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Solid State Communications 133 (2005) 681-685

solid state communications

www.elsevier.com/locate/ssc

Effect of carbon addition on synthesis of BN nanolayers encapsulating Fe fine particles and BN nanotubes

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Received 23 February 2004; received in revised form 1 October 2004; accepted 21 December 2004 by C.E.T. Gonçalves da Silva Available online 11 January 2005

Abstract

Boron nitride (BN) nanolayers encapsulating iron (Fe) fine particles and BN nanotubes were synthesized by annealing mixture powders of hematite, boron and carbon (C) at 1473 K for 2 h in a nitrogen atmosphere. The particles exhibited good soft magnetic properties. The thickness of BN nanolayers increased in the range of 10–100 nm with increasing C content in the mixture powders, which results in providing improvement of oxidation resistance of the particles. In the BN layers, no C was detected. BN nanotubes with diameters of ~ 100 nm were also synthesized, and they had cup-stacked and bamboo-like structures.

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PACS: 75.50; 68.55

Keywords: A. Metals; B. Chemical synthesis; C. Scanning and transmission electron microscopy

1. Introduction

Magnetic nanoparticles, such as iron (Fe), cobalt (Co), and Fe-based alloys, have been paid much attention, and are expected to have various magnetic applications [1–4] for their high saturation magnetization compared to Fe oxide nanoparticles. Since metal nanoparticles are easily oxidized in air, several kinds of inorganic nanolayers encapsulating them have been studied. Graphite nanolayers have been synthesized by an arc-discharge [5], modified arc-discharge [6], and electron beam irradiation [7] for the protection layers. Oxide nanolayers have also been prepared by a slight oxidation of core metals [8,9]. In addition, boron nitride

We have reported a promising method for massproduction to synthesize BN nanolayers encapsulating Fe fine particles as well as BN nanotubes (BNNTs) by using hematite (α -Fe₂O₃) and boron (B) powders as starting materials [11,12]. BN is known to exhibit good chemical stability, and its nanolayers encapsulating Fe particles have shown good oxidation resistance [12]. However, the thickness of the BN nanolayers was only a several nanometers. Thicker BN layers and control over their thickness are desired in order to enhance the resistance. The purpose of the present work is to investigate the effect of carbon addition to the starting materials on the magnetic properties, oxidation resistance and morphology of Fe fine particles with BN nanolayers.

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⁽BN) nanolayers have been prepared by arc-discharge and annealing boric acid and urea [10]. Unfortunately, these methods are not suitable to treat large quantity of nanoparticles for industrial production.

2. Experimental

 α -Fe₂O₃, B and graphite carbon (C) powders were used as starting materials, and were mixed well. Each average diameter was 0.03, 21 and 5 µm, respectively. Weight ratio of α -Fe₂O₃ to sum of B and C (denoted as B_{1-x}C_x) was 50%, that is α -Fe₂O₃: B_{1-x}C_x=1:1. The 'x' was varied in the range from 0 to 1.0. Samples were prepared by annealing the mixtures at 1473 K for 2 h in nitrogen atmosphere.

Magnetic properties were measured by a vibrating sample magnetometer (VSM) under a magnetic field of 1.6 kA/m. In order to examine oxidation resistance, the samples were exposed to atmosphere of 393 K with a humidity of 100% for 12 h, followed by measuring changes of saturation magnetization before and after the exposure. An X-ray diffractometer (Rigaku RINT-2500) was used to detect metallurgical phases under an applied power of 50 kV and 250 mA with a Cu K_{α} irradiation. Microstructures of the samples were observed by high-resolution transmission electron microscopy (HRTEM) with an acceleration voltage of 200–300 kV. An energy dispersive X-ray analysis (EDX) and an electron energy loss spectroscopy (EELS) equipped with the HRTEM were also employed to analyze chemical composition of the samples.

3. Results

Table 1 shows the magnetic properties of samples (S1– S7). Saturation magnetization (Ms) increases from 44.7 to 97.9 A m²/kg with increasing 'x', which is equivalent to 21– 45% of bulk Fe magnetization [13]. Coercivity (Hc) shows no dependence on 'x', and is in the range of 1.5-2.2 kA/m. All samples in Table 1 exhibited superior soft magnetic properties to Fe nanoparticles with C nanocoatings that have a Hc of around 20 kA/m in the previous works [14,15].

In order to investigate oxidation resistance of the samples, changes in Ms before and after an exposure test was measured. The changes were normalized by Ms before the test and expressed as percentage, and Fig. 1 shows the changes as a function of 'x'. When the carbon content increases, the change of magnetization can be as small as -10% for x=0.5 and 0.6 (sample S5 and S6). This indicates

Table 1 Magnetic properties of samples



Fig. 1. Magnetization change of samples S1–S7 exposed at 393 K for 12 h with a humidity of 100%.

that an addition of C improved oxidation resistance of Fe fine particles possible because C addition facilitates synthesis of the BN nanolayers and complete encapsulation of the Fe particles.

Metallurgical phases of the samples were detected macroscopically by an X-ray diffraction measurement. Fig. 2 shows their X-ray diffraction patterns in the range from 52 to 58° in 2 θ . The intensity of peaks assigned to hexagonal BN (h-BN) or rhombohedral BN (r-BN) decreases, while that assigned to graphite C becomes stronger with increasing 'x'. Peaks assigned to Fe–B compounds, such as Fe₂B and FeB, are detected in the S6 and S7 (x=0.6 and 0.8). The compounds are considered as intermediates under a synthesis of BN nanocoatings [11]. After the exposure test, peaks assigned to α -Fe₂O₃ and Fe₃O₄ appeared in the sample S1 and S3–S7.

The morphology of S1 and S2 has been studied in the previous work, and BN or C nanolayers encapsulating Fe fine particles were produced [12]. The morphologies of S3, S5 and S7 were observed by HRTEM in this study. From the investigation of oxidation resistance, the sample S5 was selected for detailed structure analysis, and Fig. 3(a) shows a typical nanoparticle observed in the S5. The particle has core-shell structure. The core has a diameter of ~ 100 nm

No	x (B _{1-x} C _x)	(wt%)			Ms	Hc	Reference
		Fe ₂ O ₃	В	С	(A m ² /kg)	(KA/m)	
S1	0.0	50	50	0	47.3	1.5	[11]
S2	1.0	50	0	50	100.0	1.6	[11]
S3	0.2	50	40	10	51.5	1.5	This work
S4	0.4	50	30	20	59.7	2.0	This work
S5	0.5	50	25	25	66.0	1.9	This work
S6	0.6	50	20	30	69.6	2.2	This work
S7	0.8	50	10	40	77.1	1.8	This work



Fig. 2. X-ray diffraction patterns of samples S1–S7 (x=0-1.0).

and is composed of Fe by EDX analysis. The shell is a nanocoating with ~20 nm in thickness, where lattice fringes correspond to the {002} plane of h-BN (Fig. 3(b)). An EELS spectrum focused on the nanocoating is shown in Fig. 3(c). Spectrum assigned to B and N can be detected, but there is no sign of C. Spectrum indexed as π^* and σ^* in a B–K edge are similar to ones obtained from sp²-hybridized BN [16], suggesting that the nanocoatings are h-BN. The observation of ~100 particles proved that diameters of Fe



Fig. 3. TEM image of a Fe particle with BN nanocoating (a), magnified image of the BN nanocoatings (b), and EELS spectrum obtained from the nanocoating (c).

particles and thickness of BN nanocoatings were in the range of 50–500 nm and of 10–100 nm, respectively. Similar morphology to Fig. 3(a) and (b) was observed in the sample S3 and S7 as well. Half-value widths of the peak assigned to Fe(110) in the X-ray diffraction patterns showed

that there is no dependence of the particle size with the C content, *x*. It is noted that all nanocoatings were composed of only BN, and that no trace amount of C was detected in them although C was used as a starting material.

Besides the BN nanocoatings, two kinds of BN nanotubes with diameters of ~ 100 nm and lengths of several micrometers were observed as shown in Fig. 4(a) and (d). Fig. 4(a) shows a so called cup-stacked structure [17], and a HRTEM image in Fig. 4(b) reveals that lattice fringes of BN layers are inclined by 13° from nanotube axis. An EELS spectrum focused on the BN layers in Fig. 4(b) is shown in Fig 4(c). The spectrum can be assigned to a B-K and N-K edge, suggesting that the nanotube consists of h-BN without C. Intensity of a π^* peak is stronger than that of a σ^* peak, which suggests that lattice fringes of ~0.3 nm spacing in Fig. 4(b) can be indexed as {002} plane of h-BN. Another type of nanotubes in Fig. 4(d) could be classified as a bamboo-like structure [18]. Lattice fringes in Fig. 4(d) are almost parallel to the nanotube wall as shown in Fig. 4(e). An EELS spectrum is almost the same as that of the cupstacked nanotube (Fig. 4(f)), suggesting that this nanotube is also composed of h-BN without C.

4. Discussion

BN nanocoatings in the present work have thickness in the range of 10-100 nm, which results in improvement of oxidation resistance of Fe fine particles as shown in Fig. 1. Those synthesized from only Fe₂O₃ and B in the previous work showed thickness of less than $\sim 10 \text{ nm}$ [11]. Thicker coatings could be attributed to enhancement of the growth of BN layers by addition of C, by the mechanism proposed below.

Yeadon and the coworkers have reported that BN nanocages were formed by nitridation of Fe–B nanoparticles [19]. Since Fe–B compounds were generated as intermediates of the reaction process in the present work, they are considered as precursor for the growth of the BN nanocoatings. In the present work, the thicker BN nanocoatings are probably synthesized not only from the Fe–B precursor but also from the reaction proposed as follows:

$$2Fe_2O_3 + 3B + 3C \rightarrow 3Fe + FeB + B_2O_3 + 3CO\uparrow$$
(1)

$$B_2O_3 + 3CO + N_2 \rightarrow 2BN + 3CO_2\uparrow$$
(2)

The formulas suppose that carbon monoxide (CO) is generated besides boron oxide (B_2O_3) through a reduction of Fe₂O₃, forming Fe–B compounds (formula (1)). CO reduces B₂O₃ under N₂ atmosphere, resulting in formation of BN at high temperatures (formula (2)). C reacts with neither B nor N in the formulas, as it was found in the present experiment that C was not contained in either BN nanolayers or nanotubes. Appearance of Fe–B compounds (Fe₂B, FeB) as shown in Fig. 2 would reveal that BN nanolayers formed through the formula (2) encapsulated Fe–B precursors before nitridation of them, and as a result, the BN nanocoatings prevented them from reacting with N₂ atmosphere.



Fig. 4. TEM images of BN nanotubes analyzed by EELS; (a,d) low magnification images and (b,e) enlarged HREM images of white arrow area in (a) and (d). (c,f) EELS spectra obtained from BN layers in (b) and (e).

The bamboo-like BNNTs as shown in Fig. 4(d) have been synthesized by nitridation of Fe-B nanoparticles with N_2/NH_3 mixture [20], by annealing a mixture of iron oxide and B in flowing NH₃ gas [21], and by annealing a h-BN powder under a nitrogen atmosphere [18]. Though metal catalysts were needed for growth of these BNNTs, BNNTs in the present work would grow without the catalysts because they have no nanoparticle at the tip. As straight BNNTs have been synthesized from B2O3 and C (nanotubes) flowing in N₂ gas [22], BNNTs in the present work would also grow through a reduction of B_2O_3 following the formula (2) as well as the BN nanocoatings. Although the reason for the formation of two kinds of BNNTs in Fig. 4 is under consideration, it is clear that addition of C to the mixture of Fe₂O₃ and B is effective in synthesis of BNNTs with the cup-stacked or bamboo-like structures.

5. Conclusion

Annealing mixtures of α -Fe₂O₃ and B with C powders at 1473 K in a nitrogen atmosphere resulted in the growth of BN nanocoatings, with 10–100 nm in thickness, encapsulating Fe fine particles with diameters of 50–500 nm. In addition, BN nanotubes with cup-stacked or bamboo-like structures with 100 nm in diameter and several microns in length were synthesized without metal nanoparticles by addition of C. The addition of C contributed to the synthesis of thick BN nanocoatings with good oxidation resistance of Fe fine particles and excellent soft magnetic properties.

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