Mechanism of Titanium Boride Nanoparticle Formation in RF Thermal Plasma Method

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Abstract: Experimental and computational studies have been conducted for boride functional nanoparticles fabrication by radio frequency induction plasmas. Titanium-based boride was selected as model of the investigation. In the thermal plasma, the mixed powders of titanium with boron were evaporated immediately and nanoparticles were produced through the cooling process. The nanoparticles were characterized based on phase composition in the product and crystalline diameter. The nanoparticles of titanium-based boride had the average crystalline diameter from 10 to 45 nm, with crystalline diameter increasing as the powder feed rate and titanium content in the feed powders were increased. The mass fraction of TiB in the product of TiB and TiB₂ had the range from 0% to 99.58%, with TiB content increasing as the powder feed rate and boron content in the feed powders were decreased. The experimental and computational results show good agreement in the crystalline diameter and the composition.

Keywords: RF thermal plasma, titanium boride nanoparticle, numerical simulation

1. Introduction

Radio frequency thermal plasmas have been used for production of high-quality materials, such as synthesis of nanoparticles. The attractive material processes with RF thermal plasmas result from attractive advantages of high enthalpy to enhance reaction kinetics, high chemical reactivity, and oxidation and reduction atmospheres in accordance with required chemical reactions. Furthermore, the residence time of treated materials is comparatively long due to the low plasma velocity. Its extremely unique thermofluid field can completely vaporize a large amount of raw materials even with high melting/boiling points. Moreover, since the tail of an RF-thermal plasma exhibits a high cooling rate (10⁴–10⁵ K/s), effective formation of nanoparticles is simultaneously achieved by nucleation and condensation in a highly supersaturated state. Additionally, an RF thermal plasma is inherently contamination-free because it is produced without any internal electrodes [1-5].

Boride nanoparticles have attracted considerable interest, due to high-performance properties, such as high melting temperature, high strength, durability, hardness, wear resistance, high electrical conductivity and low work function. Therefore, titanium boride is expected to be used for the electromagnetic shielding, wear-resistant coatings, and solar control windows with interaction with IR and UV lights [5, 6]. However, the synthesis of titanium boride with high-purity is difficult by conventional methods due to the high melting/boiling points. Even combustion process is substantially impossible to be applied to the fabrication of these functional nanoparticles in spite of its high temperature, because oxidation atmosphere in combustion process leads to production of contaminants (CO₂, H₂O). Therefore, RF thermal plasma synthesis provides an attractive alternative to conventional methods.

The titanium boride nanoparticle is of great interest from the scientific viewpoint of physics and chemistry as well as engineering, although the detailed mechanism of their collective growth remains poorly understood. This is true because it is impossible to observe every process using experimental approaches directly; only the characteristics of the final products can be evaluated.

In this paper, the effects of powder feed rate and boron content in the feed powders in the formation of titanium boride nanoparticles by an RF thermal plasma were studied. Moreover, numerical studies have also been carried out to clarify the binary growths and to predict the profiles of nanoparticles that will be synthesized. By combining our solution algorithm with the theory for binary homogeneous nucleation and heterogeneous condensation, the model which can reveal the growth behavior of...
nanoparticles in a binary system [7] is adopted with some modification.

In order to investigate the mechanism of titanium boride nanoparticle formation in an RF thermal plasma, numerical calculations are demonstrated for comparison with the present experiment results.

2. Experimental procedure

A schematic diagram of experimental set-up for the production of boride nanoparticles is shown in Fig. 1. The system consists of a plasma torch, a reaction chamber, a particle collection filter and a power supply. The plasma torch is composed of a quartz tube and an induction coil (3 turns) which are both cooled by water, coupling its electromagnetic energy to the plasma at a frequency of 4 MHz. Feed powders were metal titanium (Wako Pure Chemical Industries, Ltd., particle size: 45 µm, purity: 98%) and crystalline boron (High Purity Materials, Co. Ltd., particle size: 45 µm, purity: 99%). Precursors were fed with carrier gas. After the precursors were injected into the plasma, and were instantaneously evaporated completely due to the high enthalpy of the RF thermal plasma. The vapors of the injected titanium and boron were transported with the plasma flow to the reaction chamber and became supersaturated due to the rapid temperature decrease in the tail flame, which leads to homogeneous nucleation. Subsequently, the vapors co-condensed on the surface of nucleated particles. Nanoparticles of titanium borides were consequently synthesized from the gas phase.

Table 1 summarizes the operating conditions. Argon was introduced as carrier gas, plasma supporting gas and sheath gas. Helium was also injected as sheath gas, which was injected from the outer slots to protect the inner surface of the quartz tube. The range of powder feed rate was from 100 to 1000 mg/min. The boron molar content in feed powders was from 25% to 83.3%.

The structures of the prepared nanoparticles were determined by X-Ray Diffractometry (XRD, Mac Science MXP3TA). The size of the particles was measured from the photographs of Transmission Electron Microscopy (TEM).

3. Experimental Results

The XRD patterns of as-prepared nanoparticles at different powder feed rates are demonstrated in Fig. 2. Ti, TiB, and TiB₂ are identified from the XRD spectrum peaks of the as-prepared particles. As seen from Fig. 2, the full widths at the half maximum (FWHM) become smaller with increasing the powder feed rate. According to the Debye-Scherrer equation, the crystalline diameter becomes larger.

Effect of powder feed rate on the crystalline diameter of as-prepared nanoparticles is shown in Fig. 3. The crystalline diameter of the prepared nanoparticles increases with the powder feed rate. From a numerical simulation [1], nanoparticles are formed at earlier stage at larger feed rate, because the larger amount of vapor reaches the supersaturation state at a more upstream position, the nucleation positions shift upstream and the vapor consumption rate by condensation increases due to the larger vapor concentration with the higher powder feed rate. The temperature in upstream is high so that the nucleation rate is low which means a small number of stable nuclei are generated. The smaller number of nuclei shares a larger amount of vapor, consequently the particles can grow larger. Furthermore, since the powder feed rate increases,

![Figure 1. Schematic diagram of experimental set-up](image1)

![Figure 2. XRD patterns of prepared nanoparticles at different powder feed rates; Ti: B = 1:1.](image2)

Table 1. Experimental operating conditions

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheath gas and flow rate</td>
<td>Ar-He(45:5)</td>
</tr>
<tr>
<td>Inner gas and flow rate</td>
<td>Ar</td>
</tr>
<tr>
<td>Carrier gas and flow rate</td>
<td>Ar</td>
</tr>
<tr>
<td>Feed rate</td>
<td>100 ~ 1000 mg/min</td>
</tr>
<tr>
<td>Plasma power plate</td>
<td>30.7 kW</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>101.3 kPa</td>
</tr>
<tr>
<td>Frequency</td>
<td>4 MHz</td>
</tr>
<tr>
<td>Boron molar content in feed powders</td>
<td>25 at% ~ 83.3 at %</td>
</tr>
</tbody>
</table>
the monomer density increases which leads to the higher growth rate. Therefore, the particles have larger diameter.

Effect of powder feed rate on the prepared nanoparticles composition is displayed in Fig. 4. The mass fraction of TiB in the product of TiB and TiB₂ decreases with the increase of the powder feed rate. From a numerical simulation, the nucleation positions shift upstream at larger feed rate. TiB₂ is a thermodynamically dominant material, while TiB is a metastable material. Therefore, it is easier to produce TiB₂ at an equilibrium state. The temperature in the boron nanoparticles growth region is mainly higher than the melting point of boron. The nucleation positions shift upstream, and the time in which boron nanoparticles grow becomes longer. As a result boron nanoparticles have longer time to grow and reach the equilibrium state; the growth tendency of titanium nanoparticles is similar with that of boron nanoparticles. Therefore, in the case of larger feed rate, it is easier to generate TiB₂; on the contrary, metastable materials TiB can be obtained at lower feed rate.

The TEM graphs of the prepared titanium-based boride nanoparticles for different boron contents in the feed powders were shown in Fig. 5. The particles with different morphology and size exist. Most particles seemed spherical and the average grain size was less than 35 nm.

4. Numerical Analysis

The growth processes of titanium boride nanoparticles in thermal plasma synthesis are investigated numerically using our previous unique model [7]. Considering the free energy gradients for particle formation in a binary system, the present model simulates the collective and simultaneous combined process of binary nucleation and binary co-condensation of high temperature vapors, and coagulation among nanoparticles. The gradients of the free energy of particle formation, $W$, composed of the chemical potentials and the surface energy are evaluated for nanoparticles with each size and each composition. The nanoparticles are allowed to grow by condensation if the gradient is negative or zero:

$$\frac{\partial W}{\partial n_M} \leq 0 \quad (M = \text{Ti, B}),$$

where $n_M$ is the monomer number of material $M$ in a particle. Also, the melting point depressions due to nano-scale sizes and a mixture effect are taken into account. It is assumed that the nanoparticles having the temperature lower than their melting point cannot grow by coagulation.

Fig. 6 shows the computational result of the evolution of the particle size and composition distribution (PSCD), which describes the growth behavior of titanium boride nanoparticles. The computation was conducted under a typical cooling condition in the plasma tail [7]. The feed rate of the precursor material was set to be 1000 mg/min with the initial ratio of Ti:B = 1:1. Around 3000 K, nucleation starts and boron-rich nanoparticles are generated (Fig. 6(a)). Immediately, the vapors of boron and titanium condense on the existing nanoparticles. It is noted that the boron vapor has a higher rate of condensation than the titanium vapor (Fig. 6(b)) because the saturation pressure of boron is much lower than that of titanium. Following the consumption of boron vapor, titanium vapor is consumed with a high rate of condensation (Fig. 6(c)). In addition to such binary nucleation and
condensation processes, coagulation among those nanoparticles themselves takes place. In this way, as a computational prediction, titanium boride nanoparticles grow up and reach the final state (Fig. 6(d)). Fig. 7 presents the effect of the feed rate on the crystal volume mean diameter of TiB₂. For the initial condition of Ti:B =1:1, both of the experiment and the computation show the same tendency that the higher feed rate of the precursor material results in the larger mean diameter of TiB₂.

5. Conclusions

Experiments and numerical simulations were performed to investigate the nucleation and condensation of mixture of titanium with boron in an RF thermal plasma for the preparation of titanium-based boride nanoparticles. The study concluded that RF thermal plasmas were notably effective even for the difficult co-condensation processes with the large vapor pressure differences. The experimental parameters of powder feed rate and boron content in the feed powders played an important role in generating titanium-based boride nanoparticles. Therefore, RF thermal plasmas provide a powerful tool for the preparation of functional nanoparticles because the crystalline diameter and the composition of as-prepared nanoparticles can be controlled.

References