Magnetic properties of CoFe₂O₄/CoFe₂ bi-magnetic nanocomposites synthesized by reduction process using activated charcoal in argon atmosphere

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Abstract. The core-shell architecture of CoFe₂O₄/CoFe₂ nanocomposite was synthesized in a controlled flowing argon atmosphere by reduction reaction of CoFe₂O₄ nanoferrite with activated charcoal at 900 °C. The parent $CoFe_2O_4$ nanoferrite was synthesized at 200 °C by glycol-thermal method and was subsequently followed by partial and full reduction to $CoFe_2O_4/CoFe_2$ and $CoFe_2$ respectively. Full reduction was achieved at a $CoFe_2O_4$ to C ratio of at least 1:6. The phase identification, morphology and magnetic properties of the parent sample and the nanocomposites were performed by X-ray diffraction (XRD), high resolution scanning electron microscopy, high resolution transmission electron microscopy, ⁵⁷Fe Mössbauer spectroscopy and vibrating sample magnetometer. The parent sample had an average crystallite size of about 10 nm, XRD density of 5.41 g/cm³ and an average lattice parameter of a = 8.382 ± 0.008 Å. The fully reduced CoFe₂ compound had an increased crystallite size of about 65 nm. Its XRD density was estimated at about 7.9 g/cm³ based on bcc atomic arrangement of Co and Fe atoms with an average lattice parameter of $a = 2.869 \pm 001$ Å. The coercive field measured at room temperature decreased from 230 Oe to about 13 Oe after the reduction process. The nanocomposites show evidence of exchange coupling interaction and enhanced magnetizations with an increase in the energy product $(BH)_{max}$ from 0.143 MGOe for the parent sample to 0.528 MGOe for the bi-magnetic nanocomposites.

Keywords: Nano-ferrites; Nanocomposites, Bi-magnetic; Exchange interaction; (*BH*)_{max} product; Reduction reaction

1. Introduction

 $CoFe_2O_4$ ferrite has interesting properties due to its high crystalline anisotropy energy, moderate saturation magnetization, good chemical stability and wear-resistance [1-3]. It has an inverse spinel structure where the octahedral B-sites are occupied by Co^{2+} ions and half of the Fe^{3+} ions. The other half of the Fe^{3+} are contained in the tetrahedral A-sites of the spinel structure, aligned in parallel and in opposite direction to the moments of Fe^{3+} ions at the B sites. This leaves the magnetization and source of high anisotropy to the Co^{2+} ions in the B site [4]. On the other hand, the $CoFe_2$ alloy is a soft ferromagnetic material with high saturation magnetization and low coercivity. Nanocomposites complexed by the exchange coupling interaction between hard and soft phases create interesting and

mutually compensating effects on the magnetic properties leading to enhanced magnetic properties such as the saturation magnetization and maximum energy product in the hysteresis loops [5]. The exchange coupling behavior of $CoFe_2O_4/CoFe_2$ was studied by Leite et al [6] who used a parent $CoFe_2O_4$ sample synthesized by hydrothermal method with an initial crystallite size of 16 nm. Full reduction to $CoFe_2$ was obtained at a ferrite to carbon ratio of 1:10. Nanocomposites of $CoFe_2O_4/CoFe_2$ microfibers have also been studied by Liping et al [7] who used the sol-gel technique to synthesize the parent sample and performed the reduction reaction in a mixture of hydrogennitrogen gas environment. In the present work, we report on structural and magnetic studies of similar nanocomposites. We have used $CoFe_2O_4$ ferrite with smaller crystallite size.

2. Experimental details

CoFe₂ O_4 nano-ferrite was synthesized by glycol-thermal method from stoichiometric amounts of Sigma-Aldrich iron chloride FeCl₃.6H₂O (99%) and Cobalt chloride CoCl₂.6H₂O (98%) that was initially dissolved in deionized water. Different CoFe₂O₄/CoFe₂ nanocomposites were produced by the reduction reaction of the parent sample with activated charcoal at 900 °C for 3 hours in flowing high purity argon gas (99.999%) atmosphere in a Sentro-Tech Corp tube furnace. The samples produced and studied consisted of 1 mole of CoFe₂O₄ that was each reacted with 0.5, 1, 2, 4, 5, 6, 8, and 10 moles of carbon. The powder X-ray diffraction (XRD) patterns of the samples were performed on an Empyrean Analytical diffractometer type PW 1710 with CoK α radiation. The structural morphology of the samples was studied using Joel_JEM-2100 high-resolution transmission electron microscopy (HRTEM) and Zeiss high resolution scanning electron microscopy (HRSEM) The Mössbauer measurements were performed at room temperature using a convectional constant acceleration spectrometer with velocity calibration by an alpha-iron foil. Magnetic measurements were performed on a LakeShore model 735 vibrating sample magnetometer (VSM) at room temperature in applied fields of up to 14 kOe.

3. Results and discussion

Figure 1 shows the XRD patterns of the as-prepared CoFe₂O₄ nanoferrite, sample annealed at 900 °C and nanocomposites formed with 1, 2, 4, 6 and 10 moles of activated carbon. No impurity phases are detected in the parent and annealed samples as all peaks are indexed to the expected spinel structure (JCPDS no. 022-1086) associated with the Fd3m spatial group for CoFe₂O₄. The average lattice parameters, crystallite sizes and XRD densities for the pure phases are presented in Table 1. The values for the lattice parameter in the ferrite samples are close to the value of 8.3957 Å reported for bulk CoFe₂O₄ [8]. A slight increase in the lattice parameter for the annealed sample can be attributed to different distribution of metal cations and the surface distortions of particles as a result of increased crystallite size [9]. Figure 1 also shows the evolution of XRD patterns with increasing carbon used in the reduction reaction. Full reduction to CoFe₂ was achieved at the ferrite to carbon ratio of at least 1:6 in the present case compared to 1:10 elsewhere [6]. These results show evidence of systematic reduction of the ferrite phase at the expense of the alloy phase. The XRD peaks for the CoFe₂ phase have been indexed with respect to the Miller indices (110) and (200) corresponding to the body centered cubic (bcc) atomic arrangement. The crystallite sizes (D) were calculated using the Scherrer's formula using the most prominent peaks (311) for $CoFe_2O_4$ and (110) for $CoFe_2$. Figure 2 shows the evolution of the average crystallite sizes (D) for $CoFe_2O_4$ and $CoFe_2$ components as a function of the initial carbon content of the nanocomposites. The point of intersection shows equal crystallite sizes of the hard to soft phases corresponding to a ferrite to carbon molar ratio of 1:2. This confirms the transition phase for the growth of CoFe₂ phase on the CoFe₂O₄, thereby increasing the nanocomposite crystalline diameter. The morphology of the as-prepared sample is shown in Figure 3 (a) with no evidence of shell-like features on the surface. As one progresses through the images of the morphologies, it is clearly seen that the shells begin to develop all over the surface. However, this decrease, as the optimum ferrite to carbon molar ratio of 1:6 is approached. The fully reduced samples do not show a high degree of surface shelling.





Fig. 1. XRD patterns of CoFe₂O₄: (a) as-prepared (b), annealed at 900 °C (c), reduced with C = 1 (d), C = 2 (e), C = 4 (f), C = 6 and (g) C = 10

Fig. 2. Crystallite size variation with carbon molar content.



Fig. 3. Morphology of $CoFe_2O_4 + xC$ nanocomposites with carbon molar content: (a) x = 0, (b) x = 1, (c) x = 2, (d) x = 4, (e) x = 6 and (f) x = 8.

Table 1. Crystallite sizes (D), lattice parameters, (a) and X-ray densities $\rho_{_{XRD}}$.

| Sample | D (nm) | a (Å) | ρ_{XRD} (g/cm ³) | |
|--|--------|-------------|-----------------------------------|--|
| | ±0.02 | ± 0.005 | ±0.02 | |
| Parent CoFe ₂ O ₄ | 9.68 | 8.382 | 5.41 | |
| CoFe ₂ O ₄ at 900 °C | 68.49 | 8.390 | 5.28 | |
| CoFe ₂ | 64.83 | 2.869 | 7.85 | |

Table 2. Mössbauer parameters includes hyperfine fields, (B_{hf}) , isomer shifts, (δ) , quadrupole shifts, (Δ_{EQ}) , line widths, (LW), and fraction populations of Fe³⁺, (f), of the parent sample and nanocomposites formed at 0.5, 2, 4, 8 and 10 moles of carbon.

| С | Sub- | $B_{ m hf}$ | δ | $\Delta_{\rm EQ}$ | LW | f(%) |
|-------|---------|-------------|--------|-------------------|--------|-----------|
| (mol) | pattern | (kOe) | (mm/s) | (mm/s) | (mm/s) | ± 2.3 |
| | | ±1.3 | ±0.022 | ±0.019 | ±0.04 | |
| 0 | А | 445.3 | 0.305 | 0.008 | 0.35 | 29.5 |
| | В | 482.3 | 0.309 | 0.006 | 0.28 | 70.5 |
| 0.5 | А | 469.0 | 0.744 | 0.057 | 0.26 | 43.3 |
| | В | 489.7 | 0.268 | -0.024 | 0.22 | 56.7 |
| 2 | А | 357.8 | 1.696 | 0.671 | 0.30 | 26.4 |
| | В | 360.8 | -1.504 | 0.580 | 0.23 | 30.1 |
| | B_2 | 141.3 | 2.156 | 0.994 | 0.31 | 25.2 |
| | B_3 | 335.9 | -1.052 | -1.199 | 0.23 | 18.3 |
| 4 | А | 362.5 | 0.084 | -0.067 | 0.32 | 41.4 |
| | В | 377.1 | -0.588 | -0.369 | 0.11 | 13.2 |
| | B_2 | 365.0 | 2.347 | 0.043 | 0.19 | 11.6 |
| | D | - | 2.000 | - | - | 33.4 |
| 8 | А | 371.0 | 0.046 | -0.150 | 0.25 | 42.0 |
| | В | 370.7 | 0.061 | 0.112 | 0.20 | 58.0 |
| 10 | А | 367.5 | 0.027 | 0.002 | 0.26 | 66.0 |
| | В | 382.8 | 0.029 | -0.001 | 0.24 | 28.0 |
| | D | - | 1.315 | - | - | 5.3 |

Mössbauer spectra for the parent sample and nanocomposites formed at 0.5, 2, 4, 8 and 10 moles of carbon are shown in Figure 4. The data was fitted by a minimum of two sextets and a doublet. The sextets are associated with Fe³⁺ ions at A-sites (tetrahedral) and B-sites (octahedral) of the spinel crystal structure [10]. A doublet was added in the analysis to account for the complex oxidation state of Fe atoms in the nanocomposites formed at 4 and 10 moles of activated carbon. The fitted parameters obtained are shown in Table 2. At room temperature, the parent sample has typical hyperfine field values at A-and B-sites of 445 ± 1.3 and 482 ± 1.3 kOe respectively for Fe³⁺. The obtained isomer shift values are in the range for Fe³⁺ [11], with the Δ_{EQ} value nearly zero, which is a characteristic associated with Fe ion. Therefore this excludes the possible existence of Fe²⁺ in the parent sample. However, considering the nanocomposite at 0.5 moles of carbon, an increase in isomer shift values was observed on A-site, showing the evidence of Fe²⁺ [11], but B-site still retains in the Fe³⁺ range. Therefore, there is a resultant magnetic spin moment which can account for the enhanced magnetization observed at this mole ratio in VSM measurements.

Magnetic hysteresis loops for the parent sample and the bi-magnetic nanocomposites are shown in Figure 5. The magnetic properties such as coercivity, (H_c) , saturation magnetization (M_s) and remanent magnetization (M_r) can be deduced from the hysteresis curves. At room temperature we find $H_c = 0.198$ kOe, $M_s = 32.8$ emu/g and $M_r = 2.6$ emu/g was obtained for the as-prepared sample. An optimum saturation magnetization of 104.7 emu/g was observed at 6 moles of activated carbon. Excess of activated carbon was observed to reduce the saturation magnetization as seen in the hysteresis curve.



Fig. 4. Mössbauer spectra of parent sample and nanocomposites formed at 0.5, 2, 4, 8 and 10 moles of carbon.

4. Conclusions

Bi-magnetic nanocomposites of $CoFe_2O_4/CoFe_2$ were successfully synthesized by reduction reaction. Full reduction was achieved with 6 moles of activated carbon for 1 mole of the ferrite. An enhanced maximum energy product $(BH)_{max}$ was obtained. Our results suggest that there is a critical crystallite size of the parent sample to achieve the best enhanced magnetic property and (BH)max for $CoFe_2O_4/CoFe_2$ bi-magnetic nanocomposite. Excess carbon was observed to reduce the saturation magnetization due to the diluting effect of the carbon.

Acknowledgments

We express our gratitude to the National Research Foundation (NRF), South Africa for the NNEP grant for the VSM equipment, EM unit (UKZN, WC) for HRSEM measurements and the Nigerian National Centre for Technology Management (NACETEM) for study leave (IPE).

In Figure 6 we show the variations of H_c , M_s , M_r , squareness ratio Mr/Ms, and maximum energy product $(BH)_{max}$ with mole ratios of activated carbon. H_c has a maximum value of 230 Oe at C = 0.5 moles and decreases to about 13 Oe after the reduction process. The Ms is observed to increase from 32.8 emu/g to 104.7 emu/g. The abrupt drop at 2 moles could be attributed to the complex covalence phase formed as confirmed in Mössbauer analysis. The optimum magnetization value was achieved at an optimum carbon ratio of 6 moles. An enhanced maximum energy product of 0.528 MGOe as against 0.143 MGOe of the as prepared sample was achieved at 0.5 moles of carbon, which suggests the most effectively coupled bimagnet in our observation. This is a smaller value than that reported by Leite et al [6] (1.22 MGOe).using the same technique, with full reduction reported at 10 moles of carbon, but with bigger grain size of 16 nm parent sample. They suggested that the $(BH)_{max}$ depends on the magnetic properties of the precursor material. Our findings confirm this to be valid. Cabral et al [2], reported 0.6 MGOe, using hydrogen reduction technique, with a parent sample coercivity of 1.32 kOe and grain size of about 30 nm.



Fig. 5. Hysteresis loops for $CoFe_2O_4$ and $CoFe_2O_4/CoFe_2$ nanocomposites.

Fig. 6. Coercivity (H_c) , saturation magnetization (M_s) , squareness ratio (M_r/M_s) , remanence magnetization (M_r) , and maximum energy product $(BH)_{max}$ of CoFe₂O₄/CoFe₂ at different mole ratio of activated carbon.

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