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Heat treatment of strontium hexaferrite powder in nitrogen, hydrogen and carbon atmospheres: a novel method of changing the magnetic properties

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Strontium hexaferrite powder has been treated in nitrogen, hydrogen and carbon atmospheres. The results show that the phase composition and morphology, and hence, the magnetic properties of the strontium hexaferrite are affected significantly by these gas/vapour treatments. Generally, the coercivity decreased to below 0.8 kOe (regardless of the initial coercivity) and the magnetization at 14 kOe increased significantly, when strontium hexaferrite powder had been treated in a nitrogen, hydrogen or carbon atmosphere. However, it was found that a post-gas treatment of calcination in air, under appropriate conditions, resulted in a recovery of the hexaferrite structure (i.e. it is a reversible reaction). However, the particle/grain sizes of the calcined samples were significantly smaller than those of the non-treated samples, and it is believed that they were single domain particles/grains. In some cases, the coercivity increased by about 400%. The magnetization at 14 kOe and the remanence were either not affected or sometimes increased; magnetic measurements indicated a preferred orientation of the grains.

1. Introduction

In addition to their permanent magnet applications [1], barium hexaferrite ($BaFe_{12}O_{19}$) or strontium hexaferrite ($SrFe_{12}O_{19}$) in powder form exhibit excellent chemical stability, and are promising materials for perpendicular and longitudinal high-density recording media [2–4]. As a means of increasing the suitability of hexaferrite powders for use in recording media such as hard disks, floppy disks and video tapes, and in order to lower the coercivity somewhat, the substitution of Co–Ti, Co–Ni–Zn and Co–Zr for some of the iron in the hexaferrites has been proposed [5–8]. However, as a consequence, the saturation magnetization is also decreased markedly. Conversely, in order to increase the coercivity, so as to make these hexaferrites suitable for use as the recording medium in identification cards and credit cards, or for the fabrication of permanent magnets, the practice is either to substitute the hexaferrites with elements such as aluminium and chromium or to produce the hexaferrites using chemical methods, which are more expensive than the conventional ceramic mixed-oxide production methods [8, 9]. However, increasing the degree of substitution, e.g. with elements such as aluminium and chromium, again results in a significant decrease in the saturation magnetization.

The authors have developed a method of processing hexaferrites (Patent Cooperation Treaty patent pending) in order to produce the desired coercivity in a relatively economical manner without decreasing the saturation magnetization to an unacceptable level, and in some cases, actually increasing the saturation magnetization [10]. In the first instance, low coercivity materials, which might be of use in recording media such as hard disks, floppy disks and video tapes, can be prepared by heat treating strontium hexaferrite powder in the presence of nitrogen, hydrogen or carbon. In order to produce powders of higher coercivity for permanent magnet applications, such gas-treated materials can then be calcined to recover the hexaferrite phase. This paper reports the results of these studies.

2. Experimental procedure

Commercial strontium hexaferrite powders (supplied by Swift Levick Magnets) and strontium hexaferrite powder produced hydrothermally at 220 °C for 1 h in the presence of NaOH (the details of which have been described previously [11]) were treated in static nitrogen, hydrogen and carbon atmospheres. It should be noted that the starting materials were calcined at 850 °C for 2 h prior to the nitrogen, hydrogen or carbon gas/vapour treatments. Table I lists the

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TABLE I Coercivity, remanence and saturation magnetization of the starting materials after calcination at 850 °C for 2 h

Starting material	Production route	H_{ci} (kOe)	σ_r (e.m.u. g^{-1})	σ (at 14 kOe) (e.m.u. g^{-1})
Sr-hexaferrite	Hydrothermal	1.2	20	56
Sr-hexaferrite	Commercial	2.77	40	69

magnetic properties of the commercial and hydrothermally produced strontium hexaferrite powders after they had been calcined under the above conditions.

The nitrogen treatment was carried out within a static nitrogen atmosphere (1 bar) inside a resistance-heated vacuum tube furnace at > 500 °C for a few hours. The hydrogen treatment was effected by hydrogen gas (static) in a resistance-heated vacuum furnace under various pressures at < 1000 °C for a few hours. The strontium hexaferrite powders were carburized using granular charcoal in a ceramic crucible sealed by alumina–silica clay in a resistance-heated muffle furnace at < 1000 °C for a few hours. The treated strontium hexaferrite samples were then calcined at various temperatures for different times in air using a resistance-heated muffle furnace.

X-ray powder diffraction (cobalt radiation) was used to analyse the powders after treatment at the various stages in the process. The powder particle size and morphology were studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A vibrating sample magnetometer (VSM) operating up to a maximum field of 14 kOe, and a Sucksmith balance, were employed to evaluate the magnetic properties of the samples. It should be mentioned that the magnetic properties were measured in the non-aligned state except for the data shown in Fig. 11.

3. Results and discussion

3.1. Nitrogen treatment

The results obtained show that the coercivity of the nitrogen-treated (NT) samples decreased (from 1.2 kOe to about 0.4 kOe for the hydrothermally produced powders, and from 2.77 kOe to about 0.7 kOe for the commercial powders), whilst their magnetization at 14 kOe increased to 71 e.m.u. g^{-1}. The formation, *in situ*, of soft magnetic phase(s) with increased magnetization(s) is believed to be responsible for these changes. Fig. 1 shows the powder X-ray diffraction patterns for (a) the non-nitrogen treated strontium hexaferrite sample (produced hydrothermally), (b) the sample nitrogen treated at < 1000 °C for a few hours, and (c) the nitrogen-treated sample subsequently calcined. It can be seen, comparing Fig. 1a and c, that post-nitrogen treatment calcination recovers the hexaferrite structure, thus showing that the process is reversible.

Recovery of the hexaferrite phase due to the post-nitrogen treatment calcination can also be observed in Fig. 2, which shows the Curie temperature measurements of the above mentioned samples. The initial slope change is the magnetic contribution of the sample holder and acts as a calibration point. This shows a constant value of about 140 °C in all three plots but the upper Curie point exhibits a marked reduction in the nitrogen-treated material. The recovered hexaferrite has a slightly enhanced Curie point of 421 °C; this corresponds with a change in the lattice parameters.

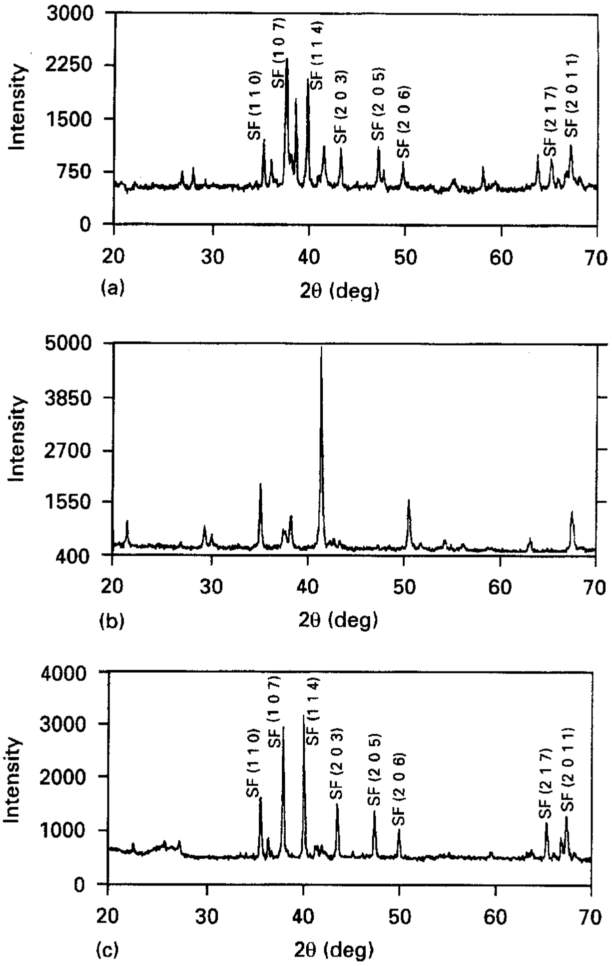

Figure 1 Powder X-ray diffraction patterns for (a) the non-NT strontium hexaferrite sample (produced hydrothermally), (b) the sample NT at < 1000 °C for a few hours, and (c) the NT sample subsequently calcined.

While the hexaferrite structure is recovered by the post-nitrogen treatment calcination, SEM studies indicate that the mean particle size of the sample is then significantly smaller than that of the non-nitrogen treated sample. The lattice parameters of the nitrogen-treated then calcined sample were different from the original state, exhibiting about 0.1% contraction along the *a*-axis and about 0.25% expansion along the *c*-axis (see Table II). This change is consistent with the increased Curie temperature.

Scanning electron micrographs (Figs 3–5) indicate that the plate-like particles of the hydrothermally produced strontium hexaferrite with an average particle

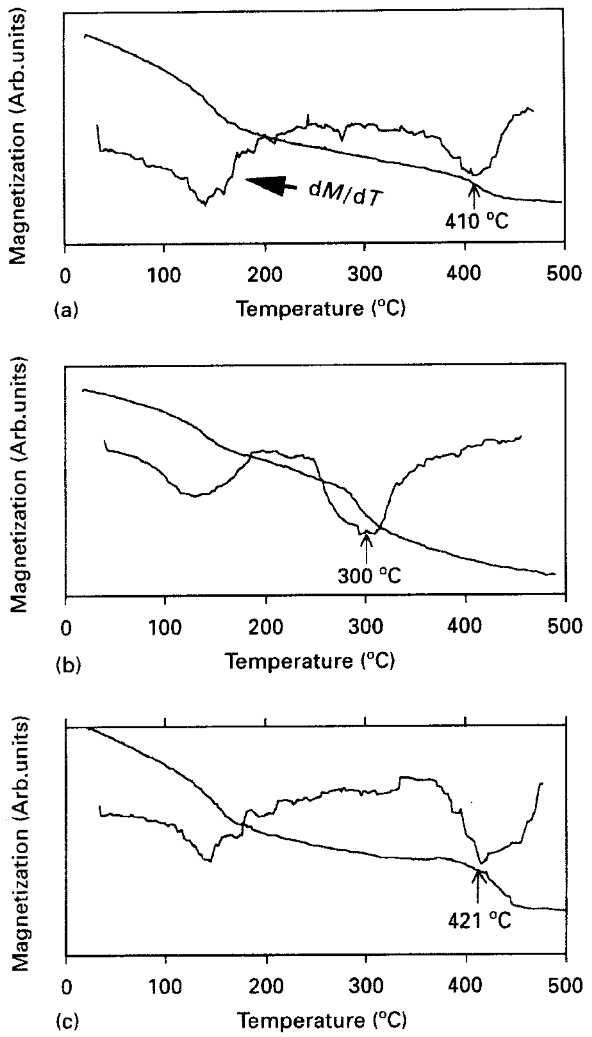

Figure 2 Magnetization and dM/dT as a function of temperature for (a) the non-NT strontium hexaferrite sample (produced hydrothermally), (b) the sample NT at above 500 °C for a few hours, and (c) the NT sample subsequently calcined.

TABLE II Lattice parameters of the non-nitrogen treated and nitrogen-treated calcined hydrothermal and commercial strontium hexaferrite samples

Sample	a(± 0.0001 nm)	c(± 0.0001 nm)
Non-NT hydrothermal strontium hexaferrite	0.5874	2.2926
Non-NT commercial strontium hexaferrite	0.5857	2.2939
NT-calcined hydrothermal strontium hexaferrite	0.5866	2.2982
NT-calcined commercial strontium hexaferrite	0.5853	2.2982

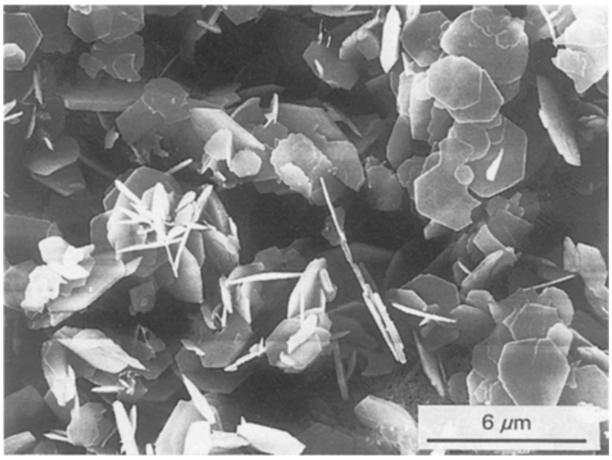

Figure 3 Scanning electron micrograph of strontium hexaferrite particles produced hydrothermally showing plate-like particles of strontium hexaferrite with an average particle size of 1.5 μm.

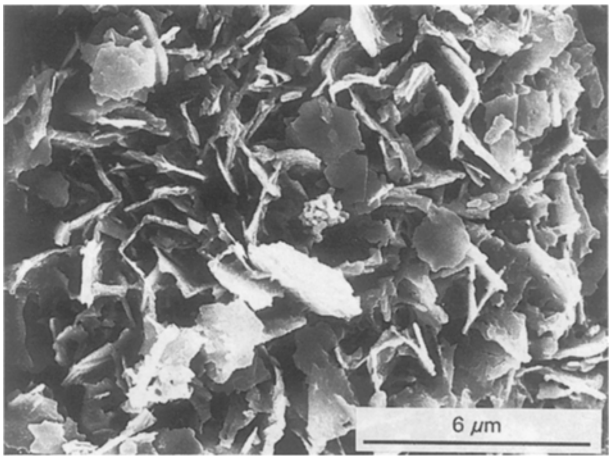

Figure 4 Scanning electron micrograph of NT strontium hexaferrite powder (produced hydrothermally) showing ruffled edges of the platelets.

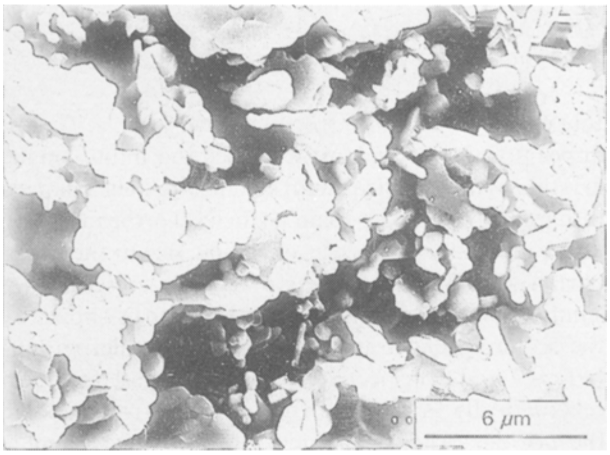

Figure 5 Scanning electron micrograph of NT and then calcined strontium hexaferrite powder (produced hydrothermally) showing tablet-like particles of strontium hexaferrite with an average particle size of < 0.5 μm.

size of 1.5 μm (see Fig. 3), were converted to tablet-like particles with an average particle size of less than 0.5 μm (see Fig. 5) after the nitrogen treatment-calcination. The decrease in the particle aspect-ratio may be attributed to the changes in the lattice parameters. The "ruffled" edges of the platelets in Fig. 4 suggest a restructuring of the particles to a finer grain microstructure as a consequence of the nitrogen treatment.

It is believed that the nitrogen-treated calcined samples consist of single-domain particles/grains of strontium hexaferrite, as indicated by the shape of the initial magnetization curve shown in Fig. 6. It can be seen that the nitrogen-treated calcined sample exhibits a very low initial susceptibility in comparison with

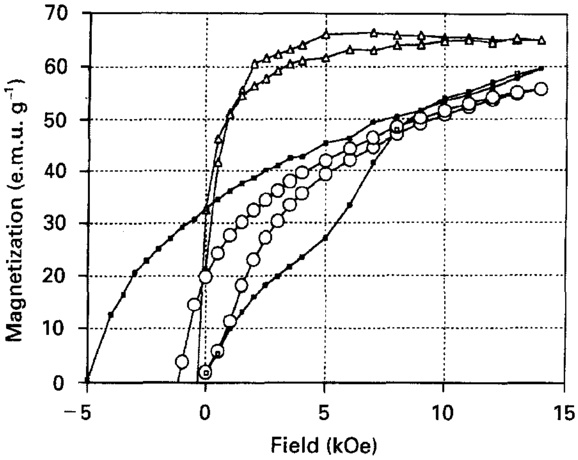

Figure 6 Magnetization as a function of applied field for (○) the initial strontium hexaferrite sample (produced hydrothermally), (△) the sample NT at > 500 °C for a few hours, and (□) the NT sample subsequently calcined (samples not pre-aligned).

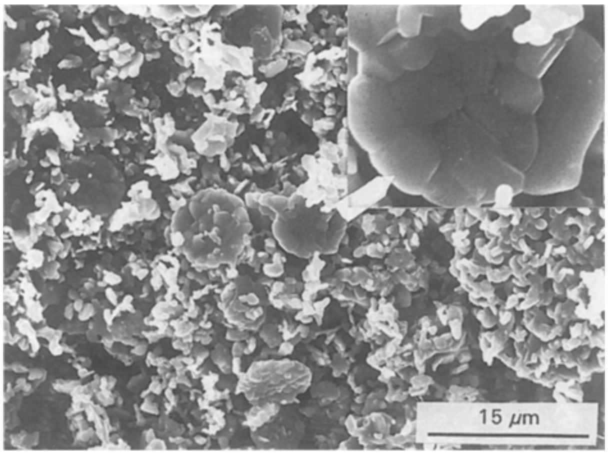

Figure 7 Scanning electron micrograph of strontium hexaferrite powder (produced hydrothermally) after it had been nitrogen-treated and then calcined, showing the polycrystalline nature of the larger particles. The central large particle is magnified in the top right-hand corner insert.

that of the initial non-nitrogen treated sample. Thus, it appears that this treatment causes the initial single-crystal particles of strontium hexaferrite to be changed into much finer single-grain particles (i.e. the majority) and a minority of particles of similar size to the initial particles but now consisting of smaller sub-grains (of similar size to the single-grain particles), as shown by the scanning and transmission electron micrographs in Figs 7 and 8, respectively. These changes are shown schematically in Fig. 9. In the nitrogen-treated state the powder exhibits a much lower coercivity, but a higher magnetization, which reaches saturation, thus indicating a softer magnetic state compared with that of strontium hexaferrite.

The coercivity of the nitrogen-treated and then calcined samples increased significantly compared with that of the initial samples (i.e. from 1.2 kOe to 5 kOe for the hydrothermally produced sample, and from 2.77 kOe to 3.66 kOe for the commercial sample). In Fig. 10, the magnetic property values of the hydrothermally produced strontium hexaferrite powder are

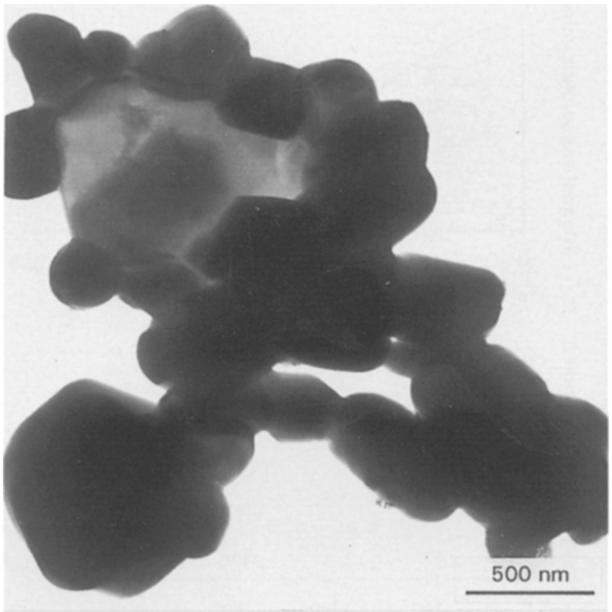

Figure 8 Transmission electron micrograph of strontium hexaferrite powder (produced hydrothermally) after it had been NT and then calcined, showing the polycrystalline nature of the particles; see top left-hand corner.

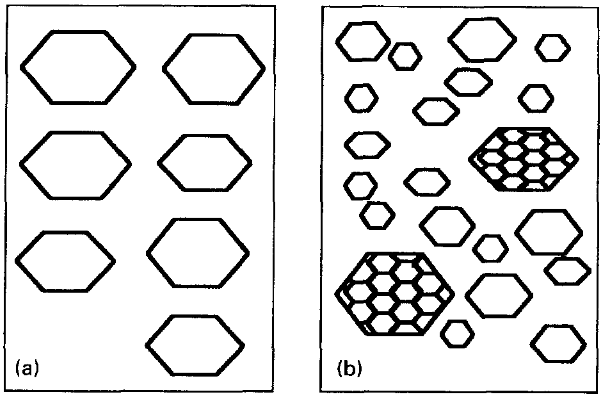

Figure 9 Schematic diagram illustrating the changing of (a) the initial particles into (b) multicrystalline particles and finer single-crystal particles of a similar size to the sub-grains, as a consequence of NT and subsequent calcination.

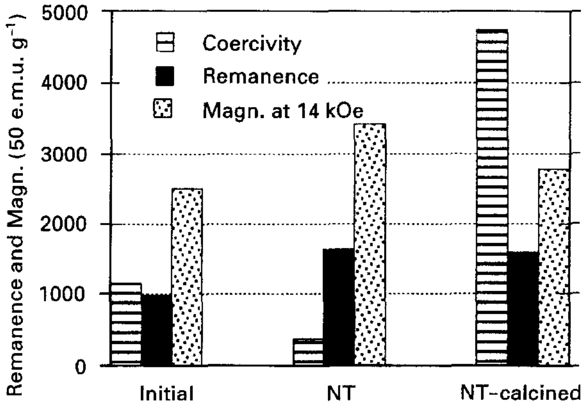

Figure 10 Magnetic properties of (a) the initial strontium hexaferrite sample (produced hydrothermally), (b) the sample NT at > 500 °C for a few hours, and (c) the NT sample subsequently calcined.

compared with the corresponding values for the nitrogen-treated and the nitrogen-treated calcined samples. The VSM data (shown in Fig. 11) reveal that the nitrogen-treated calcined powders are magnetically

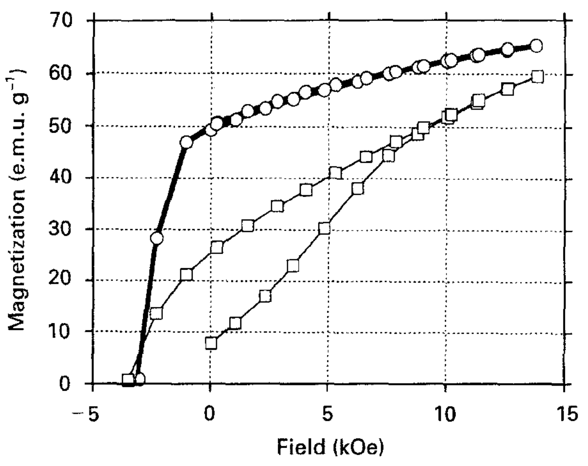

Figure 11 Magnetization as a function of applied field for the NT calcined commercial strontium hexaferrite powder along the (○) easy and (□) hard magnetization directions, showing the anisotropic nature of the powder.

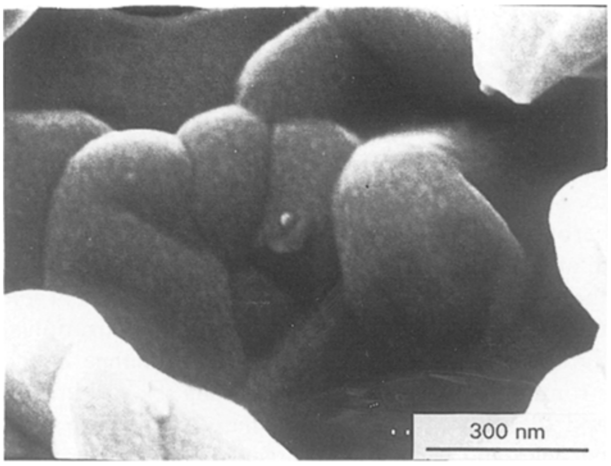

Figure 12 Scanning electron micrograph of strontium hexaferrite powder (produced hydrothermally) after it had been HT and then calcined, showing the re-structuring of an individual particle into several sub-grains.

anisotropic in nature, thus indicating that the grain structure shown in Figs 7 and 8 is probably highly aligned.

In summary, the nitrogen treatment and subsequent calcination leads to a very significant refinement of the single-crystal particle size; the presence of a minority of multi-grain particles could indicate incomplete particle separation in these cases.

3.2. Hydrogen treatment

In comparison with the non-hydrogen treated sample, the coercivity of the hydrogen treated (HT) samples was significantly lower. In contrast, the magnetization at 14 kOe increased significantly from 56 e.m.u. g^{-1} to 156 e.m.u. g^{-1}. The remanence did not exhibit any marked change. The decrease in the coercivity and the increase in saturation magnetization may both be attributed to the reduction in the proportion of the strontium hexaferrite phase present and the formation of magnetically soft phase(s) with increased magnetization value(s).

When the hydrogen-treated samples were calcined under appropriate conditions, the strontium hexaferrite phase was recovered (i.e. it is a reversible reaction). However, the coercivity of the hydrothermal samples exhibited about a 400% increase in comparison with the initial sample, from 1.2 kOe to 4.7 kOe. This marked increase in the coercivity may be attributed to the smaller grain size of the strontium hexaferrite particles. As with the powder heat treated in a nitrogen atmosphere, it appears that each single grain is changed into several sub-grains during the hydrogen heat treatment as shown by the scanning electron micrograph in Fig. 12.

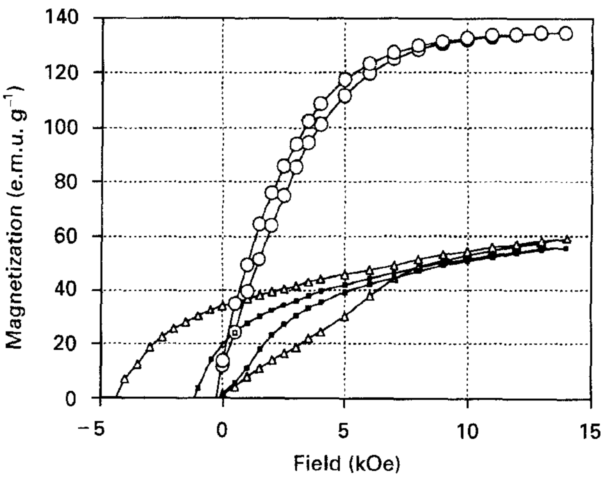

Figure 13 Magnetization as a function of applied field for (□) the initial strontium hexaferrite sample (produced hydrothermally), (○) the sample HT at < 1000 °C for a few hours, and (△) the HT sample subsequently calcined (samples not pre-aligned).

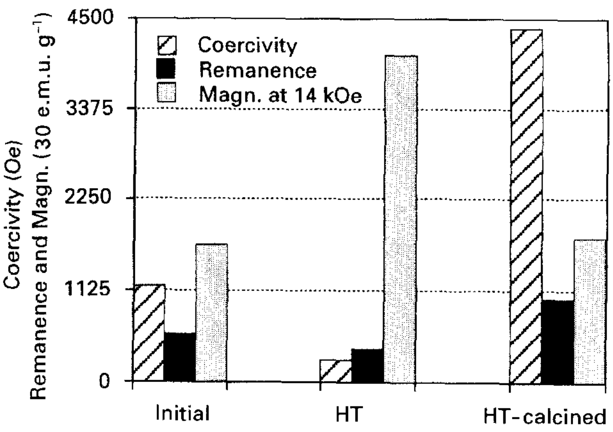

Figure 14 Magnetic properties for (a) the initial strontium hexaferrite sample (produced hydrothermally), (b) the sample HT at < 1000 °C for a few hours, and (c) the HT sample subsequently calcined.

Both the remanence and saturation magnetization of the hydrogen-treated calcined samples are also increased. These samples are believed to consist of single-domain grains of strontium hexaferrite; the shape of the initial magnetization curve in Fig. 13 is consistent with this claim. Fig. 14 shows the magnetic properties for the sample hydrogen treated at < 1000 °C for a few hours and then calcined, in comparison with those for the initial non-hydrogen treated sample and for the hydrogen-treated sample.

3.3. Carburizing

The coercivity of the commercial hexaferrite powder decreased from 2.77 kOe to 0.37 kOe when it was carburized at < 1000 °C for a few hours, while the magnetization at 14 kOe increased from 69 e.m.u. g^{-1} to 107 e.m.u. g^{-1}. These magnetic properties changed to 4.34 kOe and 60 e.m.u. g^{-1}, respectively, after the carburized sample had been calcined at < 1000 °C for a few hours. Both the reduction in the proportion of the hexaferrite phase present and the formation of soft magnetic phase(s) with increased magnetization(s) during carburizing, together with the change of the strontium hexaferrite particles during the carburizing and the post-carburizing calcination into both finer particles and particles comprising sub-grains, can explain the changes in the magnetic properties.

It was found that the carburizing process, like the nitrogen and hydrogen treatments, is reversible, as shown by the X-ray diffraction patterns in Fig. 15. The diffraction pattern of the carburized sample indicates clearly the presence of α-Fe. The lattice parameters of the carburized then calcined samples are different to those of the non-carburized samples, exhibiting a contraction along the *a*-axis and an expansion along the *c*-axis (see Table III).

Fig. 16 shows the magnetic properties of the non-carburized, carburized, and carburized then calcined commercial strontium hexaferrite sample, the magnetization curves of which are shown in Fig. 17.

TABLE III Lattice parameters of the non-carburized and carburized calcined hydrothermal strontium hexaferrite sample

Sample	*a*(± 0.0001 nm)	*c*(± 0.0001 nm)
Non-carburized hydrothermal strontium hexaferrite	0.5874	2.2926
Carburized calcined hydrothermal strontium hexaferrite	0.5865	2.3007

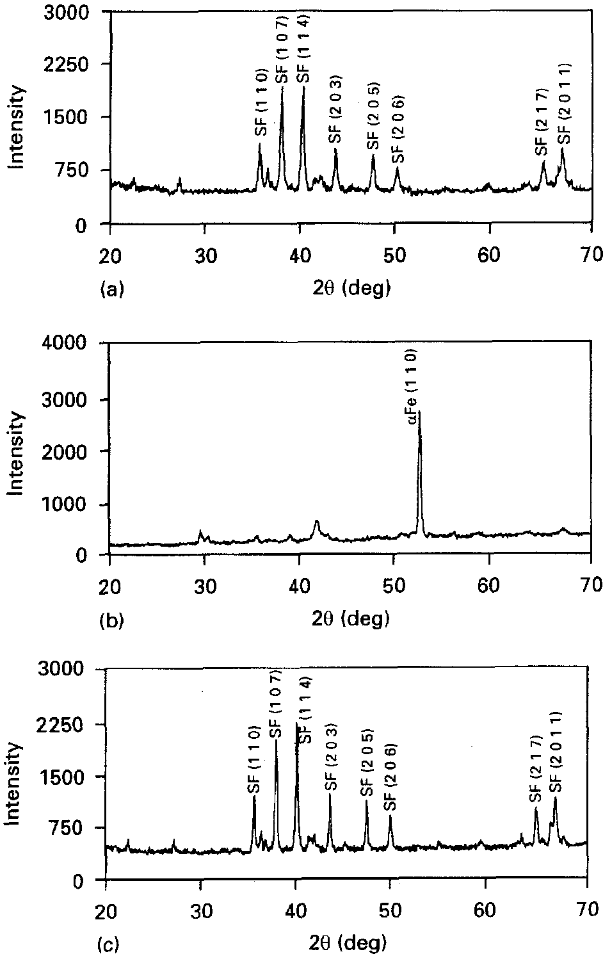

Figure 15 Powder X-ray diffraction patterns for (a) the non-carburized commercial strontium hexaferrite sample, (b) the sample carburized at < 1000 °C for a few hours, and (c) the carburized sample subsequently calcined.

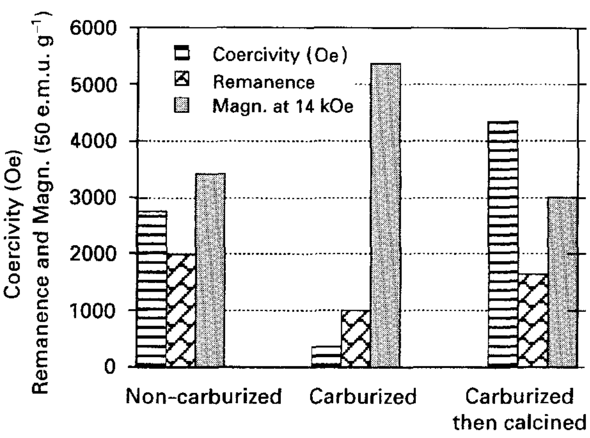

Figure 16 Magnetic properties for (a) the non-carburized commercial strontium hexaferrite sample, (b) the sample carburized at < 1000 °C for a few hours, and (c) the carburized sample subsequently calcined.

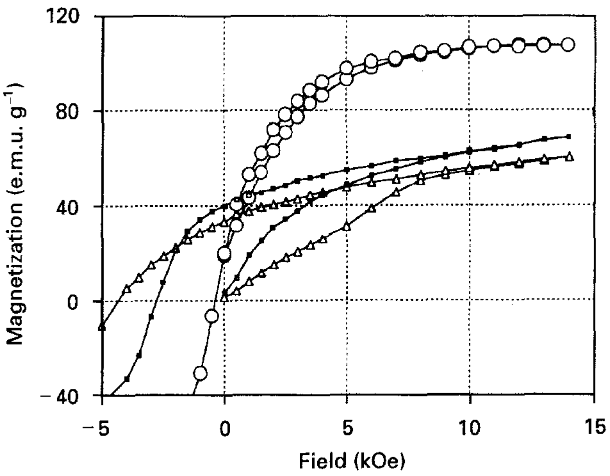

Figure 17 Magnetization as a function of applied field for (☐) the non-carburized commercial strontium hexaferrite sample, (○) the sample carburized at < 1000 °C for a few hours, and (△) the carburized sample subsequently calcined (samples not pre-aligned).

4. Conclusion

Both hydrothermally produced and commercial strontium hexaferrite powders have been processed in two stages. In the first stage, the strontium hexaferrite powders were heat treated in the presence of either nitrogen, hydrogen or carbon. It was found that all the treatments produced a variety of magnetic properties, with the common features of a coercivity reduction and an increase in the magnetization at 14 kOe. The magnetic properties of the gas/vapour treated materials are influenced by the characteristics of the starting materials as well as the process conditions, i.e. temperature, time, and gas/vapour pressure. The treated materials prior to calcination exhibit a relatively reduced coercivity and enhanced magnetization at 14 kOe, thus making them potentially suitable for use in recording media.

In the second stage, the nitrogen-treated, hydrogen-treated, and carburized samples were calcined in air under the appropriate conditions. The calcination treatment recovered the hexagonal ferrite phase with a large increase in the coercivity compared with that of the initial sample. The significant increase in the coercivity can be attributed to the change in the ferrite particles, from micrometre-sized particles to sub-micrometre-sized particles and a minority of micrometre-sized preferentially oriented particles comprising sub-grains. The initial magnetization curves of these samples imply that they consist of single-domain particles/grains of strontium hexaferrite. The remanence and magnetization at 14 kOe were both increased for the hydrothermally synthesized samples. The magnetic measurements on pre-aligned samples exhibit both easy and hard magnetization directions, thus indicating a preferred orientation of the sub-grain structure. The resulting calcined powders exhibited a coercivity as high as 4.5 kOe or above, together with an acceptable remanence and saturation magnetization, thereby making these materials potentially suitable for use either as the recording medium in identification and credit cards, or for the fabrication of permanent magnets.

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