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Thermal Stability of a Metal Alloy—Spinel Ferrite Composite Prepared by Disproportionation in a Liquid Medium

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An original method for obtaining a composite made up of cobalt–iron alloy and cobalt doped magnetite is described. This method is based on a disproportionation reaction in a liquid medium at 110°C. Chemical analysis and crystallographic measurements allow a schematic chemical formula for the composite $(Fe_{0.2}Co_{0.8})_{0.8}[Fe_{2.38}Co_{0.62}O_4]$ to be given. The crystallographic parameter of the cobalt doped magnetite of spinel structure is a = 8.396(1) Å. Cobalt–iron alloy presents BCC and FCC structures and does not oxidize up to 320°C. At room temperature this composite is characterized by a saturation magnetization of 90 emu/g and a coercive field of 1700 Oe. A further heating at 200°C increases the concentration of metallic phase of the BCC structure and the saturation magnetization, decreases the crystallographic parameter of spinel phase and the coercive field. Above 320°C, the alloy oxidizes; the spinel $CoFe_2O_4$ crystallizes at 900°C.

INTRODUCTION

Magnetite Fe_3O_4, maghemite γ-Fe_2O_3 and cobalt doped γ-Fe_2O_3 are the most known compounds among ferrites of spinel structure. The latter has been widely used till now as recording material when coercive fields of about 250-1250 Oe are required [1–3]. Fine particles of iron are also very attractive because they offer the possibility to combine higher moment and higher coercivities that can be achieved with any known oxide particles. However, they are highly reactive towards atmosphere and must be protected. Our recent works in that area have shown that it was possible to obtain, by disproportionation in a liquid medium at 110°C, small grains of metal–ferrite composite [4]. Furthermore, this composite presents very interesting magnetic properties, a saturation magnetization of 90 emu/g and a coercive field of about 2000 Oe. We present here the thermal stability of such a composite, its structural transformations and modifications of magnetic properties.

EXPERIMENTAL

Cobaltous and ferrous chlorides, $CoCl_2\,6H_2O$ and $FeCl_2\,4H_2O$, taken in $\frac{1}{2}$ ratio have been dissolved in water, mixed, and added to boiling potassium hydroxide. A black powder precipitates. It has been filtered and washed with boiling water. The precipitate was then analyzed; it was found [Fe]/[Co] = 2 and Fe^{III}/Fe^{II} = 0.17. Two hours annealing at temperatures between 100 and 900°C have been performed under air. Then, the samples have been quenched in air.

The samples have been studied by means of X-ray diffraction measurements, thermal gravimetric and thermal *differential analysis, and magnetization measurements.* X-ray diffraction data have been collected at room temperature with a D500 Siemens diffractometer equipped with a primary beam quartz monochromator ($CoK\alpha_1$ λ = 1.78897 Å). Silicon has been used as internal standard in order to estimate the diffraction line intensities. Thermal gravimetric and thermal differential analyses were carried out in platinum crucibles under air by using a SETARAM 92 apparatus. The temperature increase rate was 1°C/min. The weight variation was calculated after removing the signal of empty crucible. Magnetization was measured by means of a FONER apparatus at room temperature. SEM examinations have been performed by means of a JEOL scanning electron microscope.

RESULTS

1. *Characterization of the Precipitate*

The X-ray diffraction pattern of the precipitate appears in Fig. 1a: the three phases are detected: a spinel phase (●), a phase isomorphous of α-Fe of BCC structure (■), and a phase isomorphous of cobalt of FCC structure (O). Their crystallographic parameters have the following values: spinel a = 8.396(1) Å, BCC phase a = 2.838(1) Å, and FCC phase a = 3.561(1) Å. Let us note that the diffraction lines 531 of spinel phase and 200 of BCC phase are superposed. Examinations of the precipitate with the

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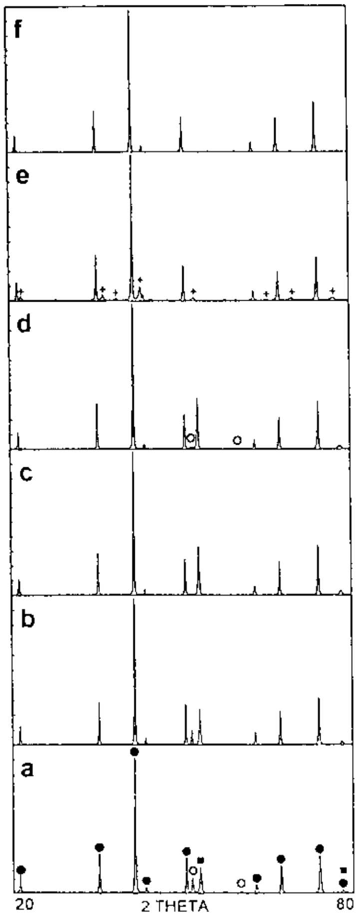

FIG. 1. (a) X-ray diffraction of the composite after precipitation at 100°C (●) indicates diffraction lines of spinel phase, (■) of the BCC phase, and (○) of the FCC structure; (b) to (f) X-ray diffraction pattern of the composite heated at 200°C (b), 300°C (c), 400°C (d), 500°C (e), and 900°C (f) for 2 hr. (+) indicates Fe_2O_3 and Co_3O_4.

electron beam microscope show that the grains have sizes of 0.1–0.5 μm (Fig. 2). They exhibit geometrical shapes, most of them having an octahedral form.

The precipitate hysteresis curve is displayed in Fig. 3. One can note a saturation magnetization of 90 emu/g and a coercive field of 1700 Oe.

2. *Thermal Stability*

The modifications of the precipitate by heating under air have been studied by X-ray diffraction measurements, TG and DTA analysis, and magnetization.

(*a*) *X-ray diffraction measurements.* When heating the precipitate, several modifications occur in the X-ray diffraction pattern (Fig. 1):

—A spinel is observed whatever the temperature may be while metallic phases have disappeared at 400°C.

—The crystallographic parameter of spinel phase changes during the thermal treatment (Fig. 4). It takes a minimum value a = 8.365 (2) Å at 400°C.

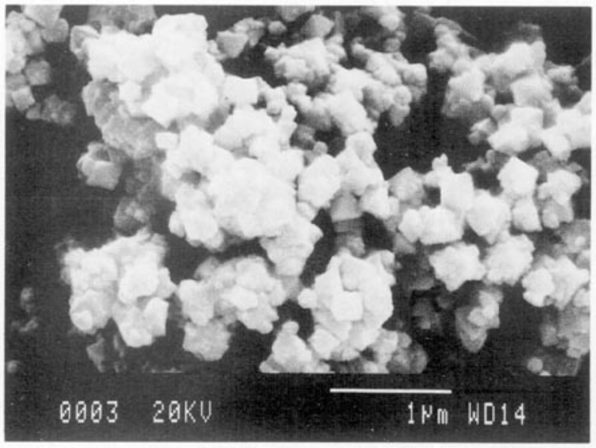

FIG. 2. Scanning electron microscope examinations of the precipitate.

—The phase of BCC structure is stable up to 300°C. Its crystallographic parameter does not change between room temperature and 300°C.

—The diffraction lines intensities of BCC phase increase at 200°C, while the spinel ones do not change.

—The phase of FCC structure with a = 3.561 (1) Å is not observed at 200°C. Another phase of FCC structure with a = 3.545 (3) Å, corresponding to metallic cobalt, is crystallized at 300 and 400°C.

—At 400°C, the composite oxidizes; CoO and Co_3O_4 are detected.

—At 500°C, the composite is mainly composed of a spinel phase. But small amounts of α-Fe_2O_3 and Co_3O_4 are observed.

—By heating up to 900°C, α-Fe_2O_3 and cobalt oxide

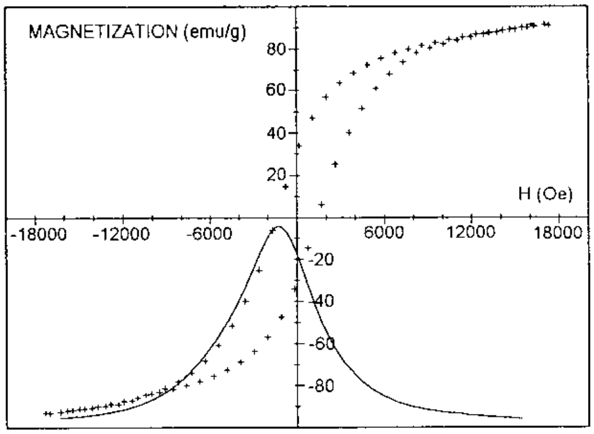

FIG. 3. Hysteresis cycle (+) observed at room temperature for the precipitate and derivative (–).

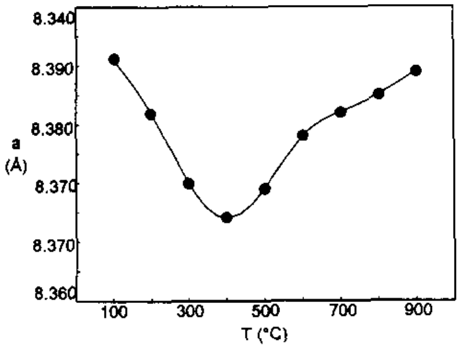

FIG. 4. Variation of spinel crystallographic parameter versus annealing temperature.

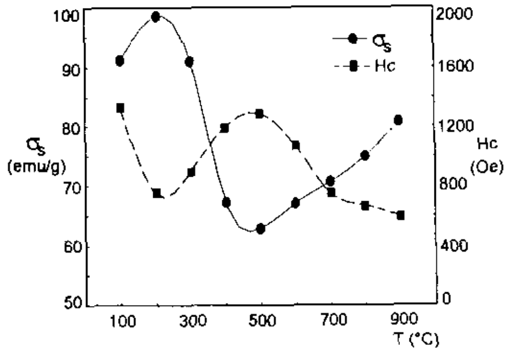

FIG. 6. Variation of saturation magnetization (σ_s) and coercive field (H_c) versus annealing temperature.

react in order to give a pure spinel phase with $a = 8.391$ (1) Å.

(*b*) *TG and DTA analysis.* Thermal gravimetric and thermal differential analysis of the composite are schematically represented in Fig. 5. It can be noted:

—A constant weight (no loss, no gain) below 320°C. On the one hand, the precipitate is totally dehydrated and does not contain hydroxides, which would decompose below 200°C. On the other hand, the precipitate does not oxidize below 320°C. This has been checked by keeping the temperature equal to 300°C for 24 hr. No weight variation has been observed.

—A weight increase of 6.4% between 320 and 500°C accompanied by an exothermic effect in the DTA curve resulting from the composite oxidation.

—A slight weight decrease between 500°C and 800°C, so that the total increase between 320°C and 800°C is of 5.9%.

—A weak and broad exothermic peak in the DTA curve between 200 and 300°C.

(*c*) *Magnetization measurements.* The magnetization variation versus magnetic field, measured at room temperature, is characteristic of ferro- or ferrimagnetic behavior for every samples and every annealing temperatures and times. The saturation magnetization versus annealing temperature increases up to 98 emu/g at 200°C, then decreases up to 62 emu/g at 500°C and increases again up to 80 emu/g at 900°C (Fig. 6). The coercive field presents the inverse variation, decreasing when saturation magnetization increases, increasing when the latter decreases. The highest values are observed below 100°C. Another maximum exists at 500°C (Fig. 6).

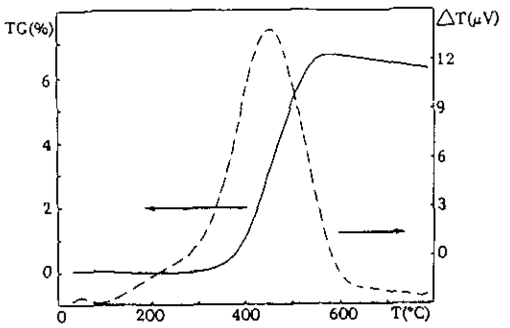

FIG. 5. Thermogravimetric and thermal differential analysis of the precipitate in air (increasing rate 1°/min).

DISCUSSION

While the precipitation of cobaltous and ferric chlorides, taken in a ½ ratio in a basic medium, gives a pure spinel phase $CoFe_2O_4$, the same method used with cobaltous and ferrous chlorides and a strongly basic medium leads to a metal–spinel composite. This is thus the result of a disproportionation reaction in a liquid medium: $Co\,Fe_2(OH)_6$ precipitates; immediately, a dehydration into $CoFe_2O_3$, a disproportionation of Fe^{II} into Fe^0 and Fe^{III}, and a reduction of cobalt into Co^0 occur simultaneously. A similar disproportionation has been encountered for FeO at 400–500°C following the reaction $4FeO \rightarrow Fe_3O_4 + Fe$ (5). It has also been reported for $Fe(OH)_2$ following the reaction $4Fe(OH)_2 \rightarrow Fe + Fe_3O_4 + 4H_2O$ (6–8). However, metallic iron was not pointed out by X-ray diffraction measurements, due to the reduction of water by iron.

The crystallographic parameters of the alloy phases and the chemical analyses allow a chemical formula of the composite to be given. The crystallographic parameters of alloy phases, $a = 2.838$ Å for BBC phase and $a = 3.561$ Å for FCC phase, both of which correspond to an alloy containing about 20% Fe. Taking into account the chemical analysis which gives $CoFe_2O_{3.14}$; i.e., $Co_{1.27}Fe_{2.55}O_4$, the composite chemical formula can be expressed by $(Fe_{0.2}Co_{0.8})_{0.8}[Fe_{2.38}Co_{0.62}O_4]$. This composite, obtained by using this simple synthesis, is characterized by a high thermal stability with regard to the properties of Fe–Co alloys and spinel ferrites with grains of 0.1–0.5 μm, and interesting magnetic properties. Both saturation magnetization and coercive field are high. Let us note that such a high coercive field has never been encountered neither for an alloy $Fe_{0.2}Co_{0.8}$ nor for a cobalt doped magnetite (1, 9). Taking into account the results of thermal treatment, two temperature ranges corresponding to distinct properties are pointed out, below and above 320°C, i.e., before and after oxydation:

—Below 320°C, the phase does not oxidize. One observes the increase of BCC phase concentration at 200 and 300°C and a decrease of the spinel crystallographic parameter. These structural transformations have to be related to the weak exothermic and broad peak in the DTA curve in the 200–300°C temperature range. The increase of BCC phase concentration can result from a crystallographic transformation of FCC phase into the BCC structure at 200°C. However, it can be also related to the decrease of the spinel crystallographic parameter: one can imagine that the disproportionation reaction which has occurred at 110°C in the liquid is not finished, that some metallic ions are transferred to the alloy resulting in a decrease of the spinel crystallographic parameter. Moreover, the decrease of the spinel crystallographic parameter cannot be assigned to a simple oxydation of spinel phase, independently of the alloys; indeed, such an oxydation would occur at about 200°C, and no weight increase is observed in that temperature range. Until now it was not possible to conclude about the thermal magnetization variation. Both magnetizations of spinel and alloy can change with annealing temperature, or one of them can be constant. The maximum at 200°C can arise from the crystallographic modifications of spinel or the higher concentration of alloy. Further studies are necessary to conclude: the elimination of one phase by a chemical process would allow the other to be studied.

—Above 320°C, the composite oxidizes as the strong exothermic peak in the DTA curve and the strong weight increase in the TG curve shows. Fe–Co alloy and metallic Co oxidizes; CoO and Co_3O_4 are detected at 400°C, then α-Fe_2O_3 and Co_3O_4 at 500°C. The reaction between α-Fe_2O_3 and Co_3O_4 leads to the formation of $CoFe_2O_4$, which explains the slight weight decrease in the TG curve above 500°C. The saturation magnetization decreases up to 500°C, the temperature for which all of the alloy has oxidized and the spinel concentration is the smallest. At 900°C, the saturation magnetization of 81 emu/g is consistent with the $CoFe_2O_4$ formula.

Numerous questions come now to mind: how the different phases are bonded together, why is this composite so stable, while spinel and metal alloy taken separately and made up of submicronic grains oxidize? For the moment, we can state positively that the grains are small; so, spinel and metal alloys are protected towards oxydation probably by a layer impermeable to oxygen. This layer necessarily develops in the liquid medium since the powder is protected as soon as the filtration is performed. It is thin or amorphous since it is invisible by X-ray diffraction measurements. It may be made up of Co_3O_4, the most impermeable to oxygen among iron and cobalt oxides.

CONCLUSION

This paper describes a simple method to synthesize a metal–ferrite composite at 110°C. This method was unknown until now. It is based on a dehydration of hydroxides in a basic media and a disproportionation of Fe^{II}. The composite made up of an Fe–Co alloy and cobalt ferrite spinel is very stable in air. It presents outstanding magnetic properties H_c = 1700 Oe and M_s = 90 emu/g. This composite has probably a promising future in magnetic recording as well as catalysis.

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