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Preparation of strontium hexaferrite nano-crystalline powder by carbon monoxide heat treatment and re-calcination from conventionally synthesized powder

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ABSTRACT

In this work strontium hexaferrite nano-crystalline powders were prepared by carbon monoxide heat treatment and re-calcination from conventionally synthesized powder. First strontium hexaferrite was obtained by the conventional route with calcination of strontium carbonate and hematite at 1100 °C for 1 h. Then strontium hexaferrite was isothermally subjected to carbon monoxide dynamic atmosphere at various temperatures and flows for different times. Optimum carbon monoxide heat treatment was achieved at 850 °C with 20 cm³/min flow for 0.5 h. The resultant powder was then calcined at 900 and 1000 °C for 1 h. The single-phase strontium hexaferrite nano-crystalline powder was finally obtained after calcination at 1000 °C. The phase identification of the powders was recorded by an X-ray diffractometer (XRD) with Cu K α radiation. Morphology and size of the particles were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The magnetic properties were also measured by a vibration sample magnetometer (VSM). The results show a good enhancement in the coercivity by applying this method on the hexaferrite powder.

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1. Introduction

M-type hexaferrites have been widely used as permanent magnets due to their low cost of production, high uniaxial magnetic anisotropy and excellent corrosion resistivity [1].

The conventional method of production of this material is solid-state reaction between $SrCO_3$ and Fe_2O_3 at temperatures higher than $1100 \,^{\circ}C$ [2]. For preparation of strontium hexaferrite nano-particles, different production methods such as mechanical alloying [3], hydrothermal [4], co-precipitation [5] and sol-gel auto-combustion [6,7] have been employed in the last few years. Gas heat treatment and re-calcination is a novel method which produce the hexaferrite nano-particles from conventionally synthesized powder. Hydrogen and nitrogen heat treatments and re-calcination have been investigated in the last decade [8–11]. In this work, the effects of carbon monoxide heat treatment and re-calcination on the microstructure and magnetic properties of conventionally synthesized strontium hexaferrite have been reported.

2. Experimental procedure

M-type strontium hexaferrite was produced conventionally by calcination of hematite (α -Fe₂O₃) and strontium carbonate (SrCO₃). The weight ratio of iron oxide to strontium carbonate was 5.5:1 without using any additives. The calcination was carried out at 1100 °C for 1 h in air. Carbon monoxide heat treatment was also carried out in a dynamic atmosphere at different temperatures with various flows. A tube furnace with quartz reactor was used for heat treating of strontium hexaferrite in CO atmosphere. Subsequent calcination processes also consisted of heating up to various temperatures in a muffle furnace, dwelling for 1 h and then cooling. The heating and cooling rates were 10 °C/min. X-ray diffraction analysis (Cu K α radiation) was used for phase identification. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were also used to determine the morphology and size of the particles. Finally, the magnetic properties were measured by a vibration sample magnetometer.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the powder calcined at 1100 °C for 1 h which indicates the formation of single-phase strontium hexaferrite by the conventional route.

Fig. 2 also shows the SEM micrograph of this sample. The particles size is below 500 nm with hexagonal shape, smooth surfaces and sharp edges.

Fig. 3 shows the XRD patterns of strontium hexaferrite powders heat treated in carbon monoxide dynamic atmosphere at 550-850 °C with flow of 30 cm^3 /min for 1 h.

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Fig. 1. The X-ray diffraction pattern of strontium hexaferrite synthesized conventionally at 1100 °C for 1 h (SH, strontium hexaferrite).

During carbon monoxide heat treatment at different temperatures, strontium hexaferrite decomposed into Fe_2O_3 and SrO according to the following reaction:

$$SrO \cdot 6Fe_2O_3 \rightarrow SrO + 6Fe_2O_3 \tag{1}$$

The resultant Fe_2O_3 was then reduced to Fe_3O_4 , FeO and finally Fe according to reactions (2), (3) and (4), respectively. Fig. 3 shows that the extent of reduction depends on the temperature of carbon monoxide heat treatment. The traces of Fe_3O_4 and FeO in Fig. 3a shows that the reduction process of hematite was not completed yet. The disappearance of Fe_3O_4 and FeO in Fig. 3b also shows the progress of the reduction process to the formation of the Fe phase. Then according to reaction (6), the Fe phase and the carbon which resulted from reaction (5), reacted again to form Fe_3C phase. $SrCO_3$ also formed according to reaction (7).

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{2}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \tag{3}$$

 $FeO + CO \rightarrow Fe + CO_2$ (4)

$$2CO \rightarrow C + CO_2 \tag{5}$$

 $3Fe + C \rightarrow Fe_3C$ (6)

$$SrO + CO_2 \rightarrow SrCO_3$$
 (7)

With increasing the temperatures up to 750 and $850 \degree C$ (Fig. 3c and d) it could be seen that the cementite phase decomposed again to carbon and iron phases. This is more visible at $850 \degree C$ rather than at $750 \degree C$.



Fig. 2. The micrograph of the powder synthesized conventionally, showing hexagonal-like particles.



Fig. 3. The X-ray diffraction patterns of the powders heat treated in carbon monoxide atmosphere with $30 \text{ cm}^3/\text{min}$ flow for 1 h at: (a) $550 \degree$ C, (b) $650 \degree$ C, (c) $750 \degree$ C and (d) $850 \degree$ C (C, Fe₃C; W, FeO; M, Fe₃O₄; SC, SrCO₃; F, Fe).



Fig. 4. X-ray diffraction pattern of strontium hexaferrite heat-treated at $850 \degree C$ for 1 h with flow of 20 cm³/min (F, Fe; SC, SrCO₃; C, Fe₃C).



Fig. 5. The X-ray diffraction pattern of the strontium hexaferrite after carbon monoxide heat treatment at $850 \degree$ C for $30 \min$ with $20 \degree$ cm³/min flow (SC, SrCO₃; F, Fe).

Fig. 4 shows the X-ray diffraction pattern of strontium hexaferrite heat treated at 850 °C for 1 h with flow of $20 \text{ cm}^3/\text{min}$. As it is shown in this figure the extent of iron carbide has been decreased with $20 \text{ cm}^3/\text{min}$ flow of carbon monoxide at 850 °C for 1 h compared to the sample prepared with flow of $30 \text{ cm}^3/\text{min}$.

For further decrease of the non-magnetic iron carbide phase, carbon monoxide heat treatment was carried out at $850 \,^{\circ}$ C with $20 \,\text{cm}^3$ /min flow for 30 min rather than 1 h. The X-ray diffraction pattern of this powder which has been shown in Fig. 5 confirms that the cementite is eliminated totally. Therefore, the optimum condition of carbon monoxide heat treatment was selected at $850 \,^{\circ}$ C with $20 \,\text{cm}^3$ /min flow for 30 min.

Fig. 6 shows the morphology of nano-powder heat treated in CO atmosphere at $850 \,^{\circ}$ C for 30 min with flow of $20 \, \text{cm}^3$ /min. It can be seen that the size of the particles was below 200 nm. Comparison of Fig. 2 with Fig. 6 indicates that the particle size of the initial powder decreased dramatically after the gas heat treatment. The average crystallite size of the heat-treated powder was also calculated by the X-ray line broadening technique employing the Scherrer formula as 33 nm.

The resultant optimized powder was then calcined at 900 and 1000 °C for 1 h. Fig. 7 shows the X-ray diffraction patterns of the powders calcined at 900 and 1000 °C for 1 h. Fig. 7a shows that after re-calcination at 900 °C the formation of single-phase strontium hexaferrite was not completed and Fe₂O₃ and Sr₇Fe₁₀O₂₂ phases are still present. The single-phase Sr hexaferrite was only obtained at temperatures higher than 1000 °C as it is shown in Fig. 7b.

The morphology of $SrFe_{12}O_{19}$ powders after re-calcination at 1000 °C for 1 h is shown in Fig. 8. Compared to Fig. 2, it is clear



Fig. 6. The morphology of the powder after CO heat treatment at $850 \,^\circ$ C for 30 min with $20 \, \text{cm}^3$ /min flow.



Fig. 7. X-ray diffraction patterns of the optimized powder which calcined at (a) 900 °C and (b) 1000 °C for 1 h (SH, $SrFe_{12}O_{19}$; S, $Sr_7Fe_{10}O_{22}$; H, Fe_2O_3).

Table 1

Magnetic properties of the initial and carbon monoxide heat treated and re-calcined powders

Powder	$M_{\rm S}$ (J/T kg)	$M_{\rm r}$ (J/T kg)	<i>H</i> _{ci} (kA/m)
Initial	66.9	37.0	262.6
Carbon monoxide	60.9	33.5	318.3
heat treated and			
re-calcined			

that the particles size of the powder after gas treatment and recalcination became much finer. This is attributed to nucleation of hexaferrite crystallites during re-calcination, on the surfaces of very fine grains obtained after gas treatment as it is shown in Fig. 6.

The TEM image of the $SrFe_{12}O_{19}$ after re-calcination is also shown in Fig. 9 showing the size of crystallites below 50 nm. This is consistent with the measurement of the crystallite size of this sample by the Scherrer formula as 38 nm.

The magnetic properties of the initial strontium hexaferrite powder before and after optimum gas heat treatment and recalcination processes have been compared in Table 1.

As it is indicated in Table 1, the carbon monoxide heat treatment and re-calcination processes resulted in a noticeable increase of the intrinsic coercivity from 262.2 to 318.3 kA/m due to the much finer



Fig. 8. SEM image of SrFe₁₂O₁₉ powders after re-calcination at 1000 °C for 1 h.



Fig. 9. TEM image of the $\rm SrFe_{12}O_{19}$ nano-crystalline powder after re-calcination at 1000 $^\circ C$ for 1 h.

structure of this powder compared to the initial one. However, there are also negligible decreases in M_r and M_S after these processes which show that the effects of these processes are mainly on the intrinsic coercivity of the initial powder.

4. Conclusions

Strontium hexaferrite decomposed into hematite and strontium oxide during the carbon monoxide heat treatment and the resultant iron oxide was then reduced by carbon monoxide mainly to metallic iron. This process made the microstructure much finer than that of the initial powder which is responsible for the very fine structure of strontium hexaferrite powder re-formed again after a re-calcination process.

Single-phase strontium hexaferrite powder with as average 38 nm crystallite size was successfully achieved by carbon monoxide heat treatment of conventionally synthesized strontium hexaferrite at $850 \,^{\circ}$ C for 0.5 h with $20 \, \text{cm}^3$ /min flow and re-calcination at $1000 \,^{\circ}$ C for 1 h.

The coercivity of strontium hexaferrite powder after carbon monoxide heat treatment and re-calcination was increased significantly due to the decrease of the crystallite size of the powder during these processes.

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