JNS 1 (1012) 7-13

Journal of
NANOSTRUCTURES
JNS NANOSTRUCTURES
JNS.kashanu.ac.ir

Chemico- thermal synthesis of nano-structured cobalt with distinct magnetic property

H. Sabarou, A. Ataie[*]

[a] *School of Metallurgy and Materials Engineering, University of Tehran, Tehran.*

Article history:
Received 3/8/2011
Accepted 9/12/2011

Keywords:
Chemical synthesis
Nano-Structured material
Magnetic material
Cobalt

**Corresponding author:*
E-mail address*:*
aataie@ut.ac.ir
Phone: 98 912 1936361
Fax: +98 21 88006076

Abstract

The synthesis of nanostructures cobalt through a controlled chemical process followed by heat treating at various temperatures is studied. The product is characterized by ICP, XRD, FESEM, and TEM, indicating that the as- synthesized particles have an amorphous structure with 1.76 for Co/B ratio, an average size of 50 nm. The transformation of intermediate phases into single phase nano-crystalline metallic cobalt during the heat treatment is investigated by DSC analysis. The mean crystallite size of obtained cobalt was 30 nm. The decrease in coercivity (4344.93A/mf) with the sharp increase in saturation magnetization (1.41×10-4 Am2/kg) presents excellent ferromagnetic properties for nano- crystallite cobalt.

1. Introduction

Magnetic nano- particles are attracting growing fundamental interest because of their potential applications in motors, electrical, power transformation, magnetic fluids, magnetic resonance imaging and high- density magnetic recording [1-3]. Cobalt nano- particles display a wealth of size dependent structural, magnetic electronic and catalytic properties. This material has been synthesized by variety of methods including thermal decomposition [4, 5], gas vapor condensation [6], reduction of cobalt salt [7, 8]. For reduction, sodium borohydride has been often used as a reducing agent [9]. It is proved that reaction between sodium borohydride and cobalt (II) chloride in aqueous media under specific experimental conditions can yield Co-B amorphous nano- particles regarding to the reaction equation mentioned below [10, 11]:

$$2CoCl_2 + 4NaBH_4 + 9H_2O \rightarrow Co_2B + 4NaCl + 12.5H_2 + 3B(OH)_3 \qquad (1)$$

Sodium borohydride is also a crystalline white substance that decomposes by hydrolysis according to the following exothermic reaction [11]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + 300\ kJ \qquad (2)$$

On the other hand, there is another side reaction coming from hydrolysis reaction [11, 12]:

$$NaBO_2 + H_2O \leftrightarrow HBO_3 + NaOH \qquad (3)$$

It is found that the extent with which reaction (3) proceeds can determines the primary solid product in borohydride reduction process [10]. According to the above reactions, Glavee *et al.* reported that borohydride reduction of cobalt ions in water has this ability to yield metallic cobalt. Nevertheless, they had no apparent evidence that Co(s) was a dominant product under their experimental conditions.

In this paper, a set of experimental conditions, which can yield metallic cobalt as a primary product with outstanding magnetic properties, has been presented.

2. Experimental procedure

The amorphous powder was prepared by chemical reduction method. Briefly, 100 mL of 1000 mmol sodium borohydride was added into 200 mL of aqueous solution of 300 mmol cobalt chloride hexahydrate through a constant pressure of argon under vigorous stirring. Preparation time of sodium borohydride and cobalt chloride hexahydrate solutions and their pH were measured. As the reduction is strongly exothermic, the mixing was performed at 278K in an ice- water bath to prevent local overheating, which may cause the gathering of small particles and/or the crystallization of the Co-B amorphous powder. Reduction mixture was stirred for 7 minutes, and the resulting black solid was washed free from Cl- and Na+ ions with distilled water. Then it was washed further with acetone, and stored in it so as to be used at a later time. The synthesis products have been heat treated at 523, 773, and 873 K for 1 h in argon flow.

The composition of the synthesized sample was analyzed by means of inductively coupled plasma (ICP, VISTA- MPX). The structure of as-synthesized and heat treated samples were determined by X- ray powder diffraction (XRD, Philips, Co Kα = 1.787 Å). After considering instrument and strain effects, the average crystallite size of heat treated powder was calculated by Scherrer's equation for the (111) peak [13]. Morphology and particle size of the synthesized and heat treated samples were observed by transmission electron microscope (TEM/Ziess EM10C, 100kV) and field emission scanning electron microscope (FESEM, Hitachi S4160).

Crystallization and thermal behavior were characterized by continuous heating in a differential scanning calorimeter (DSC) under flowing high purity argon (300 mL/min) at heating rate of 10 K/min. The magnetic properties of the samples were evaluated by vibrating sample magnetometer (VSM, 10 kOe).

3. Results and discussion

XRD pattern (Fig.1) demonstrated that as-synthesized sample had a typical amorphous structure indicated by a single broad peak around 2□ = 40◦.

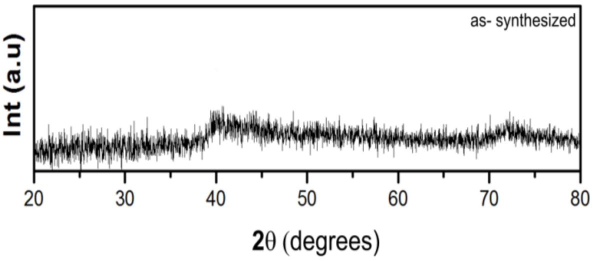

Fig.1. XRD pattern of as- synthesized sample.

ICP analysis revealed that Co/B ratio in the bulk composition of as- synthesized sample was 1.76 (Table1). Table1 also shows the Co content, B content, and Co/B ratio in equilibrium state for both cobalt boride and $Co(BO_2)_2$ compounds.

Table 1: ICP elemental analysis of the as-synthesized sample together with Co and B contents in equilibrium state for cobalt boride and $Co(BO_2)_2$ compounds.

Sample	Co [wt%]	B [wt%]	Co/B ratio
Co_2B	91.60	8.40	2
$Co(BO_2)_2$	40.77	7.48	1
As synthesized	78.60*	8.20*	1.76

Fig.2(a) and (b) are the typical TEM and FESEM micrograph of the amorphous Co- B powder, respectively, from which it can be found that the sample contains nano- particles with mean particle size of 50 nm.

Fig. 3 shows DSC analysis for as-synthesized sample. It is noted that no distinguished glass transition was identified on this curve. The curve has an endothermic peak around 600 K and three distinct exothermic peaks at 490, 744, and 810 K. It is revealed that the crystallization of the Co- B amorphous alloys included two steps. The first small exothermic peak at 490 K was indicative of a rearrangement of the Co-B amorphous alloy structure [14].

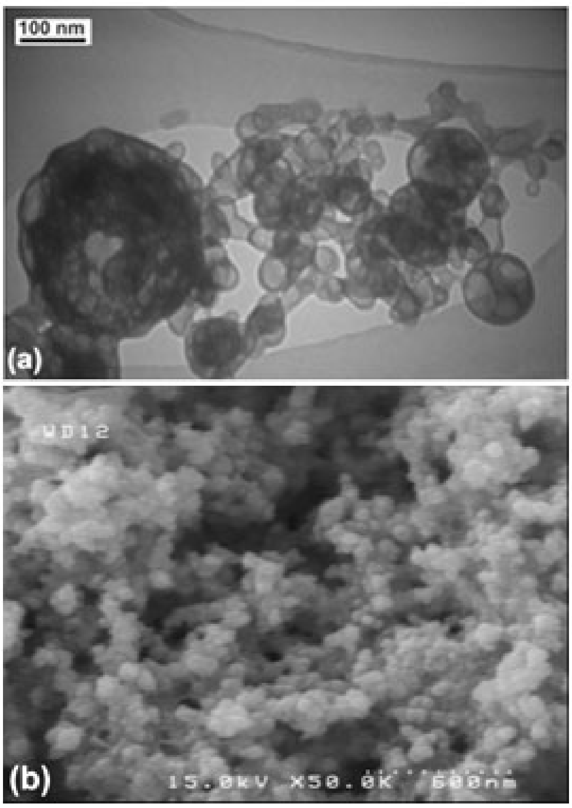

Fig.2. (a) TEM micrograph and (b) FESEM micrograph of as-synthesized sample.

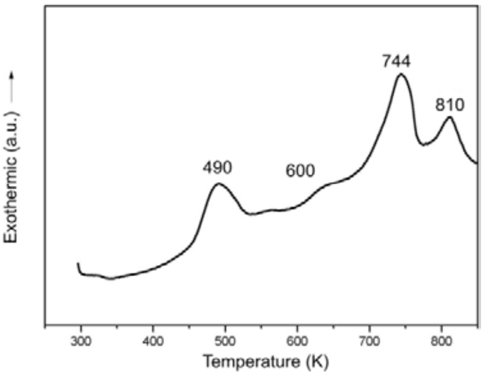

Fig.3. Continuous heating DSC plot of the amorphous Co-B powder with 10 K/min heating rate.

The second exothermic peak, around 744 K, was also related to the occurrence of the crystallization of the Co- B amorphous alloy. This crystallization behavior is already reported by Li [15] and Hernando [16]. The endothermic peak around 600 K, can be attributed to the loss of crystallization water from $Co(BO_2)_2.xH_2O$ compound [17]. The third exothermic peak around 810 K could be attributed to a solid-state reaction between cobalt boride and $Co(BO_2)_2$ to form cobalt. These results might be confirmed by means of XRD observations.

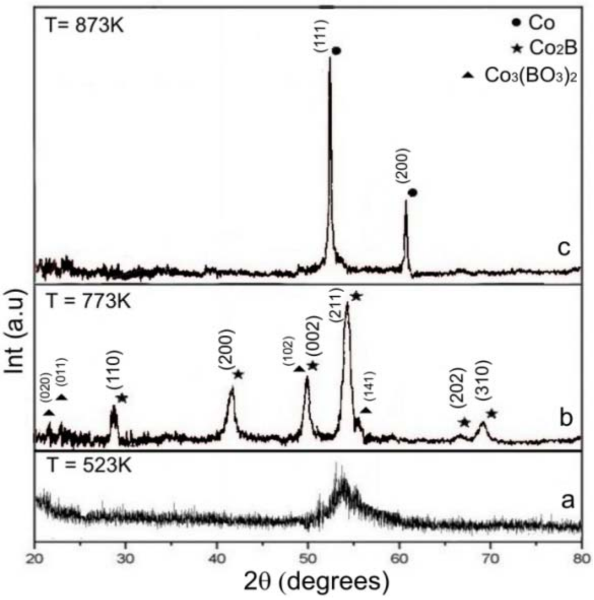

Fig.4. XRD patterns of heat treated samples at (a) 523 K, (b) 773 K, and (c) 873 K for 1 h in argon flow.

Fig.4 presents the XRD patterns of heat treated samples at different temperatures. Heat treatment at 523 K for 1h in argon atmosphere resulted in major alternation in sample structure and appearance of a diffraction peak corresponding to (211) plane, implying the occurrence of partial crystallization of cobalt boride (Fig.4a). Cobalt boride became more crystalline by increasing the heat treatment temperature to 773 K (Fig. 4b). The intensity of diffractive peaks was perfectly matched with theoretical data of JCPDS card no.25-0241. Hence, these two XRD patterns suffice to prove the nature of heat released in the process of exothermic at 523 and 773 K.

Fig.4.b also indicates diffraction of $Co_3(BO_3)_2$ compound (JCPDS card no.25-0102). After being heat treated at 873K (Fig.4c), metallic cobalt diffraction peaks appeared as a single phase (JCPDS card no.15-0806). This result is compatible with the DSC analysis. It seems that cobalt boride and $Co(BO_2)_2$ have a solid-state reaction at elevated temperatures, which can produce metallic cobalt and boron oxide [18];

$$2Co_2B+Co(BO_2)_2 \xrightarrow{T>773\ k} 5Co(s)+2B_2O \qquad (4)$$

During this reduction process and on the basis of the equation 5, Co(BO2)2 could be brought to existence as a sub- phase;

$$CoCl_{2(aq)}+2NaBO_{2(aq)} \rightarrow Co(BO_2)_{2(s)}+2Na^+_{(aq)} \qquad (5)$$

How much $Co(BO_2)_2$ could be produced is strongly related to the reaction progress of equation (3). Besides, the progress of equation (3) can be seriously affected by the progress of equation (2). In other words, increasing the rate of decomposition in equation (2) can shift equation (3) to the right, so more amount of $Co(BO_2)_2$ can yield. It seems that coexistence of cobalt boride and $Co(BO_2)_2$ is the key factor in the processing of metallic cobalt.

In order to produce these two phases simultaneously, it is necessary to consider kinetic limitations as dominating factors. In general, the decomposition rate of the aqueous borohydride solutions can be controlled by adjusting the pH and temperature of the solution and considering the pertinent time for preparing aqueous sodium borohydride solution [19]:

$$\log(t_{1/2}) = pH-(0.034T-1.92) \qquad (6)$$

$t_{1/2}$ is half- life of decomposition rate in minutes as a function of pH and temperature. T is in Kelvin degrees. By utilizing suitable pH, temperature and time, the equation (2) is shifted to the right side; therefore considerable amount of $NaBO_2$ has been obtained. Subsequently, the reactions 3 and 5 are directed to produce more amount of $Co(BO_2)_2$ as a sub- phase. Hence, by adjusting these reactions, metallic cobalt has been synthesized as a dominant product.

Equation (7) can justify the existence of $Co_3(BO_3)_2$ peaks in the XRD pattern of the sample heat treated at 773 K [17];

$$3Co(BO_2)_2 \rightarrow Co_3(BO_3)_2+2B_2O_3 \qquad (7)$$

In addition, water washing step can convert boron oxide to boric acid and remove it from heat treated samples. Equation (8) shows this reaction;

$$B_2O_3+3H_2O \rightarrow 2H_3B \qquad (8)$$

Accordingly, the XRD patterns prove the coexistence of cobalt boride and $Co(BO_2)_2$ during the heating process. The mean crystallite size of the heat treated powder at 873 K is calculated 37 nm, so the metallic cobalt has a structure in nano scale.

Fig. 5 is the FESEM image of heat treated sample at 873 K for 1 h in argon flow. It is conspicuous that particles have been grown and made an agglomerated structure. Due to the mutual magnetic attraction, reducing the magnetic energy, and growth at the high temperatures, an agglomerated morphology is formed.

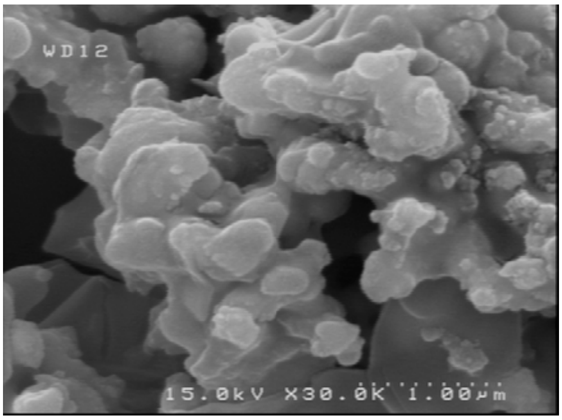

Fig.5. FESEM micrograph of heat treated sample at 873 K for 1 h in argon flow.

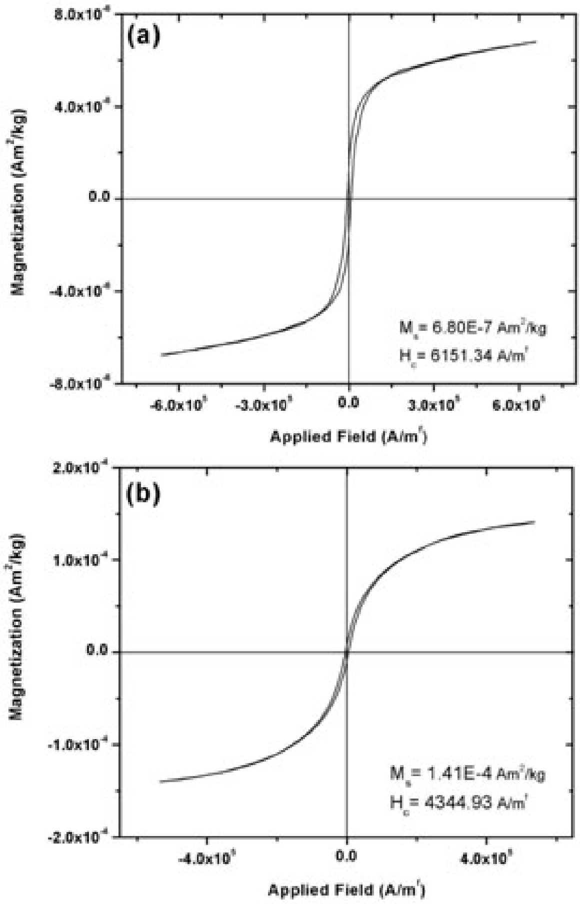

Fig.6. Magnetic hysteresis loops for (a) as-synthesized sample and (b) heat treated sample at 873 K for 1 h in argon flow.

Due to the mutual magnetic attraction, reducing the magnetic energy, and growth at the high temperatures, an agglomerated morphology is formed. Furthermore, a minuscule amount of remaining boron oxide can be another reason for the formation of morphology. The melting point for boron oxide is around 480°C [20], and so it can be effective for agglomerating particles. This oxide probably has a negligible amount (<5%) and an amorphous structure, so there is no peak of it in XRD diffraction patterns.

The hysteresis loops for as-synthesized and heat treated samples at 873 K for 1 h in argon flow are shown in Fig. 6a and b, respectively. While the coercivity decreased from 6151.34 (77.3) to 4344.93 (54.6 Oe) A/mf after heat treatment, the saturation magnetization increased sharply from 6.8×10-7 (0.5) to 1.41×10-4 (112.3 emu/g) Am2/kg. Saturation magnetization boosting is mainly related to the formation of metallic cobalt as a ferromagnetic phase and as a result increases in the long range order.

4. Conclusion

The results reported herein provide a facile and potentially general procedure for processing of nano-structured metallic cobalt with desirable magnetic properties. The results showed that single phase nano-crystalline Co(s) phase with a mean crystallite size of 30 nm was obtained through the heat treatment of as-synthesized sample at 873K for 1 hour. Magnetic properties of the heat treated samples have been improved significantly due to the formation of cobalt ferro-magnetic phase. This research divulges the bona fide potential of borohydride reduction for producing nano-structured metallic particles with desired properties.

Acknowledgment

The financial support of this work by Research Council of University of Tehran (Grant number: 8107004/NP/01 is gratefully acknowledged.

References

[1] D.V. Talapin, E.V. Shevchenko, H. Weller, G. Schmid, Nanoparticles: From Theory to Application, first ed., Wiley, Weinheim, 2004.

[2] C. Petit, S. Rusponi, H. Brune, J. Appl. Phys. 95 (2004) 4251–4260.

[3] I.W. Park, M. Yoon, Y.M. Kim, J. Magn. Magn. Mater. 272- 276 (2004) 1413–1414.

[4] V. F. Puntes, K. M. Krishnan, A.P. Alivisatos, Science. 291(2001) 2115–2117.

[5] C.B. Murray, S.Sun, W. Gaschler, IBM J. Res. Dev. 45 (2001) 47–56.

[6] X.L. Dong, C.J. Choi, B.K. Kim, Scripta Mater. 47 (2002) 857–861.

[7] S. Sun, C.B. Murray, J. Appl. Phys. 85 (1999) 4325–4330.

[8] C. Luna, M. P. Morales, C. J. Serna, M. Vazquea, Mater.Sci.Engi.C.23 (2003) 1129–1132.

[10]G.N. Glavee, K. J. Klabunde, C. M. Sorensen, G.C. Hadjipanayis, Languir. 9 (1993) 162–169.

[11]B. H. Liu, Z. P. Li, S. Suda, J. Alloys Compd. 468 (2009) 493–498.

[12] J.Shen, Z.Li, Q. Yen, Y. Chen, J. Phys. Chem. 97 (1993) 8504–8511.

[13] B.D.Cullity, S.R. Stock, Elements of X- Ray Diffraction, third ed., Addison- Wesley, Menlo Park, 2001.

[14] L. Yiping, G. C. Hadjipanayis, C.M. Sorensen, J. Magn. Magn.Mater.79 (1989) 321–326.

[15] H. Li, Y. Wu, H. Luo, M. Wang, Y. Xu, J. Catal. 214 (2003) 15–25.

[16] A. Hernando, A. Gonzalez, C. Ballesteros, A. Zern, D. Fiorani, F. Lucari, Nanostruct. Mater. 11 (1999) 783–788.

[17] G.N. Glavee, K.J. Klabunde, C.M. Sorensen. G.C. Hadjapanyis, Languir. 8 (1992) 771–773.

[18] A. K. Srivastava, S. Madhavi, R.V. Ramanujan, Phys. Status. Solidi A 207(2010) 963–966.

[19] A. Pozio, M. De Francesco, G. Monteleone, R. Oronzio, S. Galli, C. D’ Angelo, M. Marrucci, Int. J. Hydrogen Energy. 33 (2008) 51–56.

[20] P.Patnaik,Handbook of Inorganic Chemical Compounds, first ed., McGraw- Hill, NewYork, 2002.