



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

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

Conductive and magnetic glass microsphere/cobalt composites prepared via an electroless plating route



Ruihua Zhou, Huiyu Chen*, Guilin Liu, Guizhe Zhao, Yaqing Liu*

School of Materials Science and Engineering, North University of China, Taiyuan 030051, People's Republic of China

ARTICLE INFO

Article history:

Received 1 August 2013

Accepted 29 August 2013

Available online 5 September 2013

Keywords:

Composite materials

Magnetic materials

Electrical properties

Microstructure

ABSTRACT

Glass microsphere/cobalt composites were successfully prepared by an electroless plating method in alkaline solution. The as-obtained samples were characterized by XRD, SEM, and VSM techniques. It was found that the concentrations of cobalt salt and aqueous ammonia greatly influenced the microstructure of cobalt coatings. A compact, uniform and continuous cobalt coating could be deposited on the surface of the glass microspheres by adjusting the synthetic parameters. The cobalt layer possessed hexagonal-close-packed phase structure. The magnetic measurement demonstrated that the glass microsphere/cobalt composites exhibited ferromagnetic nature with saturation magnetization of 21.1 emu/g and coercivity of 382.9 Oe, respectively. Compared to the cobalt bulk, the composites showed a decreased saturation magnetization value but an enhanced coercivity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently, electromagnetic shielding material has attracted considerable attention, and the traditional metallic shielding materials are increasingly limited because of their high density [1,2]. Thus, the conductive core-shell structural composites with lower density were more promising for such applications [3–5].

Glass microspheres possess excellent chemical and thermal stability, low thermal conductivity, and high mechanical strength, and have been widely used in electronic devices [6], polymer industry [7,8], and insulation fields [9]. When the glass microspheres were deposited on a layer of magnetic metal materials, e. g., Fe, Ni, and Co, more applications would be achieved as electromagnetic wave absorbers and magnetic recording heads [10]. In the previous reports, An et al. successfully synthesized hollow glass/cobalt core-shell composites by hydrothermal reduction process [11]. Meng et al. obtained a cobalt layer on the surface of cenosphere particles using heterogeneous precipitation thermal reduction method [12]. Special equipments were needed in the above work, and it was difficult to synthesize in large scale. Electroless plating process is low cost, simple handle, and energy-saving compared to the vapor deposition method.

Herein, glass microsphere/cobalt composites were prepared via an electroless plating approach. Sodium hypophosphite and sodium citrate were served as reductant and complexing agent, respectively. The magnetic properties of such composite were also

examined at room temperature. The chemical reaction process can be expressed as the following:



2. Experimental procedure

Materials and method: All chemical reagents were analytical grade and used without further purification. In a typical synthesis, 3 g of glass microspheres were firstly etched in 100 mL aqueous solution which contained 3 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and 6 mL of sulfuric acid (H_2SO_4 , 98 wt%), stirred at 30 °C for 15 min, collected, and then were sensitized for 15 min in 100 mL solution containing 2 g of tin(II) chloride (SnCl_2), and followed by the activating treatment in 100 mL solution composed of 0.01 g palladium(II) chloride (PdCl_2). Subsequently, 100 mL of an aqueous solution was prepared in a beaker by dissolving 3 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 4 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ in distilled water. Then 8 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added into the above solution to adjust the pH of the bath. After adding 3 g of the activated glass microspheres into the mixture, the beaker was placed in a electric-heated thermostatic water bath at 80 °C with vigorous mechanical stirring, and 10 mL (30 g/L) of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ aqueous solution was dropwise added to the above solution. After 50 min, the sample was filtered off and rinsed with distilled water and ethanol for several times, then collected and dried at 60 °C for 5 h. Controlled experiments were conducted by changing the concentrations of cobalt salt and $\text{NH}_3 \cdot \text{H}_2\text{O}$, respectively, while kept other parameters and procedures unchanged.

* Corresponding authors. Tel./fax: +86 3513559669.

E-mail addresses: hychen09@sina.com (H. Chen), zfflyq98@sina.com (Y. Liu).

Characterizations: XRD pattern was recorded on a Bruker D8 focus diffractometer with Cu K α radiation ($\lambda=0.15406$ nm). SEM images were taken with a Hitachi SU-1500 scanning electron microscope. The volume resistivity values were obtained by a SB120 four-point-probe instrument. Magnetic measurement was conducted at room temperature using a VSM (Lakeshore 7407, USA) with a maximum magnetic field of 15 kOe.

3. Results and discussion

Powder XRD has been used to determine the crystal structure and chemical composition of the resultant product. Fig. 1a displays the XRD pattern of the product obtained in the typical synthesis. All peaks can be indexed as the hexagonal-close-packed phase of cobalt (JCPDS Card no. 05-0727). No characteristic peaks due to the impurities of cobalt oxides or hydroxides could be observed, which indicated that high purity of cobalt layer on glass microspheres was achieved. The morphology of the as-prepared composites was investigated by SEM. It could be seen from Fig. 1b that the diameter of the composite microspheres was ca. 10–50 μm , and the broad distribution of the diameter was due to the size variation of the pure glass spheres. A close-up view of the single composite particle revealed that the cobalt coating was composed of compact particle-like clusters with average size of about 500 nm (Fig. 1c and d).

Fig. 2 shows the SEM images of the glass/cobalt composite microspheres prepared with different $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations. It could be clearly observed that the morphologies of cobalt coatings varied remarkably, although all the microspheres were deposited with a thin layer of cobalt. Fig. 2a is the SEM image of core-shell composite obtained with lower concentration of Co^{2+} (10 g/L), the coating possessed some small cracks and easily be peeled off. As the concentrations of Co^{2+} cations increased (Fig. 2b–d), the layer changed from coarse to compact. In addition, both the weight and the thickness of the cobalt layer also increased accordingly. However, the electroless plating process

did not take place when the concentration of cobalt salt was further increased to 40 g/L. Such morphology variations of the cobalt depositions might be attributed to the following interpretations: at lower Co^{2+} concentration of 10 g/L, the reducing agent was relatively sufficient and the reaction was fast, so the small amount of Co^{2+} was easily reduced to elemental cobalt and then deposited on the surface of glass microspheres. Additionally, the cobalt layer was thin enough to be fractured, and poor binding force existed between the cobalt layer and the surface of glass microspheres. However, with the Co^{2+} concentrations increasing, the electroless plating rate was gradually decreased, and the reaction would stop when the concentration of the Co^{2+} exceeded 40 g/L. The optimal mass ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was 1/1 in the current synthesis. The minimum value of volume resistivity was $0.0082 \Omega \text{ cm}$ when the concentration of Co^{2+} was 30 g/L. It proved that uniform and compact cobalt layer was beneficial to electrical conductivity.

Fig. 3 presents the SEM images of the products synthesized with $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentrations ranging from 20 to 200 mL/L. When the concentration of aqueous ammonia was low, the deposition of cobalt would be very slow and tended to form tiny grain on the Pd activation point. So the coating was thin and easily destroyed (Fig. 3a), which indicated that the binding force between the cobalt layer and glass surface was weak. As the $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration increased, the coating layer gradually became compact and uniform, and the cobalt crystals grew bigger (Fig. 3b–d). Such phenomena might result from the acceleration of hypophosphite oxidation in higher pH value systems. According to the chemical reaction (Eq. (1)), the reaction process was greatly improved in the stronger base solution, and such reaction was previously reported [13]. And hence, the interaction between the glass microspheres and cobalt layers became stronger. However, the solution became unstable at higher pH value, and the microcrystals-based cobalt coatings possessed obviously porous clusters (inset of Fig. 3d) owing to the tremendous release of H_2 bubbles. On the basis of the controlled experiments, the optimal concentration of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was 80 mL/L in this work to obtain compact cobalt deposits.

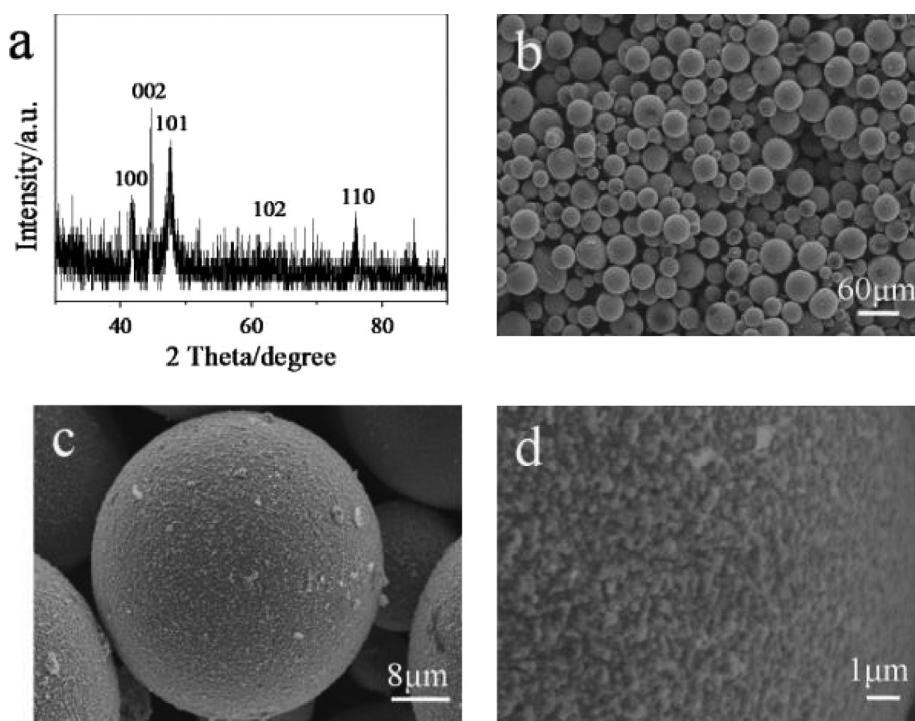


Fig. 1. XRD pattern (a) and SEM images of the glass microsphere/cobalt core-shell microstructures prepared in the typical synthesis with a low magnification (b), high magnification view of a single composite particle (c), and smaller particle-like clusters on the surface (d).

Download English Version:

<https://daneshyari.com/en/article/8021278>

Download Persian Version:

<https://daneshyari.com/article/8021278>

[Daneshyari.com](https://daneshyari.com)