Magnetism and Structural Phase Transformation in Fe / Fe oxide Nanopowders

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Abstract. Fe / Fe₃O₄ (magnetite) powders obtained by ball milling at room temperature, undergo an incomplete redox reaction with formation of FeO. This reaction is favoured due to the high energy developed during the milling and alloying. Concurrent effects of the milling, such as grain refinement down to the nanometric scale lead at the end of the milling processes to a mixed multiphased nanopowder, with a homogeneous dispersion of Fe and Fe oxide grains. Such ferromagnetic – antiferromagnetic systems are extensively studied due to their exchange bias properties, extremely useful in technological applications. We study the phase transformation that leads to a multiphased metal / oxide microstructure with an energy-dispersive in-situ X-ray diffraction experiment using the synchrotron radiation. This study allows direct collection of X-ray spectra after few minutes exposure, at selected temperatures, ranging between 20°C and 1000°C. Magnetic behavior has been studied for as-milled and annealed samples and the obtained magnetic parameters are correlated to the microstructure and phase composition at each stage of annealing. A significant exchange bias effect, related to FeO content, is observed for as-milled sample, the effect being less pronounced upon annealing the nanogranular powder.

1. Introduction

Granular systems of Fe nanoparticles embedded in iron oxide matrix have attracted a great deal of interest due to the observed magnetic exchange bias effect in such systems [1-3]. The exchange bias effect, extremely useful for magnetic applications, arises in granular systems due to the coupling between ferromagnetic (FM) and antiferromagnetic (AFM) grains at the interfaces. It has been shown that this FM/AFM interfacial coupling strongly influences the exchange bias observed in such systems [3]. The size distribution of the grains as well as the phase composition within the granular mixed FM/AFM powders is shown to be also of great importance for the exchange bias in such materials [2]. It has been reported that ball milled Fe and magnetite powders may induce the formation of wüstite during milling and this wüstite decomposes into the constituent powders upon annealing [4]. The phase composition in such mixtures needs though to be strictly controlled during annealing, if the granular systems are to be used for technological applications based on the exchange bias effect. We have synthesized a non-equimolar mixture of iron and magnetite by ball milling to achieve a nanogranular structure and we have studied the phase transformation that occurs during dynamic annealing in such systems via a unique tool of in-situ characterization: temperature dependent X-ray diffraction of synchrotron radiation.
2. Experiment
The Fe / Fe$_3$O$_4$ mixed powder (2:8 wt%) has been prepared by ball milling in a Retzsch PM
400 planetary ball mill with 4 vials. The total amount of the sample was 10 grams, powders of
high purity (99.99+%). The experimental conditions were: sun wheel frequency 200 rpm, sun
wheel / vial frequency ratio 1.5, the loading constant 8; ball size 20 mm and number of balls
used was 8. The powder and balls were sealed together with hexane as protective media,
against uncontrolled oxidation. Total milling time was 50 hours. The energy-dispersive in-situ
X-ray diffraction study was done at DESY-HASYLAB Hamburg at Max 80 F2.1 beamline,
dedicated to the diffraction studies of materials under extreme conditions (high temperature/
high pressure). The diffraction patterns are recorded with step-scanning mode single runs
using synchrotron radiation wavelength close to 1.2 Å. The energy range covered by the high-
purity Ge solid state detector is between 2 and 80 keV. Pure NaCl mounted in the sample
boron cube was used for energy calibration and the resulting diffraction spectra are therefore
given directly in units of reticular distance, for simplicity. The temperature was controlled by
a PtRh thermocouple placed inside the cube and the sample was heated in steps of 25°C or
less. Each pattern is collected using an average exposure of 2 minutes. Magnetic
measurements have been done using a vibrating sample magnetometer (VSM) in a
temperature range between 4.2 K and 300 K. The hysteresis loops were recorded as follows:
(i) cooling to 4.2 K without the presence of external field and first loop (ZFC at 4.2 K) was
measured; (ii) heated up and recording the loop at 280 K; (iii) again, cooling to 4.2 K in 5 T
applied field (FC) and the loop was measured.

Figure 1: XRD patterns taken at selected temperatures between 45°C and 450°C (left) and 500°C
and 900°C (right). The following phases are indexed on the figure: # - α-Fe, * - FeO and § - Fe$_3$O$_4$.
The spectra are given in units of reticular distances.
3. Results and discussions

In Figure 1 we present the XRD spectra taken at several, selected temperatures, from 45°C to 900°C. The pattern at 45°C present broad lines typical for nanostructured materials. We are able to identify the main Bragg reflections of the \( \alpha \)-Fe, FeO (wüstite) and Fe\(_3\)O\(_4\) (magnetite). As the initial mixed powders were \( \alpha \)-Fe and Fe\(_3\)O\(_4\) the observation of the Bragg reflections of the wüstite is the prove of an uncomplete redox reaction that develops during the milling, in agreement with previous results [4]. We are interested in following the evolution of the phase structure with the temperature. With increasing the temperature, as expected, the Bragg reflections continuously narrow due to the coarsening of the structure by agglomeration of the nanograins. We observe the gradual decrease of the relative intensity of the main Bragg peak of the wüstite, with increasing the temperature up to around 450°C. In the mean time, the relative contents of the other constituent phases, \( \alpha \)-Fe and Fe\(_3\)O\(_4\), are more or less the same. It seems that the redox reaction that formed the FeO phase is reversible and with increasing temperature iron and magnetite become the predominant phases.

At 450°C the main reflection of the wüstite is only about 12% of the main diffraction peak of the iron. But, at around 500°C (Figure 1 right), upon further increase of the temperature, the wüstite phase starts to form again, its main Bragg peak, increasing to about 63% of the iron peak. The new reduction of the magnetite to wüstite occurs quite fast, such as at 600°C, the diffraction pattern sees no more magnetite peaks, but only FeO and \( \alpha \)-Fe Bragg reflections, with FeO becoming the dominant phase. The oxidation of the iron continues with increasing temperature. Thus, at 900°C the iron main diffraction peak represents only about 6% of the main FeO (2 0 0) Bragg reflection. The evolution of the phase structure with the temperature and the transformation occurring in the different stages of annealing may be followed by plotting the ratio between the main Bragg reflections of the constituent phases. In Figure 2 we plot the intensity ratios R1 between Fe\(_3\)O\(_4\) (3 1 1) and \( \alpha \)-Fe (1 1 0) and R2 between FeO (2 0 0) and \( \alpha \)-Fe (1 1 0) diffraction lines, respectively.

![Figure 2: Intensity ratios between main Bragg peaks of the Fe\(_3\)O\(_4\) and \( \alpha \)-Fe phases, and respectively between main Bragg peaks of the FeO and \( \alpha \)-Fe phases at different temperatures.](image)

This approach constitutes only an estimation of the relative proportion of different phases, since it does not take into account the whole profile of all the diffraction lines observed in the spectrum. In this Figure the tendency from XRD spectra is better observed. Wüstite is the predominant phase at 45°C and then decreases and reaches a minimum at 450°C. After 450°C, the intensity of FeO increases very fast, and at about 900°C, the iron represents only 6% of the FeO intensity.
Figures 3-5 (left to right): Hysteresis loops for the as-milled sample (Fig. 3), sample annealed at 250 C (Fig. 4) and at 400 C (Fig. 5): a) ZFC at 4.2 K; b) ZFC at 280 K and c) FC@5T at 4.2 K, magnified in the low field part. Inset: the exchange bias field measured as a function of the annealing temperature.

This phase transformation is, as we already mentioned, irreversible, the sample quenched down to the ambient temperature presenting only the diffraction pattern of FeO.

The strict control of the stoichiometry and the phase composition at every temperature stage is essential for the use of such mixed powders made of ferromagnetic and antiferromagnetic phases.

Magnetic measurements have been performed in order to investigate the expected exchange bias effect but also to obtain important magnetic parameters such as the saturation magnetization, coercive field, etc. To correlate these parameters with the observed microstructure of the mixed nanogranular powders, we have performed two different isothermal annealings at 250°C and 400°C for 1 h.

The room temperature hysteresis loops of the annealed at 250°C and 400°C samples have been performed and compared with the RT loops of the as-milled sample. These loops are presented in Figures 3-5.

Magnetic behaviour is similar in the case of the 3 samples: as-milled and annealed at 250°C and 400°C. Saturation magnetization is about 55 Am²/kg, with a shape typical for soft FM / AF systems. The occurrence of the coercivity in such systems is due to the enhanced exchange coupling between FM and AFM layers of atoms at the nanograins interfaces and/or grain boundaries.

The field cooling produces partial alignment of the magnetic domains. Thus, for temperatures below $T_{Neel}$ one observes slight increase of the magnetization and of the coercive field. It is also worth noticing that the exchange bias effect decreases with the enhancement of the annealing temperature (as in the inset of Figure 3) down to 8 mT for the sample annealed at 400°C. This tendency is in agreement with the high amount of FeO observed in the phase composition in a-milled sample, while this relative proportion is diminished at higher temperatures due to the redox reaction (see Figure 1), or for the annealed samples compared with the as-milled one.

4. Conclusions

The temperature evolution of the phase structure of a mixture of Fe and Fe₃O₄ (magnetite) powders, obtained by ball milling for 50 hours at room temperature, has been studied by energy-dispersive in-situ X-ray diffraction of synchrotron radiation. The nanocomposite powder is proven to undergo during preparation an incomplete redox reaction with formation of FeO. This reaction is favored due to the high energy developed during the milling and alloying. Two different stages of phase transformation are identified. In the first stage, between 45°C and 450°C, the FeO content decreases continuously in the sample and α-Fe and magnetite are the main phases identified in the XRD patterns. In the second stage, between 500°C and 900°C, the FeO phase starts to appear again in the detriment of the magnetite that completely disappear at around 600°C. Magnetite and iron powders are gradually transformed via redox reaction and wüstite is the main phase observed in the sample at the end of this heating stage. A significant exchange bias effect, related to FeO content, is observed for as-milled sample, the effect being less pronounced upon annealing the nanopowders.

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