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Optimization of hydrogen dynamic heat treatment and re-calcination for preparation of strontium hexaferrite nanocrystalline powder

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ABSTRACT

Strontium hexaferrite is a hard magnetic material which under hydrogen treatment and re-calcination, its phase composition and also particles size and morphology change completely. Strontium hexaferrite was prepared by conventional route with calcination of strontium carbonate and hematite at 1100 °C for 1 h. Then strontium hexaferrite was heat treated in hydrogen dynamic atmosphere at various temperatures and gas flows for different times. Optimum conditions of hydrogen treatment were obtained at 850 °C with 60 cm^3/min flow for 1 h. Subsequent re-calcination was carried out at various temperatures for the optimum hydrogen treated powder and its optimum conditions were obtained at 1000 °C for 1 h. The effect of dynamic hydrogen treatment and re-calcination on the phase composition and particles size and morphology characterized by X-ray diffraction (XRD) and scanning and transmission electron microscopes (SEM and TEM). The results showed decomposition of strontium hexaferrite and reduction of the resultant hematite mainly to iron during hydrogen treatment. Nanocrystalline powder of strontium hexaferrite was also reformed after the re-calcination. The magnetic properties of the initial and final strontium hexaferrite powder were measured by a vibration sample magnetometer (VSM). The results showed about 30% increase in the coercivity by application of this process on the strontium hexaferrite powder.

1. Introduction

M-type hexaferrites with $MFe_{12}O_{19}$ (M = Ba, Sr and Pb) chemical formula have been widely used as permanent magnets due to their low cost of production, high uniaxial magnetic anisotropy and excellent corrosion resistivity [1]. Hexagonal ferrites are also promising materials for microwave devices and perpendicular recording Media [2]. The conventional method of production of this material is the solid-state reaction between $SrCO_3$ and Fe_2O_3 at temperatures higher than 1100 °C [3]. In order to get single domain particles of strontium hexaferrite, different synthesis techniques have been developed such as hydrothermal synthesis [4], salt melt method [5], co-precipitation [6], self-propagating high temperature synthesis [7] and sol–gel auto combustion method [8,9].

Static gas heat treatment and re-calcination is a method which produces hexaferrite nanoparticles from conventionally synthesized powder and have been investigated in last decade [10–13]. Dynamic carbon monoxide heat treatment and re-calcination has also been reported recently [14].

In this work the effects of dynamic hydrogen heat treatment and re-calcination on the microstructure and magnetic properties of conventionally synthesized strontium hexaferrite have been studied systematically.

2. Experimental procedure

Starting materials for M-type strontium hexaferrite conventionally synthesis were hematite (α-Fe_2O_3) and strontium carbonate ($SrCO_3$) without using any additives. The calcination was carried out at 1100 °C for 1 h in air. Hydrogen 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 H_2 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 Kα radiation) was used for phase identification. Scanning and transition electron microscopy was 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

X-ray diffraction pattern of the single phase strontium hexaferrite synthesized conventionally has been shown in Fig. 1. Fig. 2 also shows SEM image of the microstructure this powder. The hexagonal shape particles with size of below 500 nm can be observed clearly.

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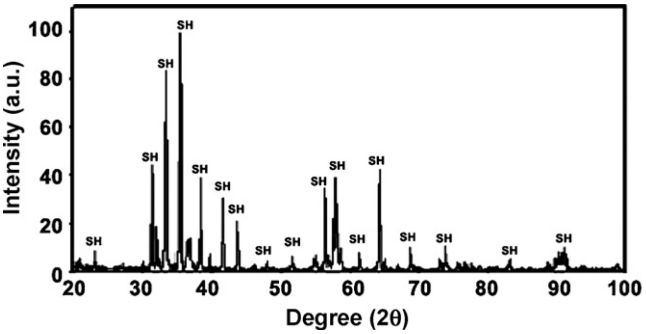

Fig. 1. X-ray diffraction pattern of Sr-hexaferrite synthesized conventionally at 1100 °C for 1 h (SH = Sr-hexaferrite).

X-ray diffraction patterns of the strontium hexaferrite powder subjected to hydrogen atmosphere at various temperatures with 30 cm^3/min flow for 1 h have been shown in Fig. 3.

Hydrogen heat treatment makes the initial powder to decompose into hematite and $Sr_7Fe_{10}O_{22}$. Then the resultant hematite was reduced by hydrogen to metallic iron and other iron oxides. Fig. 3 indicates that the extent of reduction increases with increasing the temperature. XRD pattern of the powder heat treated in hydrogen atmosphere at 550 °C in Fig. 3a shows that the reduction products are iron and magnetite. There is no trace of wustite (FeO) because it is unstable at temperatures lower than 570 °C. With increasing the temperature up to 650 °C, the magnetite was reduced totally to wustite and no traces of it could be seen any more (Fig. 3b). With further increasing the temperature, the reduction of wustite to iron became faster (Fig. 3c) and at temperature of 850 °C only a few traces of wustite would be still observed (Fig. 3d).

Fig. 4 shows X-ray diffraction pattern of the strontium hexaferrite powder heat treated at 850 °C with 60 cm^3/min for 1 h. This pattern indicates that with increasing the gas flow, the hematite was reduced completely to iron phase by hydrogen.

Since the wustite completely removed from the phase composition, the hydrogen heat treatment at 850 °C with 60 cm^3/min flow for 1 h was selected as optimum process.

The SEM image of this powder has been shown in Fig. 5. Compared to Fig. 2 the particle size has been decreased significantly due to expansion of the hydrogen penetrated inside the particles and breakage of the big grains into much finer sub-grains.

This optimum heat treated powder was then calcined at 900 and 1000 °C for 1 h in air. Their X-ray diffraction patterns have been shown in Fig. 6.

According to Fig. 6a, the present phases at the temperature of 900 °C are $SrFe_{12}O_{19}$, Fe_2O_3 and $Sr_7Fe_{10}O_{22}$. Therefore, this temper-

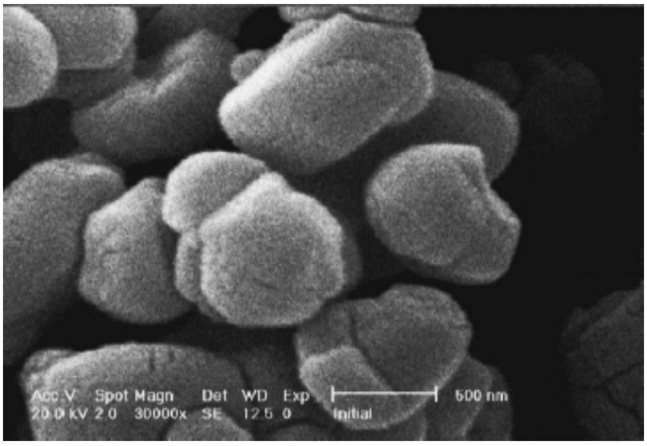

Fig. 2. SEM image of the powder synthesized conventionally.

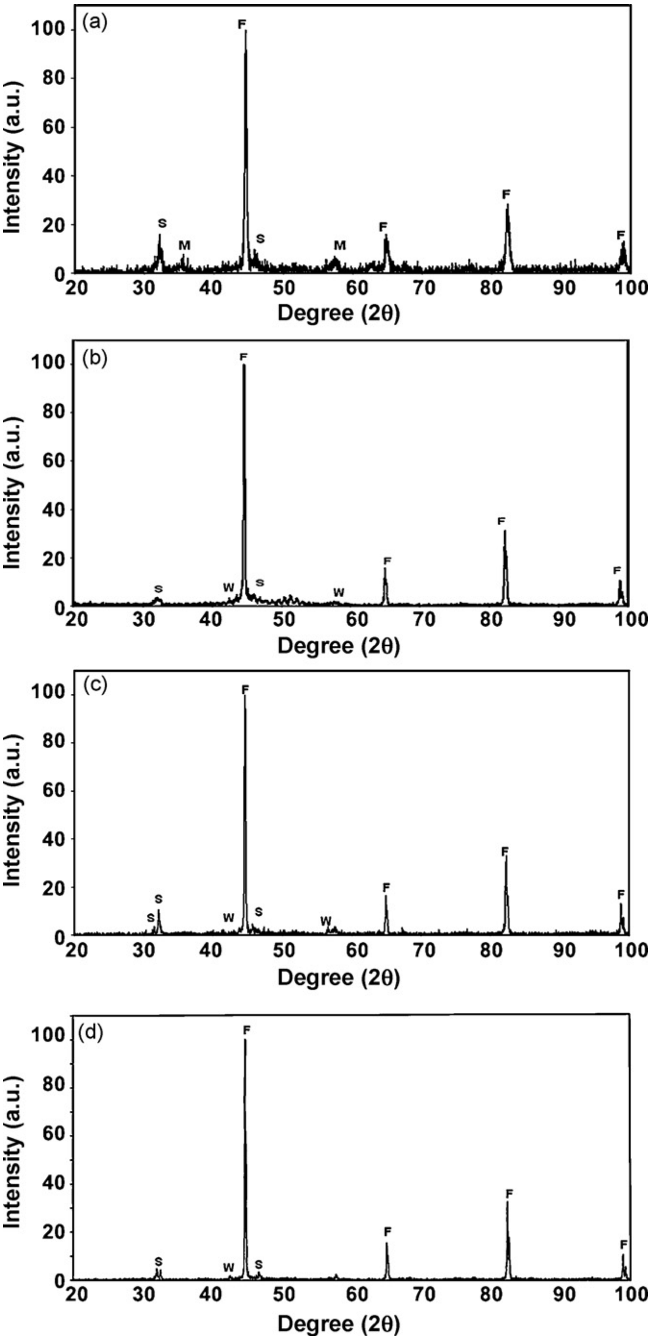

Fig. 3. X-ray diffraction patterns of the strontium hexaferrite powder heat treated in hydrogen atmosphere at (a) 550 °C, (b) 650 °C, (c) 750 °C and (d) 850 °C with 30 cm^3/min flow for 1 h (F = Fe, W = FeO, M = Fe_3O_4, S = $Sr_7Fe_{10}O_{22}$).

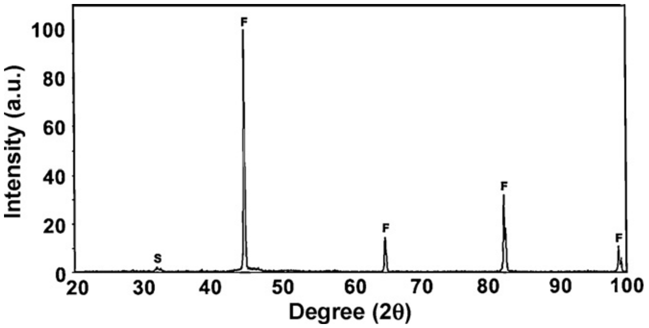

Fig. 4. X-ray diffraction pattern of the strontium hexaferrite powder heat treated at 850 °C with 60 cm^3/min for 1 h (F = Fe, S = $Sr_7Fe_{10}O_{22}$).

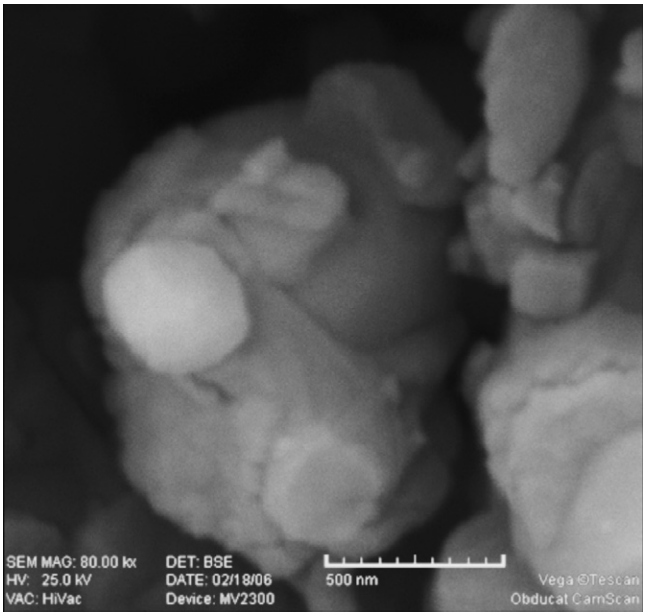

Fig. 5. SEM image of the hydrogen treated sample at 850 °C with 60 cm^3/min gas flow for 1 h.

ature is not enough to form the single phase strontium hexaferrite. With further increase of the calcination temperature up to 1000 °C, the single phase strontium hexaferrite was formed as it is shown in Fig. 6b. During the re-calcination process, the metallic iron was oxidized to hematite and then by reaction with $Sr_7Fe_{10}O_{22}$ the single phase strontium hexaferrite was re-formed.

The SEM image of the strontium hexaferrite powder after re-calcination at 1000 °C has been shown in Fig. 7.

This image shows that the strontium hexaferrite particles after re-calcination are much finer than those of the initial powder (Fig. 2) due to reformation of the hexaferrite phase on the surfaces of very fine grains obtained after hydrogen heat treatment.

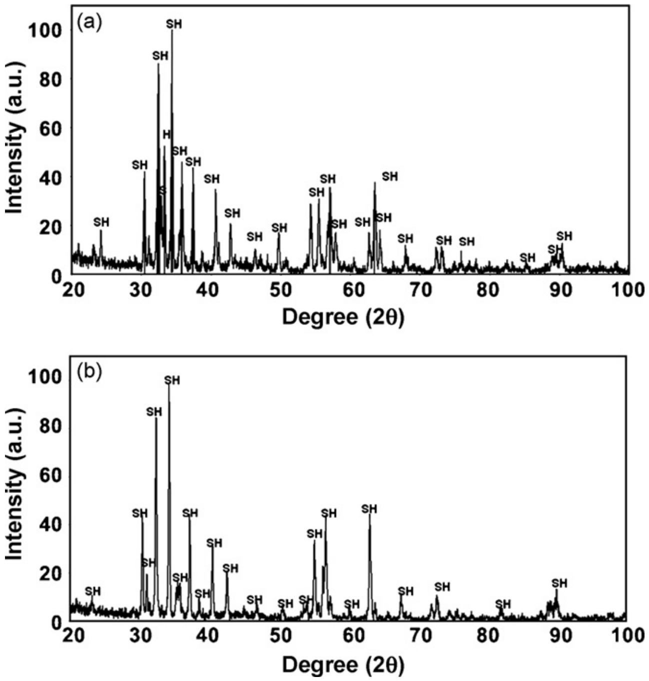

Fig. 6. X-ray diffraction pattern of the optimum powder which calcined at (a) 900 and (b) 1000 °C for 1 h (SH = $SrFe_{12}O_{19}$, S = $Sr_7Fe_{10}O_{22}$, H = Fe_2O_3).

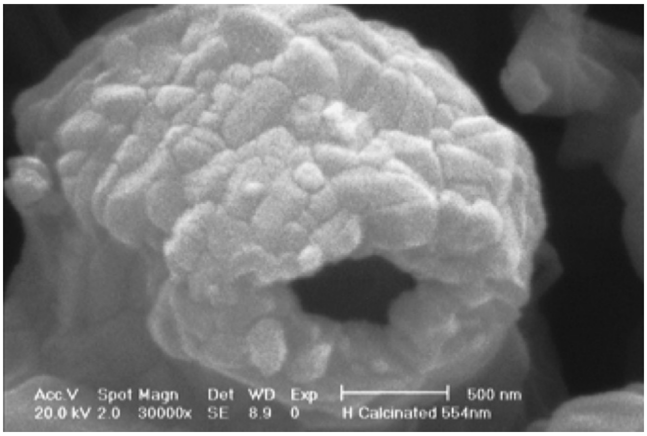

Fig. 7. SEM image of the strontium hexaferrite powder after re-calcination at 1000 °C for 1 h.

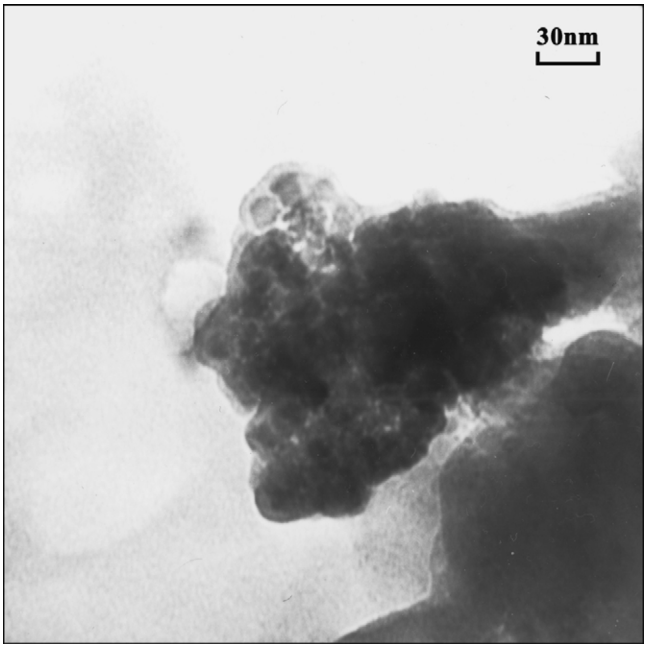

Fig. 8. The TEM image of the strontium hexaferrite nanocrystalline powder after re-calcination at 1000 °C for 1 h.

Fig. 8 also shows the TEM image of this powder. It seem that the size of the particles is below 50 nm which is in consistence with the measurement of the crystallite size of this sample by the X-ray line broadening technique employing the Scherrer formula as 38 nm.

The magnetic properties of the initial powder along with the powder hydrogenated and re-calcined optimally have been indicated in Table 1.

As it is shown in this table, the intrinsic coercivity of the initial strontium hexaferrite powder increased markedly after hydrogen heat treatment and re-calcination from 263 to 342 kA/m due to much finer structure obtained after this process. However, there are also small decreases in M_r and M_s after the process.

Table 1
Magnetic properties of the initial powder and the powder hydrogenated and re-calcined optimally.

Powder	M_s (J/Tkg)	M_r (J/Tkg)	H_{ci} (kA/m)
Initial	66.9	37.0	263
Hydrogenated and re-calcined optimally	55.8	31.9	342

4. Conclusions

During the hydrogen heat treatment, the strontium hexaferrite decomposed into Fe_2O_3 and $Sr_7Fe_{10}O_{22}$ and then the resultant Fe_2O_3 was reduced to iron with soft magnetic nature. After hydrogen treatment, the coarse microstructure of the initial strontium hexaferrite also changes to a much finer microstructure. Optimum conditions of hydrogen treatment obtained at 850 °C with 60 cm^3/min gas flow for 1 h.

Single phase strontium hexaferrite was formed again by recalcination of the optimum powder at 1000 °C having much finer microstructure than that of the initial powder. The crystallite size of the optimum powder was measured below 50 nm.

The main effect of this very fine microstructure was on the noticeable increase of the intrinsic coercivity from 263 to 342 kA/m.

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