Journal of Magnetism and Magnetic Materials 339 (2013) 20–29

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Self-grown core/shell nanoparticles of cobalt: Correlation of structure, transport and magnetism

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ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form
13 February 2013
Available online 6 March 2013

Keywords:
Nanoparticle
Core–shell
Tunneling
Magnetoresistance

ABSTRACT

The structure, electrical and magnetic transport properties of cobalt nanoparticles having core–shell structure are presented. The nanoparticles were prepared by a borohydride reduction method followed by heat treatments. X-ray diffraction shows that the as-prepared samples are amorphous while annealed samples are crystalline having a majority of fcc-Co along with metastable Co_3B. The particles are spherical in shape and the average grain size increases with increasing anneal temperature. The core–shell structure is confirmed by high resolution transmission electron microscopy. The structural study reveals that the cores of the as-prepared and the annealed samples are of fcc-Co, while there is a profound microstructural change of the shells with annealing. A large change in the resistivity is observed between the as-prepared and annealed samples. The electrical transport properties at low temperature are interpreted in terms of tunneling between ferromagnetic cobalt cores through the non-magnetic shell. Improvements of the magnetic and the transport properties of the nanoparticles with annealing are observed with microstructural changes of the core–shell structure. The saturation magnetization (M_s=40 emu/g) at room temperature suggests that air annealed (500 °C) samples are protected from oxidation due to the formation of a B_2O_3 protective layer. These results suggest that this kind of nanocomposite systems might have significant potentiality in recording media and in medical diagnostic or therapy applications.

1. Introduction

Magnetic fine particles have attracted a constant interest among the scientific community during the last few decades because of their increasing number of applications [1]. Nanostructured materials with different dimensionalities in the submicron range have been possible to prepare due to the availability of new synthesis techniques and the never ending demand for miniaturization. With the reduction in the particle size, new magnetic, optical and electrical properties emerged, which is observed to be different from their bulk counterparts [2–4]. Thus it has opened up the field of nanomagnetism to new opportunities [5] and has found application in wide areas of science ranging from magnetic recording and quantum computing [6] to Earth sciences [7] and biomedicine [8,9]. Recently, much attention has been focused on the magnetic properties and unidirectional exchange anisotropy in oxide-passivated magnetic transition metal particles including iron (Fe) [10], cobalt (Co) [11–13] and nickel (Ni) [14,15], because of their potential application in memory devices. They show appreciable enhancement in the value of magnetoresistance (MR) at low temperature with values much larger than those observed for the conventional metal insulator granular system. A giant magnetoresistance (GMR) arises due to a metallic non-magnetic barrier in structures of two ferromagnetic (FM) layers (electrodes) separated by a thin insulating (I) layer [16]. Depending upon the relative orientation of the magnetization of the FM electrodes, the electrical conduction is governed by the electrons tunneling through the insulating layer in the FM/I/FM structure. The relative orientation of the magnetization of the FM layers is achieved by applying a magnetic field and tunneling type magnetoresistance (TMR) is observed [17–19]. In the FM–I granular system, where the magnetic metal granular or clusters are embedded in an insulating matrix, a large TMR effect has been detected recently [20]. The tunneling current between randomly oriented magnetic granules is found to be smaller than that between the magnetically aligned ones. In polycrystalline compounds and thin films, the tunneling through grain boundaries strongly influences the conductivity at low temperature. The grain boundary effect on the transport property has been experimentally studied in magnetites [21,22] as well as cuprate superconductors [23], where large TMR values are reported. Although several models have been proposed for understanding the tunneling mechanism [24–26] through the

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http://dx.doi.org/10.1016/j.jmmm.2013.02.035

oxide grain boundaries, a better understanding of the transport properties is yet to be addressed.

The interface between Co (FM) and CoO has been used as a prototype for studying the exchange bias (EB) effect, because it has a large unidirectional anisotropy and ordering temperature of bulk CoO, that is the Neél temperature (T_N) near room temperature at 293 K [27]. Meiklejohn and Bean [28] were the first to discover the EB anisotropy effect between Co-core and antiferromagnetic (AFM) CoO layer in oxide coated Co particles prepared by depositing onto a mercury cathode. Various aspects of conductivity mechanism, such as the EB effect through magnetoresistance (MR) [29], reversing of the training effect through anisotropic MR, etc., have been investigated for the Co/CoO core–shell nanostructures. The present work explores in detail the structural, and electrical and magnetic transport properties in the cobalt nanoparticles having core–shell structure, with Co at its core. The temperature dependence of the conductance in the nanoparticles has been studied through the non-linear current–voltage (*I*–*V*) characteristics. It is observed that the conductance between metallic ferromagnetic Co particles involves tunneling of the charge carriers through the localized and non-magnetic shell layers present at the grain boundary of the Co particles. Magnetic property and the magnetoresistive (MR) characteristics of the nanoparticles have been studied as a function of applied magnetic field and temperature. All the aforesaid characterizations have been done on the as-prepared sample as well as on the samples annealed at 250 °C and 500 °C. Annealing at higher temperature resulted in the increase of the average grain size along with a significant structural change. The electrical and magnetic properties of the nanoparticles seem to have a strong co-relation with the microstructural change.

2. Experiment

Cobalt rich fine particles were prepared by reducing the corresponding salt $CoCl_2 \cdot 6H_2O$ (cobalt chloride) with sodium borohydride ($NaBH_4$) as the reducing agent (the borohydride reduction technique). 100 ml of a 1 M solution of sodium borohydride ($NaBH_4$) was added drop wise over a period of 1 h to 250 ml of a 0.5 M $CoCl_2 \cdot 6H_2O$ aqueous solution in a beaker with constant magnetic stirring. An instantaneous exothermic reaction ensued with the formation of black slurries of Co nanoparticles and evolution of H_2 gas. The average temperature of the solution rises by 10–20 °C. However, dropwise addition of $NaBH_4$ controls the reaction and maintains the average temperature of the solution near room temperature. The reaction in air monitors the *in-situ* surface reaction of the resulting Co sample with H_2O in the solution, forming a stable spontaneous surface oxide (SSO) layer as an integral part of each individual Co particle. After the $Co^{2+} \rightarrow Co$ reaction, the sample (slurries of Co nanoparticles) was filtered and washed thoroughly with distilled water and acetone. This recovery powder was then dried in vacuum at 10^{-2} mbar pressure and at a temperature of 70 °C for 6–8h. The sample thus obtained is black in color and stable in ambient atmosphere. The as-prepared sample was finally heated at 250 °C and 500 °C, for further characterizations.

The structural identification and qualitative analysis of the as-prepared and annealed samples have been done using a PW 1718 X-ray diffractometer with Co-Kα ($\lambda = 1.789$ Å) radiation. The constituent of the as-prepared and annealed samples was analyzed by an electron probe X-ray microanalyzer (EPMA) (CAMECA-SX100) at 15 kV operating voltage. High resolution transmission electron microscopy (HRTEM) was used for visualizing the core–shell nanostructure using a JEOL JEM, 2010 microscope. The particle size, morphology and chemical composition were investigated with a field emission scanning electron microscope (FESEM) (Carl ZIESS-SUPRA 40). The transport property of the core–shell structures was studied as a function of applied bias (voltage), magnetic field (*H*) and temperature (*T*). A conventional linear four probe technique was used to measure the transport property of the nanoparticles (NPs) in the pelletized form. The powder sample was pressed to form a pellet of diameter 10 mm and four linear contacts were made with a gap of 1.5 mm between each probe. Electrical measurements were done using a Keithley make 2400 source meter, 6220 current source, 2182A nanovoltmeter and 6514 electrometer. For low temperature measurements, a closed chamber of He cryostat (make: Cryo Industries Inc., USA) was used along with a Bruker BIOSPIN electromagnet for the application of magnetic field. The magnetization measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

3. Results and discussions

3.1. Structural characterizations

Fig. 1 compares the X-ray diffraction (XRD) pattern of the as-prepared and annealed samples. The diffractogram of the as-prepared sample exhibits a broad hump near $2\theta = 51°$, suggesting that the prepared sample is Co rich. However, the absence of any sharp peak indicates that the sample is amorphous with pronounced structural disorder. Due to annealing at 250 °C, it is observed that the as-prepared sample crystallizes to form two metastable crystalline phases of fcc-Co and orthorhombic-Co_3B structures. The indexing (*hkl*) of the intense peaks has been done using standard JCPDS (Joint Committee on Powder Diffraction Standards) file no. 15-0806 (for Co) and no. 13-0133 (for Co_3B). However, comparing the most intense peak, the volume fraction

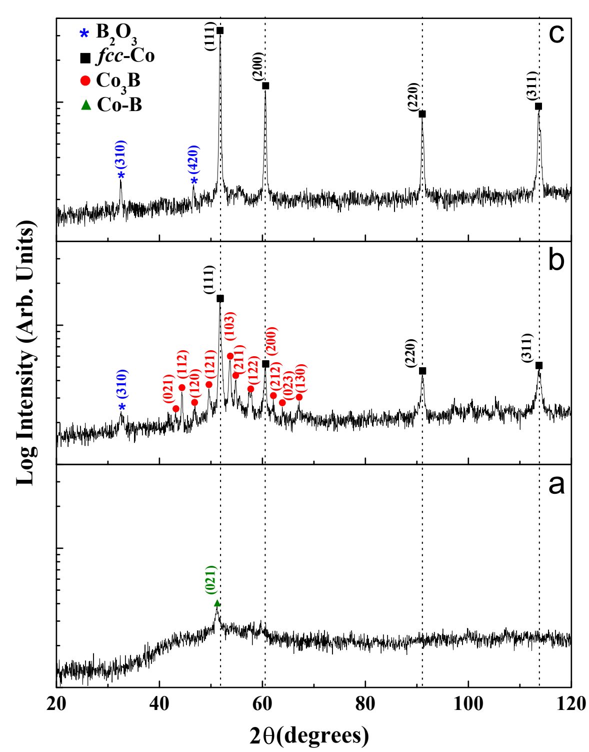

Fig. 1. Comparison of the XRD plots for the as-prepared, 250 °C and 500 °C annealed samples. The intensity is normalized to the same incident intensity for all the samples, and the scale is set accordingly.