Synthesis of cobalt boride nanoparticle in triple DC thermal plasma jet system

J. H. Oh[1], M. Kim[1], Y. H. Lee[1], S. H. Hong[1], T. H. Kim[2*], and S. Choi[1,2,*]

[1]*Department of Nuclear and Energy Enginerring, Jeju National University, Jeju, Republic of Korea*
[2]*Institute for Nuclear Science and Technology, Jeju National University, Jeju, Republic of Korea*

Abstract: The cobalt boride nanoparticles were synthesized in triple DC thermal plasma jet system. The mixed powder of cobalt and boron was used as starting material. The effect of plasma forming gas composition and quenching rate was investigated on view of crystal phase and morphology. The major crystal phase of synthesized powder was CoB with Co_2B phases in minor. The size distribution of cobalt boride was varied in accordance with quenching rate by plasma forming gas.

Keywords: Cobalt boride, nanoparticles, synthesis, triple DC thermal plasma

1. Introduction

During the past two decades the risk and reality of environmental degradation have become more apparent due to increasing consumption of fossil fuel and growth of economy and industry. In case of fossil fuel, it has caused global warming by carbon dioxide, so renewable promotion of clean energy is essentially required [1,2].

Among the various renewable energy resources such as hydrogen, solar, wind and bioenergy, particularly, hydrogen energy is promising power source to solve energy and pollution problem. However, it has not become viable because of low efficiency towards hydrogen production. In addition, when it generates hydrogen evolution, the expensive platinum-based alloys are used at the electrode for the hydrogen evolution reaction (HER) [3].

Noble catalysts (e.g. Ru, Pt, Rh, etc.) have high catalytic performance and stability. But, their cost is too expensive and deposites is very limited. Therefore, extensive research is advenced towards replacing those with abundant material in the earth. Transition materal such as Ni, Cu, and Co have the potential to be low cost and efficient substitute. In particular, the cobalt boride displays better catalytic activity for hydrolysis or electrolysis, beacause boron protect the active cobalt metal from oxidizing by playing the role of enhances catalytic activity of cobalt by electron transfer from boron to cobalt [4].

The catalytic system using nano-sized promising metal might improve the efficiency and cost problem due to the high surface and volume of nanomaterial. Therefor, we synthesized cobalt boride nanoparticles from vapor phase of cobalt and boron evaporated from the soild startimg materials in triple DC thermal plasma jet system. In order to understand synthesis process and chracteristic of synthesized powder such as the morphology and size distribution, we carried out plasma process in accordance with change of plasma forming gas composition and quenching gas rate.

2. Experiment setup

The cobalt boride nanoparticles were synthesized by triple DC thermal plasma jet system. The schematic of triple DC thermal plasma jet system is indicated in Fig. 1. The system consists of DC power supply, plasma torch, water pump, and powder feeder for injection of the starting material. The water cooled reactor chamber was separated from R-1 to R-7. For generating plasma flame, the mixed gas, which was composed of Ar and H_2, was used for plasma forming gas.

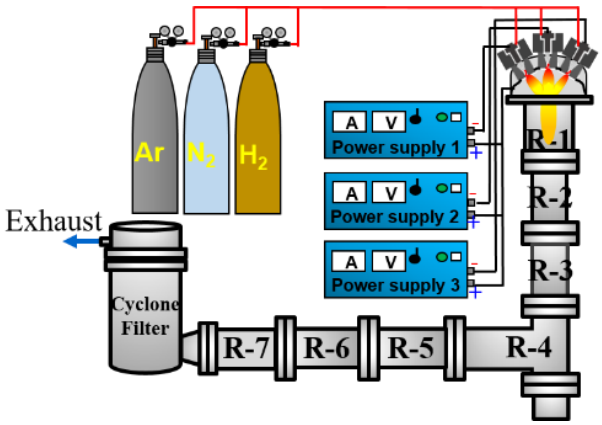

Fig. 1. Schematic for the synthesis of cobalt boride nanoparticles by triple DC thermal plasma jet system.

Table 1. Experiment condition for the synthesis of cobalt boride nanoparticles by DC thermal plasma jet system.

Exp. No.	1	2	3	4
Molar ratio of starting material	Co:B=1:3			
Plasma forming gas	14 L/min Ar 14 L/min N_2	14 L/min Ar 14 L/min H_2	11 L/min Ar 11 L/min H_2	8 L/min Ar 8 L/min H_2
Plasma in put power	27 ~ 28 kW		23.6 kW	21 kW
Powder feed rate	0.5 g/min			
Carrier gas	5 L/min Ar			

Table 1 shows the summarized operating condition. The cobalt and boron were mixed at 1 to 3 molar ratio, and it was injected into the plasma flame with the carrier gas of Ar 5 L/min through the injection tube between three torches. The condition of molar ratio for starting

materialwas referred to previous research results [5]. The crystallinity of synthesized powder was observed by X-ray diffraction (XDR, DMAX 2200, Rigaku Co., Akishima, Japan). The morphology and particles size were observed by field emission transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Japan).

3. Result and discussion

3.1 The effect of plasma forming gas composition

Fig. 2 shows XRD graph for synthesized powder according to collected position in Exp. 1 condition. In oerder to analyz morphology and characteristic of synthesized powder with collected position, XRD graphs for Reactor-1 and -6 were expressed in Fig. 2 The cobalt peak was only observed at $2\theta = 44.26^{\circ}$, 51.52°, and 75.92° in the Reactor-1. It was described that the cobalt powder as starting material was incompletely vaporized because it was condensed as rapid as possible observed, whereas Co_2B were identified with weak intensity in Reactor-1 and -6.

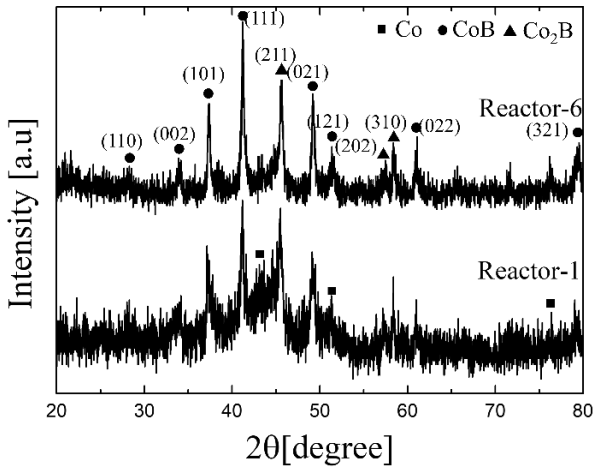

Fig. 2. XRD graph of synthesized powder in Exp. 1 condition according to collected position.

The FE-TEM and HR-TEM image of the synthesized nanoparticles in Exp 1 condition are shown in Fig. 3. Fig. 3(a) and (b) are image for powder collected from Reactor-1 and Fig. 3(c) and (d) image are for powder collected from Reacor-6. In the Fig. 3(a), particles size of synthesized powder is smaller than those of Fig. 3(c). It was analyzed that powder synthesized in Reactor-1 was rapidly condensed, because the quenching rate of vaporized starting material was relatively higher than other position. In the HR-TEM images of Fig. 3(b) and (d), the lattice fringes were indicated as CoB(2.4 Å, 2.1 Å). The layers were identified as hexagonal boron nitride (3.4 Å) at Fig. 3(b). As a result, the CoB phase composition was higher than Co_2B, h-BN were additionally synthesized by the dissociated nitrogen reacted with vaporized boron. The intensity of cobalt boride peak increased at the backside reactor. The cobalt boride nanoparticles was synthesized by using Ar-H_2 as plasma forming gas in Exp. 2. This condition was performed at the equal flow of plasma forming gas with former condition. Fig. 4 shows XRD graph of synthesized powder with collected position in Exp. 2. In the Fig. 4, the intensity of CoB and Co_2B peak in the whole reactors was higher than those of Fig. 2. Moreover, the peak of starting material could not be observed in the Fig. 4. The intensity of cobalt boride peak increased at the backside reactor.

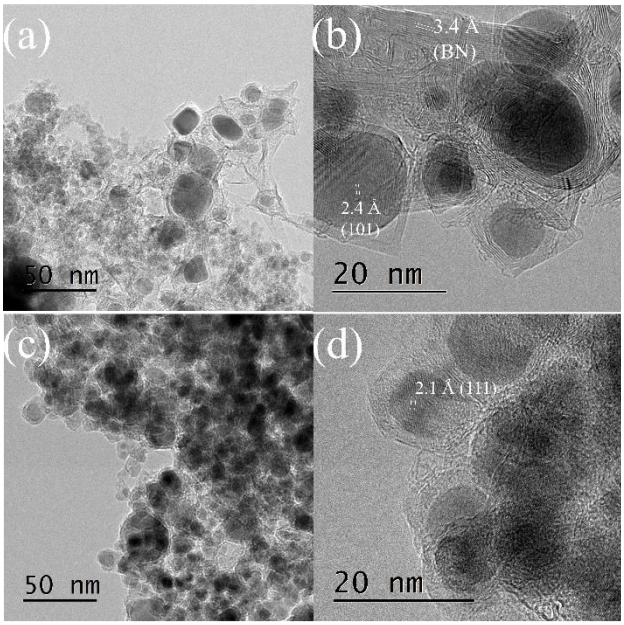

Fig. 3. FE-TEM images of synthesized powder in Exp. 1 condition according to collected position; (a), (b) collected in Reactor-1, (c),(d) collected in Reactor-6.

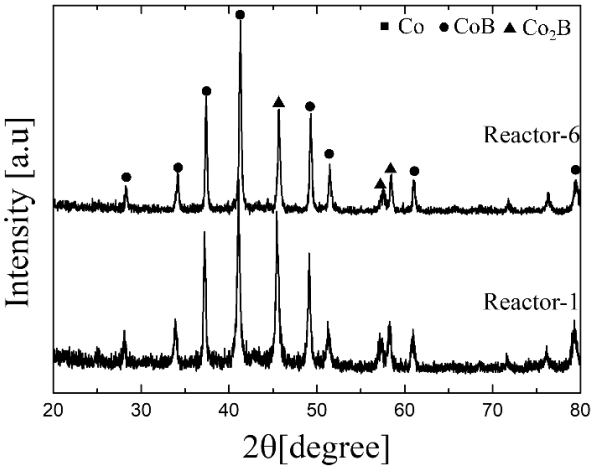

Fig. 4. XRD graph of synthesized powder in Exp. 2 condition according to collected position.

The cobalt boride nanoparticles was synthesized by using Ar-H_2 as plasma forming gas in Exp. 2. This condition was performed at the equal flow of plasma forming gas with former condition. Fig. 4 shows XRD graph of synthesized powder with collected position in Exp. 2. In the Fig. 4, the intensity of CoB and Co_2B peak in the whole reactors was higher than those of Fig. 2. Moreover,

the peak of starting material could not be observed in the Fig. 4. The intensity of cobalt boride peak increased at the backside reactor.

Fig. 5 shows FE-TEM and HR-TEM image of the synthesized nanoparticles in Exp. 2 condition. Fig. 5(a) and (b) are image for powder collected from Reactor-1 and Fig. 5(c) and (d) image are for powder collected from Reacor-6. In the Fig. 5(a) and (c), particles size of synthesized powder was larger than those of Exp. 1 condition and the morphology of synthesized powder is spherical. It was proved that vaporized starting materials in Exp. 2 had long residence time during passing plasma flame due to relatively slow quenching rate. In the HR-TEM images of Fig. 5(b) and (d), the lattice fringes were indicated as CoB(2.4 Å).

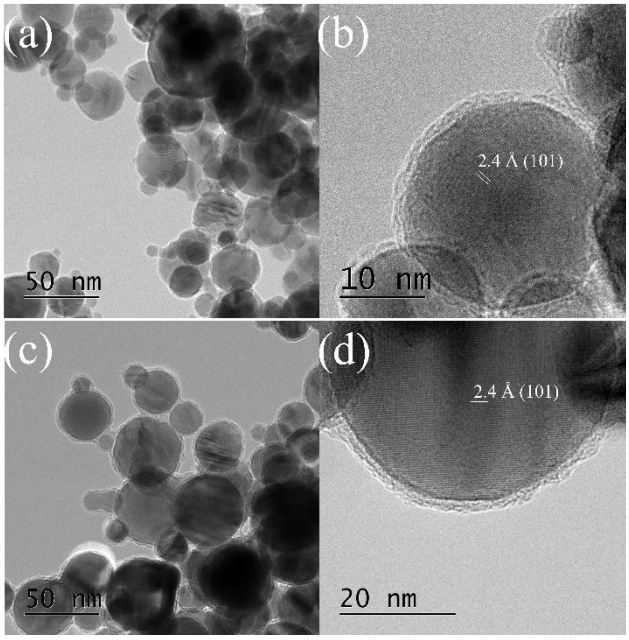

Fig. 5. FE-TEM images of synthesized powder in Exp. 2 condition according to collected position; (a), (b) collected in Reactor-1, (c), (d) collected in Reactor-6.

3.2 The effect of quenching rate

In order to identify effect of quenching rate for synthesized powder characteristic, total flow rate of plasma forming gas (Ar-H_2) was controlled from 22 to 14 L/min. Fig. 6 shows XRD pattern graph is for synthesized powder with collected Reactor-6 in Exp. 3 and 4. It was observed that the main crystal phase was CoB with Co_2B phases in minor. In addition, crystal phase of injected starting material could not be identified in the XRD patterns. Although the input power of plasma was lower than Exp. 2, starting material was completely evaporated in Exp. 3 and 4 condition.

FE-TEM and HR-TEM image of synthesized powder with collected from Reactor-6 in Exp. 3 and 4 condition were indicated in Fig. 7. In the Fig. 7, particle size of powder were was widely distributed and morphology of those had spherical shape. The morphology of synthesized powder in the Exp.3 condition has spherical. It was revealed that the evaporated starting material had residence time in the thermal plasma jet generated from Exp 3 and 4, so particle size of synthesized powder was larger than those in previous experiment due to relatively slow quenching rate.

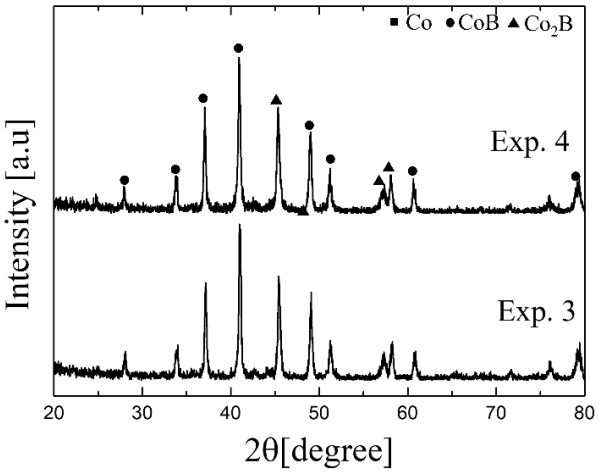

Fig. 6. XRD pattern image of synthesized powder with collected Reactor-6 in Exp. 3 and 4 condition.

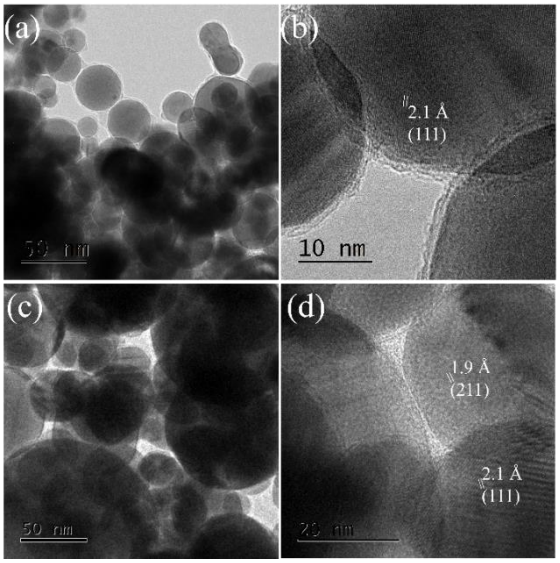

Fig. 7. FE-TEM images of synthesized powder with collected Reactor-6; (a), (b) synthesized in Exp. 3 condition, (c), (d) synthesized in Exp. 4 condition.

4. Conclusion

The cobalt boride nanoparticles were synthesized by triple DC thermal plasma jet system. The nanocomposite, which was formed with cobalt boride and h-BN, was syntheiszed in the Exp. 1 codition. Their mophology was cobalt boride nanoparticles wrapped with h-BN shell layer. In Exp.2 codition, on the other hand, only cobalt boride nanopaticle was synthesized. Their particle size was larger than the synthesized cobalt boride nanocomposite in Exp. 1 condition. In the whole conditions, cobalt boride

nanoparitlces were observed from FE-TEM images and XRD patterns. The crystal peak of CoB was mainly investigated, whereas Co_2B were indentified with weak in tensity in the XRD pattern. The particle size of synthesized cobalt boride was increased as decreasing of the flow rate of plasma forming gas with power reduction, because vaporized starting material could have long residence time in the plasma flame. As a result, characteristics of synthesized cobalt boride nanoparticle were analyzed in accordance with the effect of plasma forming gas composition and quenching rate. The h-BN was additionally synthesized as composite texture using N_2 as plasma forming gas. The particles size of synthesized powder increased in accordance with decreasing flow rate of plasma forming gas.

5. References

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