[Review Paper]

**Microwave Synthesis of Ti₄O₇ or AlN Nanoparticles by Rapid Carbothermal Reduction Process**

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Microwave processing was used to fabricate nanoparticles having a desired particle size and morphology by a simple method, carbothermal reduction method. By microwave processing, Ti₄O₇ nanoparticles (≈ 60 nm) maintaining the morphology of a pristine material were fabricated at 950 °C for 30 min. Since grain growth was observed in conventional processing, rapid heating (250 °C/min) and rapid cooling, which are features of the microwave processing, are also effective in maintaining the particle diameter even though this carbothermal reduction reaction proceeds in the high temperature region. In addition, we successfully synthesized spherical AlN nanoparticles with high nitridation rate, maintaining the morphology of pristine material by microwave processing. It is considered that the crystal structure of transition alumina (which is advantageous for formation of intermediate AlON but phase transition over 1200 °C) was maintained over 1300 °C by microwave rapid heating. In addition, by optimizing the nitrogen flow rate, spherical AlN nanoparticles having a nitridation ratio of 0.88 could be fabricated at 1200 °C for 180 min and a nitrogen flow rate of 0.2 L/min.

**Keywords**
Microwave processing, Reduced titanium oxide, Aluminum nitride, Nanoparticle, Carbothermal reduction process

1. Introduction

In solid phase processing, microwaves are beginning to be applied for sintering and synthesis of ceramics1−7, heating and sintering of metal powders8−12, synthesis of glasses13,14, and so on. Especially, in high temperature region such as ceramic synthesis process, rapid synthesis, sintering, and energy saving process is required, and are being developed utilizing the feature of microwave processing such as internal heating, volumetric heating etc., which is independent of the heat conduction law15,16. In the synthesis of materials that do not absorb microwaves, we can utilize a heat-source material called a susceptor around the container17, and get the benefit of microwave rapid heating. In addition, using a single mode cavity, which can confining the electromagnetic field in the cavity, we can heat materials with higher efficiency than the multi-mode microwave heating furnace such as microwave oven. Single mode cavity can separate the position of maximum intensity of electric field and magnetic field, and it is also used for research on the principle of microwave processing focusing on the effects of microwave electromagnetic field18,19. By devising the sample setting and microwave apparatus as described above, it is possible to synthesize almost all functional materials that can be synthesized in an electric furnace within a short period of synthesis time5. On the other hand, there are few cases of synthesis of transition-metal oxide nanoparticles, which are difficult to produce in an electric furnace. The most problem to synthesize nanoparticles is sintering and coarsening of the sample at high temperature, which needs for solid state processing. However, by taking advantage of the microwave process such as rapid heating and internal heating, it is possible to overcome this problem.

In the review, we show that reduced titanium oxide (TiO₂) nanoparticles and aluminum nitride (AlN) nanoparticles are synthesized at low temperature and short time by rapid carbothermal reduction process using microwaves. The key strength of this method is retaining the morphology of oxide nanoparticles as a pristine material. Rutile (TiO₂) and alumina (Al₂O₃) nanoparticles as pristine materials are being applied to cosmetics, electronic components, and so on in Japan, and they are produced industrially (several hundred tons), respectively. Rutile and alumina nanoparticles are also possible to control these particle size according to the application, which is very advantageous for use as a pristine material. On the other hand, these oxides
are very stable, and chemical reactions accompanied by reduction reaction (smelting, reduction nitridation, etc.) require high temperatures. Therefore, when these oxide nanoparticles are used as a starting material, it is difficult to obtain desired nanoparticles by a simple carbothermal reduction method using an electric furnace. TiO$_7$ nanoparticles and AlN nanoparticles are expected to be applied to catalysts and encapsulates, respectively; thus control of particle size and morphology is indispensable. Therefore, a method of low temperature reduction reaction using a strong reducing agent and a method for obtaining nanoparticles from an organometallic material are proposed. However, the former has problems in view of safety and convenience, the latter has a problem that cannot obtain the desired morphology. In this review, we introduce the rapid carbothermal reduction process using microwave irradiation, which can solve the above problems.

1. Application and Materials Processing of TiO$_7$ Nanoparticles

Titanium oxide having various titanium valence state exists between metallic titanium (Ti) and titanium dioxide (insulator), and they are called as reduced titanium oxides or titanium sub-oxides. Titanium oxides are classified to stoichiometric compounds such as TiO and Ti$_2$O$_3$ and nonstoichiometric compounds typified by the Magnéli phase (Ti$_n$O$_{2n-1}$ ($n\geq 4$)) in reduced titanium oxide. The Magnéli phase is based on a rutile type structure, and an octahedral structure having an O atom at the apex centered on the Ti atom is formed by a series of edges sharing and point sharing. Figure 1 shows the crystal structure of TiO$_7$, which is a typical Magnéli phase, and Table 1 shows TiO$_7$ crystal structure data. V, Mo, W based oxides has also Magnéli phase, and has been studied for a long time as reduced titanium oxides have high electric conductivity and chemical stability. Figure 2 shows the electrical conductivity of various titanium oxide. Titanium dioxide (TiO$_2$) is an insulator at room temperature and its electrical conductivity is extremely small as $10^{-13}$ to $10^{-14}$ S/cm. With TiO$_2$ reducing, the electrical conductivity increases gradually and once it reaches the maximum value on TiO$_7$. The electrical conductivity of TiO$_7$ is about $1.6 \times 10^3$ S/cm at room temperature and shows high electric conductivity equivalent to graphite (about 1000 S/cm). The utilizing of TiO$_7$ having such high electrical conductivity has been studied for use in polymer electrolyte fuel cell (PEFC), lithium sulfur batteries, etc. In any application, nanoparticles of TiO$_7$ with a large specific surface area are required. Large specific surface area can increase the reaction area, and in the catalyst support, it prevents suppressing catalyst aggregation, lead to increase the reaction point. As described above, nanoparticles are highly useful forms, but their production is difficult due to their high surface energy. High temperature is necessary for reducing TiO$_2$, and sintering and coarsening occurs even when nanoparticles are used as a raw material.

| Table 1 | TiO$_7$ Crystal Structure Data |
|---------|-------------------------------|
| Crystal system | Triclinic |
| Space group | P-1 |
| $a$ [nm] | 0.5597 |
| $b$ [nm] | 0.6903 |
| $c$ [nm] | 0.7125 |
| $\alpha$ [°] | 64.12 |
| $\beta$ [°] | 71.24 |
| $\gamma$ [°] | 75.65 |

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To synthesize reduced titanium oxide nanoparticles, a special method has been reported. One of the methods to synthesis method of reduced titanium oxide nanoparticles is using a strong reducing agent. Tominaka et al. used strong reduction agents such as CaH₂, NaBH₄ and has succeeded to reduce TiO₂ nanoparticles and nanorods to Ti₃O₅. Although a long time reaction (several days) is required, such strong reducing power can reduce TiO₂ nanoparticles at a low temperature condition of about 350 °C. Ohkoshi et al. has synthesized λ-Ti₃O₅ nanoparticles by coating titanium hydroxide Ti(OH)₄ with SiO₂ and reducing it with hydrogen. In this method, it is suggested that coated SiO₂ prevented a contact between TiO₂ nanoparticles generated from Ti(OH)₄. Other study has been reported, reduced titanium oxides was obtained by using an organic titanium compound as a raw material. Titanium isopropoxide etc. was used as the organic titanium compound and the reduced titanium oxide nanoparticles were synthesized by heating the gel obtained by polymerizing of these organic titanium compounds. In this method, fine TiO₂ nanoparticles and amorphous carbon are produced when an organic titanium compound is heated. Thus generated carbon prevented a contact between TiO₂ nanoparticles, which lead to prevent sintering of TiO₂ nanoparticles. Although these methods are useful for preparing reduced titanium oxide having a nanostructure, there are several problems. In the method using a strong reducing agent, complicated operations are required to handle the reducing agent under an inert atmosphere, and it takes a long time to reduce. The reduction by hydrogen is also not preferable from the viewpoint of safety and convenience. The carbothermal reduction method using organic titanium compounds as a raw material is an excellent method from the viewpoint of safety and convenience, but application to obtain various forms of reduced titanium oxides is difficult. Therefore, as a more versatile and convenient method, carbon thermal reduction method to prepare reduced titanium oxide nanostructures from TiO₂ nanostructures is desirable. However, in generally, carbon thermal reduction method requires high temperature and it is difficult to synthesize reduced titanium oxide nanoparticles.

In this study, we applied microwaves to synthesize reduced titanium oxide having nanostructures, especially Ti₃O₅. Microwave heating has characteristics of rapid heating and rapid cooling, and the total heating time can be shortened. To control the morphology, TiO₂ nanoparticles as a raw material and polyvinylpyrrolidone (PVP) as a reducing agent carbon source were used. It is suggested that fine Ti₃O₅ nanoparticles can be synthesized without sintering of each particles by shortening heating time.

### 1.2. Nitride Ceramics and Materials Processing of AlN Nanoparticles

Among many function ceramics, nitrides have various excellent properties such as light weight, heat resistance, corrosion resistance, and abrasion resistance. Therefore, nitride ceramics are used for various purposes as industrial materials. Recently, nitride semiconductor materials are expected to be applied to electronics, and aluminum nitride (AlN) has attracted attention as a substrate for power devices.

Nitride ceramics such as boron nitride (BN), AlN, and silicon nitride (Si₃N₄) are covalent materials and such as titanium nitride (TiN), chromium nitride (CrN), manganese nitride (Mn₃N), iron nitride (e.g., Fe₃N) are interstitial transition metal nitrides. Besides, the Group 13-15 nitrides such as GaN and InN are thermally and chemically stable and applied to a semiconductor for various electronic materials. Table 2 shows representative nitrides, their properties and applications. These nitride ceramics have high functionality and utilize in various fields.

AlN has high thermal conductivity, high electrical insulation, and thermal expansion coefficient similar to that of silicon, thus it is expected to be applied as a heat sink material. Various method is used to synthesize AlN, and typical methods are a direct nitridation method of metallic aluminum and a reduction-nitridation method of alumina (Al₂O₃). In the former method, nitriding reaction can be carried out at a relatively low temperature, but the particle size distribution of synthesized AlN particles are increased by sintering or agglomeration due to heat with the nitriding reaction. The latter is excellent method to synthesis of filler materials because AlN maintaining the particle size and morphology of raw alumina particles can be synthesized. However, this reaction requires high temperature and long time to obtain AlN. Therefore, it is desired AlN synthesis method which can proceed reduction and

| Boron nitride (BN) | Layered structure: h-BN, high hardness: c-BN | h-BN: lubricant, c-BN: cutting tool |
|--------------------|---------------------------------------------|-----------------------------------|
| Aluminum nitride (AlN) | High thermal conductivity, high insulation, corrosion resistance, antifriction, thermal shock resistance | Heat sink, substrate |
| Silicon nitride (Si₃N₄) | High hardness, good mechanical characteristics | Ball bearing, cutting tool |
| Titanium nitride (TiN) | High hardness, antifriction, high electrical conductivity | Hard coating, ornament |
| Gallium nitride (GaN) | High thermal conductivity, high insulation, corrosion resistance | Blue LED, power device |
nitriding reaction at low temperature and short time. In some previous research, AlN was synthesized at relatively low temperature, 1100 to 1400 °C, by using ammonia gas or propane gas. However, since toxic HCN gas is generated in this process, safe processing is desired.

Therefore, focusing on transition alumina which is thought to be advantageous for AlN synthesis at low temperature, we utilize microwave processing to end the reduction nitriding reaction before its structure changes. We introduce the synthesizing of AlN at low temperature and short time using microwaves by carbon thermal reduction as raw materials from γ-, δ-, θ- and α-Al2O3, and also introduce increasing nitridation ratio by controlling of nitrogen flow rate with maintaining raw alumina particles.

2. Results and Discussion

2.1. Microwave Synthesis of Ti4O7 Nanoparticles

Predetermined molar ratio of TiO2 and PVP were added to pure water (80 mL) and mixed by using ultrasonic irradiation (44.19 kHz) at 100 W for 30 min. Dried starting materials was irradiated with 2.45 GHz microwave in various temperature and holding time by using an electromagnetic-field concentration-type microwave irradiation furnace (Shikoku Instrumentation Co., Ltd.) (Fig. 3). The chamber diameter of the device is about 12 cm, and the maximum point of electric field intensity is generated at the center of the chamber. Unlike the single-mode type microwave irradiation furnace using a rectangular waveguide, by purposely lowering the Q value of the chamber, it is possible to widen the concentration zone of electromagnetic fields and heat a relatively large amount sample efficiently. Argon gas was flowed at 0.5 L/min during the experiments. Carbon (1.5 g) and titanium powder (0.5 g) were used for susceptor and oxygen absorber, respectively. As comparative experiments, samples were synthesized by conventional heating using a tube furnace by heating at a rate of 5 °C/min.

Figure 4(a) shows the results of X-ray diffraction (XRD) measurement of samples prepared at 900, 950 and 1000 °C for 30 min by microwave irradiation. As temperature increased, the product phase became more reduced phase. At 900 °C, a broad peak, which is considered to be composed of multiple Magnéli phases TiO2n–1 (5 ≤ n ≤ 10) including TiO2 and Ti6O11 phases, was confirmed. In this study, Magnéli phases other than Ti4O7 shown as broad peak, suggesting that various phases coexist. This is because these Magnéli phases are generated at similar temperature. At 950 °C, only Ti6O7 was produced, and TiO2 was not remained. It is suggested that oxygen getter, titanium, prevent re-oxidation after formation of Ti4O7. Incidentally, the standard enthalpy of formation (4TiO2 → Ti4O7 + CO) at 1200 K is 269.6 kJ mol⁻¹. Furthermore, at 1000 °C, more reduced phase such as γ-Ti3O5 (TiO1.6) and Ti2O3 (TiO1.5) was confirmed in addition to Ti4O7 (TiO1.75). Figure 4(b) shows XRD results in the case of conventional heating. Similar to the case of microwave heating, reduction reaction was proceeded with increasing the temperature. Only Ti4O7 phase was confirmed at 950 °C for 30 min, similar to microwave heating. On the other hand, at 1000 °C, the formation of Ti2O3, which is the most reduced phase in microwave case, was not confirmed. Figure 5(a) shows the results of XRD measurement of samples prepared for 10, 30 and 60 min at 950 °C by microwave irradiation. For 10 min, a broad peak consisting of TiO2n–1 (5 ≤ n ≤ 10) including TiO2 and Ti6O11 phases was confirmed, but the TiO2 phase could not be confirmed for 30 min and 60 min. Reduction reaction was proceeded with increasing the holding time. For 60 min, more reduced phase such as γ-Ti3O5 (TiO1.6) and Ti2O3 (TiO1.5) was confirmed in addition to Ti4O7 (TiO1.75). Figure 5(b) shows XRD results in the case of conventional heating on various holding time. Proceed of reduction reaction was confirmed with increasing the retention time from 10 to 30 min, but not for 60 min. For 60 min, only Ti4O7 was obtained similar to the
results at 950 °C, and the reduction reaction was not proceeded to Ti$_2$O$_3$ and $\gamma$-Ti$_3$O$_5$ phases, which were observed in microwave case. The upper row of Fig. 6 shows field emission scanning electron microscope (FE-SEM) images of the sample prepared at 900, 950 and 1000 °C for 30 min and for 10, 30 and 60 min at 950 °C by microwave irradiation. It was confirmed that reduced titanium oxides was high contrast and carbon was low contrast. The amount of this residual carbon was about 16.4 wt% from thermogravimetry-differential thermal analysis (TG-DTA). The residual carbon, however, is very likely to disappear under high-voltage and water (vapor) as following chemical equation:

$$C + 2H_2O \rightarrow 4H^+ + 4e^-$$

Thus the residual carbon has few problems for using the catalysts of fuel cell.

Grain growth was not observed at 900 °C and 950 °C for 30 min. On the other hand, at 1000 °C, large grain particles were observed with fine particles at the same time. Average particle diameter was 56 nm at 900 °C for 30 min, 60 nm at 950 °C, resulting that almost the same in particle size as compared with the raw TiO$_2$ nanoparticles (58 nm). On the other hand, at 1000 °C for 30 min, average particle diameter became larger (70 nm). This is because some grains have sintered at high temperature. The bottom row of Fig. 6 shows FE-SEM images of the sample prepared for 10, 30 and 60 min at 950 °C by microwave irradiation. Distinct grain growth could not be confirmed for 10 min and 30 min at 950 °C, but particles sintered to large grain for 60 min. Average particle diameter was for 10 min at 950 °C was 54 nm, 30 min was 60 nm, and 60 min was 74 nm, respectively. It is suggested that grain growth of TiO$_2$ nanoparticles was occurred by long heating. From the results of XRD and FE-SEM, synthesis of fine Ti$_4$O$_7$ nanoparticles with a particle diameter of 60 nm was succeeded by microwave irradiation method in the condition of 950 °C for 30 min.

The upper row of Fig. 7 shows FE-SEM images of samples prepared at 900, 950 and 1000 °C for 30 min by conventional heating. As similar to the results of microwave irradiation, the presence of titanium-oxides particles and carbon was confirmed. Although grain growth was not observed under the condition of 900 °C, grain growth was confirmed under the conditions of 950 °C and 1000 °C. The bottom row of Fig. 7 shows the FE-SEM images of the sample prepared for 10, 30 and 60 min at 950 °C by conventional irradiation. Grain growth was not observed under the condition of holding for 10 min, but grain growth was confirmed over 30 min holding.

Compared with the samples prepared under the conditions of holding at 950 °C for 30 min in each process, particle size was only retained in microwave processing, whereas grain growth was occurred in conventional heating. From the particle size distribution of samples prepared in conventional processing at 950 °C for 30 min, the average particle diameter was 81 nm, which was larger than that of the sample (60 nm) prepared by microwave irradiation under the same conditions. One of the reasons why the difference in grain size occurs in
each heating is the difference of the heating time over 700°C between microwave and conventional processing. Figure 8 shows the temperature profiles under the holding condition of 950°C for 30 min in microwave and conventional processing. In this experiment, the heating rate of microwave processing was 250°C/min or more, but the heating rate of tube furnace heating was 5°C/min. From the difference of the heating profile and the time required for temperature rise to 950°C, the heating time in microwave processing was shortened. According to previous reports, TiO₂ nanoparticles become grain growth by heating at 700°C or more. Thus short time of temperature rise to 950°C resulted in preventing of the grain growth of TiO₂ nanoparticles. In addition, it was considered that time for cool down to 700°C was short because the furnace did not warm due to selective heating, which is one of the feature of the microwave processing. With calculated the time when the sample temperature was over 700°C in this experiment from the heating profile, only 2 min (temperature increase) + 30 min (holding) + 2 min (cooling) = 34 min was required in the case of microwave heating, while it was (holding) 50 min (temperature increase) + 30 min (holding) + 18 min (cooling) = 98 min. By shortening the heating time by rapid heating/cooling by microwave heating, even though grain growth was confirmed by conventional heating under the condition of holding at 30 min at 950°C, grain growth of the microwave heated sample was not occurred.

2.2. Microwave Synthesis of AlN Nanoparticles from Spherical Al₂O₃

2.2.1. Effect of Crystal Structure of Raw Alumina on Carbothermal Reduction and Nitridation Process

Various transition alumina was obtained by calcining at 650, 800, 900, 1000, 1100, and 1400°C of γ-Al₂O₃ as a raw material. In order of the above temperature, the phases of the sample was δ-Al₂O₃ single phase, θ-Al₂O₃ + small amount of δ-Al₂O₃, θ-Al₂O₃ single phase, θ-Al₂O₃ + small amount of α-Al₂O₃, small amount of θ-Al₂O₃ + α-Al₂O₃, and α-Al₂O₃ single phase, respectively. We mixed the alumina powder of each phase with a carbon black dispersion. The molar ratio of Al₂O₃ : C was 1 : 10. The mixed solution was dried at 80°C, and we obtained a starting raw material powder. This raw material powder (0.2 g) was press into a pellet and set in a quartz tube. The surround of the quartz tube was covered with activated carbon, which is a good susceptor. With flowing a nitrogen gas through a quartz tube on 1.0 L/min, 2.45 GHz microwave was irradiated. For microwave irradiation, an electromagnetic-field concentration-type microwave irradiation furnace (Shikoku Instrumentation Co., Ltd.) was used (Fig. 3). The remained carbon in the sample after processing was removed by heating by an electric furnace at 800°C for 2 h.

Figure 9 shows XRD measurement results of samples prepared by irradiating various alumina raw materials with microwaves at 1400°C for 1 h. There is a
difference in the amount of aluminum nitride produced. When using alumina raw material $\delta$-Al$_2$O$_3$ single phase, $\theta$-Al$_2$O$_3$ + small amount of $\delta$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ single phase, the amount of AlN produced was smaller than that of other transition alumina for raw materials. Among them, the amount of produced AlN was the least when the $\alpha$-Al$_2$O$_3$ single phase was used as raw material. It was found that, a large amount of AlN was obtained as the main phase with using raw material containing $\theta$-Al$_2$O$_3$. There are two processes in the carbothermal reduction reaction of alumina. At first, the intermediate AlON is formed. Then, the process of AlN formation continues to the above process. Below 1700 $^\circ$C, it is known that the intermediate AlON quickly decomposes into $\alpha$-Al$_2$O$_3$ and AlN. Therefore, the reason why the above-described carbothermal reduction proceeded is due to a promotion of the reaction for producing the AlON intermediate. Figure 10 shows the change of the crystal structure in carbothermal reduction and nitridation process from $\gamma$- and $\alpha$-Al$_2$O$_3$. From the figure, an intermediate AlION has AlO$_4$ sites, and it has been reported that it is advantageous for AlON formation$^{41)}$. From this fact, it is considered that large amount of AlN was synthesized from raw material containing $\theta$-Al$_2$O$_3$. There are two processes in the carbothermal reduction reaction of alumina. At first, the intermediate AlION is formed. Then, the process of AlN formation continues to the above process. Below 1700 $^\circ$C, it is known that the intermediate AlON quickly decomposes into $\alpha$-Al$_2$O$_3$ and AlN. Therefore, the reason why the above-described carbothermal reduction proceeded is due to a promotion of the reaction for producing the AlON intermediate. Figure 10 shows the change of the crystal structure in carbothermal reduction and nitridation process from $\gamma$- and $\alpha$-Al$_2$O$_3$. From the figure, an intermediate AlION has AlO$_4$ sites, and it has been reported that it is advantageous for AlON formation$^{41)}$. From this fact, it is considered that large amount of AlN was synthesized from raw material containing $\theta$-Al$_2$O$_3$ having AlO$_4$ site as the main phase.

The above discussion is derived from the crystal structure of raw material alumina, but the difference in AlN synthesis behavior due to the difference in heating method is not clear. Therefore, the same experiment was conducted by using electric furnace heating. Figure 11 shows the XRD measurement results. As a result, carbothermal reduction did not proceed by using electric furnace heating. Particularly, transition alumina was changed to $\alpha$-Al$_2$O$_3$ in all raw materials. The transition of each transition alumina to $\alpha$-Al$_2$O$_3$ is known to occur at 1200 $^\circ$C or higher. In addition, it is considered that carbothermal reduction and nitridation reaction from $\alpha$-Al$_2$O$_3$ hardly occurs from the results of microwave irradiation experiment. In addition, in the temperature region, carbothermal reaction and nitridation of $\alpha$-Al$_2$O$_3$ hardly proceed because the reaction Gibbs energy becomes zero at over 1600 $^\circ$C. Thus, it is considered that AlN synthesis does not proceed even if heating time is extended at high temperature (1400 $^\circ$C). On the other hand, in microwave processing, when raw material containing $\theta$-Al$_2$O$_3$ as the main phase was used, AlN was synthesized by heating at 1300 $^\circ$C for 2 h (Fig. 12). Incidentally, the standard enthalpy of formation ($1/2\gamma$-Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$ + 3/2C +
The value when using $\theta$-Al$_2$O$_3$ as starting materials may be between the values of $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ as starting materials. One reason why the AlN synthesis reaction was promoted by microwave irradiation is the effect of rapid heating. Although the crystal structure of transition alumina is important for promoting AlN synthesis, it is required that the crystal structure of the transition alumina maintains at high temperature region. It is considered that the crystal structure of this transition alumina was kept over 1300°C in microwave processing because the sample temperature increased sharply by microwave rapid heating. Therefore, AlN synthesis could be performed at low temperature and short time. Another reason is that the reduction reaction was promoted by microwave irradiation itself. For example, Yoshihikawa et al. reported that the carbothermal reduction reaction of nickel oxide (NiO) has proceeded at low temperature compared to electric furnace heating$^{42)}$. This report indicated that the reason for this comes from a difference in heating behavior between NiO and carbon, and it is considered that the reduction reaction was promoted by selective heating of carbon. In our system, alumina absorbs microwaves weaker than carbon, thus carbon is selectively heated. Therefore, it is considered that the carbothermal reduction reaction proceeded at low temperature.

2.2.2. Effect of Flow Rate of Nitrogen on Carbothermal Reduction and Nitridation Process

Carbothermal reduction reaction forms CO gas, and reverse reaction occurs when CO remains in the system for long time, resulting that re-oxidation of AlN occurs. By flowing N$_2$ gas, it was considered that CO was flowed out from the system and the reverse reaction could be prevented, resulting that improvement of nitridation ratio is expected. Therefore, the optimum flow rate was examined by changing the nitrogen flow rate between 0.5-3.0 L/min. Figure 13 shows the XRD patterns of the samples fabricated at 1200°C for 180 min, on N$_2$ flow rate = 0.5-3.0 L/min. Here, nitridation ratio ($R_N$) was calculated by the following equation.

$$R_N = \frac{I_{\text{AlN}(00)}}{I_{\text{AlN}(00)} + I_{\theta-\text{Al}_2\text{O}_3(113)} + I_{\theta-\text{Al}_2\text{O}_3(403)} + I_{\delta-\text{Al}_2\text{O}_3(4112)}}$$

From the results of the XRD measurement, the nitridation ratio of the sample was 0.24 when the sample was fabricated on 0.5 L/min. This sample had a lower nitridation ratio than the sample prepared under other conditions. This is presumably because CO is not discharged outside the system and reverse reaction is not suppressed. As the nitrogen flow rate was increased, the nitridation rate improved with increasing nitrogen flow rate up to 2.0 L/min. This is because CO was efficiently flowed out to the outside of the system by nitrogen flowing and the reverse reaction was prevented.
as the nitrogen flow rate increases. On the other hand, when the nitrogen flow rate was increased to 3.0 L/min, the nitridation ratio was decreased. It is suggested that a part of the sample was cooled when a large amount of nitrogen was blown onto the sample. Figure 14 shows SEM images of samples prepared at 1200 °C for 180 min on 0.5-3.0 L/min. From the SEM images, the prepared particles maintained spherical shape irrespective of nitridation ratio. Accordingly, spherical AlN nanoparticles having a high nitridation ratio can be synthesized by adjusting the nitrogen flow rate.

3. Conclusion

In this review, we synthesized Ti$_4$O$_7$ nanoparticles and spherical AlN nanoparticles by microwave irradiation at low temperature in short time. In the synthesis of Ti$_4$O$_7$ nanoparticles, by a simple method of mixing TiO$_2$ nanoparticles and PVP, and then irradiating with microwaves under Ar atmosphere at 950 °C for 30 min, Ti$_4$O$_7$ nanoparticles successfully synthesized with maintain about 60 nm particle size of raw materials. On the other hand, Ti$_4$O$_7$ prepared by tube furnace heating (heating rate: 5 °C/min) sintered and had partially coarsened particles, and the superiority of microwave processing for fabrication of Ti$_4$O$_7$ nanoparticle was confirmed. It is considered that the rapid heating (250 °C/min) and rapid cooling, which are the features of microwave processing, are important role to maintain the size of nanoparticles during carbothermal reduction reaction at high temperature region. In AlN synthesis, by the experiment of focusing on the crystal structure of pristine alumina, a high nitridation ratio was achieved when θ-Al$_2$O$_3$ was used as starting materials. Moreover, it was confirmed that the nitridation rate could be improved by optimizing the nitrogen flow rate, and succeeded in producing spherical particles having a nitridation ratio of 0.88 under the conditions of 1200 °C for 180 min on 0.2 L/min of flowing N$_2$ gas.

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要 旨

急速炭素熱還元法によるTi₄O₇およびAINナノ粒子のマイクロ波合成

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炭素熱還元法という簡便な方法により望ましい粒径、形態を有するナノ粒子を得るために、マイクロ波プロセスを用いた。マイクロ波プロセスにより、原料の形態を維持したTi₄O₇ナノ粒子（〜60 nm）を、950 ℃, 30分の熱処理によって得た。通常加熱では粒成長が見られなかったため、高温領域での炭素熱還元反応においても、マイクロ波プロセスの特徴である急速加熱（250 ℃/min～）および急速冷却が粒径の維持に効果的であったと考えられる。また、マイクロ波プロセスにより、高い発熱率を有する原料形態を維持した球状AINナノ粒子の合成に成功した。遷移アルミナ（AION中間体の形成のために有利な結晶構造であるが、1200 ℃以上でα-Al₂O₃に相変化する）の結晶構造がマイクロ波急速昇温によって1300 ℃以上においても維持されたためであると考えられる。これに加えて、窒素流量を最適化することによって、0.88の窒素化率を有する球状AINナノ粒子を、1200 ℃, 180分, 窒素流量0.2 L/minの条件で得ることができた。