Thermal stability of Sm$_2$Fe$_{17}$N$_3$ magnet powders

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Abstract. The time dependence of coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powder compacts exposed in air and in He gas (oxygen-free atmosphere) was investigated at 110°C and 150°C. At 110°C in air, coercivity rapidly decreased within 5 h, reached a minimum at around 5h, and then gradually increased over 1000 h. Similar behavior was observed in the He gas atmosphere, although the minimum coercivity value was higher than that in air exposure. Since the oxygen content was confirmed to be constant, the coercivity minimum behavior is independent of oxidation. The temperature dependence of the anisotropy field, coercivity and saturation magnetization of fine Sm$_2$Fe$_{17}$N$_3$ powder compacts was measured in air at 110°C and analyzed by using Kronmüller’s formula.

1. Introduction
Sm$_2$Fe$_{17}$N$_3$ compounds are good candidates for high performance magnets because of their high saturation magnetization and strong uniaxial anisotropy [1,2]. However, it is fairly difficult to obtain fully dense magnets, because Sm$_2$Fe$_{17}$N$_3$ compounds decompose into SmN and α-Fe when heated above 600°C, and in particular, the coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powder (about 2 µm) is unstable even at 200°C [3]. For this reason, application of Sm$_2$Fe$_{17}$N$_3$ compounds is currently limited to resin bonded magnets. Recently, several researchers have reported Sm$_2$Fe$_{17}$N$_3$ powders having high coercivity of 10-23 kOe [4-7]. These works demonstrate the potential for application not only to the bonded magnets, but also to excellent bulk magnets rivalling the Nd-Fe-B magnets. Surface modification and consolidation methods for maintaining large coercivity even at high temperatures are the key techniques for realizing bulk magnets with Sm$_2$Fe$_{17}$N$_3$ powders. It is also important to know the fundamental properties of the powder at high temperatures. Therefore, in this work, we investigated the time dependence of coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powder compacts exposed in air and in He gas at 110°C and 150°C.

2. Experiment
Coarse Sm$_2$Fe$_{17}$N$_3$ powders (particle size: 30 µm) were prepared by nitrogenation of Sm$_2$Fe$_{17}$ alloy powders in a mixed gas of ammonia and hydrogen [2], and were then pulverized into fine powders (particle size: 2 µm) by jet milling. The fine Sm$_2$Fe$_{17}$N$_3$ powders were compacted at a pressure of 12 tonf/cm$^2$ under an alignment field of 15 kOe. Some Sm$_2$Fe$_{17}$N$_3$ compacts were exposed for 0 h (initial sample) to 2500 h at 110°C. The other Sm$_2$Fe$_{17}$N$_3$ compacts were encapsulated in Pyrex glass tubes with 0.3 atm helium gas, after the inner gas in these tubes had been replaced three times with helium gas through a liquid nitrogen cold trap. Subsequently, the glass tubes containing the Sm$_2$Fe$_{17}$N$_3$ compacts...
were annealed at 110°C and 150°C. The coercivities of the compacts were measured by a vibrating sample magnetometer (VSM) after magnetization with a pulse field of 60 kOe. The temperature dependence of magnetic properties from the temperature of liquid helium to room temperature was measured by VSM after magnetization with a static field of 150 kOe. The oxygen contents in the compacts were analyzed by an inert gas fusion method.

3. Results and Discussion

The time dependence of coercivity of the Sm$_2$Fe$_{17}$N$_3$ compacts at 110°C is shown in Fig. 1. The coercivity of Sm$_2$Fe$_{17}$N$_3$ decreased to about 50% (4.8 kOe) of the initial value of 9.4 kOe when the sample was exposed in air for around 5 h, then increased gradually and recovered to 70% of the initial value at 1000 h. Similar behavior was observed in the helium atmosphere, although the minimum coercivity value (6.9 kOe after 5 h exposure) was larger than that in air exposure (4.8 kOe). From this result, it does not seem that the coercivity decrease-increase process occurs with the progress of oxidation. Fig. 2 shows the time dependences of the coercivity and oxygen contents of Sm$_2$Fe$_{17}$N$_3$ at 150°C in the helium atmosphere. The significant difference between Fig. 1 and 2 is the time of minimum coercivity, which occurred at 5 hours at 110°C and 30 minutes at 150°C. The oxygen contents of all the compacts showed approximately constant values of 1.3 wt% from 0 to 8 hours. This indicates that the coercivity minimum behavior is independent of the oxygen content.

![Figure 1](image1.png)  
**Figure 1.** Time dependences of coercivity of Sm$_2$Fe$_{17}$N$_3$ compacts at 110°C in air (closed circles) and in He gas (open circles).

![Figure 2](image2.png)  
**Figure 2.** Time dependences of coercivity (closed squares) and oxygen content (closed triangles) of Sm$_2$Fe$_{17}$N$_3$ compacts at 150°C in He gas.

In order to understand the mechanism of the coercivity decrease-increase process, we measured the temperature dependence of the anisotropy field $H_A^* = 2(K_1 + K_2) / M_s [8]$, where $H_A^* M_s/2$ equals the anisotropy energy, coercivity $H_c$, and saturation magnetization $M_s$ of fine Sm$_2$Fe$_{17}$N$_3$ powder compacts which were exposed in air at 110°C for A) 0 h (non-exposure), B) 100 h, and C) 1000 h. Fig. 3 shows the temperature dependence of the coercivity values of samples A)-C). The coercivity values of all the samples monotonically increased with decreasing temperature. Since the coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powders is controlled by the nucleation process [8, 9], their coercivity can be expressed as $H_c = cH_A^* - NM_s [8]$. This formula is adapted from Ref. 10 by using $H_A^*$ instead of $2K_1/M_s$, which is another approach shown in Ref. 9. All the samples A)-C) exhibited linear relationships between $H_A^* / M_s$ and $H_c / M_s$ except at the temperature of liquid helium (Fig. 4). Consequently, the coefficients $c$ and $N$ can be derived from these results in the temperature range from −173°C to 27°C (Table 1). The initial value of $c$ (A: 0.080) decreased to 0.064 at 100 h (B) and then was constant to 1000 h (C). The $N$ value decreased monotonically (A: 7.3, B: 5.9, C: 5.2). Therefore, the initial decrease of coercivity would be
due to a reduction of the $c$ value, which suggests easier nucleation of the reversed domains in this sample. On the other hand, the gradual increase of coercivity in the 1000 h sample (C) can be attributed to a decrease in the local demagnetization factor value $N$. Such a change in the $N$ value would be related to the sharpness of the edges and corners [6, 11] of the fine Sm$_2$Fe$_{17}$N$_3$ powders. Fig. 5 shows a SEM image of fine Sm$_2$Fe$_{17}$N$_3$ powder immediately after jet milling in this work. Sharp edges and corners can be observed in all the powder particles, and these portions of the powder presumably have very high $N$ values. We speculate that these sharp edges and corners become rounder as annealing time increases, probably because of endogenous diffusion or reaction of oxygen at the surface amorphous layers of the powder [3, 12].

| Table 1. $c$ and $N$ values for Sm$_2$Fe$_{17}$N$_3$ compacts exposed in air at 110°C for 0, 100 and 1000 h. |
|---------------------------------------------------------------|
| Annealing time (h) | $c$  | $N$  |
|---------------------|-----|-----|
| 0                   | 0.080 | 7.3 |
| 100                 | 0.064 | 5.9 |
| 1000                | 0.064 | 5.2 |

Figure 3. Temperature dependence of coercivity for Sm$_2$Fe$_{17}$N$_3$ compacts exposed at 110°C for 0, 100, 1000 h in air.

Figure 4. Relationship between $H_A^* / M_s$ and $H_D / M_s$ of Sm$_2$Fe$_{17}$N$_3$ compacts exposed at 110°C for 0, 100 and 1000 h in air.

We produced Sm$_2$Fe$_{17}$N$_3$ compression-molded magnets based on this work by using the following conditions. Fine Sm$_2$Fe$_{17}$N$_3$ powders, which had been surface treated with a silane coupling agent at 150°C in a vacuum, were mixed with 3 wt% of lubricant and epoxy-resin, and subsequently compressed at a pressure of 14 tonf/cm$^2$ under an alignment field of 15 kOe. The magnets were then cured in a
vacuum at 150°C. The total annealing time at 150°C in an oxygen-free atmosphere was several hours; this was just the coercivity recovery time (see Fig. 2). Fig. 6 shows an example of the demagnetization curve of the Sm$_2$Fe$_{17}$N$_3$ compression-molded magnets. The coercivity of the compression-molded magnets recovered to 7.7 kOe as a result of annealing, but nevertheless did not reach the initial value of 9.3 kOe. Amorphous oxide layers (thickness: 10 nm) were observed on the surfaces of the Sm$_2$Fe$_{17}$N$_3$ powder particles [12]. Takagi et al. [3] reported that the coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powders was deteriorated by sintering for 1 minute at 350°C, because a soft magnetic $\alpha$-Fe phase appeared in the surface amorphous oxide layers. We consider the origin of the rapid decrease in the $c$ value observed in this work to be related to a similar appearance of the soft magnetic phase. Therefore, when using fine Sm$_2$Fe$_{17}$N$_3$ powders, a lower temperature and an oxygen-free process (e.g., explosive consolidation using water [13]) are preferable conditions for fabrication of consolidated magnets. Alternatively, techniques to remove the surface amorphous oxide layers on the fine Sm$_2$Fe$_{17}$N$_3$ powder particles, such as acid etching, coating with a stable phase (e.g., iron-ferrite [14, 15]), or surface cleaning by reaction (e.g., Zn metal coating [16]), can be proposed as possible methods for obtaining excellent consolidated magnets.

4. Conclusion
The coercivity of fine Sm$_2$Fe$_{17}$N$_3$ powders decreased rapidly and subsequently increased gradually during annealing at 110°C and 150°C. According to an analysis by Kronmüller’s formula, the initial decrease and the subsequent increase in coercivity were related to the rapid reduction in the $c$ value and the gradual decrease in the $N$ value, respectively. We speculate that the former arises from easier nucleation of reversed domains, while the latter is related to the change of sharpness in the edges and corners of the fine Sm$_2$Fe$_{17}$N$_3$ powders with increasing annealing time. In addition, sample compression-molded magnets were produced, and methods for consolidating fine Sm$_2$Fe$_{17}$N$_3$ powders while maintaining their high coercivity values were discussed.

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