High Performance Ferrite Magnets
— From the Perspective of Powder Technology

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Abstract

Coercivity in hexa-ferrite magnets originates in the magnetic behavior of so-called "single domain particles" with uniaxial magneto-crystalline anisotropy. The critical diameter, below which a single domain is stable, is estimated at around 1 micrometer ($10^{-6}$ m) for M-type Sr-ferrite, which means that control of grain size to under a micron is significant for achieving high coercivity. For this reason studies were performed on a process for obtaining submicron powder and sintered grains, as well as on techniques for obtaining high orientation under magnetic fields when using submicron powder. For analytical purposes, particle size distribution, magnetic properties, and lattice defects of Sr-ferrite particles were investigated to explain the observed behavior.

1. Introduction

In general, the crucial properties of permanent magnets are not only their high energy product (BH)$_{\text{max}}$, which allows volume reduction, but also high reliability (chemical and magnetic stability) and low price. Selection of magnet materials should be based on these criteria. Over the past few decades, many materials have been studied and proposed, but only ferrite, NdFeB, SmCo, and some AlNiCo magnets are still in use today. At 32-40 kJ/m$^3$, ferrite magnets have a considerably lower (BH)$_{\text{max}}$ than NdFeB-magnets with 320-400 kJ/m$^3$, but ferrite magnets account for an estimated 95% of world production by weight, which testifies to the unsurpassed cost efficiency of ferrite magnets. Another advantage is the chemical stability of these oxides, which makes them environmentally safe, further establishing their continued use.

The first "ferrite magnet" was Co-ferrite with a spinel structure (OP-magnet) invented by Prof. Y. Kato and Prof. T. Takei of Tokyo Institute University in 1932. The OP-magnet is now considered a landmark of scientific progress, although it was produced on a very small scale due only to its poor magnetic properties and weak mechanical strength. Later J. J. Went et al. (Philips N.V.) systematically studied Ba-ferrites with hexagonal structures and in 1952 released the M-type Ba-ferrite as a new permanent magnet material called "Ferroxdure" [1]. Since then, much basic research has been directed at improving the properties and productivities of these materials. Typical and successful examples are the discovery of Sr-ferrite with larger magnetic anisotropy (K$_{\text{f}}$), and the development of pressing technology under a magnetic field, which doubles the residual flux density (Br). For this reason anisotropic M-type Sr-ferrite is now dominant in mass production.

2. General Description of Ferrite Magnets

2.1 Crystal Structure of Ferrite Magnets

Fig. 1 shows a magnetoplumbite (M) type crystal structure. Oxygen ions that form hexagonal closed

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packing are partially substituted by strontium ions (Sr$^{2+}$). Ferrous ions (Fe$^{2+}$) lie between the oxygen ions and are magnetically connected with each other. These generate uniaxial magnetic anisotropy along the c-axis in the M-structure, which is the basic reason why M-type ferrite is a permanent magnet. Other than M-type ferrite, W- and X-type ferrites also have uniaxial anisotropy, which means they have the potential to be permanent magnets. Their compositions lie on the line between M and S (spinel) as shown in Fig. 2.

**Table 1** shows the fundamental properties of these hexa-ferrites. M-type Sr-ferrite (SrM) has a 10% larger anisotropic constant (K1) than M-type Ba-ferrite (BaM). Magnetization of W-type ferrites is 10% greater than M-type ferrite, but its K1 is relatively small in general. Despite a great number of studies concerning cation substitution in the M-type structure, very few attempts to increase magnetization have succeeded.

Similar to spinel ferrites, the saturation magnetization of M-type ferrites will increase when non-magnetic ions such as Zn occupy the tetrahedral 4f1 sites; Fe$^{3+}$ at 4f1 sites has down-spins. Recently the partial substitution of La$^{3+}$ and Zn$^{2+}$ for Sr$^{2+}$ and Fe$^{3+}$ achieved magnetization that was 5% higher than conventional M-type Sr-ferrite, while retaining the K1 value of conventional M-type Ba-ferrite, thereby resulting in the highest (BH)$_{max}$ value of 41 kJ/m$^3$, as shown in **Table 2** [7].

### 2.2 Theory of Single Domain Particles

It is assumed that coercivity in ferrite magnets originates in the magnetic behavior of “single domain particles” [8]. In general, magnetic materials form a “magnetic domain structure” in order to reduce static magnetic energy. Boundaries between two domains are magnetic walls where magnetic moments gradually change direction. When reducing the particle or

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**Figure 2** BaO-MeO-Fe$_2$O$_3$ system, showing the relationships of chemical compositions among ferrimagnetic hexagonal compounds. The symbol Me represents a divalent ion.
grain size of magnetic materials, the “non magnetic wall state” (i.e., single domain state) becomes energetically more stable as shown in Fig. 3. And once this single domain state is realized, coercivity will be maximized because magnetic reversal mechanisms are limited only to spin rotation.

2.3 Conventional Process for Sintered Ferrite Magnets

Fig. 4 shows the conventional manufacturing process of ferrite magnets. The raw materials strontium carbonate (or barium carbonate) and iron oxide are mixed and calcined at 1250-1300°C in air. Especially in the case of anisotropic ferrite production, ferrite formation must be concluded at this stage because it is necessary to orient the ferrite particles at the pressing stage. For this reason, higher calcination temperatures (higher than 1250°C) have been conventionally employed, causing grain growth. The calcined products, which are usually hard pellets of more than a few mm in size, are crushed and pulverized. For the production of anisotropic magnets, calcined pellets are first dry-pulverized and then wet-milled to submicron order.

Ferrite magnets can be classified into two groups according to their manufacturing process: isotropic magnets and anisotropic magnets. Anisotropic magnets are mainly manufactured by pressing in a magnetic field. There are two methods for pressing, wet and dry. Wet-pressing is a process for compacting a slurry of fine-milled powder mixed with a solvent such as water in a magnetic field. Although the flotation of the particles in the solvent facilitates their rotation and orientation, dewatering takes a longer time. SiO2 and CaCO3 are usually added at the pulverizing stage in order to promote densification and inhibit grain growth at the next sintering stage. Compacts are sintered at 1200-1250°C in air.

2.4 A Concept for High-Performance Ferrite Magnets

From the perspective of materials research, residual flux density (Br) and intrinsic coercivity (Hcj) are the most important properties. Both Br and Hcj consist of factors originating in the crystal structure and micro- or nano-structure, as shown in Fig. 5. All these factors should be improved simultaneously in order to improve magnetic properties.

Br is determined by the product of density, the

Crystal structure
Microstructure

Br = Magnetization (Js) x Orientation (%) x density (%)
Hcj = Anisotropic field (Hc=2K/Js) x Ratio of single domain particles (%)

Fig. 5 Factors of magnetic properties (Br and Hcj) in ferrite magnet
degree of orientation, and the saturation magnetization \( J_s \). M-type Sr-ferrite has a \( J_s \) value of about 0.465 T. The density and the degree of orientation have upper limits of about 98% for sintered magnets, which afford the highest values. Therefore, the practical limit of \( B_r \) in a sintered ferrite magnet with conventional M-type composition is around 0.445 T (i.e., \( 0.465 \times 0.98 \times 0.98 \)), resulting in \( (BH)_{max} \) of 37 kJ/m³.

The limit of \( H_C \), on the other hand, is determined by the anisotropic field \( (H_A=2K/J_s) \), which is estimated at 1.5 MA/m for M-type Sr-ferrite. Large grains in excess of one micrometer show multi-domain behavior and reduce coercivity. The ratio of single domain particles or grains should therefore be increased in order to reach the theoretical value of \( H_C \).

The critical diameter below which a single domain is stable is estimated at around 1 \( \mu \)m for SrM-ferrite. This means controlling grain size to under a micron is significant for achieving high \( H_C \) as mentioned above. Taking into account grain growth, ferrite particles for sintered magnets should be around 0.3 \( \mu \)m before sintering. There are some problems in obtaining this powder with conventional processing (e.g., simply long milling) because very fine particles (0.01-0.02 \( \mu \)m) also appear, as shown in Fig. 6. These ultrafine particles have low magnetic properties due to thermal fluctuation, and decrease productivity especially at the pressing stage. Similarly, particles prepared by the co-precipitation method, hydrothermal synthesis, or by glass crystallization are too small (under 0.1 \( \mu \)m) to be oriented in a magnetic field. Our research therefore centered on conventional ceramic methods for obtaining submicron-sized primary particles \textit{after calcination and before pulverization}, having an adequate size between 0.1 and 1 \( \mu \)m for the production of sintered magnets. From this point of view, calcination temperatures should be lowered through careful mixing of fine raw materials. In addition, the molar ratio \( \text{Fe}_2\text{O}_3/\text{SrO} \) should be nearly stoichiometric (6.0) to inhibit grain growth.

3. Process for Submicron Calcined Powder

First was a study of the wet mixing of raw materials in order to understand ideal mixing \cite{9}. Iron oxide from pickling liquors (\( \alpha\text{-Fe}_2\text{O}_3 \)) having 0.3 \( \mu \)m primary particle size was agitated milled (attritor) in a \( \text{Na}_2\text{CO}_3 \) aqueous solution. By adding a \( \text{SrCl}_2 \) solution to the slurry, fine-\( \text{SrCO}_3 \) particles were synthesized and mixed with the \( \text{Fe}_2\text{O}_3 \) particles in the mill. The reaction is indicated below. The \( \text{Fe}_2\text{O}_3/\text{SrCO}_3 \) molar ratio was about 6.0.

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\text{SrCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{SrCO}_3\downarrow + 2\text{NaCl}
\]

After removing \( \text{NaCl} \) by washing, the slurry was dried and granulated to about 50 \( \mu \)m by spray drying, and calcined at 1150-1200°C for 3 hours in air. TEM observation showed that \( \text{SrCO}_3 \) precipitated particles were uniformly fine (0.02 \( \mu \)m) and dispersed well among the \( \text{Fe}_2\text{O}_3 \) particles. By means of a SEM observation (Fig. 14) of Sr-ferrite primary particles calcined at 1200°C, the average size of the particles was around 0.3 \( \mu \)m as shown in Fig. 9. The magnetic properties of the powder were \( \sigma_s=1.12\times10^{-6} \) Hm²/kg, \( H_C=422 \) kA/m. Judging from the fact that \( \sigma_s \) was approximately the theoretical value \( (1.3\times10^{-6} \) Hm²/kg), ferrite formation was almost completed. These excellent properties are due to the high dispersion of the fine raw materials (\( \text{Fe}_2\text{O}_3 \) and \( \text{SrCO}_3 \)) and low calcination temperature. As a result of further investigation, similar powders were also obtained by using commercial-grade raw material \( \text{SrCO}_3 \), and even by a dry mixing process \cite{10}.

4. Process for High Orientation Using Submicron Calcined Powder

4.1 Experimental Process for Pulverizing Submicron Calcined Powder \cite{11}

Fig. 7 illustrates the following pulverization process. First, calcined powder was dry-pulverized with a
vibrating mill using 19 mm dia. steel rods. In Ex. 1 and Ex. 2, SiO₂ (0.6 wt%) and CaCO₃ (1.9 wt%) were added during pulverization. In Ex. 3 and Ex. 4, stearic acid (2.0 wt%) was also added. All powders were then wet-pulverized by agitation milling (attritor) or ball milling, using water or toluene, to the extent of 10⁻¹²×10³ m²/kg. After increasing slurry concentration, the slurry was wet-pressed into pellets of 30×15 mm dia. in a magnetic field of about 1.0 MA/m. Pellets were sintered at 1180°C in air. Table 3 shows the magnetic properties of the pressed and sintered samples. Pulverization with stearic acid in toluene (Ex. 4) achieved a remarkable improvement in orientation. Orientation degree was over 97%. This resulted in the highest magnetic properties, such as Br=0.44 T, HcJ=320 kA/m, and (BH)max=37 kJ/m³. Sintered density was about 97% of the theoretical value. As shown in Fig. 8, SEM examination revealed highly uniform and well oriented grains. Fig. 9 shows particle (grain) size distribution measured by counting 300-400 particles (grains) in the SEM micrographs of Fig. 7 and Fig. 8. Average grain size was about 0.7 μm. A combination of oleic acid and xylene,
instead of stearic acid and toluene, yielded similar or improved results.

The orientation degree decreased in the conventional process (water-based without surfactant, Ex. 1). The following subsection considers the reasons for this change in orientation.

### 4.2 Mechanism for Magnetic Agglomeration of Sr-Ferrite Particles

It is believed that single domain particles attract each other magnetically, thereby creating agglomerates that prevent orientation. Fig. 10 shows an expected B-H hysteresis curve of one Sr-ferrite particle. Magnetic flux density at the working point (B1), which is determined by the particle shape, relates to magnetic agglomeration force. Thus, the surface flux density of the particle must be reduced (B1→B2) by reducing HcB. The magnetic moment of the particle in the magnetic field (Hex) is proportional to Js, which is best maximized. It was found that dry-vibration pulverization in particular was effective in reducing Hc values. This is treated in Section 5.

### 4.3 Wet Pressing Using an Organic Solvent and Surfactant

The wet process using an organic solvent (e.g., toluene or xylene) and a surfactant (e.g., stearic acid or oleic acid) brought about a remarkable improvement in the degree of orientation for submicron particles, as shown in Fig. 11. In a magnetic fluid, for instance, it is well known that fine ferrite particles (0.01 μm) are dispersed well in organic solvents with an added surfactant such as oleic acid. In the same way, it appears that Sr-ferrite particles coated with oleic acid or stearic acid dispersed well in toluene or xylene during milling and pressing. This gave rise to the improvement of orientation under a magnetic field. The relation between the amount of stearic acid

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**Fig. 9** Particle size distribution of calcined powder and sintered grains. Size of the sintered grains was measured from the c-plane SEM micrograph.

**Fig. 10** Magnetic agglomeration forces of single domain particles

**Fig. 11** XRD patterns of submicron Sr-ferrite particles
Fig. 12  Relationship between amount of stearic acid and orientation degree

and the degree of orientation (Jr/Js) of the pressed samples was investigated. More than 2 wt% of stearic acid seems to be required for optimum orientation, as shown in Fig. 12. This corresponds to a complete coating by stearic acid, as calculated for particles of 10 m²/g surface area based on a cross sectional stearic acid area of about 2.0 nm².

5. Analysis of Sr-Ferrite Powder

5.1 Influence of Pulverization on Magnetic Properties

Fig. 13 shows the changes in magnetic properties of submicron Sr-ferrite powder when pulverized by dry-vibration milling. As pulverization proceeded, and the specific surface area of the powders increased, both magnetization and coercive force decreased. However, the respective changes are very different. Compared at 8×10⁵ m²/kg for example, the pulverized powder's HcJ decreased to 40% of the initial value, HcJ=438 kA/m, HcB=366 kA/m→HcJ (=HcB) =199 kA/m, while the decrease of σs (saturation magnetization per weight) was within 10%. These changes can be utilized to avoid magnetic agglomeration of the Sr-ferrite particles as mentioned in the previous section. Furthermore, with wet-pulverization by agitation milling (attritor), the changes are relatively small, as shown in Fig. 13. In addition to σs and HcJ, the temperature dependence of HcJ was considerably changed by pulverization, although Tc was not, as shown in Table 4. The torque curve of the pulverized powder was measured by using a highly sensitive torque measurement. The dependence of K2/K1 on the applied magnetic field increased [12].

5.2 SEM and TEM observation

Fig. 14 shows SEM images of pulverized Sr-ferrite particles prepared by dry-vibration milling. Primary particle size distribution differed little from the initial state, which means that the change in powder HcJ cannot simply be explained by a change in particle size. Fig. 15 is a TEM image of pulverized Sr-ferrite particles. Moire fringes (parallel) indicate lattice defects.
5.3 XRD Analysis

Lattice defects can cause a decrease in pulverized powder HcJ. Pulverized powder was analyzed by XRD in order to characterize lattice defects. The crystal system (hexagonal) did not change, and lattice constants were almost the same. Fig. 16 shows the XRD profile of the (206) peak of Sr-ferrite powder. Apparently the diffraction peak broadened as pulverization proceeded. In consideration of crystallite size reduction as well as the crystal strain responsible for this broadening, the XRD profiles were analyzed with the Warren and Averbach method [13], yielding the conclusion that the strain induced by pulverization is isotropic and closely related to the coercivity of the particles, as shown in Fig. 17.
6. Conclusions

Processes for preparation of submicron-sized powder, for high orientation, and for high density are significant for high performance ferrite magnets. However, this study found that submicron sized particles (with high He) are oriented with great difficulty in a magnetic field at the pressing stage. A detailed study of the pulverization process to solve this problem revealed that over 97% high orientation and high density could be achieved, with an average grain size of 0.7 μm, by dispersing this powder with surfactant (stearic or oleic acid) into an organic solvent (toluene or xylene), while at the same time reducing the coercive force of the powder by introducing lattice defects [14].

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Author’s short biography

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Dr. H. Taguchi is a chief scientist at the Materials Research Center of TDK Corporation. He graduated in Electronics Engineering from Saitama University and joined TDK in 1981. He has been engaged mainly in developing high performance ferrite magnets. He received his Doctorate in Engineering from Saitama University in 1995. He received “Technology Advancement Award” from the Japan Society of Powder and Powder Metallurgy in 1995. He is a member of the Magnetics Society of Japan.