Magnetic properties of mechanochemically prepared iron–wüstite (Fe–Fe₇O₃) nanocomposites

M. Mozaffari a,*, M. Gheisari a, M. Nyiafar b, J. Amighian a

a Department of Physics, Faculty of Science, University of Isfahan, Isfahan, 81746-73441, Iran
b Physics Department, IAU-KSRC, Ahvaz, Khuzestan, Iran

1. Introduction

Composites have been generally classified based on the matrix such as metal-matrix composites (MMCs), ceramic-matrix composites (CMCs) and polymer-matrix composites (PMCs). Nano-composites are a new class of materials in which at least one of the phases (the matrix, the reinforcement or both) is of nanometer dimensions. Magnetic nanocomposites containing fine (single domain) magnetic particles, isolated electrically and magnetically by a nonmagnetic, nonmetallic component, also exhibit interesting magnetic properties and they are attracting increasing attention for magnetic application [1]. Magnetic nanocomposite materials show remanence enhancement and improved mechanical and chemical properties in comparison with single-phase magnets [2,3]. Recently, ceramic-matrix and/or metal-matrix nanocomposites have also received increased attention because of their unique mechanical, electrical and interesting magnetic properties [4,5] such as high coercivity at room temperature [6,7], giant magnetoresistance [8] and superparamagnetism [9]. Also, ceramic/Fe magnetic nanocomposites, such as Al₂O₃/Fe, SiO₂/Fe and Fe₃O₄/Fe [10–13], have shown high values of coercivity and so are, therefore, interesting for application as recording media [10].

Nanocomposites are prepared using various physical [14–17] and chemical [18–20] methods. Among these methods mechanical alloying (MA) or high-energy ball milling (HEBM) [11] is a powerful method to synthesize nanomaterials. Mechanochemical processing (MCP) is the term applied to powder processing in which chemical reactions and phase transformations take place due to application of mechanical energy. Most of the mechanochemical processing reactions studied in recent years have displacement reactions of the type: MO+R=M+RO where the metal oxide (MO) is reduced by a more reactive metal (reductant, R) to the pure metal, M [1]. In this work, iron–wüstite (Fe–Fe₇O₃) nanocomposites with different mole ratios have been synthesized by HEBM and their structures and magnetic properties have been studied.

In this work, iron–wüstite (Fe–Fe₇O₃) nanocomposites have been prepared via high-energy ball milling (HEBM), using high-purity hematite (α-Fe₂O₃) and iron (Fe) powders as the raw materials with different Fe/Fe₂O₃ mole ratios (MR) = 0.6, 0.9, 1.0, 2.3, 4.9 and 13.6. X-ray diffraction studies of the as-milled powders show that a single-phase wüstite was formed for the lowest mole ratio (MR = 0.6) and mixtures with MRs higher than 0.6 result in iron–wüstite nanocomposites, except for MR = 13.6 that is dominantly a pure iron phase. The mean crystallite sizes of the iron and wüstite in the nanocomposites have been calculated by Scherrer’s formula, which were 9 ± 1 and 7 ± 1 nm, respectively. Using the formula a = 3.856 ± 0.478y, for Fe₇O₃, where “a” is the lattice parameter of wüstite, it is possible to estimate the value of “γ” for different nanocomposites and a composition of Fe₇O₃/O was estimated for the wüstite single phase (MR = 0.6). In addition, a gradual decrease in “γ” from 0.87 to 0.85 was obtained by increasing MR values from 0.9 to 4.9, respectively. The room-temperature Mössbauer spectrum of the single-phase wüstite shows considerable asymmetry due to two overlapping quadrupole doublets. For higher MRs, room-temperature Mössbauer spectra exhibit sextets, which confirm the existence of iron in the samples. The Mössbauer spectrum of the sample with the highest mole ratio (MR = 13.6) shows only a sextet related to α-Fe without any detection of wüstite, which is in agreement with the XRD results. The nanosized prepared wüstite shows ferrimagnetic like behavior, which was interpreted according to spinel-like defect clusters. The M values obtained from VSM measurements and those calculated based on the Mössbauer data and chemical reaction are in good agreement. By increasing MR from 0.6 to 2.3, the coercivity (Hc) increases sharply to its maximum value at about MR = 2.3, for which the value of Fe content is 45% and then drops off. This behavior is discussed based on α-Fe contents in the nanocomposites and percolation threshold.
2. Experimental procedure

A mixture of 30 g of the raw materials (Fe powder from Merck Co. with a minimum purity of 99% and a refined z-Fe2O3 from a domestic source with minimum purity of 99.8% [21]) with the mole ratios MR = Fe/Fe2O3, where MR = 0.6, 0.9, 1.0, 2.3, 4.9 and 13.6, together with 270 g hardened steel balls with different sizes were loaded into a 500 cc hardened steel vial. The ball to powder mass ratio was 9:1. The mechanical milling was performed for 20 h in air in a high-energy planetary mill (Fritsch, model Pulverisette 6) with a rotational speed of 500 rpm. Phase identification of the as-milled powders was studied by an X-ray diffractometer (Bruker, Advanced D8 model), using CuKα radiation (λ = 1.5406 Å). The mean crystallite size of the powders was calculated from the broadening of XRD peaks, using Scherrer's formula [22]. Lattice parameters have been obtained from "Tune Cell" part of software named EVA, supplied by Bruker Company. This program uses X-ray diffractometer data.

57Fe-Mössbauer spectroscopy was used for phase analysis at room temperature. Room-temperature magnetic measurements were carried out by a vibrating sample magnetometer (Oxford Instruments) with a maximum field of 50 kOe. Also, saturation magnetization (Ms) of the nanocomposites were calculated based on Mössbauer data and chemical reaction. The Ms calculation based on Mössbauer data was performed by the following formula:

\[
Ms = \alpha[M_{sFe} + (1 - \alpha)M_{swustite}],
\]

where \(\alpha\) is the Fe fraction in the nanocomposites and \(M_{sFe}\) and \(M_{swustite}\) are the saturation magnetizations of Fe and wüstite, respectively, were obtained from the VSM measurements. A non-zero magnetization of 12 emu/g has been considered for wüstite phase, which is due to formation of spinel-like defect clusters [23]. In addition, the Ms value of Fe nanopowders, which were obtained by VSM measurements is 170 emu/g, which is lower than the value of bulk Fe (217.2 emu/g) [24].

Ms calculation based on the chemical reaction was performed by

\[
Ms = \beta[M_{sFe} + (1 - \beta)M_{swustite}],
\]

where \(\beta = \frac{55.9(MR+2-3y) + 3(55.9y+16)}{55.9(MR+2-3y)}\) and \(M_{s}\) of Fe and wüstite are defined as above. The chemical reaction used in this calculation is: (MR) Fe+Fe2O3→3FeO+(MR+2-3y)Fe. The measured Fe uptake in the course of milling was about 2 g and was taken into account.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-milled samples with different mole ratios, as labeled on the figure. As can be seen, milling a mixture of the raw materials with an equimolar Fe and Fe2O3 resulted in formation of an iron–wüstite composite, instead of wüstite single phase, as is expected from the chemical reaction of Fe+Fe2O3→3FeO. But the XRD pattern of a mixture with MR = 0.6 shows that the product is a wüstite single phase. This MR value was obtained by the trial and error method. This difference is mainly due to extra Fe uptakes from wear of the vial and balls in the course of mechanical milling. All mixtures with MRs higher than 0.6 result in iron–wüstite composites, except for MR = 13.6. As can be seen on the XRD pattern of the sample with MR = 13.6, there are no detectable peaks related to wüstite. Of course this sample should be an iron–wüstite composite, but because of the detectability limit of the XRD method all peaks are related to z-Fe.

The mean crystallite sizes of the iron and wüstite in the nanocomposites were obtained, using Scherrer’s formula [22] and are about 9 ± 1 and 7 ± 1 nm, respectively. Also, from Fig. 1 it can be seen (refer to vertical line drawn on the figure) that by increasing MR, the main diffraction peaks of wüstite shift, noticeably, to higher angles which is a result of reduction in its lattice parameter.

Fig. 2 shows the variation of wüstite lattice parameters with respect to MR. This reduction can be due to: (i) iron deficiency [12,23] and (ii) nano-sized particles [25].

But as the average crystallite sizes of the wüstite in the nanocomposites have more or less the same values for all MRs, the reduction can be due to different Fe deficiency. Wüstite is almost nonstoichiometric with some Fe deficiency and can be denoted as Fe2O [12,23]. Using the formula \(y = 3.856 + 0.478y\) [26], where \(y\) is the Fe content, a composition of FeO.93O was estimated for the wüstite single phase (with MR = 0.6), while the lattice parameters in the samples with higher mole ratios, MR = 0.9–4.9, corresponded to the compositions Fe0.85O–Fe0.83O. It should be noted that to achieve electroneutrality, an appropriate proportion of iron ions should be considered as Fe3+, therefore one could consider wüstite as Fe3+.85O–Fe0.83O, where \(O\) shows a vacancy.

The Mössbauer spectra of the samples are shown in Fig. 3. The observed asymmetry of spectrum for the single-phase
wüstite sample is due to two overlapping quadrupole doublets [27]. The doublet with $\delta = 0.95$ and $\Delta = 0.85$ mm/s is assigned to occupation of octahedral sites and to the feature of electronic exchange between Fe$^{3+}$ and Fe$^{2+}$ ions both in octahedral sites. Also another doublet with $\delta = 0.65$ and $\Delta = 0.57$ mm/s is assigned to Fe$^{3+}$ ions on tetrahedral sites which interact with Fe$^{2+}$ ions on octahedral sites [27]. For higher MR, Mössbauer spectra exhibit sextets, which show the existence of iron in the samples. From the area of the peaks, corresponding to each sample, the relative contents (%) of Fe and wüstite were determined and shown in Table 1. Mössbauer spectrum related to the sample with MR = 13.6, shows a single sextet which is related to a$-Fe and confirms the XRD results. This also, is due to lack of high detectability in Mössbauer method.

Fig. 4 shows room-temperature hysteresis loops of the cold-pressed powders with different MRs.

The variation of $M_s$ value with respect to MR, that was obtained from VSM measurements and those obtained from the calculations from Mössbauer data and chemical reaction are shown in Fig. 5. As can be seen, a non-zero $M_s$ of 12 emu/g has been attributed to wüstite single phase (MR = 0.6), which is related to the formation of spinel-like defect clusters which has been fully discussed in our previous work [23].

Increase $M_s$ with respect to MR is due to the increase of a-Fe content in the samples. As can be seen, the calculated values of $M_s$ are in good agreement with the experimental ones.

Fig. 6 shows the variation of coercivity with respect to MR for the nanocomposite as-milled powders. As can be seen, the values of $H_c$ are not zero for the lowest MR (0.6) [23]. Also, it can be seen that as MR increases from 0.6, the coercivity increases sharply to a value of 480 Oe, and drops off at the percolation threshold at about MR = 2.3 [28–31], in which the value of Fe content is 45% (Table 1). This behavior has been seen in other granular magnetic systems, exactly, when the percolation threshold is crossed [32].

![Fig. 3. Mössbauer spectra of the samples with different mole ratios (Fe/Fe$_2$O$_3$), as labeled on the spectra.](image)

![Fig. 4. Room-temperature hysteresis loops of the powders with different MRs (a) 1.0, (b) 2.3, (c) 4.9 and (d) 13.6. Inset shows low-field part of the loops.](image)

![Fig. 5. The variation of saturation magnetizations with respect to MR, for VSM measurements (●) and calculation based on Mössbauer data (X) and chemical reaction (▲).](image)

<table>
<thead>
<tr>
<th>MR</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$H_{hf}$ (kOe)</th>
<th>% Fe (obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>$A = 0.65$</td>
<td>B = 0.95</td>
<td>Fe = 0.05</td>
<td>$A = 0.57$</td>
</tr>
<tr>
<td>1</td>
<td>$A = 0.63$</td>
<td>B = 0.95</td>
<td>Fe = 0.05</td>
<td>$A = 0.68$</td>
</tr>
<tr>
<td>2.3</td>
<td>0.57</td>
<td>0.97</td>
<td>0.03</td>
<td>0.78</td>
</tr>
<tr>
<td>4.9</td>
<td>0.43</td>
<td>0.83</td>
<td>0.03</td>
<td>0.85</td>
</tr>
<tr>
<td>13.6</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
</tr>
</tbody>
</table>
The decreases in the $H_c$ for MR values greater than the percolation threshold is due to an increase in $\alpha$-Fe phase in the sample, in which the low $H_c$ value of Fe dominates the composite coercivity and reaches the $H_c$ value of Fe less than 10 Oe. The same behavior has been reported in Fe–Fe$_3$O$_4$ systems [33].

4. Conclusion

Iron–wüstite nanocomposites were obtained by mechanochemical processing of different values of Fe and Fe$_2$O$_3$. Mössbauer spectrum related to the sample with MR = 0.6 shows two overlapping quadruple doublets with considerable asymmetry, where as for the samples with 0.6 < MR < 13.6, a sextet related to $\alpha$-Fe has appeared, as well. The values of $M_s$ were calculated based on Mössbauer data and chemical reactions and the values are in good agreement with VSM measurements. By increasing Fe in the wüstite matrix, the coercivity starts to increase and reaches a critical maximum value of $H_c = 480$ Oe for MR = 2.3. This increase has been explained based on the percolation theory. For MR > 2.3, the value of the coercivity decreases as the Fe content is increased, and reaches a value of less than 10 Oe, which is roughly the coercivity of pure nanosized Fe.

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