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RESEARCH PAPER

Magnetic field assisted polyol synthesis of cobalt carbide and cobalt microwires

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Abstract Cobalt–cobalt carbide [Co_xC ($x = 2$ or 3)] and cobalt (FCC-Co) microwires have been synthesized using a polyol method in the presence of a high external magnetic field of 4.3 kOe. It was reported before that the synthesis of these particles in the absence of magnetic field leads to the formation of spherical particles. Analysis of the X-ray diffraction (XRD) scans indicates that the synthesized Co_xC wires consist of four phases' α-Co, β-Co, Co_3C, and Co_2C. The percent composition of these phases was 53.3 % Co_3C, 26.8 % Co_2C, 12.5 % α-Co, and 7.4 % β-Co. XRD analysis of the as-synthesized cobalt wires shows that it consists of single-phase FCC-Co. Based on Scherrer analysis of the XRD data, the average crystallite sizes of the cobalt carbide and the cobalt particles are 18.5 and 16.3 nm, respectively. Scanning electron microscopy (SEM) studies show that the diameter of Co_xC wires is in the range of 1.6($\pm$0.2) μm with their length varying between 18 and 30 μm while the diameter of the cobalt wires is 1.65($\pm$0.1). The SEM results infer that the morphology of the growing particles was controlled by the magnetic field with the applied field directs the growth of the particles into wires. The magnetic measurements indicate a superparamagnetic character of the cobalt wires and a soft ferromagnetic nature of the synthesized Co_xC chains. The degree and field range of the interactions between magnetic domains have been investigated using a Henkel plot.

Keywords Polyol synthesis · Cobalt carbide · Cobalt · Microwires · One-dimensional (1D) magnetic structures

This article is part of the topical collection on nanomaterials in energy, health and environment

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Introduction

For decades, soft ferromagnetic materials especially one-dimensional (1D) magnetic structures have attracted a lot of interest due to their unique characteristics such as high saturation induction, high permeability, low core loss, and ability to concentrate and shape magnetic flux with great efficiency (Fish 1990). 1D magnetic structures have many potential applications such as permanent magnets, high density magnetic storage media, sensors, catalysts, and power electronic circuits (Fert and Piraux 1999; Kind et al. 2002; Wang et al. 2001; Whitney et al. 1993). To date, there are few reports about convenient and practical methods to synthesize 1D structures due to the strong

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forces arising from magnetic dipole interaction, Van der Waals forces, and partially filled bands (Puntes et al. 2001; Cha et al. 2005).

In this study, cobalt and cobalt/cobalt carbide 1D magnetic structures were synthesized using a polyol process under an external applied magnetic field. It is reported that the absence of the applied magnetic field leads to the formation of spherical particles (Cheng and Cheng 2009; Kamal et al. 2009; Osorio-Cantillo et al. 2012; Zhang et al. 2011). The cobalt/cobalt carbide system is interesting because cobalt is a soft magnetic material with high magnetization while cobalt carbides possess hard magnetic properties (Harris et al. 2010; Kyler et al. 2012). Hence by synthesizing Co/Co_xC composites, the exchange coupling interactions between the hard and soft magnetic phases could be investigated. While only cobalt-based 1D magnetic structures are being presented, the application of an external magnetic field in conjunction with the polyol process can be used for the synthesis of many other magnetic particle systems. The applicability of this technique to prepare other magnetic materials has been investigated through the successful synthesis of cobalt wires.

Experimental section

Preparation of the Co_xC arrays

In a typical experiment, tetraethylene glycol (TEG) was mechanically stirred, and heated to 275 °C, with 2 mmol of KOH under distillation conditions (Carroll et al. 2011). Once the solution reached the desired temperature, a 4.3 kOe uniform magnetic field is applied using a computer controlled Lakeshore model 7304 12-in. electromagnet. At 4.3 kOe magnetic field, a total of 10 quantities of 2.0×10^{-4} mol of $Co(Ac)_2 \cdot 4H_2O$ were added incrementally at 1 min intervals. The solution is stirred at 275 °C for an additional 20 min before the heat and magnetic field are removed. The reaction mixture was centrifuged at 8,000 rpm for 4 min to remove the solvent. The resulting precipitate was then rinsed with methanol several times, magnetically separated, and allowed to dry at room temperature in a vacuum oven. A similar approach has been used to synthesize cobalt chains using $CoCl_2 \cdot 6H_2O$, NaOH, and ethylene glycol at 190 °C.

Characterization

X-ray diffraction (XRD) scans were collected using a PANalytical X'Pert Pro MPD series diffractometer, with Cu Kα radiation ($\lambda = 0.154056$ Å) in θ–2θ geometry to determine the crystal phases of the as-synthesized Co_xC and Co arrays. Crystal phase identification, phase percent composition, and crystal structure refinement were carried out using X'Pert Highscore Plus software, which utilized the ICDD/JCPDS database. The average crystallite size was determined using Scherrer equation. Scanning electron microscopy (SEM) micrographs were obtained using a HITACHI SU-70 SEM operated at an acceleration voltage of 5 kV. Magnetic properties were determined using a Quantum Design–Versalab vibrating sample magnetometer. Isothermal remanence magnetization (IRM) plots were collected from 0 to 10 kOe. The direct current demagnetization (DCD) plots were collected in the same manner as the IRM plots, except that the particles were first saturated in a field of −10 kOe. A Henkel plot was then constructed using the formula: $\Delta M = M_{DCD} - [1 - (2 \times M_{IRM})]$ (Wohlfarth 1958).

Results and discussion

In the XRD patterns of the as-prepared particles (Fig. 1), four crystal phases were identified: α-Co, β-Co, Co_3C, and Co_2C. The percent phase composition was 53.3 % Co_3C, 26.8 % Co_2C, 12.5 % α-Co, and 7.4 % β-Co. Scherrer analysis of the XRD data revealed average crystallite sizes of 18.5 nm. XRD of the as-synthesized cobalt chains displayed peaks consistent with single-phase FCC-Co with an average crystallite size of 16.3 nm (Fig. 1). Crystal structure refinement of the Co_xC and Co microwires showed each crystal phase to possess consistent peak widths (Fig. 2). This lack of variance implies that little anisotropic crystal growth was induced by nucleating the particles under the influence of a magnetic field.

SEM images of the as-prepared Co_xC particles show them to display a long chain like morphology made up of smaller spherical particles (Fig. 3a, b). The length of the as-prepared chains varies between 18 and 30 μm and their width is 1.6(±0.2) μm. The surface of the chain like assemblies reveals a low density surface layer, made up of smaller spherical particles averaging

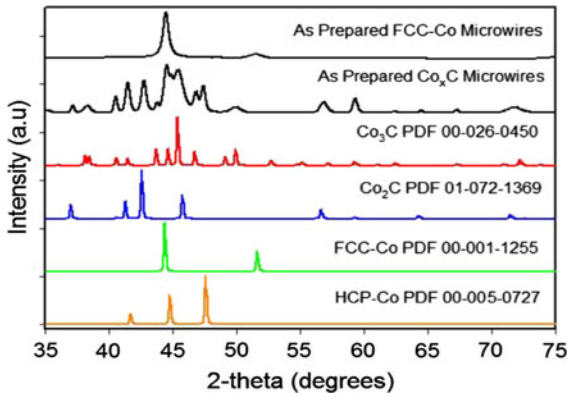

Fig. 1 XRD patterns of the as-synthesized cobalt carbide and cobalt wires

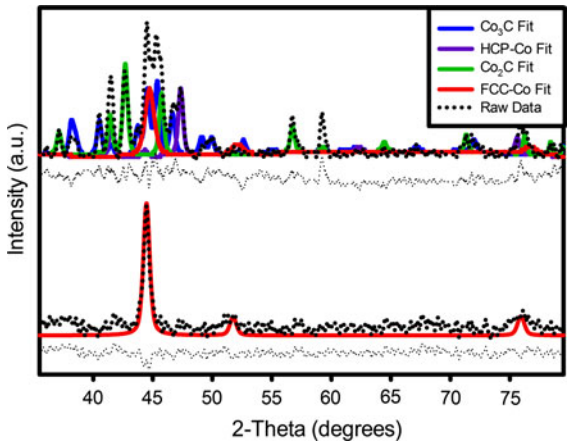

Fig. 2 Reitveld refinement of the XRD patterns for as-synthesized cobalt carbide (*top*) and cobalt (*bottom*) wires

150 nm in diameter. The low density surface layer has previously been identified as a surface glycolate layer (Kyler et al. 2012). The impurity particles appear in the figure may be attributed some broken chains by the effect of the mechanical stirring. Low magnification SEM images (Fig. 3c) of the as-synthesized cobalt particles display the formation of a long chain like structures extended up to tens of micrometers with average widths of 1.65(±0.1) μm. Higher magnification SEM images (Fig. 3d) indicated that the surface of the as-synthesized cobalt chains consists of smaller particulates layer of 118 nm average size. The chain like morphology and lack of anisotropic diffraction patterns implies that the particles first nucleate, then aggregate into larger spheres and the applied magnetic field causes the spheres to agglomerate into the observed chains.

The room temperature hysteresis loops of the as-synthesized cobalt carbide and cobalt chains are shown in Fig. 4. For cobalt carbide chains the magnetic saturation (M_s), remanent magnetization (M_r), and coercivity (H_c) of these wires are 74.32 emu/g, 15.11 emu/g, and 393 Oe, respectively. A 151.66 emu/g magnetic saturation has been observed for the superparamagnetic cobalt chains. The presence of the carbide phases accounts for the lower magnetic saturation of the carbide chains with respect to the metallic cobalt chains. Similarly, the presence of α-Co and β-Co phases are responsible for the observed low coercivity in the cobalt carbide chains compared to the high coercivity reported for the pure cobalt carbide phases (Harris et al. 2010; Kyler et al. 2012). The slope of the magnetization curve near zero field was used to determine the magnetic domain size. Near zero field the primary contribution to the slope of the magnetization curve is derived from the largest magnetic domains allowing for an approximation as to the upper limit of magnetic domain size (Yaacob et al. 1994). Based on the room temperature, hysteresis loop of the as-synthesized cobalt carbide chains (Fig. 4) and the equation (Yaacob et al. 1994)

$$d_{\max} = \left[\frac{18kT\left(\frac{dM}{dH}\right)_{H=0}}{\pi\rho M_S^2}\right]^{\frac{1}{3}},$$

where k is the Boltzmann constant, T is the absolute temperature (300 K), for cobalt carbide wires dM/dH is the slope near zero field (97.106 emu/g Oe), and ρ is the density of the cobalt carbide (7.65 g/cm^3), M_s is the saturation magnetization (74.32 emu/g), the magnetic domain size of the carbide wires was determined. The magnetic diameter of the cobalt carbide particles is 37.92 nm which is nearly twice the crystallite size. The as-synthesized cobalt chains have a magnetic domain size of 1.73 nm based on dM/dH = (0.06172 emu/g Oe), ρ is the density of the cobalt (8.90 g/cm^3), and M_s = (151.66 emu/g). The larger domain size of the carbides compared to the crystallite size indicates that the grains of the carbide are exchange coupling together to form a single magnetic phase. The hysteresis loop in Fig. 4 shows magnetic saturation to occur at high fields, implying domain–domain interactions to be present.

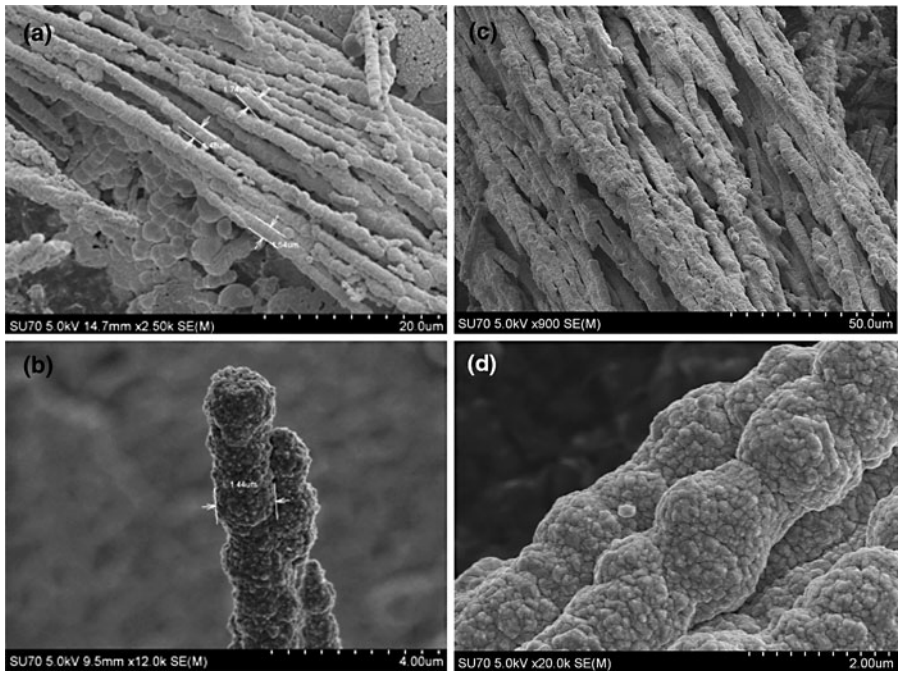

Fig. 3 SEM images of the as-synthesized cobalt carbide (**a**, **b**) and cobalt (**c**, **d**) chains

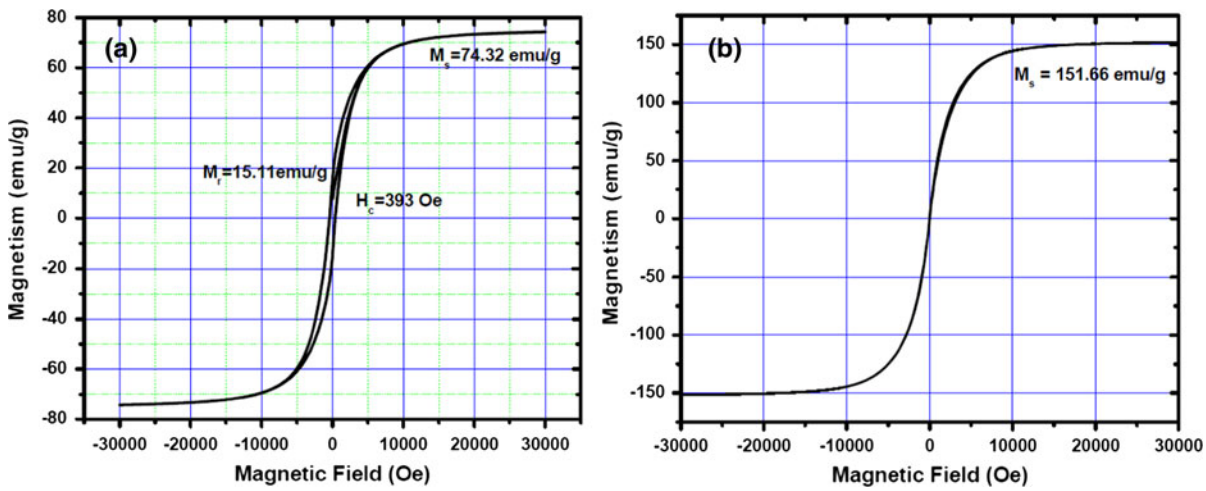

Fig. 4 Hysteresis loop of the as-synthesized cobalt carbide (**a**) and cobalt wires (**b**)

To further investigate the degree and field range of the interactions between domains, a Henkel plot was constructed from collected IRM and DCD plots (Fig. 5). The Henkel plot identified demagnetizing magnetostatic interactions to be present at low fields (0 Oe–4 kOe). Previous studies have reported coercivities exceeding 3 kOe for cobalt carbide particles (Kyler et al. 2012). However, the presence of the soft ferromagnetic metallic cobalt phases, cause cooperative switching of the magnetically hard carbide phases at low fields, resulting in the reduced coercivity observed.

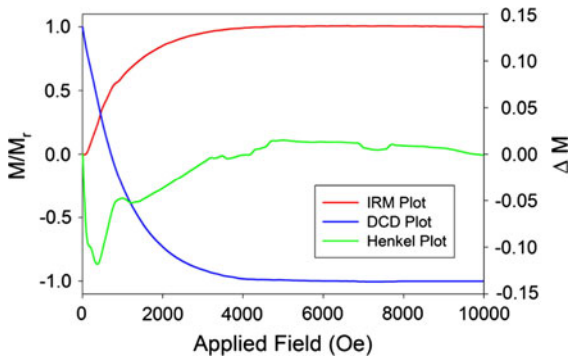

Fig. 5 Henkel plot for the cobalt carbide wires

Conclusions

Synthesis of 1D microwires was achieved by using a polyol process under an external applied field. The nanoparticles nucleate and grow spherical nanoparticles which in the presence of a magnetic field aggregate into larger exchange coupled domains. The larger domains further aggregate along the flux lines to create larger 1D microwires. This facile and convenient strategy can be used on any magnetic nanoparticles system, it should be a promising technique to synthesize other 1D magnetic materials.

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