produced by the SPS-DC method. The magnetic properties of the Fe-N magnets are summarized in Table 3. The Fe-N magnets produced at 373 K and 473 K had wide hysteresis loops, but that produced at 573 K had a narrow hysteresis loop. Since the consolidation temperature of 573 K is above the decomposition temperature of the α'' -Fe₁₆N₂ phase, this narrow hysteresis loop was due to the decomposition of the α'' -Fe₁₆N₂ phase during the consolidation. The magnet produced at 373 K showed a saturation magnetization of 1.07 T with a coercivity of 0.20 MA/m. In contrast, the Fe-N magnet produced at 473 K showed a saturation magnetization of 1.12 T with a coercivity of 0.17 MA/m. Although the saturation magnetization of the Fe-N powder is comparable to that of Nd-Fe-B magnets, that of the Fe-N magnet produced by the SPS-DC method was smaller than that of the Nd-Fe-B magnets, owing mainly to the lower density of the Fe-N magnets, of around 80%. Thus, the next step is to increase the density of the Fe-N magnets.

Table 3. The magnetic properties of the Fe-N magnets produced at 373, 473, and 573 K by the SPS-DC method.

Sintering	Saturation Magnetization I_s (T)	Coercivity H_c (MA/m)
373 K	1.07	0.20
473 K	1.12	0.17
573 K	1.06	0.05

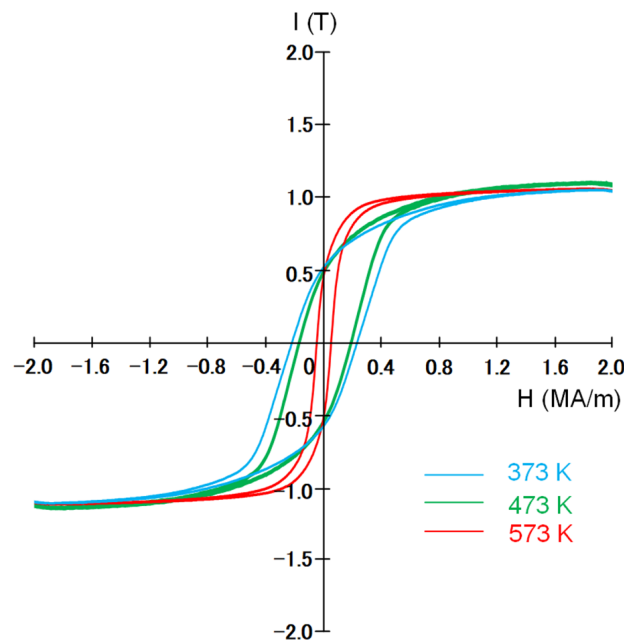


Figure 12. The hysteresis curves of the Fe-N magnets produced at 373, 473, and 573 K by the SPS-DC method.

4. Conclusions

This study confirmed that the Fe-N powder with the α'' -Fe₁₆N₂ phase shows a high saturation magnetization of 1.53 T with a coercivity of 0.21 MA/m. Thus, we aimed at producing rare-earth-free magnets from it. The SPS-DC method can consolidate the Fe-N powder into bulk magnets at as low as 373 K. The resultant Fe-N magnet exhibits a high saturation magnetization of 1.07 T with a coercivity of 0.20 MA/m. The achieved magnetic properties of the Fe-N magnet were not yet comparable to those of Nd-Fe-B magnets. Further work is still necessary to improve the magnetic properties of the Fe-N magnet.

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Conflicts of Interest: Author Hitoshi Yamamoto was employed by the company Neoji-consul. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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