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The effect of hydrogen on composition, microstructure and magnetic properties of strontium hexaferrite

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Abstract

Strontium hexaferrite powder, synthesised conventionally, has been treated in a hydrogen atmosphere and subsequently calcined in air. The phase identification studies showed decomposition of strontium hexaferrite into Fe_2O_3 and $Sr_7Fe_{10}O_{22}$ and the reduction of the resultant Fe_2O_3 during reaction with hydrogen. The magnetic measurements indicated a substantial increase in the saturation magnetisation and a marked decrease in the remanence and intrinsic coercivity during hydrogenation due to the formation of the α-Fe phase. After re-calcination, the hexaferrite phase re-formed and the remanence and saturation magnetisation exhibited values close to the initial ones but there was a significant improvement in the intrinsic coercivity. This was attributed mainly to very fine grains formed as a result of hydrogenation and subsequent re-calcination. The highest intrinsic coercivity obtained in this work was 400 kA/m (5 kOe) which occurred after hydrogenation at 700°C for 1 h under an initial pressure of 1.3 bar followed by re-calcination at 1000°C for 1 h. These studies show that strontium hexaferrite powder with an enhanced value of intrinsic coercivity can be produced from the conventionally synthesised powder.

Keywords: B. Microstructure; C. Magnetic properties; Hydrogen effect; Composition; Strontium hexaferrite

1. Introduction

A new method of processing hexaferrites in order to produce an increased intrinsic coercivity has been reported for commercial and hydrothermally synthesised materials [1,2]. By this method, low coercivity can be produced by heat treating the powders in the presence of hydrogen, nitrogen or carbon. High coercivities can then be achieved by a post-calcination in air. This method has recently been investigated for hydrogen and nitrogen and improved values of the intrinsic coercivity have been obtained [3].

In this work, the hydrogenation and re-calcination processes applied to the conventionally synthesised strontium hexaferrite powder have been studied using vibrating sample magnetometer (VSM), X-ray diffraction (XRD) and high resolution scanning electron microscopy (HRSEM) techniques. The phase transformations during these processes have been identified. A more detailed study of the phase products is given in Ref. [4].

2. Experimental procedure

The starting material was M-type strontium hexaferrite produced conventionally by calcining of strontium carbonate and hematite (α-Fe_2O_3). The ratio of iron oxide to strontium carbonate was 5. 5 to 1 without using any additives. The calcination was carried out at 1100°C for 1 h in air. The hydrogenation was carried out in a static atmosphere at various initial pressures. The hydrogenation process consisted of heating the powder at a rate of 5°C/min up to various temperatures, dwelling for various times and then cooling at the same rate. Subsequent calcination processes also consisted of heating to various temperatures, dwelling for 1 h and then cooling. The heating and cooling rate was 5°C/min and 10°C/min respectively. The magnetic properties were measured at room temperature by a VSM operating up to a maximum field of 1100 kA/m. The majority of VSM samples were mounted in molten wax but were not subject to a magnetic alignment field and hence were magnetically isotropic. On applying a field, there was no evidence of anisotropy in the treated powders. X-ray diffraction analysis (Co-Kα radiation) was used for phase identification.

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3. Results and discussion

The comparative magnetisation curves (quadrants 1 and 2) of the conventionally synthesised powder prior to hydrogenation, after hydrogenation and after a subsequent calcination are shown in Fig. 1.

It can be seen that after hydrogenation at 700°C for 1 h, under an initial pressure of 1.3 bar, the remanence and intrinsic coercivity decreased markedly to values close to zero. However, the magnetisation at 1100 kA/m increased considerably and approached a completely saturated value of $\sim$110 J/Tkg.

At the next stage, when this powder was re-calcined at 1000°C for 1 h in air, the remanence and magnetisation at 1100 kA/m showed values close to the initial values but, the intrinsic coercivity exhibited an increase to 400 kA/m compared with the initial value of 314.6 kA/m.

The XRD traces of these three powders are exhibited in Fig. 2. All the peaks in Fig. 2a belong to the stoichiometric M-type strontium hexaferrite, $SrFe_{12}O_{19}$ (or $Sr0.6Fe_2O_3$) [5]. Thus, the initial powder consisted predominantly of the strontium hexaferrite phase.

The XRD traces in Fig. 2b shows that a radical change in the phase constitution occurred during hydrogenation. There are almost no traces of the hexaferrite phase and the main peaks can now be ascribed to Fe [6], FeO [7] and $Sr_7Fe_{10}O_{22}$ (or $7SrO.5Fe_2O_3$) [8]. These results show that during hydrogenation the strontium hexaferrite decomposed into $7SrO.5Fe_2O_3$ and Fe_2O_3 and the resultant Fe_2O_3 was then reduced by hydrogen to form α-Fe. Thus, the very high magnetisation at 1100 kA/m and very low intrinsic coercivity after hydrogenation (Fig. 1) can be attributed to the strong presence of the magnetically soft α-Fe phase. The presence of FeO after hydrogenation indicated the partial reduction of Fe_2O_3 to Fe by hydrogen.

In Fig. 2c only the strontium hexaferrite peaks were observed and this indicated that, after subsequent calcination, the reduction reactions were completely reversed.

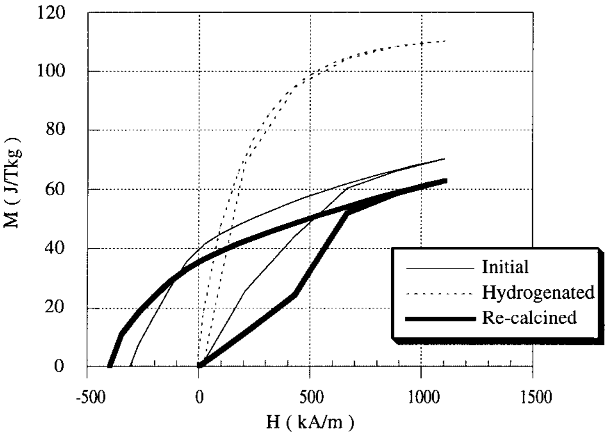

Fig. 1. The comparative magnetisation curves for the initial, hydrogenated and re-calcined conventional powders.

The microstructures of the powders are exhibited in Figs. 3–5. Fig. 3 shows the hexagonal-like grains of the initial hexaferrite. The surfaces of the grains are smooth and the grains edges are sharp. The mean grain size in this powder was below 500 nm.

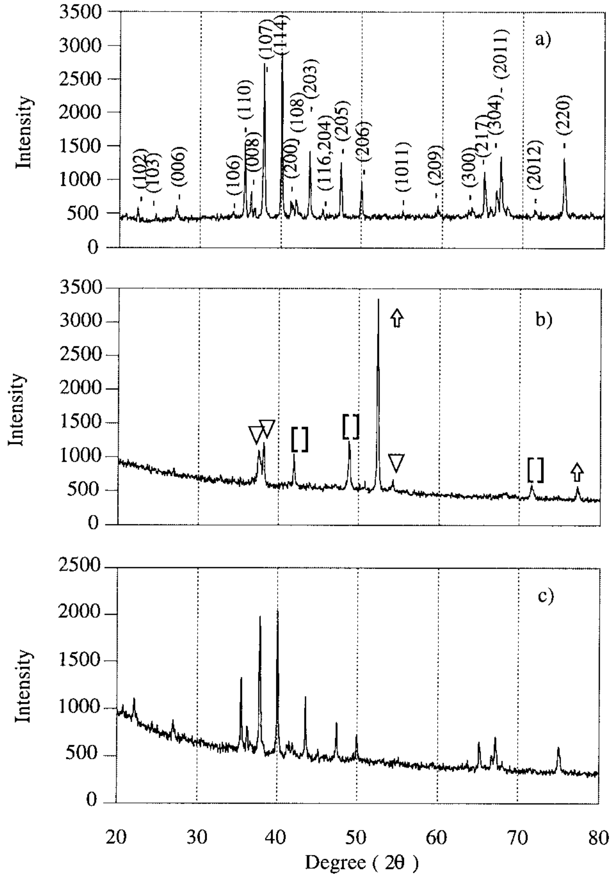

Fig. 2. The XRD patterns of (a) initial powder indexed according to hexagonal $SrFe_{12}O_{19}$, (b) hydrogenated at 700°C for 1 h under initial pressure of 1.3 bar, (c) subsequently calcined at 1000°C for 1 h in air indicating the same pattern as that shown in (a).($\Uparrow$ = Fe, $\nabla = Sr_7Fe_{10}O_{22}$, [] = FeO).

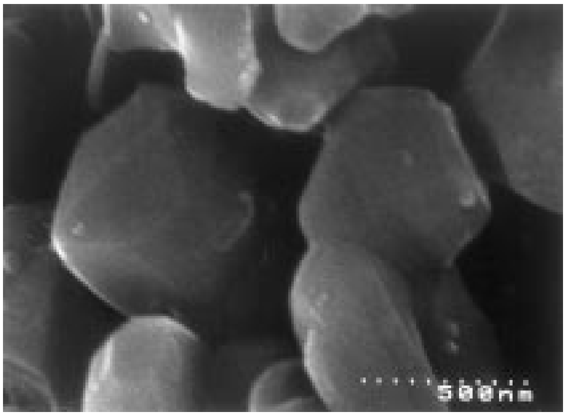

Fig. 3. The micrograph of initial powder, showing hexagonal like grains.

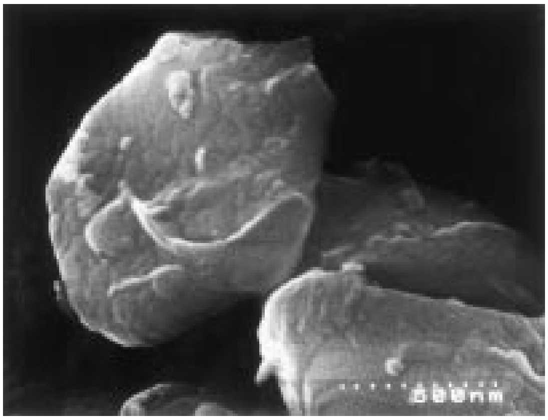

Fig. 4. The micrograph of hexaferrite powder after hydrogenation at 700°C for 1 h under 1.3 bar pressure, indicating a very fine substructure within the individual particles.

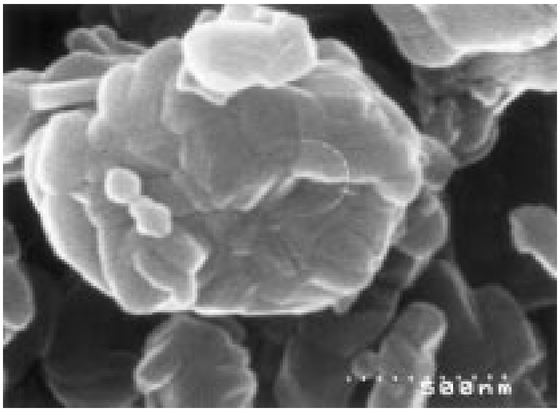

Fig. 5. The micrograph of recovered hexaferrite during subsequent calcination after hydrogenation. The smaller grains appear within what was originally an individual particle.

In Fig. 4, it can be seen that some of the original grains are sub-divided into very fine sub-grains. The mean size of these sub-grains was below 100 nm. This refinement of the microstructure which occurred during hydrogenation, apparently has a big influence on the subsequent refinement of the Sr-hexaferrite grains formed during re-calcination.

Fig. 5 shows that the hexaferrite grains after re-calcination are much finer than those of the initial powder (Fig. 3). The original individual particles now appear to be subdivided into finer grains. The mean size of the grains shown in Fig. 5 is below 300 nm.

The increase in the intrinsic coercivity in the re-calcined powder in comparison with that of the initial powder can be attributed to this finer structure. With respect to the size of grains shown in Fig. 5 they are much less than the single domain size for Sr-hexaferrite (~1 μm). The shape of the initial magnetisation curves in Fig. 1 also support this finding as these show that the initial susceptibility of the re-calcined sample is much lower than that of the initial powder.

4. Conclusions

The strontium hexaferrite decomposed during the hydrogenation process to Fe_2O_3 and $Sr_7Fe_{10}O_{22}$ and then the resultant iron oxide was -reduced by hydrogen to α-Fe. The effect on the magnetic properties was a significant increase in the magnetisation at 1100 kA/m and a marked decrease in the intrinsic coercivity and remanence due to the presence of the magnetically soft α-Fe phase. With a subsequent calcination process, the reactions were reversed and the Sr-hexaferrite phase recovered, thus indicating that the hydrogenation and re-calcination were reversible processes. Consequently, the magnetisation at 1100kA/m and remanence recovered to their initial values but the intrinsic coercivity exhibited a much higher value due to a finer, single domain grain size. The highest coercivity obtained was 400 kA/m, after hydrogenation at 700°C for 1 h under 1.3 bar initial pressure in a static hydrogen atmosphere and then calcination in air at 1000°C for 1 h.

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