

## Magnetic Properties of Sr-ferrite Powder Prepared by Intensive Mechanical Milling Technique

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As an alternative promising way of producing high coercivity Sr-ferrite for a permanent magnet application, intensive mechanical milling process was applied to the raw materials of the Sr-ferrite with different composition. Synthesising reactivity for the Sr-ferrite of the mechanically milled raw material containing SrCO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and SiO<sub>2</sub> was inferior to that of the raw material containing SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The Sr-ferrite prepared from mechanically milled raw materials had profoundly improved magnetic properties compared to the Sr-ferrite prepared by conventional method. Beneficial effect of the substituting (La<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>) and additive (SiO<sub>2</sub>) oxides for improving the magnetic properties was not exploited in the Sr-ferrite prepared from the mechanically milled raw material. The Sr-ferrite powder prepared from the mechanically milled raw materials was magnetically isotropic in nature.

**Key words :** SrO·6Fe<sub>2</sub>O<sub>3</sub>, SrFe<sub>12</sub>O<sub>19</sub>, Sr-ferrite, intensive mechanical milling

### 1. Introduction

For a permanent magnet application of Sr-ferrite, high coercivity is one of the important requirements. The high coercivity in Sr-ferrite can be achieved by obtaining a fine grain structured particle, and grain size comparable to the critical single domain size ( $d_c \cong 0.8\sim 1.0 \mu\text{m}$ ) [1] of the Sr-ferrite compound is desirable. The Sr-ferrite powder prepared by a conventional process consisting of a mixing and pre-firing usually has coarser grain structure because of the high pre-firing temperature of 1250 °C ~1300 °C, thus coercivity of the conventionally prepared powder is usually far lower compared to the anisotropy field ( $H_A \cong 20 \text{ kOe}$ ) [2] of the compound. Recently, an intensive research effort has been made to prepare a Sr-ferrite powder with high coercivity using other new techniques than the conventional process. As an alternative promising way of producing high coercivity Sr-ferrite, the mechanical alloying (MA) and mechanical milling (MM) processes have been proposed [3-9]. In the present study, high coercivity Sr-ferrite was prepared using intensive mechanical milling, and the effects of intensive mechanical milling

variables and raw material composition on the synthesising reactivity and magnetic properties of the prepared Sr-ferrite powder have been investigated.

### 2. Experimental Process

Two types of raw materials were used to synthesise Sr-ferrite (SrFe<sub>12</sub>O<sub>19</sub>), and chemical compositions of the raw materials are tabulated in Table 1. The binary raw material containing SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is referred to as material A, hereafter. The other type of raw material contains some amount of substituting and additive oxides. In this type material some part of the SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> was substituted with La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, respectively, and small amount of SiO<sub>2</sub> was added. This material with substitution and addition is referred to as material B, hereafter. Material B has almost the same chemical composition as the so-

**Table 1.** Chemical composition of raw materials (wt%)

	SrCO <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	SiO <sub>2</sub>
purity			> 99.9%		
average particle size			10~20 μm		
material A	14.5	.	85.5	.	.
material B	10.8	3.6	83.9	1.5	0.2

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called 'F9 ferrite' in the commercial market. The mixed raw materials were mechanically milled using a shaker mill. For the intensive mechanical milling, hardened steel vial and balls were used, and the mass ratio of the milling balls (8 mm $\phi$ ) and raw material was selected to be 10 : 1. The vial was charged with the raw material in air, and milling was undertaken for 5~25 hrs. The mechanically milled raw material in a powder form was compacted into a disc-shaped tablet (5 mm $\phi$   $\times$  2 mm $t$ ) and then annealed at temperature range of 600~1200  $^{\circ}$ C in air to synthesise the Sr-ferrite. Phase analysis and microstructure of the synthesised material were carried out by XRD and TEM. Magnetic characterization of the prepared Sr-ferrite was performed by VSM with maximum field of 15 kOe. In the VSM measurement, magnetic field was applied along the direction perpendicular to the flat surface of the disc-shaped specimen, and the demagnetising factor associated with the geometry of the specimen was not compensated.

### 3. Results and Discussion

Fig. 1 shows XRD spectrum of the raw material A after the intensive mechanical milling for 25 hrs. Also included is the spectrum of the raw material A after low energy roller milling for 25 hrs for comparison. This low energy milling is thought to cause a simple mixing of the raw material. Reflected peaks in the spectra are corresponding mainly to the  $\text{Fe}_2\text{O}_3$ . It is noted that the reflected peaks for the mechanical milled raw material are severely broadened with respect to the simply mixed material. This indicates that the mechanical milled raw materials have been milled down to ultra-fine particles with nano-scale size, and it is expected, therefore, that the mechanical milled material may have an enhanced synthesising reactivity for Sr-ferrite due to the ultra-fine particle structure.

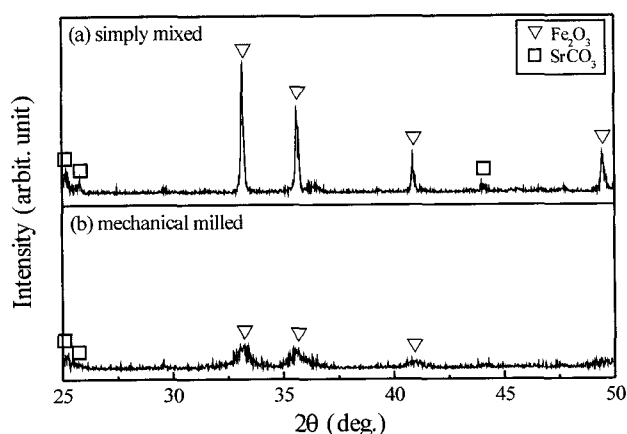


Fig. 1. XRD spectra of the raw material A (a) simply mixed and (b) mechanical milled for 25 hrs.

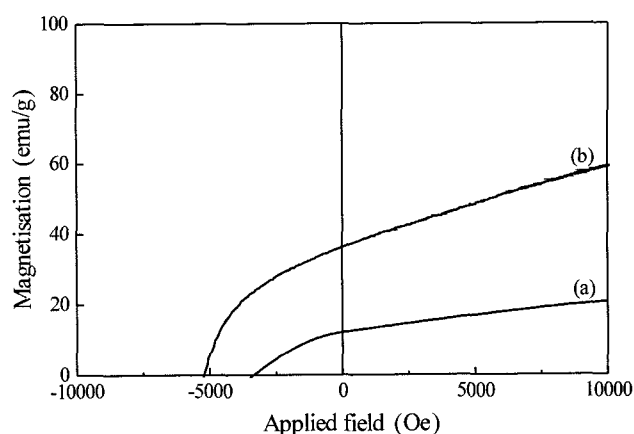


Fig. 2. Demagnetisation curves of (a) simply mixed and (b) mechanical milled material A after annealing at 900  $^{\circ}$ C for 1 hr.

Fig. 2 shows the demagnetisation curves of the material A mechanical milled or simply mixed for 25 hrs after synthesising annealing at 900  $^{\circ}$ C for 1 hr. It can be seen that the mechanical milled materials has remarkably higher saturation magnetisation (magnetisation at 15 kOe) compared to the simply mixed material. The higher magnetic parameters, in particular, the higher saturation magnetisation, are surely occurring as a result of greater extent of the Sr-ferrite synthesis. This indicates that the mechanical milled material has highly enhanced synthesising reactivity for the Sr-ferrite. The enhanced reactivity due to the intensive mechanical milling is also evidenced by the XRD phase analysis. Fig. 3 shows XRD spectra of the material A mechanical milled or simply mixed for 25 hrs after annealing at 900  $^{\circ}$ C for 1 hr. It can be seen that the mechanical milled raw material has been synthesised almost completely into Sr-ferrite, while the simply mixed raw material has only been partially synthesised.

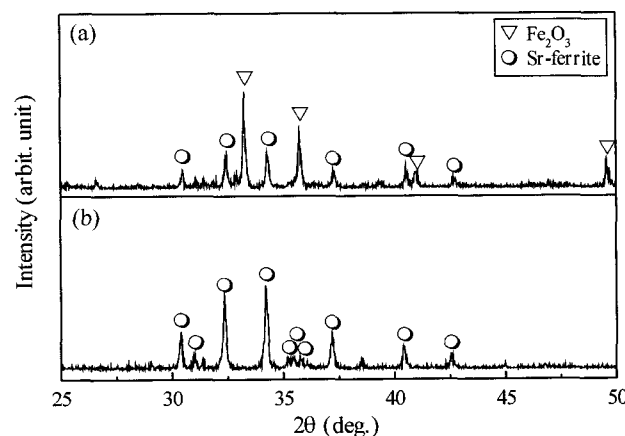
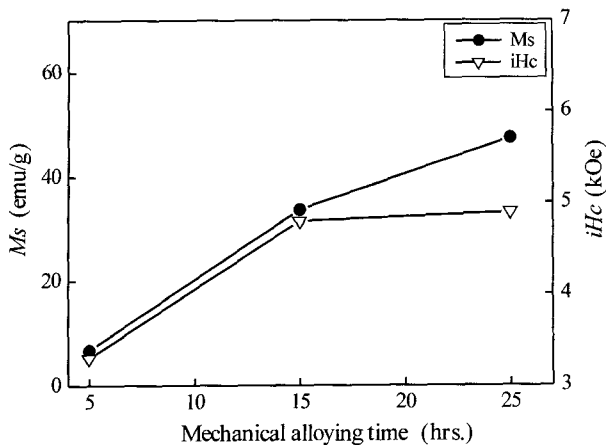


Fig. 3. XRD spectra of (a) simply mixed and (b) mechanical milled material A after annealing at 900  $^{\circ}$ C for 1 hr.



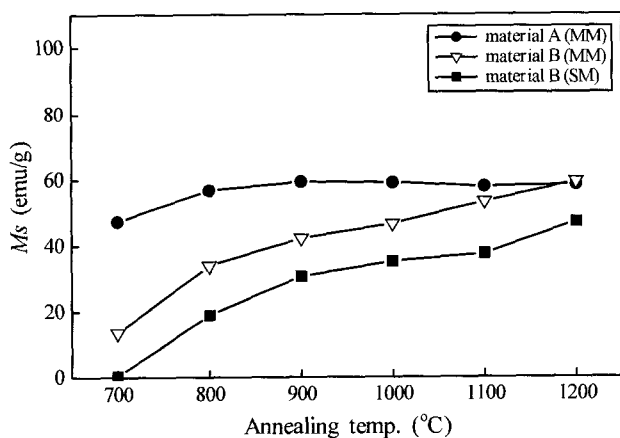
**Fig. 4.** Effect of intensive mechanical milling time on the saturation magnetisation and intrinsic coercivity of material A annealed at 700 °C for 1 hr.

Fig. 4 shows the effect of intensive mechanical milling time on the synthesising reactivity of the material A. The raw material A was annealed at 700 °C for 1 hr after intensive mechanical milling for various time periods. It can be seen that the saturation magnetisation of the annealed material increases with increasing the intensive mechanical milling time, indicating that the synthesising reactivity is improved with increasing intensive mechanical milling time. This can be explained by the remarkably increased specific surface area of the milled particle in the raw material. Intensive mechanical milling time dependence of the synthesising reactivity of mechanical milled material B was also investigated, and a similar trend was observed. Also included in Fig. 4 is the variation of coercivity of the material A with intensive mechanical milling time. The material milled for longer than 15 hrs exhibits high coercivity, and this is attributed to the improved synthesis

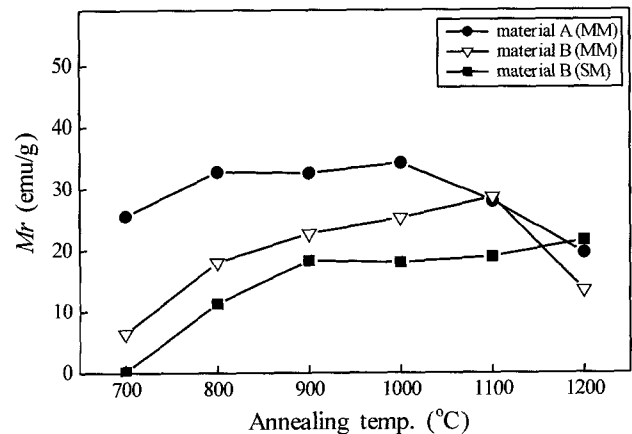
of the raw material.

Fig. 5~8 show the variations of magnetic parameters with synthesising annealing temperature (annealing for 1 hr) for the materials A and B mechanical milled for 25 hrs. Also included in Fig. 5~8 are the variations of magnetic parameters for the simply mixed (SM) material B for comparison. As can be seen in Fig. 5, the material A annealed at 700 °C has high saturation magnetisation, and it almost saturates from above 800 °C. However, the saturation magnetisation of the material B synthesised at 700 °C is remarkably low with respect to that of material A, and it increases gradually with increasing annealing temperature up to 1100 °C. This indicates that the mechanical milled material A has been synthesised almost completely above 800 °C, while the mechanical milled B above 1100 °C. This suggests that the synthesising reactivity of material B is far inferior to that of material A, and this may be attributed to the addition and substituting oxides contained in material B. It can also be seen that saturation magnetisation of the simply mixed material B is consistently lower compared to the mechanical milled material B, indicating that the mechanical milled material has highly enhanced synthesising reactivity.

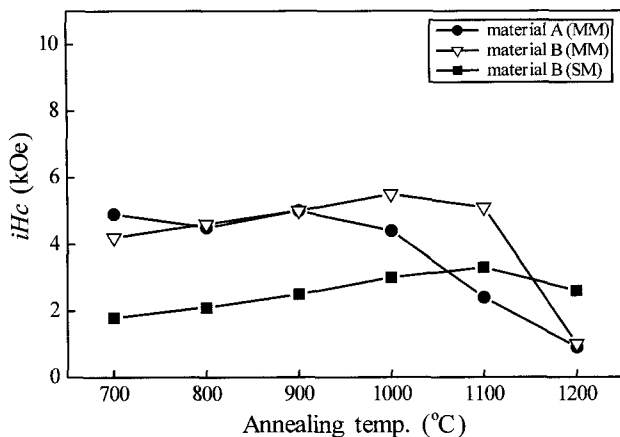
Variations of remanence with annealing temperature for the materials A and B mechanically milled for 25 hrs are shown in Fig. 6, and it can be seen that the remanence increases with increasing the annealing temperature and then decreases radically at higher temperature. At higher annealing temperature, the formed Sr-ferrite grains may probably be over-grown. The coarse grain structure may lead to a deterioration of demagnetisation character, and reducing the remanence. It is noted that although the simply mixed (SM) material B shows lower remanence compared to the mechanical milled material B, it shows



**Fig. 5.** Variations of the saturation magnetisation with annealing temperature for the materials A and B mechanical milled (MM) or simply mixed (SM) for 25 hrs and annealed for 1 hr.



**Fig. 6.** Variations of the remanence with annealing temperature for the materials A and B mechanical milled (MM) or simply mixed (SM) for 25 hrs and annealed for 1 hr.

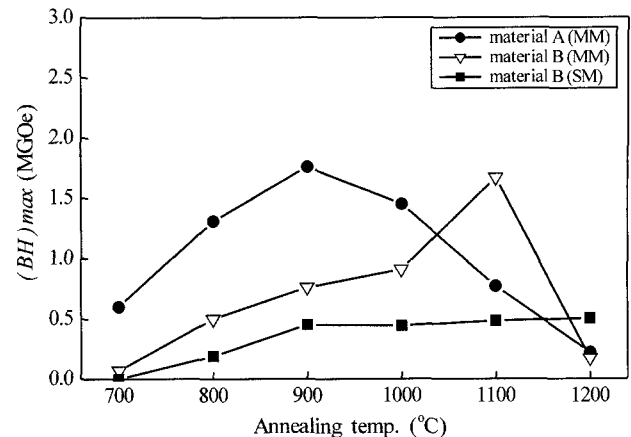


**Fig. 7.** Variations of the intrinsic coercivity with annealing temperature for the materials A and B mechanical milled (MM) or simply mixed (SM) for 25 hrs and annealed for 1 hr.

no radical remanence degradation at high synthesising temperature. This may be explained by the retarded synthesising reactivity of the simply mixed material B. In this material, an excessive grain growth is thought not to take place.

Coercivity variations with annealing temperature for the materials A and B mechanical milled for 25 hrs are shown in Fig. 7. As can be seen, coercivity increases with increasing the annealing temperature and decreases radically at higher temperature. This coercivity reduction is also attributed to an excessive grain growth of the formed Sr-ferrite. The coercivity degradation at higher temperature appears to be more profound in the mechanical milled material A than in mechanical milled material B. The temperature where a radical coercivity reduction onsets in material A is lower than in material B. These results indicate that excessive grain growth of the formed Sr-ferrite takes place more easily in the mechanical milled material A than in mechanical milled material B. This suppressed grain growth at higher synthesising temperature in the mechanical milled material B may be attributed to the substitution and addition of oxides contained in this material, in particular to the addition of  $\text{SiO}_2$ . The addition of  $\text{SiO}_2$  is known to suppress the grain growth in the Sr-ferrite prepared by conventional method consisting of simple mixing and pre-firing [10]. The suppression of grain growth by addition of  $\text{SiO}_2$  is expected to occur also in these mechanical milled materials. The coercivity deterioration at high synthesising temperature in the simply mixed (SM) material B appears not to be radical compared to the mechanical milled material B. This may be explained by the retarded synthesising reactivity of the simply mixed material B.

Fig. 8 shows the effect of synthesising annealing temper-



**Fig. 8.** Variations of the maximum energy product with annealing temperature for the materials A and B mechanical milled (MM) or simply mixed (SM) for 25 hrs and annealed for 1 hr.

ature on the maximum energy product of the mechanical milled materials. The mechanical milled material A and B show highest  $(BH)_{max}$  when annealed at  $900^\circ$  and  $1100^\circ$   $^\circ\text{C}$ , respectively, and the mechanical milled material A has slightly higher  $(BH)_{max}$  than the mechanical milled material B. The substituting and additive oxides contained in material B are known to improve magnetic properties (in particular,  $(BH)_{max}$ ) in the Sr-ferrite produced by conventional method [10-13]. However, this is not the case for the Sr-ferrite prepared by intensive mechanical milling. This result, therefore, leads us to make a conclusion that the beneficial effect of the substituting and additive oxides in the conventionally prepared Sr-ferrite is not exploited in the Sr-ferrite prepared by intensive mechanical milling. It can also be seen that the Sr-ferrite (material B) prepared by intensive mechanical milling has much higher  $(BH)_{max}$  with respect to the Sr-ferrite prepared from the simply mixed (SM) raw material.

In order to see if the Sr-ferrite powder prepared by intensive mechanical milling has an anisotropic nature, the prepared tablet samples were crushed briefly for 10 seconds using a mortar and pestle. The milled powder was aligned by applying magnetic field (10 kOe) and wax-bonded. Then demagnetisation curves of the aligned powder were measured along the direction parallel or transverse to the aligning direction. For an examination of anisotropic nature, the material A and B synthesised at optimum condition (with peak  $(BH)_{max}$ ) were used. The material A and B mechanical milled for 25 hrs were synthesised for 1 hr at  $900^\circ\text{C}$  and  $1100^\circ\text{C}$ , respectively. Fig. 9 shows the demagnetisation curves measured along the two different directions. For the both Sr-ferrite powders prepared by intensive mechanical milling, the remanence values along the two directions are not significantly

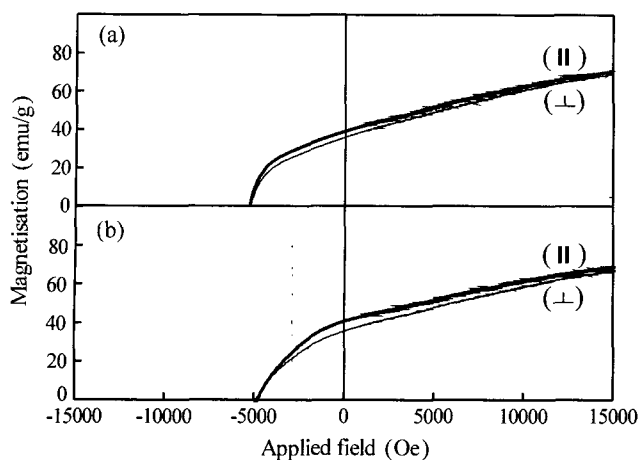


Fig. 9. Demagnetisation curves of the Sr-ferrites prepared from mechanical milled material (a) A and (b) B.

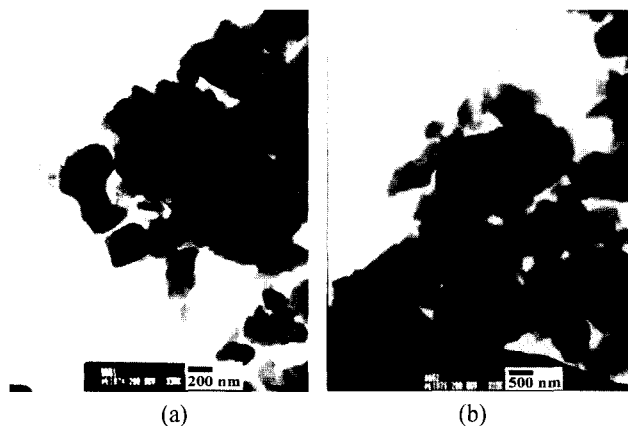


Fig. 10. TEM photographs showing morphology of the Sr-ferrite particle prepared from the mechanically milled raw material (a) A and (b) B.

different with each other. This indicates that these Sr-ferrite powder are magnetically almost isotropic in nature.

Fig. 10(a) and (b) shows morphology of the Sr-ferrite particles prepared from the material A and B mechanical milled for 25 hrs. The materials were synthesised at optimum condition in terms of  $(BH)_{max}$ , that is, the material A and B were synthesised for 1 hr at 900 °C and 1100 °C, respectively. The prepared tablet sample was crushed briefly for 10 seconds using a mortar and pestle before TEM observation. As can be seen, the Sr-ferrite particle prepared from the raw material B has larger particle size compared to that from the raw material A (note the magnification difference between two photographs). This is simply because of the higher annealing temperature for the raw material B. The coarse particles in the both Sr-ferrites prepared from the mechanical milled raw material A and B are not considered to be a

single crystal particle, rather they may consist of aggregate of fine grains. The individual grains in a coarse particle may probably orient randomly, thus the Sr-ferrite powder prepared from the mechanical milled raw materials shows magnetically almost isotropic nature.

#### 4. Conclusion

The mechanical milled raw materials for the synthesis of Sr-ferrite had ultra-fine particle size in nano-scale, and these raw materials had highly enhanced synthesising reactivity into the Sr-ferrite phase. The Sr-ferrite prepared from mechanical milled raw materials had profoundly improved magnetic properties compared to the Sr-ferrite prepared by conventional method. The synthesising reactivity of the raw material B containing the substituting ( $\text{La}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ) and additive ( $\text{SiO}_2$ ) oxides was inferior to that of the raw material A without the substituting and additive oxides. Beneficial effect of the substituting and additive oxides for improving the magnetic properties was not exploited in the Sr-ferrite prepared from the mechanical milled raw material. The Sr-ferrite powder prepared from the mechanical milled raw materials was magnetically isotropic in nature.

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