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Effects of catalytic metals for synthesis of BN fullerene nanomaterials

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Abstract

Boron nitride (BN) fullerene nanomaterials were synthesized by an arc-melting method from Al/B, TiB_2, VB_2, Ga/B, YB_6, YB_6/Ni, NbB_2 powder in N_2/Ar mixture gas, and various structures were confirmed by high-resolution electron microscopy. From comparing of formation enthalpy with nitrogen and boron, tendency of catalysis metal for BN nanotube was characterized, which is a useful guideline for synthesis of BN fullerene nanomaterials.

Keywords: BN; Nanoparticles; Nanotubes; High-resolution electron microscopy

1. Introduction

Carbon nanocage structures, such as fullerene clusters, nanotube, nanocapsules, nanopolyhedra, cones, cubes and onions, have great potential for studying nanomaterials of low dimensions in an isolated environment [1–6]. Recently, boron nitride (BN) nanotubes and nanocapsules have also been synthesized by an arc-discharge method using boride-based rods such as HfB_2 and ZrB_2 [7,8]. The properties of BN fullerene nanomaterials would be better than those of carbon fullerene nanomaterials, from the viewpoint of wide band gap and heating resistance in air [5,9–11]. However, it is difficult to produce the BN fullerene nanomaterials with the ordinary arc-discharge method because of the difficulty in the control of arc conditions.

Recently, BN nanocapsules, nanocages and nanotubes have been produced successfully by an arc-melting method from boron and metal powder compacts in a nitrogen/argon gas atmosphere [5,11–14]. These nanomaterials are expected as gas storage materials, single-electron transistors and magnetic refrigeration. However, the yield for BN fullerene nanomaterials by this method is very small. Therefore, it is necessary to investigate catalytic element and to develop new process such as chemical reaction [15–20].

The purpose of the present work was to investigate effects of catalytic metals for synthesis of BN fullerene nanomaterials. It would be a useful guideline for synthesis of BN fullerene nanomaterials, such as nanocapsule, nanocage and nanotube. To investigate effects of catalytic metals, MgB_2, Al/B, TiB_2, VB_2, Ga/B, YB_6, YB_6/Ni, NbB_2 powders are used as starting materials for arc-melting in a nitrogen/argon gas atmosphere. Since these compounds and mixture powders have good conductivity, easier arc-melting is expected. Especially, boride compounds have good conductivity as well as metal, though only boron powder is difficult to start arc-discharge. Then, since niobium (Nb) and yttrium (Y) easily react to nitrogen than boron, these metals would enhance the reaction of boron and nitrogen. In addition, Y and Y/Ni metal had been reported to show excellent catalytic properties for producing single-walled carbon nanotubes [21]. To confirm the formation of BN fullerene nanomaterials, high-resolution electron microscopy (HREM) and electron dispersive X-ray spectroscopy were carried out. These studies will give us useful guideline for the selection of catalysis metal of BN fullerene nanomaterials.

2. Experimental

The MgB_2 powder (2.0 g, 99%) was set on a copper mold in an electric-arc furnace, which was evacuated down to 1.0×10^{-3} Pa. After introducing a mixed gas of Ar (0.025 MPa) and N_2 (0.025 MPa), arc-melting

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Table 1
Produced BN fullerene nanomaterials

Material	Structure	Encapsulated nanoparticle	Size (nm)	Number of BN layers
MgB_2	Non BN fullerene materials	–	–	–
Al/B	Nanocapsules	AlB_{10}	30–100	5–15
TiB_2	Nanocapsules	TiN	5–30	2–10
	Nanocages	–	20–50	5–10
VB_2	Nanocapsules	VN	10–50	5–10
Ga/B	Nanocages	–	50–250	5–10
YB_6	A large of nanotubes	–	Length: 4–6 μm, width: 20–50 nm	2–15
YB_6/Ni	Vary large of nanotubes	–	Length: 4–6 μm, width: 20–50 nm	2–15
	Bundled nanotubes	–	Length: 4–6 μm, width: 100–200 nm	–
NbB_2	A few of nanotubes	–	Length: 80–120 nm, width: 12–150 nm	5–15

was applied to the samples at an accelerating voltage of 200 V and an arc current of 125 A for 60 s. Arc-melting was performed with a vacuum arc-melting furnace (NEV-AD03, Nissin Engineering Co., Ltd). Similarly, arc-melting was carried out for Al (0.6 g, 99%) with boron (2.4 g, 99%), TiB_2 (4.0 g, 99%), VB_2 (4.0 g, 99%), Ga (4.0 g, 99.99%) with boron (4.0 g, 99%), YB_6 (4.0 g, 99.6%), YB_6 (2.0 g, 99.6%) with Ni (0.8 g, 99.9%) and NbB_2 (4.0 g, 99%) powder. Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with a 300 kV electron microscope (JEM-3000F). To confirm the formation of BN fullerene nanomaterials, EDS analysis was performed by the EDAX system.

3. Results

For BN fullerene materials produced in the present works, relationships between structures and catalytic metals are summarized in Table 1.

A low magnification and a HREM image of BN nanocapsules produced from Al/B powder are shown in Fig. 1a and b, respectively. In Fig. 1a, some nanoparticles with amorphous boron are confirmed. The size of the nanoparticles is 30–100 nm. In addition, some nanoparticles with BN layers were observed, as shown in Fig. 1b. The nanoparticle size and number of BN layers are approximately 100 nm and 10 layers, respectively. The lattice fringe of included nanoparticle is {1 1 3} of AlB_{10}.

A low magnification and a HREM image of BN nanocages produced from Ga/B powder are shown in Fig. 1c and d, respectively. The size of BN nanocages and number of the BN layer are approximately 50–250 nm and 5 layers, respectively.

A low magnification and a HREM image of BN nanotubes produced from YB_6/Ni powder are shown in Fig. 1e and f, respectively. The length and width of BN nanotubes is 4–6 μm and 20–50 nm, respectively. In Fig. 1e, bundled BN nanotubes are indicated by arrows. The width of bundled BN nanotubes is approximately 100–200 nm.

4. Discussion

Catalytic metals for BN fullerene nanomaterials, which were confirmed by experiments on arc-method, are summarized in Fig. 2 as periodic table. In the present works, Nb and Y works as a good catalytic element to produce BN nanotubes. As well as, it has been reported that Zr, Hf, Ta, W and La can be good catalytic metal for synthesis of BN nanotube [5,7,8,11,14,22–25]. On the other hand, other metals could not form BN nanotubes, although BN nanocapsules or nanocages were formed. The relationship between catalytic metals and structures of BN fullerene materials would be summarized by formation enthalpy with nitrogen and boron.

About some metals, formation enthalpies with boron ($H^{for}B$) and nitrogen ($H^{for}N$) are indicated in Fig. 3a and b, respectively. The data were from theoretical calculations [26]. Difference of formation enthalpy ($H^{for}N-H^{for}B$) is also shown in Fig. 3c. The difference of formation enthalpy ($H^{for}N-H^{for}B$) is very important for the formation of BN fullerene nanomaterials. Because, reactivity with nitrogen and boron is decided by this enthalpy. Basically, BN nanotubes are formed when rare earth metals are used as catalytic metals, such as Y, Zr, Nb, Hf, Ta, W and La. These elements have minus enthalpy, as shown in Fig. 3c. It means that catalytic elements for synthesis of BN nanotubes should be selected from those with minus formation enthalpy ($H^{for}N-H^{for}B$). From the guideline, Sc element could be a good catalytic element to form BN nanotubes.

In the case of YB_6/Ni powder, the Y and Ni worked as good catalytic elements to produce bundled BN

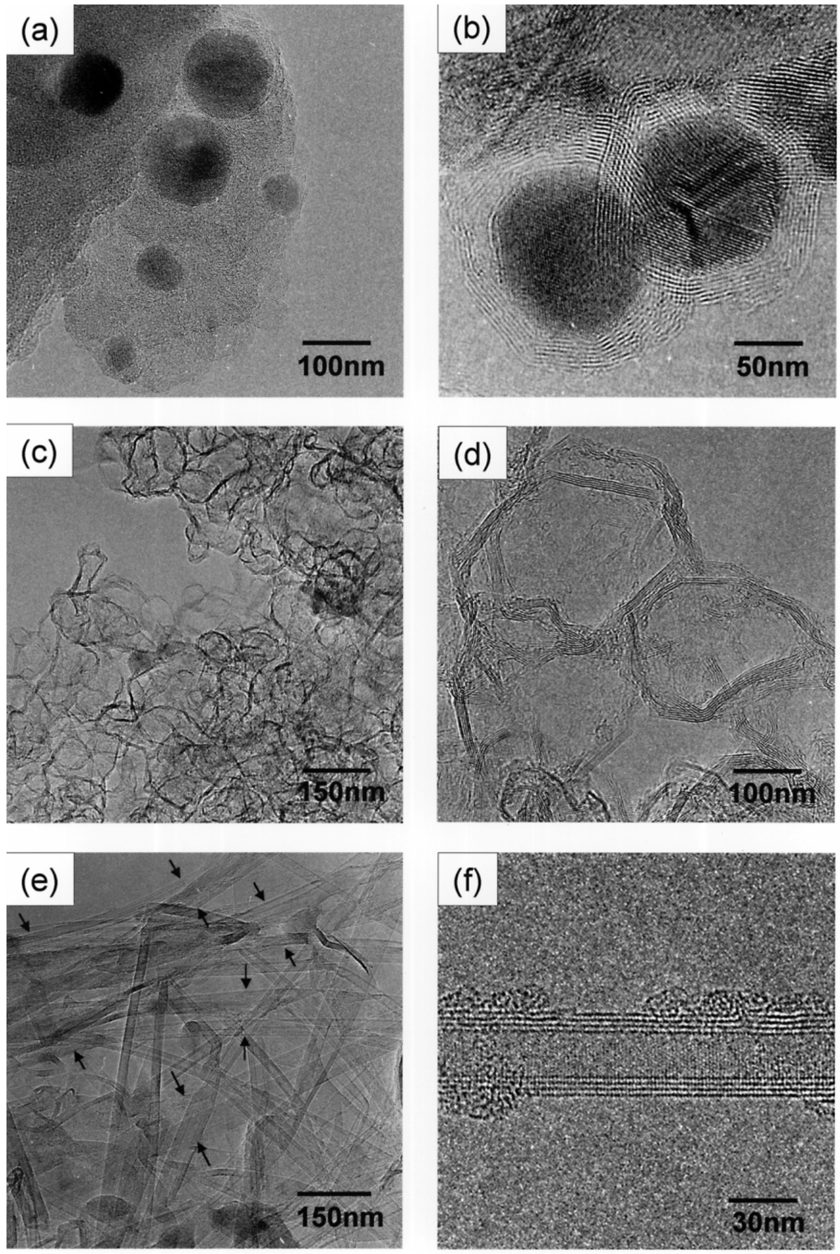

Fig. 1. (a) Low magnification and (b) HREM images of BN nanocapsules produced from Al/B powder; (c) Low magnification and (d) HREM images of BN nanocages produced from Ga/B powder; (e) Low magnification and (f) HREM images of BN nanotubes produced from YB_6/Ni powder.

nanotubes. From the results of only YB_6 powder, Y atoms would work as core element to produce BN nanotubes, and Ni atoms would have a role for combination of each BN nanotubes. Therefore, existence of Ni atoms would have an effect on formation of bundled BN nanotubes, and the Ni atoms might exist among BN nanotubes. Further studies will be needed for the role of Ni atoms in bundled BN nanotubes and the effects for synthesis as catalysis.

5. Conclusion

BN fullerene nanomaterials were produced by arc-melting of Al/B, TiB_2, VB_2, Ga/B, YB_6, YB_6/Ni, NbB_2 powder in N_2/Ar mixture gas, which was confirmed by HREM and EDS. Nb and Y atoms worked as catalytic elements to produce BN nanotubes in the present work. The present work indicates that catalysis metals for BN nanotubes are characterized by formation

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	× Mg											● Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	○●☆ Ti	● V	Cr	Mn	● Fe	● Co	● Ni	○● Cu	Zn	○ Ga	● Ge	As	Se	Br	Kr
5	Rb	Sr	☆ Y	☆ Zr	●☆ Nb	Mo	Tc	Ru	Rh	● Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La ∼Lu	☆ Hf	☆ Ta	☆ W	Re	Os	Ir	Pt	● Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac ∼Lr	Rf	Db	Sg	Bh	Hs	Mt									

○●☆ La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Fig. 2. Catalysis metals for BN fullerene nanomaterials confirmed by experiments on arc-method (×, non BN fullerene nanomaterials; ●, BN nanocapsule; ○, BN nanocage; ☆, BN nanotube).

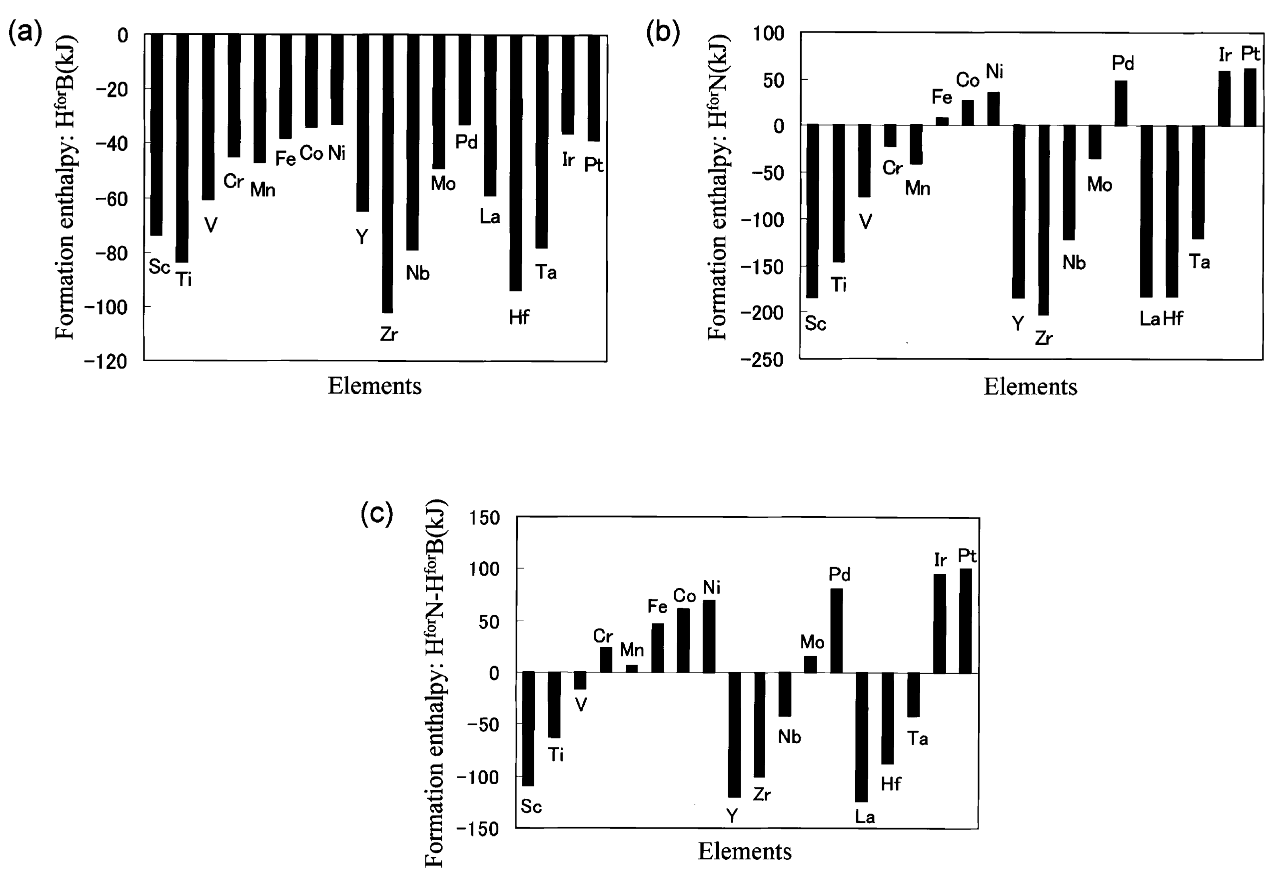

Fig. 3. (a) Formation enthalpy with boron (H^{for}B) and (b) nitrogen (H^{for}N); (c) Difference of formation enthalpy (H^{for}N − H^{for}B).

enthalpy with nitrogen and boron. It is a useful guideline for BN nanotube synthesis, and Sc element could be a good catalytic element to form BN nanotubes by arc-melting method.

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