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Formation mechanism of titanium boride nanoparticles by RF induction thermal plasma

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ABSTRACT

The formation mechanism of titanium boride functional nanoparticles by the radio frequency induction thermal plasma was investigated by experiment and numerical analysis. The mixed powders of titanium and boron were injected into the plasma and evaporated immediately, and then nanoparticles were produced through the quenching process. The nanoparticle products were characterized by phase composition and crystalline diameter. TiB_2 was easily synthesized with a low powder feed rate in the boron-rich condition, because the molar ratio of evaporated and nucleated boron in plasma was enhanced. The prepared titanium boride nanoparticles had the average crystalline diameter ranging from 10 to 30 nm, and it was reduced with decreasing the powder feed rate and titanium content in the raw material due to abundant number of boron nuclei. This paper demonstrates the feasibility of the control of titanium boride nanoparticles' crystalline mean diameter and phase composition with different raw material condition in the RF induction thermal plasma synthesis.

1. Introduction

Radio frequency (RF) induction thermal plasma has attracted extensive attention in recent years, and it is expected to be utilized for a number of industrial applications such as plasma spraying, deposition of thin films, treatment of harmful materials, recovery of useful materials from wastes [1–3], and synthesis of high-quality and high-performance nanoparticles [4,5]. The unique advantages of RF thermal plasma including high enthalpy to enhance reaction kinetics, high chemical reactivity, and large volume with low velocity, long residence time, and oxidation or reduction atmospheres in accordance with required chemical reactions are beneficial to synthesize particles. Compared with conventional synthesis methods, the high temperature of thermal plasma makes a large amount of raw materials with high melting point evaporated completely and sufficient reaction between raw materials in gas phase reality [6]. Particularly, homogeneous nucleation and heterogeneous condensation make the formation of nanoparticle during the saturation state due to the high quenching rate (10^4–10^5 K/s) in the tail flame of the plasma [7]. Additionally, the preparation of nanoparticle with high purity is available by RF thermal plasma, because there is no internal electrode in the plasma torch [7–12].

Nanoparticles have excellent and interesting performance in hardness, ductility, electronic characteristics, optical property, and catalytic effect, which are highly enhanced compared to bulk materials. Thus, they are strongly expected to be applied in various field including electronic, biomedical, and environmental technologies. In particular, titanium boride nanoparticles have high melting point, strength, hardness, durability, wear resistance, electrical conductivity, and low work function. Therefore, titanium boride nanoparticle is very attractive from the scientific viewpoint of physics and chemistry as well as engineering including the electromagnetic shielding, wear-resistant coatings, and solar control windows interacting with IR and UV lights [12–14]. Furthermore, TiB_2 is remarkably stable materials with a unique structure, and it has more various applications than TiB. However, the synthesis of such a phase-controlled titanium boride with high-purity is very difficult by conventional methods due to the high melting points of raw materials. Even combustion process is substantially impossible to be applied on the fabrication of such nanoparticles in spite of its high temperature, because oxidation atmosphere in combustion process leads to production of contaminants of metal oxide and CO_2. Meanwhile, RF thermal plasma provides an attractive alternative to conventional methods in the nanoparticle synthesis with short reaction time in a compact reactor.

The large difference of the saturation vapor pressures of constituents makes the phase-controlled nanoparticle preparation more difficult; what is worse is that the detailed growth mechanism of those nanoparticles has not been clarified due to the

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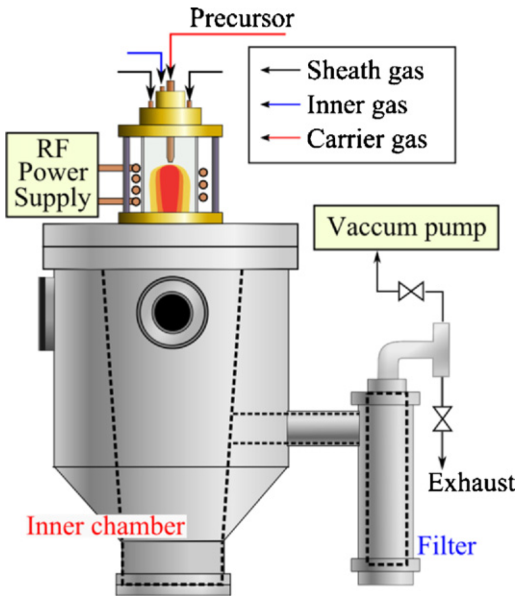

Fig. 1. The experimental setup of RF induction thermal plasma for the preparation of titanium boride nanoparticles.

complicated interaction in the system and the limitation of experimental approach. In experiments, because neither direct observation nor measurements are possible, only the characteristics of the final products can be evaluated. As mentioned, the ratio of the saturation vapor pressures is a critical factor affecting the growth process of the binary-material nanoparticles (e.g. Ti/B: 10^2) [12]. The different vapor pressures lead to different nucleation temperatures. Therefore, theoretical and numerical studies for such a system are also required to understand the formation mechanism and the effects of operating variables, as conducted in Ref. [7].

The purpose of this study is to prepare phase-controlled titanium boride nanoparticles by RF induction thermal plasma and also to clarify their formation mechanism in the term of condensational growth. The parametric studies with an experiment and numerical analysis were carried out with controlling the powder feed rate and the boron content in the feeding powders. The crystalline mean diameter and the phase composition of the final product were examined.

2. Experiment

2.1. Experimental setup

Fig. 1 shows a schematic diagram of an RF induction thermal plasma experiment set-up for the synthesis of titanium boride nanoparticles. The set-up mainly consists of an injector 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 a water-cooled induction coil (3 turns), coupling its electromagnetic energy to the plasma at a frequency of 4 MHz. In the experiment, the total system was operated at the atmosphere pressure. Raw materials were metal titanium (particle size 45 μm, purity 98%, Wako Pure Chemical Industries, Ltd.) and crystalline boron (particle size 45 μm, purity 99%, Kojundo Chemical Lab. Co., Ltd.), which were fed with the carrier gas. After the injection of precursors into the plasma from the central nozzle, they are instantaneously evaporated due to the high enthalpy of the thermal plasma. The vapors of the injected titanium and boron are transported with the plasma flow to the reaction chamber and become to be supersaturated due to the rapid temperature decrease in the tail flame, which leads to homogeneous nucleation. Subsequently, the vapors are co-condensed on the surface of the nucleated particles.

Table 1
Experimental operating conditions for the preparation of titanium boride nanoparticles.

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
Plasma power plate	30.5 kW
Reactor pressure	101.3 kPa
Frequency	4 MHz
Feed rate	0.1–1.0 g/min
Boron molar content in feeding powders	25.0–83.3 at.%

The operating conditions are summarized in Table 1. Argon was introduced as the carrier gas and the plasma supporting inner gas. Mixture of argon and helium was used as the sheath gas [15], which was injected from the outer slots to protect the inner surface of the quartz tube and stabilize the plasma discharge. The range of powder feed rate was from 0.1 to 1.0 g/min, and boron molar content in feeding powders was controlled from 25.0 to 83.3%.

The synthesized nanoparticles were characterized for phase identification by X-ray diffractometry (XRD, MXP3TA, Mac Science). The mean crystalline diameter was calculated from the full width at the half maximum (FWHM) of the most intensive diffraction according to the Debye Scherrer equation [16]. The morphology of the particles was observed from transmission electron microscopy (TEM, JEM-1010BS, JEOL Ltd.). Quantitative phase analysis by XRD was carried out based on the adiabatic method [17]. This method is used for quantitative analysis by powder diffraction in the XRD pattern and based on the ratio of the diffraction data for each phase in the product to the diffraction of standard reference materials selected. The mass fraction of X phase can be calculated by the following equation:

$$W_X = \frac{I_X}{K_A^X \sum_{X=A}^{N} I_X / K_A^X} = \frac{I_X}{K_A^X((I_A/K_A^A) + (I_B/K_A^B) + \cdots + (I_X/K_A^X) + \cdots + (I_N/K_A^N))} \quad (1)$$

here, A can be any phase selected in the product and $X(=A, B, \ldots N)$ denotes each phase in the product. I_X presents the intensity of X phase in the product from the XRD spectrum. K_A^X is the ratio of the reference intensity ratio (RIR) value of X phase to that of the reference phase A, i.e., $K_A^X = \mathrm{RIR}_X/\mathrm{RIR}_A$. In the experimental measurement, three peaks for Ti, TiB, and TiB_2 were shown in XRD data, and Ti was selected as the reference sample. Based on the powder diffraction file (PDF) cards, RIR values for Ti, TiB, and TiB_2 were determined to be 6.44, 1.72, and 4.11, respectively. Therefore, $K_{Ti}^{TiB} = \mathrm{RIR}_{TiB}/\mathrm{RIR}_{Ti}$, $K_{Ti}^{TiB_2} = \mathrm{RIR}_{\mathrm{TiB}_2}/\mathrm{RIR}_{\mathrm{Ti}}$, and $K_{Ti}^{Ti} = 1$ can be calculated. Therefore, the equation for W_X in the present work can be derived from Eq. (1) as follow;

$$W_X = \frac{I_X}{K_{\mathrm{Ti}}^X((I_{\mathrm{Ti}}/K_{\mathrm{Ti}}^{\mathrm{Ti}}) + (I_{\mathrm{TiB}}/K_{\mathrm{Ti}}^{\mathrm{TiB}}) + (I_{\mathrm{TiB}_2}/K_{\mathrm{Ti}}^{\mathrm{TiB}_2}))} \quad (2)$$

2.2. Experiment results and discussion

The TEM image of the as-prepared titanium-based boride nanoparticles is shown in Fig. 2. Particles are almost spherical shape. Fig. 3 shows the particle size distribution of as-prepared nanoparticles with the powder feed rate of 1.0 g/min at the fixed initial composition of Ti:B = 1:1. As shown in Fig. 3, the average grain size is about 15 nm.