Synthesis of AlB$_{12}$ and YB$_{66}$ Nanoparticles by RF Thermal Plasmas

Sooseok Choi, Jiro Matsuo and Takayuki Watanabe
Dept. Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259-G1-22, Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan
E-mail: watanabe@chemenv.titech.ac.jp

Abstract. Boron-rich compounds of AlB$_{12}$ and YB$_{66}$ nanoparticles were synthesized in radio frequency (RF) thermal plasmas. Yttrium tetraboride or aluminium powders with 10 μm in diameter and boron powder with 45 μm in diameter were evaporated in the high temperature region of the thermal plasma, and then metal boride nanoparticles were formed in the tail region of the plasma with rapid quenching. Boron-rich compounds were identified by X-ray diffractometry in the product. Polyhedral shaped nanoparticles about 20 nm in size were measured in Al-B system by transmission electron microscopy, while YB$_{66}$ particles about 50 nm in size were cubic in morphology. The composition of raw powder and the input power of RF thermal plasma were controlled to enhance the content of boron-rich metal borides in as-prepared nanoparticles. Since boron has very high melting point and evaporation temperature, high boron content in the raw powder and high input plasma power were preferable to synthesize AlB$_{12}$ and YB$_{66}$ nanoparticles.

1. Introduction
Boron-rich metal borides composed of polyhedral boron subunits and metal atoms have excellent material properties of high melting point, hardness, corrosion resistance, thermionic electron emission, and neutron absorption ability with low density [1]. Since they have various applications including mechanical tools, chemical catalysts, electronic devices and nuclear materials, typical production methods such as chemical vapour deposition and a long-time solid reaction in high temperature have been introduced [2, 3]. Although boride nanoparticles are strongly required in many applications due to advantages of nanoparticles in optical, chemical, mechanical, electromagnetic characteristics, they are difficult to be obtained from solution which is typically used for the preparation of nanoparticles. In this work, boron-rich compounds of AlB$_{12}$ and YB$_{66}$ were prepared by radio frequency (RF) induction thermal plasmas. The RF thermal plasma is receiving much attention to synthesize nanoparticles, because it has sufficiently high temperature for the evaporation of any kinds of precursor and rapid quenching rate for nucleation and condensation [4]. In order to increase the content of boron-rich compounds in final products, effects of boron composition ratio in raw feeding powders and the input power of RF thermal plasma on the synthesis of AlB$_{12}$ and YB$_{66}$ were examined in the present work.

2. Experimental setup
Experimental setup and operating conditions are presented in figure 1 and table 1, respectively. Raw materials composed of boron (size: 45 μm, purity: 99%, Kojundo Chemical Laboratory Co. Ltd.)
powder and aluminum (size: 10 μm, purity: 99%, Kojundo Chemical Laboratory Co. Ltd.) or yttrium tetraboride (size: 10 μm, purity: 99%, Japan New Metals Co. Ltd.) powder are injected into the RF thermal plasma by a powder feeder. The composition ratio of metal to boron was 1:2, 1:12, and 1:15 for Al-B system, while it was controlled at 1:12, 1:40, 1:66, and 1:100 for Y-B system. The feed rate of raw material was fixed at 100 mg/min. The RF thermal plasma was operated at atmospheric pressure and the input power was controlled from 24 kW to 33 kW. Argon was used for the carrier gas of the raw powder, and argon and helium were used for plasma supporting gases. Evaporated boron and metal were nucleated and condensed in the RF thermal plasma producing nanoparticles that were found on a water cooling inner chamber and a filter. Collected particles were analyzed by transmission electron microscopy (TEM, JEM-2010F, JEOL Ltd.) and X-ray diffractometry (XRD, Miniflex, Rigaku Corp.).

Figure 1. Experimental setup for the synthesis of boron-rich metal boride nanoparticles.

Table 1. Experimental conditions.

| Parameter                              | Conditions                                      |
|----------------------------------------|-------------------------------------------------|
| Raw powder size                        | Al and YB₄ = 10 μm, B = 45 μm                   |
| Metal to boron ratio (R)               | Al:B = 1:2, 1:12, 1:15                         |
|                                       | Y:B = 1:12, 1:40, 1:66, 1:100                   |
| Powder feed rate                       | 100 mg/min                                      |
| Operating pressure                     | 101.3 kPa                                       |
| Radio frequency                        | 4 MHz                                           |
| Input power (P)                        | 24, 27, 30, 33 kW                               |
| Sheath Gas                             | Ar 60 L/min and He 5 L/min                      |
| Inner Gas                              | He 5 L/min                                      |
| Powder Carrier Gas                     | Ar 3 L/min                                      |
3. Results and discussion

TEM images of synthesized nanoparticles in Al-B and Y-B systems are presented in figures 2 and 3, respectively. These images were obtained at the highest boron composition ratio in the raw powder among used conditions in the present work at the fixed input plasma power of 30 kW. In a RF thermal plasma process for the synthesis of nanoparticles, spherical shaped products are typically produced. In the present work, however, polyhedral nanoparticles which were about 20 nm in average diameter were synthesized in the case of Al-B system as seen in figure 2. Such polyhedral morphology seems to be caused by the structure of icosahedral \(B_{12}\) and \(B_{20}\) units which compose \(\text{AlB}_{12}\) [5]. In figure 3, rectangular shaped nanoparticles about 50 nm in the length of each side were found in the product when \(\text{YB}_4\) and B powders were used as raw materials. The cubic shape is unique morphology for \(\text{YB}_{66}\) nanoparticles [6]. Therefore, successful synthesis of boron-rich metal borides nanoparticles of \(\text{AlB}_{12}\) and \(\text{YB}_{66}\) were confirmed from the observation of TEM images.

![Figure 2. TEM image of nanoparticles prepared by the RF thermal plasma in Al-B system at operating conditions of 1:15 for Al to B ratio in the raw powder and 30 kW for the input plasma power.](image2)

![Figure 3. TEM image of nanoparticles prepared by the RF thermal plasma in Y-B system at operating conditions of 1:100 for Y to B ratio in the raw powder and 30 kW for the input plasma power.](image3)

In order to increase the quantity of boron-rich compound in the product, the composition ratio of boron in the raw powder and the input plasma power were changed. Figures 4 and 5 present XRD data for the final product from the RF thermal plasma treatment of Al and B raw powders. First, the intensity of \(\text{AlB}_{12}\) is increased with increasing boron composition ratio in the raw powder as seen in figure 4. The nucleation temperature of boron is higher than that of aluminum according to the synthesis mechanism of metal borides based on the homogeneous nucleation model [7, 8]. As a result, boride nanoparticles are produced from the condensation of boron and aluminum monomers on boron nuclei. Therefore, enough quantity of boron nuclei and monomers should be secured by increasing the composition ratio of boron in the raw powder for the synthesis of boron-rich metal boride nanoparticles. In addition, the peak for \(\text{AlB}_{10}\) is also produced together with \(\text{AlB}_{12}\) as shown in figure 4, because both \(\text{AlB}_{12}\) and \(\text{AlB}_{10}\) nanoparticles are composed of icosahedral \(B_{12}\) units. Therefore, boron clustering from boron nuclei and monomers takes place at first, followed by chemical reactions between boron clusters and Al monomers in the high temperature environment of RF thermal plasma forming \(\text{AlB}_{12}\) and \(\text{AlB}_{10}\) nanoparticles.
In the synthesis of boride nanoparticles in the RF thermal plasma, boron vapour should be reach at the saturation vapour pressure for nucleation. Since boron has very high melting point and evaporation temperature of 2 349 K and 4 200 K, respectively, high temperature and enthalpy of the RF thermal plasma are required to produce large amount of boron nuclei and monomers. Therefore, the content of AlB$_{12}$ in the product is increased with increasing the input plasma power as shown in figure 5.

Experimental results on the synthesis of YB$_{66}$ from evaporated YB$_4$ and B powders are presented in figures 6 and 7. The composition ratio of boron in the raw powder was controlled at the fixed input plasma power of 30 kW. As shown in figure 6, peak intensity for YB$_{66}$ is increased with increasing the

---

**Figure 4.** XRD data for products in Al-B system in different composition ratio of aluminium to boron in raw material at the fixed input power of 30 kW: (a) 1:5, (b) 1:12, and (c) 1:15.

**Figure 5.** XRD data for products in Al-B system in different input plasma power at the fixed raw material composition of Al:B = 1:15: (a) 24 kW, (b) 27 kW, (c) 30 kW, and (d) 33 kW.
composition ratio of boron in the raw material. Although YB$_{66}$-related peaks at 22° and 25° for 2-theta values are appeared in the lowest boron contents in the raw material as shown in figure 6 (a), these two peaks also correspond to YB$_{4}$. In addition, XRD pattern only for YB$_{66}$ was very weak to be detected in figure 6 (a). Therefore, high boron content in the raw material is essentially required for the synthesis of YB$_{66}$ nanoparticles in the RF thermal plasma. However, the peak intensity of YB$_{66}$ is still weak compared with that of YB$_{4}$ even in the highest boron composition ratio in the raw material as depicted in figure 6 (d). In order to synthesize YB$_{66}$ nanoparticles in the RF thermal plasma, large amount of boron nuclei and monomers are required because YB$_{66}$ is composed of 13-icosahedron unit of $(B_{12})_{12}B_{12}$ which is called supericosahedron [9].

![Figure 6](image6.png)  
**Figure 6.** XRD data for products in Y-B system in different composition ratio of yttrium to boron in raw material at the fixed input plasma power of 30 kW: (a) 1:12, (b) 1:40, (c) 1:66, and (d) 1:100.

![Figure 7](image7.png)  
**Figure 7.** YB$_{66}$ particle ratio in synthesized nanoparticles evaluated by TEM images according to boron composition ratio in raw material.
Since YB$_{66}$ has unique cubic morphology, TEM images for nanoparticles produced in Y-B system were analyzed to evaluate the ratio of YB$_{66}$ nanoparticles in the final product. From the analysis of 200 particles for each condition, the ratio of rectangular nanoparticle in TEM images is presented in figure 7. The number of YB$_{66}$ nanoparticle is increased with increasing the composition ratio of boron in the raw material, and this result is in a good agreement with XRD results in figure 6.

4. Conclusion
Boron-rich metal boride nanoparticles of AlB$_{12}$ and YB$_{66}$ were successfully synthesized from the vapour phase of raw powders in the RF thermal plasma. Boron nuclei and monomers form boron clusters, and they react with metal monomers in the high temperature environment of the RF thermal plasma producing boron-rich metal boride nanoparticles. Since AlB$_{12}$ is composed of icosahedral B$_{12}$ and B$_{20}$ units, polyhedral nanoparticles is observed in the TEM image of final products synthesized from Al and B raw powders. Whereas cubic YB$_{66}$ nanoparticles is found when YB$_{4}$ and B powders is used as the raw material. Because boron clusters are required to form boron-rich compound, the content of boride nanoparticles in final products is increased with increasing the composition ratio of boron in the raw material. In addition, boron-rich compound is more easily synthesized in the condition of high input plasma power due to high melting point and evaporation temperature of boron.

References
[1] Albert B and Hillebrecht H 2009 Angew. Chem.Int. Ed. 48 8640
[2] Wang G, Brewer J R, Chan J Y, Diercks D R and Cheung C L 2009 J Phys. Chem. C 113 10446
[3] Liu Y, Lu W J, Qin J N and Zhang D 2007 J Alloys Compd. 431 337
[4] Kruis F E, Fissan H and Peled A 1998 J Aerosol Sci. 29 511
[5] Higashi I 2000 J Solid State Chem. 154 168
[6] Huang J Y, ishigaki T, Tanaka T and Horiuchi S 1998 J Mater. Sci. 33 4141
[7] Girshick S L, Chiu C P and McMurry P H 1990 Aerosol Sci. Technol. 13 456
[8] Cheng Y, Shigeta M, Choi S and Watanabe T 2012 Chem. Eng. J 183 483
[9] Richards S M and Kasper J S 1969 Acta Cryst. B25 237