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Journal of Magnetism and Magnetic Materials 205 (1999) 261–269

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Magnetic properties of Ba hexaferrite and Fe compounds produced by milling and annealing in air

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Received 10 March 1999

Abstract

The structure and magnetic properties of different magnetic compounds are studied. The compounds are produced by first milling 80% Ba hexaferrite and 20% Fe for 40 h (giving severely deformed hexaferrite plus Fe), and for 60 h (giving magnetite plus Ba carbonate). These two precursors are annealed at 850, 900 and 1000°C in air and characterized by their structure and magnetic properties. When the precursor consists of deformed hexaferrite and Fe, the thermal treatment promotes the elimination of defects in the hexaferrite and the oxidation of Fe to hematite and some magnetite. In the other case, that is, when the precursor is magnetite and Ba carbonate the annealing produces the re-transformation to the original hexaferrite and the excess of magnetite transforms to hematite. In this situation the annealing at 1000°C produces a compound with a coercivity of 4.4 kOe and a maximum magnetization at 15 kOe of over 51 emu/g, values which are comparable to the ones in the literature for this material considering that the fraction of hexaferrite in the samples is 80%. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 75.50.Gg; 75.60.Jp; 81.40.Rs

Keywords: Hexaferrites; Fine particles; Magnetic properties

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1. Introduction

The available hard magnetic materials have a lower saturation magnetization M_s than many soft magnetic materials. Researchers in the fields of both soft and hard magnetic materials have recently turned their attention to the use of composite materials. According to the theory of exchange spring magnets [1] it would be possible to make composite hard magnetic particles that consist of oxide and metal in order to increase the M_s of the particles, without losing their high coercivity. It is known that the magnetic properties of this kind of compounds improve as the mean grain size diminishes because the formation of single domain particles is propitiated and the exchange coupling among nanometric particles is favored [2].

Based on this idea, some work has been done trying to improve the magnetic properties of a compound consisting of 80% Ba hexaferrite and 20%

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PII: S0304-8853(99)00471-0

Fe, produced using the technique of high-energy ball milling (HEBM) [3]. It was observed that the presence of Fe produces a faster degradation of the hexaferrite structure and that in certain conditions a magnetic composite material of Ba hexaferrite and magnetite is obtained.

The aim of this work is to produce a magnetic composite of Ba hexaferrite and magnetite starting from two different precursors obtained by HEBM: one of them composed of highly deformed hexaferrite and free iron, and the other with magnetite and barium carbonate. Keeping in mind that the processing costs at an industrial level should be as low as possible, heat treatments in air are performed. It is expected that with the adequate annealing in the first precursor the free iron will oxidize to form magnetite while the hexaferrite will recover its structure, and in the second precursor it is expected that part of the magnetite will remain in that state and the rest will react with the Ba carbonate to form the hexaferrite. However, for long annealing times hematite will prevail over magnetite.

The maximum magnetization at 15 kOe $M_{\max}$ and the coercivity H_c are used to characterize the samples. These parameters are very sensitive indicators of the details of the reaction involved. $M_{\max}$ reflects the variation of the phase composition; the changes in H_c sensitively follow the microstructure and composition.

2. Experimental

The technique of HEBM is used to produce the precursors. 20% of pure Fe and 80% of pure $BaFe_{12}O_{19}$ (phase M of Ba hexaferrite) are milled in air atmosphere using a hardened steel vial and balls of the same material at 200 rpm, with a 10 : 1 ball-to-powder ratio.

The first sample (m40) is taken out after 40 h of milling, when the crystalline structure of phase M is very deformed but there is still free Fe in the powder. This can be seen in Fig. 1, where a diffractogram of the sample shows that the peaks corresponding to the hexaferrite are broadened and less intense with respect to the sample before milling, and the peaks (1 1 0) and (2 0 0) of Fe are still present. Using the Scherrer formula the crystallite mean size s is calculated, giving a value of 15 nm. $M_{\max}$ is 52 emu/g and the coercivity measured for this sample is 0.42 kOe.

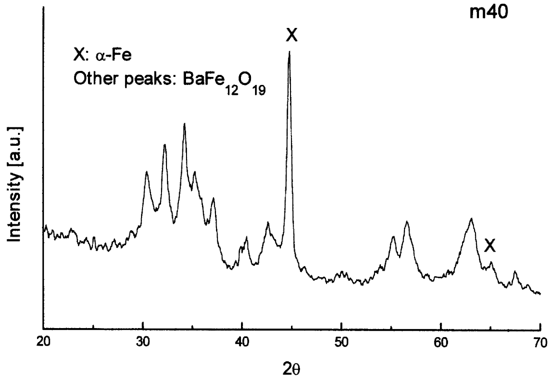

Fig. 1. Diffractogram of the as-milled sample, after 40 h of HEBM (m40).

The second sample (m60) is obtained after milling the initial powders for 60 h, in the same conditions as m40. In this case, due to the process of HEBM, a transformation of the powder structure is produced. This is shown in the diffractogram of Fig. 2, where the peaks corresponding to phase M and Fe have disappeared, giving rise to magnetite (Fe_3O_4) and small amounts of $BaCO_3$, as a result of performing the milling in air atmosphere [4]. The crystallite mean size is $s \cong 10$ nm. The magnetic properties of these samples are very deteriorated with respect to m40, being $M_{\max} = 45$ emu/g and $H_c = 0.05$ kOe.

Different thermal treatments are carried out in samples m40 and m60 at 850, 900 and 1000°C, for periods up to 8 h. The heating atmosphere is air in all cases.

The magnetic properties of the samples are measured with a vibrating sample magnetometer and the crystalline structure is monitored with an X-ray diffractometer using Cu K_α radiation.

3. Results

3.1. Heat treatment at $T = 850°C$

The diffractograms of m40 for $t = 0.5$ and 8 h are shown in Figs. 3a and b. Very similar spectra are

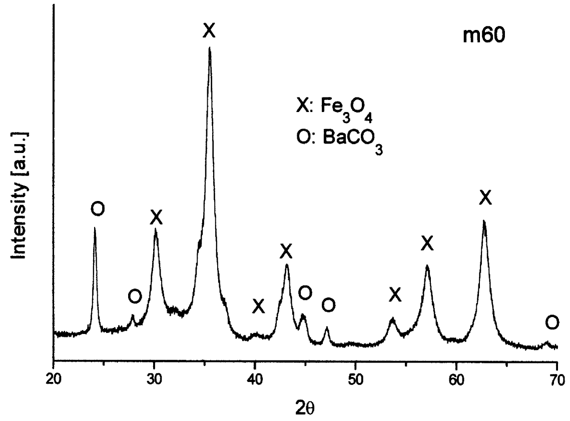

Fig. 2. Diffractogram of the as-milled sample, after 60 h of HEBM (m60).

obtained for m60. The structural changes observed during heat treatment are principally related to changes in relative peak intensities.

The phases present after the treatment are mostly α-Fe_2O_3 (hematite or phase α) and $BaFe_{12}O_{19}$. Small traces of Fe_3O_4 (magnetite) are also noticeable.

It is a remarkable fact that even when m40 and m60 are originally composed of different phases (phase M and iron in the first, and magnetite and barium carbonate in the second) the resulting structures after the heating are basically the same. This can be explained considering that the free iron in m40 transforms first to magnetite and then to hematite during the heat treatment, and phase M recovers its structure. There is an increase in the relation of hematite to phase M in the corresponding diffractograms for 0.5 and 8 h due to oxidation of Fe_3O_4.

The situation is different in m60, where the Ba in $BaCO_3$ reacts with magnetite (which is one of the structural units of Ba $Fe_{12}O_{19}$ [5]) to form phase M, and the rest of Fe_3O_4 either stays in that phase or transforms to Fe_2O_3. It is observed that hematite maintains its volume fraction relative to phase M during the treatment, as revealed by the relative intensities of the most intense peaks of both phases, i.e. the $(1\,0\,4)_\alpha$ peak and the $(1\,1\,4)_M$ peak.

However, even when the resulting crystalline structures are similar, the evolution of the magnetic properties is somewhat different in both samples, as Fig. 4a shows for m40 and Fig. 4b for m60. There, the coercivity H_c and maximum magnetization at 15 kOe M_{max} are plotted as a function of annealing time t.

In m40 the magnetization starts with a value of 38 emu/g and shows a maximum at 46 emu/g after 4 h of treatment; further heating produces a slight fall in the magnetization. The coercivity starts at 3.31 kOe and hardly increases with t up to 3.39 kOe.

This behavior is somewhat altered in m60, where there is a sustained increase in coercivity from 3.62 to 4.07 kOe, while the magnetization remains almost constant around 43 emu/g. The structure of

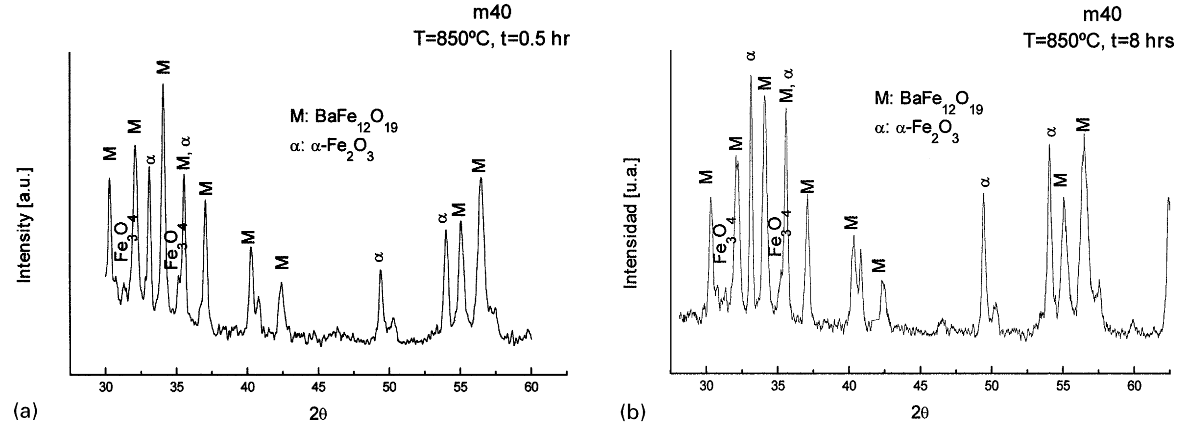

Fig. 3. Diffractogram of m40 after annealing at $T = 850°C$ for (a) 0.5 h and (b) 8 h.

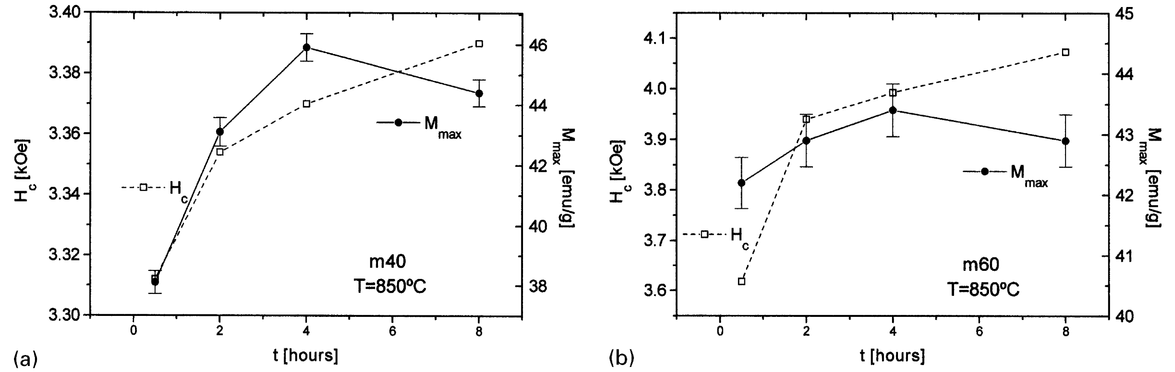

Fig. 4. Coercivity H_c and maximum magnetization at 15 kOe M_{max} as a function of annealing time t, for (a) m40 at 850°C and (b) m60 at 850°C.

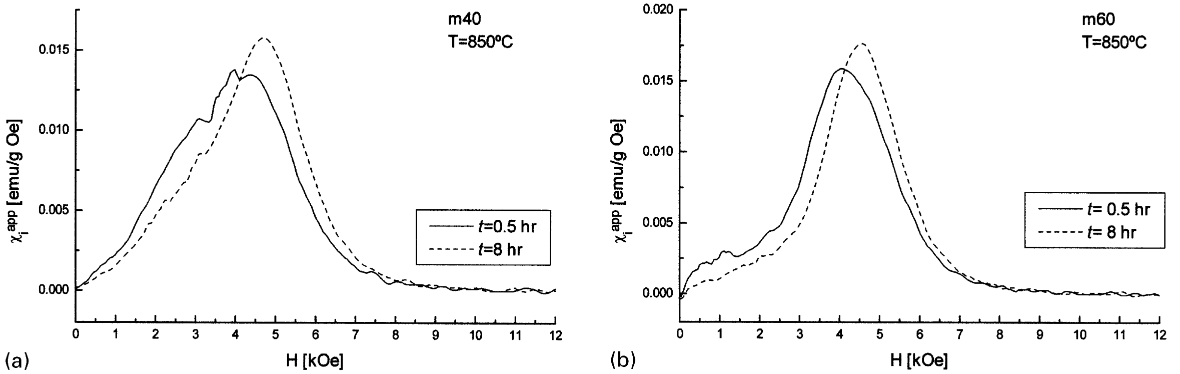

Fig. 5. Apparent irreversible susceptibility χ_i^{app} as a function of applied field H, for the annealing of (a) m40 and (b) m60 at 850°C. The solid line corresponds to $t = 0.5$ h, and the dashed line to $t = 8$ h.

this sample has a progressive evolution for different values of t. In the corresponding diffractograms a change in the relative peak intensities is observed, without any changes in the positions of the peaks.

In both m40 and m60 s remains constant during the whole treatment with a value of approximately 28 nm.

As defined in a previous paper [3], the apparent irreversible susceptibility χ_i^{app} is derived from the expression $\chi_i^{app} = \chi_{tot} - \chi_{rev}^{app}$, where $\chi_{tot} = \mathrm{d}M/\mathrm{d}H$ and the apparent reversible susceptibility χ_{rev}^{app} is the susceptibility for H in the first quadrant. The fields at which the plot χ_i^{app} versus H shows a peak are related to the reversion fields of the system.

In Fig. 5a χ_i^{app} is plotted as a function of H for m40. It can be seen that after 0.5 h of thermal treatment there are two peaks in the curve, corresponding to two nucleation fields: one at 3.1 kOe and the other at 4.5 kOe. This indicates that there are mainly two groups of magnetic particles that nucleate at different fields. As the only magnetic phase significantly present in the sample is $BaFe_{12}O_{19}$ and s remains constant, it may be inferred that there is a bimodal distribution in the nucleation fields in this phase. It is thought that the smaller particles would have a higher nucleation field than the bigger ones because the elimination of defects is completed in shorter times. As t increases the low-coercivity particles become hardened and

χ_i^{app} evolves into a narrower curve shifted to higher values of H (Fig. 5a).

The behavior for m60 is shown in Fig. 5b, where the corresponding curve for χ_i^{app} has only one maximum at 4.0 kOe. This peak becomes narrower and shifted to higher fields after the treatment.

3.2. Heat treatment at $T = 900°C$

Phase M, hematite and a small amount of magnetite are initially present. When continuing with the heat treatment the phases observed are only hematite and phase M in both samples. The structural evolution presents variations during the annealing process, this affecting the magnetic properties, which are plotted in Figs. 6a and b for m40 and m60, respectively.

It can be seen that in both samples M_{max} initially drops with heating time, while the coercivity increases. This behavior is more gradual in m60. The fall of M_{max} is accompanied by a structural change in the powders, as revealed by the diffraction patterns of the two samples, where the initially present peak of magnetite disappears and the proportion of phase α relative to phase M increases with t.

In m40 the coercivity increases with t and diminishes slightly after 8 h. In m60 it raises from 3.75 kOe up to 4.40 kOe, a higher value than the one obtained for any of the heat treatments at 850°C.

In both samples M_{max} levels off at around 46 emu/g.

The calculated mean grain size for both m40 and m60 is approximately 32 nm and is constant throughout the thermal treatment.

As it can be seen in Figs. 7a and b, the curves χ_i^{app} versus H for both m40 and m60 have a very similar behavior as those observed for these samples at 850°C.

3.3. Heat treatment at $T = 1000°C$

The phases formed after the heat treatment are hematite and phase M in both m40 and m60.

In m40, both H_c and M_{max} have similar behavior: there is an increase of these magnitudes up to $t = 2$ h and from then on they remain almost constant, as it can be seen in Fig. 8a. This is not the case in m60, where a maximum in coercivity is achieved for $t = 2$ h and further heating leads to a decrease in this property (Fig. 8b). M_{max} shows the same tendency as for m40.

The structure evolution of these samples does not show any peculiarity like the one observed for the treatment at $T = 900°C$, but the diffraction peaks become narrower with t, indicating an increase in the mean grain size. For m40, $s \cong 32$ nm at the beginning of the treatment and $s \cong 42$ nm for $t = 8$ h. In m60, s grows from 29 nm up to 38 nm.

The apparent irreversible susceptibility χ_i^{app} has two superposed distributions for m40 at $t = 0.5$ h, which converge to the same peak at 5.0 kOe at the end of the treatment (Fig. 9a).

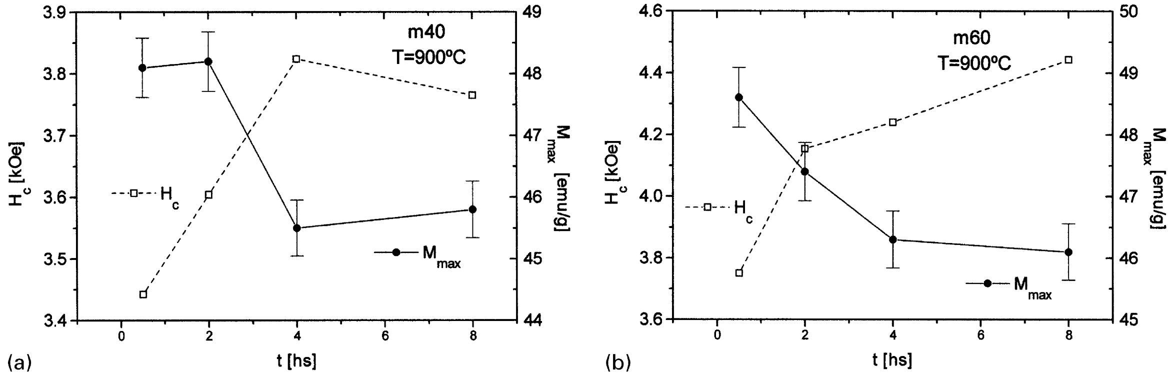

Fig. 6. Coercivity H_c and maximum magnetization at 15 kOe M_{max} as a function of annealing time t, for (a) m40 and (b) m60 at 900°C.

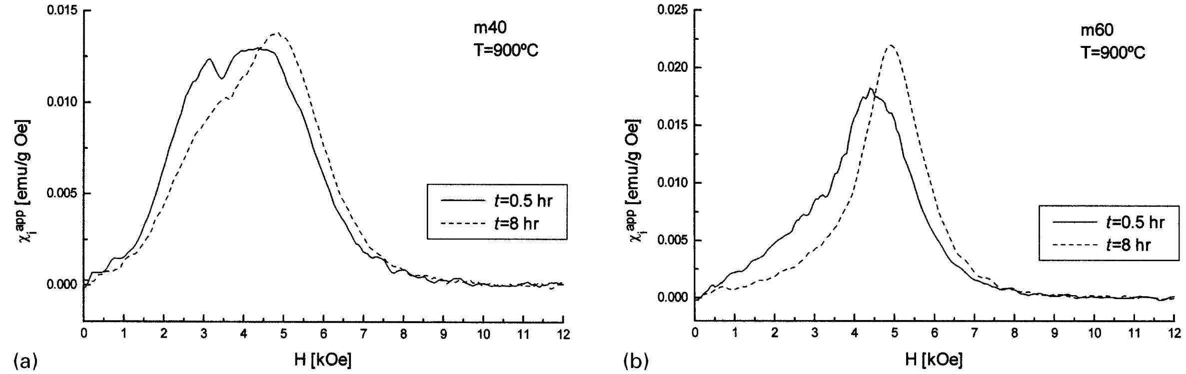

Fig. 7. Apparent irreversible susceptibility χ_i^{app} as a function of applied field H, for the annealing of (a) m40 and (b) m60 at 900°C. The solid line corresponds to $t = 0.5$ h, and the dashed line to $t = 8$ h.

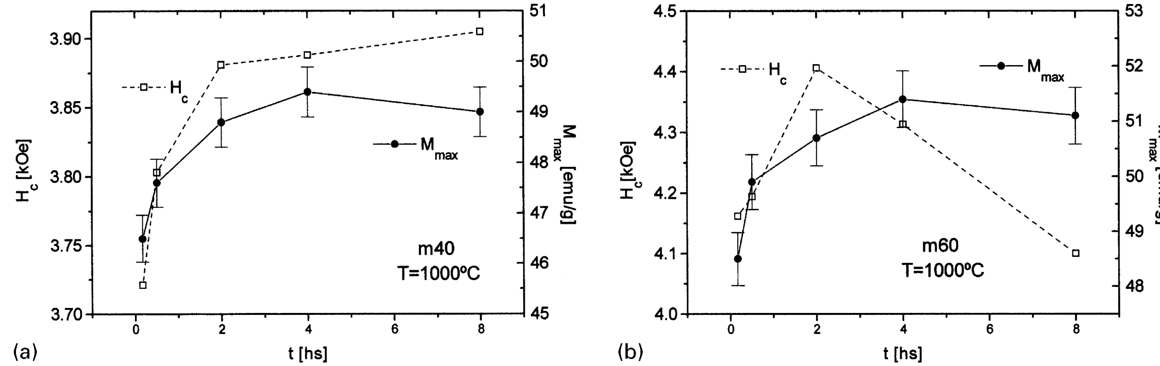

Fig. 8. Coercivity H_c and maximum magnetization at 15 kOe M_{max} as a function of annealing time t, for (a) m40 and (b) m60 at 1000°C.

The situation is different for m60 (Fig. 9b), as there is one narrow peak already for $t = 0.5$ h at 5.0 kOe. The maximum in this case is higher and shifted to 5.2 kOe at $t = 2$ h; from then on the peak moves back to lower values of H, reaching 4.8 kOe at the end of the treatment.

It is worth mentioning that for both kinds of samples the remanence M_r is 0.55 of M_{max}, in every treatment.

4. Discussion

It is clear that the temperature at which the thermal treatment is performed is fundamental in determining the structural and magnetic properties of the as-milled material. Very different mechanisms are observed at lower and higher temperatures.

4.1. m40

Magnetite and phase α are developed starting from the free Fe in the powder, independently from phase M. The crystalline structure and magnetic properties of m40 evolve starting from the original phase M, damaged during the process of HEBM.

Despite some magnetite being present in the powder in the treatment at 850°C, it is not enough to contribute significantly to the total magnetization. M_{max} increases during the treatment due to the evolution of phase M. It is also observed at this temperature that H_c increases with t but very slightly. As during the treatment s remains

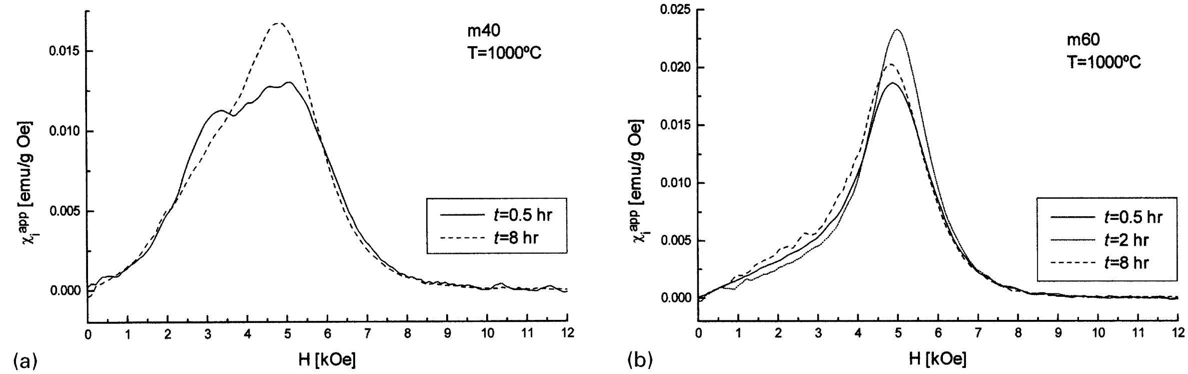

Fig. 9. Apparent irreversible susceptibility χ_i^{app} as a function of applied field H, for the annealing of (a) m40 and (b) m60 at 1000°C. The solid line corresponds to $t = 0.5$ h, and the dashed line to $t = 8$ h.

constant, no change in H_c due to the particle growth is expected. It is suggested that this raise in coercivity is related to an increase in the anisotropy of phase M as the structure eliminates its defects. Fig. 5a supports this assumption; χ_i^{app} shifts to higher fields for longer heat treatments, where there is a reduction in the defects present in the powder as a result of the diffusion processes held in the sample.

A reduction in the anisotropy field due to crystalline defects, stresses and strains is also observed by other authors [6] in hexaferrites. The anisotropy field distribution they measure for phase M has the same shape of the χ_i^{app} curves obtained in this work for m40 and m60 after the thermal treatment. The broad distribution of the anisotropy fields is associated to the structural non-uniformity, particle size distribution and irregularity in particle shapes of the powders. The irreversible susceptibility χ_{irr} in the usual definition [7] is related to the nucleation fields of the particles, so it depends on the grain size and the anisotropy. If the particle size is constant, changes in χ_{irr} are related to changes in the anisotropy of the particles. In this paper it is considered that the apparent irreversible susceptibility, as defined in Section 3, is also a measure of the grain size distribution and the anisotropy distribution, and therefore χ_i^{app} is closely related to the defect distribution of the samples.

In the case of the treatment at 900°C the temperature is high enough to produce a fast oxidation of Fe to Fe_3O_4 during the first stages of the treatment and to transform magnetite completely into hematite after $t = 2$ h. This loss in magnetite is supposed to be responsible for the 4% drop in magnetization after 2 h of treatment. Similar to the case of $T = 850$°C, the increase in coercivity is attributed to the elimination of defects and structure readjustment of phase M, as s remains constant during the treatment. This is in accordance with the behavior of the corresponding curves of χ_i^{app} for different values of t (Fig. 7a).

In the treatment at 1000°C the temperature is so high that it avoids the formation of magnetite and it is assumed that the structure evolution of phase M is responsible for the changes in the magnetic properties. Both M_{max} and H_c follow the same tendency with t. The maximum magnetization starts growing and after 2 h stabilizes around 49 emu/g. Coercivity presents a steady increase and reaches a maximum of 3.89 kOe after 8 h. According to the reported data for small particles of $BaFe_{12}O_{19}$ [6], M_{max} reaches the expected value for an applied field of 15 kOe considering that the fraction of this phase in the sample is 80%. This indicates that phase M has reached a fairly stable structure. However, the shape of the χ_i^{app} versus H curve is still wide after 8 h of heat treatment (Fig. 9a) which indicates that there are still many defects lowering the anisotropy and thus the coercivity. The fact that χ_i^{app} is asymmetric and displaced to lower values of H for $t = 8$ h indicates that there are still many particles with low nucleation fields (low anisotropy). This is because there still remain many crystalline defects. Further heating is needed to get rid of them and improve the anisotropy of the sample.

4.2. m60

Phase M precipitates from the $BaCO_3$ and part of the Fe_3O_4 present in the starting powder. The rest of magnetite either stays in that way or oxidizes to Fe_2O_3. The crystalline structure and magnetic properties of m60 evolve starting from a new phase M, originated from the products of HEBM. Phase M in m60 has less structural damage than m40, as it is generated from Ba carbonate and Fe oxide and therefore it has a better 'quality' than the one present in m40, which has been severely damaged during HEBM.

$M_{\max}$ increases very slightly during the treatment at 850°C, and it could be said that it is almost constant. This is possibly a result of two compensating effects: the gradual loss of magnetite (lowering the magnetization) and the structural evolution of phase M due to the elimination of damage (raising $M_{\max}$), resulting in a steady value of this magnitude. The increase in coercivity is evidenced by the displacement of χ_i^{app} to higher values of H (Fig. 5b).

In the treatment at 900°C it is observed that $M_{\max}$ falls due to the gradual extinction of magnetite. In this case the temperature is high enough to make this process faster than at 850°C and the magnetization is not able to remain almost constant throughout the treatment. The final value is about the same as the corresponding value for m40, but higher than that obtained for m60 treated at a lower temperature. The coercivity is also increased in this situation and χ_i^{app} evolves to a narrower peak at higher fields after 8 h, as shown in Fig. 7b.

When considering the case of annealing at 1000°C, it is seen that $M_{\max}$ has the same behavior as in the previous cases; here the maximum value attained is the highest and it reaches over 51 emu/g. This is assigned to the fact that the temperature of the treatment is about the same as the optimum one for synthesizing phase M from simple oxides [2,8]. Coercivity reaches a value of 4.40 kOe after 2 h of heat treatment, a value that is very close to that obtained for this phase without defects or stresses [6] and it drops with further heating as a consequence of grain growth. This behavior is reflected in the apparent irreversible susceptibility, as it can be seen in Fig. 9b; it is a striking fact that already for $t = 0.5$ h m60 has a narrow peak in χ_i^{app}. This peak becomes even narrower and higher after 2 h of thermal treatment, moving a little towards higher fields. After 8 h of heating there has been an increase in s, this causing the shift in χ_i^{app} to lower fields and diminishing the coercivity. Other authors [6,9] have also noticed this effect. In this case, phase M originated from a reaction of oxides and there are hardly any defects in the crystalline structure, as in the case of m40.

It is found that for both the precursors and in every treatment hematite was the main Fe oxide obtained instead of magnetite, indicating that the kinetic of the reaction $Fe_3O_4 + O_2 \rightarrow Fe_2O_3$ is very fast and is completed during the very first stages of the treatments. As a result of this, there was only one magnetic phase in every case and the composite could not be formed.

5. Conclusions

It was not possible to obtain the desired phases to form the composite, as in every case the iron or the magnetite oxidized to hematite. The reaction that leads to hematite is very fast at the high levels of O_2 used and the transformation is completed in short times.

It is observed that phase M recovers its structure and magnetic properties between 2 and 4 h at 1000°C. The values of coercivity and saturation magnetization are comparable to the ones obtained when this phase is prepared from the elemental oxides in similar milling conditions and posterior annealing at 1000°C [6,9].

Acknowledgements

P.G. Bercoff acknowledges a fellowship from CONICOR. This work was partially financed by CONICOR and SECYT - UNC (PID 275/98), Argentina.

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