

RF thermal plasma synthesis of core-shell structured metal boride nanoparticle

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Abstract: Core-shell structured titanium boride nanoparticles were synthesized by the radio frequency thermal plasma. The composition of the shell was controlled through the variety of boron content in feeding powders. The thickness of the shell was about 1.5 nm. The shell included titanium in boron poor condition, while it composed of boron in boron rich condition due to the excess of boron on supercooled liquid state.

Keywords: RF thermal plasma, titanium boride nanoparticle, core-shell structure.

1. Introduction

Radio frequency (RF) thermal plasma has been applied for the production of high-quality and high-performance materials. It has unique advantages such as large volume of high temperature, high enthalpy to enhanced reaction kinetics, high chemical reactivity, and selective oxidation or reduction atmosphere. These advantages of RF thermal plasma can be utilized to vaporize a large amount of raw materials, followed by the formation of nanoparticles in the tail of plasma flame with a rapid quenching rate up to $10^6 \text{ K}\cdot\text{s}^{-1}$ [1]. Therefore, the RF thermal plasma is considered as an innovative tool that transforms raw materials into functional nanoparticles [1- 6].

Titanium boride is an advanced ceramic material with special properties of high melting points, hardness, electric conductivity, catalyst activity, and great thermal stability. Therefore, titanium boride nanoparticles are widely applied for crucibles, electrode materials, protective coatings, armor materials, cutting tools, electromagnetic shielding, wear-resistant coatings, and solar control windows [7, 8]. Core-shell structured titanium boride can be defined as the core of titanium boride with the shell of titanium or boron. The synthesis of titanium boride nanoparticle with high-purity is difficult by conventional methods due to the high melting and boiling points of raw materials. Moreover, few studies have been carried out for the fabrication of core-shell structured titanium boride nanoparticle.

Core-shell nanoparticles have received significant attention recently, because these nanoparticles can be used in a wide range of applications, including material science, electronics, biomedical, pharmaceutical, optics and catalysis. Core-shell nanoparticles with improved properties are highly functional materials compared with single phase nanoparticles. Generally the constituent composition and the ratio of the core radius to the shell thickness play an important role in properties of core-shell nanoparticles. The advantages of the shell coating on the core particle include surface modification, improving the

functionality, stability, dispersibility, and so on [9].

In this work, the synthesis of core-shell structured titanium boride nanoparticles by RF thermal plasma is investigated. The properties of titanium boride core can be improved by the shell, such as thermal and chemical stabilities. The shell results from the large temperature gap between melting points of boron and titanium. In addition, the high quenching rate of plasma plays an important role in the synthesis of core-shell structured titanium boride nanoparticle. The composition of the shell is controlled by the boron content in feeding powders.

2. Experiment

2.1 Experimental apparatus

A schematic diagram of experimental set-up for the production of titanium boride nanoparticles is shown in **Fig. 1**. The set-up mainly consists of a powder feeder for raw materials, a plasma torch, a reaction chamber, and a particle collection filter. The plasma torch works with a water-cooled quartz tube and an induction coil which is operated at the frequency of 4 MHz. in the experiment,

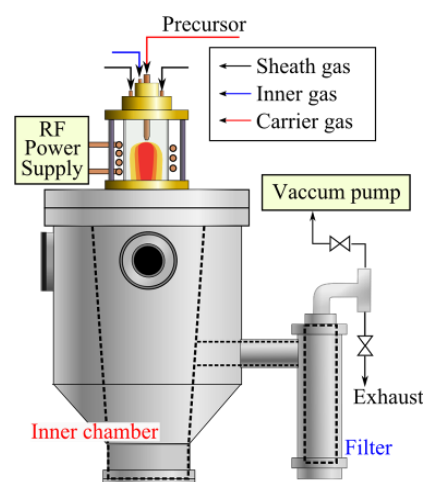


Fig.1 Schematic diagram of RF thermal plasma for the synthesis of boride nanoparticle.

RF thermal plasma system was operated at the atmosphere pressure.

2.2 Experimental conditions

Feeding powders were metal titanium (Wako Pure Chemical Industries Ltd., particle size 45 μm , purity 98%) and crystalline boron (Kojundo Chemical Laboratory Co. Ltd., particle size 45 μm , purity 99%). After the injection of precursors into the plasma from the central nozzle, they are instantaneously evaporated due to the high enthalpy of thermal plasma. The vapors of injected titanium and boron are transported with the plasma flow to the reaction chamber and become supersaturated due to the rapid temperature decrease in the tail of plasma flame, which leads to the homogeneous nucleation. Subsequently, titanium and boron vapors are co-condensed on the surface of nucleated particles. As a result, nanoparticles of titanium borides are synthesized from the gas phase.

Table 1 summarizes operating conditions. Argon was introduced as carrier gas and inner plasma supporting gas at fixed flow rates of 3 L/min and 5 L/min, respectively. Mixture of argon and helium was used as the sheath gas, which was injected from the outer slots to protect the inner surface of the quartz tube and stabilize the plasma discharge. The powder feed rate was 0.2 g/min, and boron molar content in feeding powders was controlled from 33.3% to 83.3%.

2.3 Analysis methods

The phase composition of prepared nanoparticles was determined by X-ray diffractometry (XRD, Mac Science MXP3TA). The morphology of the particles was observed from transmission electron microscopy (TEM, JEM-2010, JEOL) images. Scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS, JEM-2100, JEOL) allows the identification of elements.

3. Results and Discussion

Figure 2 shows XRD spectrum of product prepared at the fixed initial composition of Ti:B = 1:5. Characteristic

peaks of TiB_2 are identified with the unreacted raw material of Ti. The dominant product is TiB_2 and boron is not observed due to the amorphous boron in the product.

Figure 3 presents TEM and STEM-EELS images of synthesized particles at fixed initial composition of Ti:B = 1:5. Fig. 3 (a) is TEM image of the as-prepared particles; (b) shows STEM image of a titanium boride-B core-shell nanoparticle; (c) and (d) are EELS maps of B and Ti, respectively. EELS measurements in the STEM are conducted to analyze chemical components of the core and shell separately. In EELS result, the color presents the

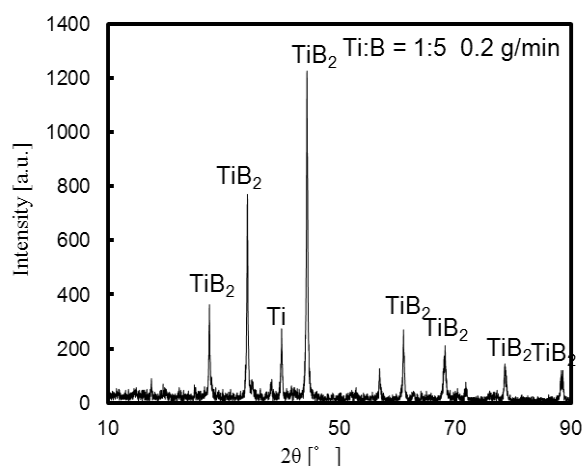


Fig.2 XRD spectrum of product at Ti:B = 1:5 with powder feed rate of 0.2 g/min.

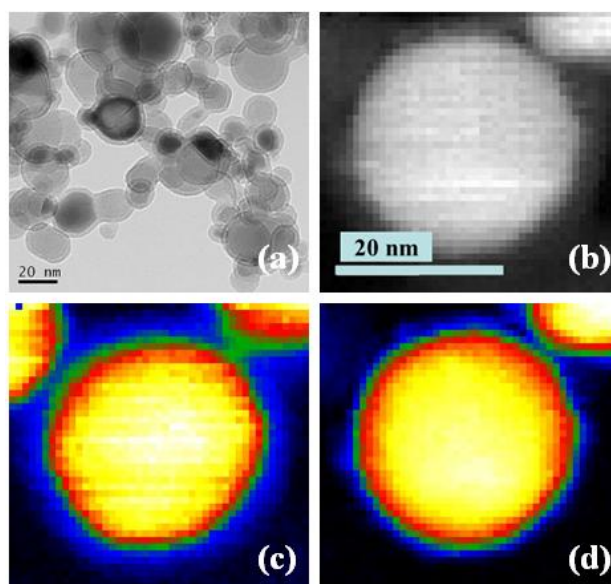


Fig.3 TEM, STEM, and EELS images of product at Ti:B = 1:5 for initial condition: (a) TEM image of as-prepared particle, (b) STEM image of a core-shell nanoparticle, and EELS maps of (c) B and (d) Ti.

Table 1. Experimental operating conditions

Process parameter	Value
Sheath gas and flow rate	Ar-He(60:5) 65 L/min
Inner gas and flow rate	Ar 5 L/min
Carrier gas and flow rate	Ar 3 L/min
Powder feed rate	0.2 g/min
Plasma power	30.0 kW
Reactor pressure	101.3 kPa
Frequency	4 MHz
Boron molar content in feeding powders	33.3 at% ~ 83.3 at %

concentration of each element. White and black displays the highest and the lowest concentrations of element, respectively. The concentration of element is changed in the order of color as follows: white > yellow > orange > red > green > blue > black. According to Fig. 3 (a), core-shell structured nanoparticles are observed in TEM image of as-prepared product and the particles are spherical shape. Based on EELS results, diameters of boron and titanium elements are 32 nm and 28.8 nm, respectively. Therefore, the thickness of boron shell is estimated to be 1.6 nm.

XRD spectrum of the product prepared at raw material composition of Ti:B = 2:1 is demonstrated in Fig. 4. Although the dominant product is TiB, unreacted Ti is also observed.

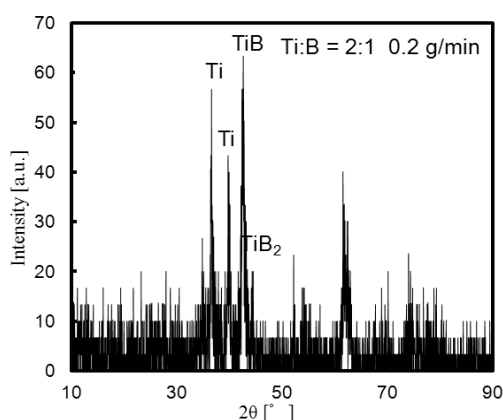


Fig.4 XRD spectrum of product at Ti:B = 2:1 with the powder feed rate of 0.2 g/min.

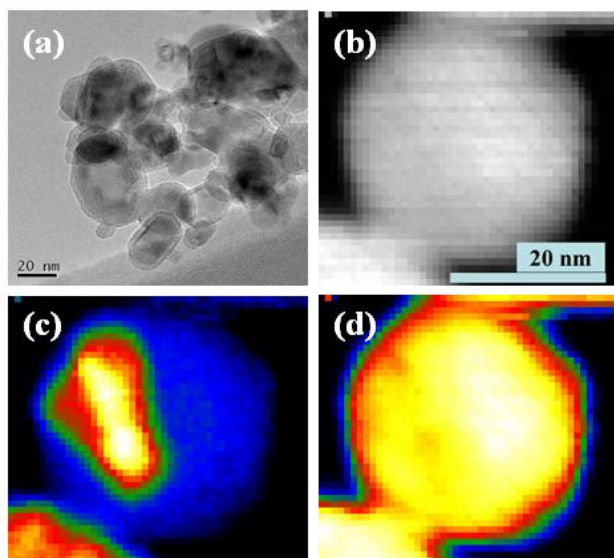


Fig.5 TEM, STEM, and EELS images of product at Ti:B = 2:1 for initial condition: (a) TEM image of as-prepared particle, (b) STEM image of a core-shell nanoparticle, and EELS maps of (c) B and (d) Ti.

Figure 5 presents TEM and STEM-EELS images of the product at Ti:B = 2:1 for initial composition and 0.2 g/min for powder feed rate. Fig. 5 (a) shows the TEM image of as-prepared nanoparticles; (b) is STEM image of a titanium boride-Ti core-shell nanoparticle; (c) and (d) are EELS maps of B and Ti, respectively. In the EELS result, the concentration of each element is changed according to the color like as Figs. 3 (c) and (d). According to Fig. 5 (a), core-shell nanoparticles are observed in TEM image of as-prepared product. On the basis of EELS results, the diameters of boron and titanium are 29.6 nm and 32.4 nm, respectively. Therefore, the thickness of Ti shell is estimated to be 1.4 nm.

The formation mechanism of core-shell structured titanium boride nanoparticle was examined with the calculation of nucleation temperature [8]. Metal or boron reaches its supersaturated state leading to the formation of nuclei with the decrease of the saturation vapor pressure of raw material along with plasma flow. At this time, corresponding values of saturation ratio and temperature at the nucleation rate of $1.0 \text{ cm}^{-3} \text{ s}^{-1}$ are defined as the critical saturation ratio and the nucleation temperature, respectively. The nucleation temperature at the critical saturation ratio is presented in Fig. 6 for constituent components of titanium boride at the boron molar content of 66.7% with different powder feed rate. The nucleation temperature was calculated by the following nucleation rate [10].

$$J = \frac{\beta_{ii} N_s^2 S}{12} \sqrt{\frac{\Theta}{2\pi}} \exp \left[\Theta - \frac{4\Theta^3}{27 n_s^2} \right] \quad (1)$$

where n_s is the equilibrium saturation monomer concentration at temperature T , the collision β_{ij} is frequency function between monomers, and S is the saturation ratio.

For Ti-B system, the formation mechanism of titanium boride nanoparticles is considered as displayed in Fig. 7. After the precursors are injected into the plasma, they instantaneously start to evaporate. The evaporated vapors are transported with the plasma flow to the reaction

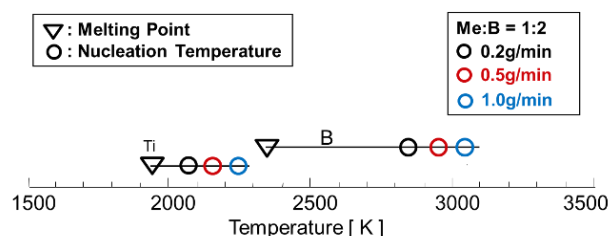


Fig.6 Nucleation temperatures at critical saturation ratios for constituent components of titanium borides at the boron molar content of 66.7% with different powder feed rates.

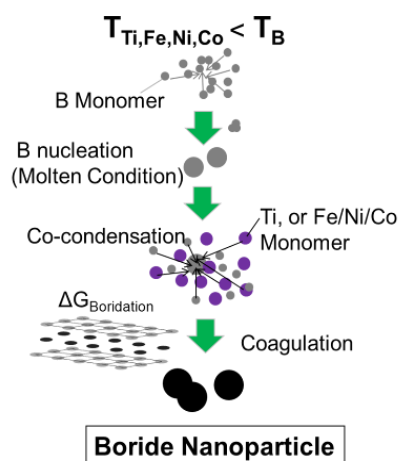


Fig.7 Formation mechanism of transition metal boride nanoparticles in RF thermal plasma.

chamber where the temperature decreases rapidly. The saturation vapor pressure of each element decreases drastically along with the temperature decrease. Therefore, the saturation vapor pressure will fall below the partial pressures of each element reaching supersaturated state. This supersaturated state consequently leads to the production of nuclei by homogeneous nucleation. At the upstream in plasma, boron vapor become supersaturated due to its higher nucleation temperature, then the nucleation process of boron occurs homogeneously only around the boron nucleation temperature. Subsequently, the heterogeneous co-condensation of titanium and boron dominantly takes place on the surface of the nucleated boron nuclei in the temperature region between the nucleation temperature and melting point of boron forming titanium boride nanoparticles. This combined mechanism makes nanoparticles grow.

In the boron poor condition as shown in Figs. 4 and 5, the large temperature gap between melting points of titanium and boron leads to excessive titanium on the molten state promoting the formation of titanium shell. During this period, titanium boride nanoparticles act as nucleation sites for titanium monomers creating metal covered boride nanoparticles.

In the boron rich condition as shown in Figs. 2 and 3, the plasma temperature is lower than the melting point of boron when the excessive boron condenses on the generated titanium boride nanoparticles. This indicates the impossible synthesis of the titanium boride-B core-shell nanoparticle, because boron on the solid state is difficult to condense on the solid of titanium boride nanoparticles. However, the shell of element boron is observed in the EELS result. The shell of boron is considered to be formed in the supercooled liquid state even at the lower plasma temperature than the melting point of boron by the high quenching rate at the tail of the RF thermal plasma [11].

Therefore, boron on supercooled liquid state exists in the temperature range from the melting point boron to the melting point of titanium. In the boron rich condition, excessive boron on the supercooled liquid state leads to the forming of the shell of boron. Titanium boride nanoparticles act as nucleation sites for excessive boron monomers creating boron covered boride nanoparticles.

4. Conclusions

RF thermal plasma was used to prepare titanium boride core-shell nanoparticles. Boron content in feeding powders is an important factor in the synthesis of core-shell nanoparticles with controlled composition of the shell. In the boron poor condition, the shell includes titanium due to the excessive titanium on liquid state in the growth region between the melting point of titanium and nucleation temperature of boron. However, the shell consists of boron in the boron rich condition due to the excessive boron on the molten state which results from the high quenching rate existing in the plasma when the plasma temperature is below the melting point of boron.

5. References

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