Nanoparticle synthesis using high-power modulated induction thermal plasmas with intermittent synchronized feeding of raw materials

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Abstract: The titanium dioxide (TiO₂) nanoparticles were synthesized by direct evaporation of titanium powders using Ar-O₂ pulse-modulated induction thermal plasmas (PMITP). The PMITP has been developed to control the temperature of thermal plasma and gas flow fields in time domain. In addition to the PMITP, a system was developed for intermittent feeding of raw materials synchronized with the modulation of the coil current. Effect of the intermittent feeding was investigated on synthesized particles with the PMITP in terms of the mean particle diameter, the morphology, and the weight fraction of anatase-TiO₂. The delay timing of the intermittent feeding was also studied on the synthesized particles.

Keywords: Pulse-modulated induction thermal plasmas (PMITP), TiO₂ nanoparticle synthesis, intermittent powder feeding

1. Introduction
Inductively coupled thermal plasmas (ICTPs) around at atmospheric pressure have been widely used as effective heat and chemical species sources for various materials processings such as syntheses of diamond films, thermal barrier coatings, and surface modifications, etc. The advantages of ICTPs are their high enthalpy and high radical density without any contamination. Such an ICTP is also useful to synthesize nanoparticles of various kinds [1, 2].

On the other hand, the authors previously developed a pulse modulated induction thermal plasmas (PMITP) system and an arbitrary-waveform-modulated induction thermal plasma (AMITP) system [3]. The PMITP and AMITP are established by the coil current modulated into a rectangular or other waveforms. Such a millisecond modulation can perturb the thermal plasma markedly, and then it can change the temperature and radical densities as well as the gas flow field in the thermal plasma in time domain [3]. Through this modulation, the temperature and radical densities can be controlled. We found actually that the Ar-N₂ PMITP provides simultaneous control of the nitrogen radical flow and the enthalpy flow [4].

We have been trying to adopt the Ar-O₂ PMITP to nanoparticle synthesis of titanium dioxide (TiO₂) in anatase phase. The TiO₂ nanoparticles in anatase phase are continuously receiving attention for use as photocatalysts [5], photonic crystals [6], photovoltaic cells [7], gas sensors [8], and a strong deoxidation material used for producing hydrogen gas from water for fuel cells [9]. The TiO₂ nanoparticle properties depend on the particle size, crystal structure, phase constituents. Thus, particle size and phase constituent control are extremely important to obtain the specified performance of TiO₂ nanoparticles. In our previous works, we found that the modulation of the coil current can control the size of synthesized nanoparticles, and that the weight fraction of anatase-TiO₂ in synthesized nanoparticles is about 85%–90% almost independent of the modulation condition [10]. It was also found that the size of synthesized nanoparticles depends on the temperature decay rate in the cooling period in the PMITP [11].

In this paper, in addition to the PMITP, a system was developed for intermittent feeding of raw materials synchronized with the modulation of the coil current. In our previous work, the raw materials was continuously fed to the plasma although the coil current was modulated into a rectangular waveform [10, 11]. Effect of the intermittent feeding was investi-
gated on synthesized particles with the PMITP. The synthesized nanoparticles were analyzed using FE-SEM for the morphology and the size distribution, and using XRD for the surface compounds. The influence of the delay timing of the intermittent feeding was also studied on the synthesized particles.

2. Concept of intermittent feeding of raw materials synchronized with the PMITP

Fig. 1 illustrates the concept of the intermittent and synchronized feeding of raw material to the PMITP. The PMITP can repetitively produce a high-temperature field during the ‘on-time’ and low-temperature field during the ‘off-time’ in thermal plasmas. Here, the on-time means the time period with the higher current level, while the off-time is the time period with the lower current level. If the raw materials are continuously fed to the PMITP as a conventional way, they can be supplied to the thermal plasma both during the on-time and off-time. In this case, the supplied particles experience different temperature histories in the thermal plasma. On the other hand, if we use the intermittent and synchronized feeding of raw materials to the PMITP, the raw material particles can be supplied to the thermal plasma only when the high-temperature plasma is established in the torch during the on-time. This may promote complete and efficient evaporation of the supplied raw material. Furthermore, evaporated materials in the high-temperature thermal plasma is rapidly cooled during the successive off-time in the reaction chamber. This may provide the efficient nucleation for nanoparticle, and then prevent synthesized particles from growing up.

3. Experimental setup

3.1. The developed system for intermittent feeding of raw materials

Fig. 2 shows the whole nanoparticle synthesis system using the PMITP used in the present work. The upper side in Fig. 2 portrays the newly developed system for intermittent feeding of raw material to the PMITP. The system contains the trigger circuit, the delay circuit and a high speed solenoid valve. The pulse generator provides the modulation control signal with 0–10 V to the gate signal circuit for the metal oxide semiconductor field effect transistor (MOSFET) and also the trigger circuit. The FET gate signal circuit controls the fire angle of the MOSFET elements for rf power supply with the pulse modulation of the coil current. On the other hand, the trigger circuit and then the delay circuit control opening and closing a high-speed solenoid valve. Use of this system enables us to intermittently feed the raw material powder to the thermal plasma with controlling feed timing. The solenoid valve has a time constant of less than 2 ms.

3.2. Plasma torch and rf power source

The plasma torch in Fig. 2 is configured identically to that used in our previous work; its details are described in an earlier paper [10, 11]. The plasma torch has two coaxial quartz tubes. The inner diameter of the interior quartz tube is 70 mm; its length is 370 mm. An argon-oxygen gas mixture was supplied as a sheath gas along the inside wall of the interior quartz tube from the top of the plasma torch. Titanium raw material was fed using a powder feeder with Ar carrier gas through the solenoid valve and a water-cooled probe inserted from the top of the plasma torch head, as depicted in Fig. 2. Downstream of the plasma torch, the water-cooled chambers are installed in vertical and then in horizontal, as depicted in Fig. 2. Further downstream, a powder-collecting filter is set up and then a vacuum pump. Synthesized particles were collected in the filter.

3.3. Experimental conditions

The total sheath gas flow rate was fixed at 100.0 standard liters per minute (slpm) (=1.33 × 10⁻³ m³ s⁻¹). The oxygen gas admixture ratio to Ar was fixed at 10% in the gas flow rate. The Ar carrier gas flow rate was 4 slpm. Titanium powder with a diameter less
than 45 μm was used as raw material. The powder feed rate \( g \) of the Ti raw material was set from 3.3 to 4.0 g/min for any feeding condition. The pressure inside the chamber was controlled, actually fixed at 300 Torr (=40 kPa). The time-averaged input power to the rf power supply was fixed at 20 kW. The SCL, which is the ratio of the lower current level to the higher current level, was set to 80%. The on-time and the off-time were set to 12 ms and 3 ms, respectively. In this case, the duty factor DF is 80%.

4. Effect of intermittent feeding with synchronized to pulse modulation

4.1. SEM images and particle diameter distribution

Fig. 3 presents examples of FE-SEM micrographs of particles for four conditions: (a) non-modulation and intermittent feeding (NM/IMF), (b) pulse modulation and continuous feeding (PM/CWF), (c) pulse modulation and intermittent feeding with delay time \( t_d \) of 0 ms (PM/IMF & \( t_d = 0 \) ms), and (d) pulse modulation and intermittent feeding with delay time \( t_d \) of 8 ms (PM/IMF & \( t_d = 8 \) ms). From these micrographs, the particle size distribution was subsequently obtained from observation of 200 randomly sampled particles in Fig. 4. This figure also includes the mean diameter \( \bar{d} \), the median diameter \( d_{50} \) and the standard deviation \( \sigma \). In addition to this, we have had results for non-modulation / continuous feeding (NM/CWF) which has \( \bar{d} = 63.2 \) nm, \( d_{50} = 54.5 \) nm, and \( \sigma = 30.6 \) nm. First, the comparison between NM/CWF and PM/CWF results indicates that the coil current modulation provides smaller nanoparticles. This was already obtained in our previous results [10]. NM/CWF and NM/IMF results were compared to imply that the intermittent feeding of raw materials also produce smaller nanoparticles. Moreover, PM/IMF conditions, in particular PM/IMF & \( t_d = 8 \) ms condition, provide smaller nanoparticles than conditions NM/CWF, NM/IMF and PM/CWF. Fig. 5 shows the dependence of \( \bar{d} \) on the delay time of intermittent feeding of raw materials. As seen, the conditions of PM/IMF & \( t_d = 6–8 \) ms are ones that provide the smaller nanoparticle synthesized in the present work. This feeding timing of \( t_d = 8 \) ms was found to be synchronized between the feeding of raw material and the high temperature timing in the PMITP.

4.2. Weight fraction of anatase-TiO₂ analyzed using XRD

The phase constitutes of synthesized nanoparticles were analyzed using X-ray diffraction technique (XRD). Almost identical XRD spectra were found for particles synthesized for any operation conditions. These XRD spectra were all related to TiO₂. Thus, this re-
Mean particle diameter [nm]

Weight fraction of anatase TiO₂

Result shows that the modulation and intermittent feeding conditions do not affect the phase of TiO₂ nanoparticles. From the XRD spectra, the weight fraction of anatase to rutile phase of synthesized TiO₂ nanoparticles was estimated as indicated in Fig. 6 as a function of tₙ. The weight fraction of anatase-TiO₂ is between 0.82 and 0.9. This value is close to those in other reports [2].

Fig. 6. Weight fraction of anatase-TiO₂ estimated from XRD analysis.

5. Conclusions

The TiO₂ nanoparticles were synthesized using the PMITP with intermittent feeding system of raw materials. It was found that combination of the PMITP and the intermittent feeding of raw materials provides smaller nanoparticles, keeping high weight fraction around 0.85 for anatase-TiO₂.

References