Effect of Alternating Gas Injection on Temperature Fields in Reaction Chamber using Inductively Coupled Thermal Plasmas for Nanoparticle Synthesis

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Abstract:
Effect of alternating injection of quenching gas was studied in inductively coupled thermal plasma (ICTP) for nanoparticle synthesis. First, three dimensional (3D) numerical simulation was conducted to obtain temperature and gas flow fields with and without alternating injection of quenching gas. Furthermore, nanoparticle synthesis for Fe^{3+}-doped TiO_2 was experimentally done with and without modulation of quenching gas. Results showed that alternating injection of quenching gas can offer more rapid cooling of the thermal plasma, which results in smaller nanoparticles.

Keywords: Thermal plasma, Nanoparticles, Modulation, Alternating quenching gas

1. Introduction

Recently, nanoparticles or nanopowder (NPs or NP) are receiving great attention in the fields of electronics, environmental and energy applications, etc. This is due to the fact that nanoparticles have unique characteristics and functions compared to its bulk, and it also has a potential to improve some of their electromagnetic or thermodynamic properties. For inductrical application of such nanoparticles, it is desired to develop a method to synthesize functional nanoparticles with high production rates. For this aim, we have so far developed the 'PMITP+TCFF' method: the 'PMITP' indicates the pulse modulated induction thermal plasma, while 'TCFF' means the time controlled feeding of feedstock[1]−[5]. The PMITP can generate a periodical varying gas-temperature fields in on-time and off-time of the modulated coil current [1]. Furthermore, the TCFF method offers synchronous feeding of feedstock to the PMITP[1]. The combination of PMITP and TCFF results in high efficient evaporation of feedstock and also high efficient nucleation of evaporated material. This PMITP +TCFF method can thus provide a high rate production of oxide nanoparticles around ~500 g/h at an input power of 20 kW for PMITP [1]. In addition, the PMITP + TCFF method can produce Si nanowires with a high production rate [4]. For further enhancement in production rate of nanoparticles, new approaches are under investigation in addition to the modulation of coil current and feedstock feeding.

This paper describes a trial of modulation or alternating injection of quenching gas in the reaction chamber for nanoparticle synthesis using inductively coupled thermal plasma (ICTP). Such a modulation or alternation of quenching gas injection is expected to control cooling rate of thermal plasma in the reaction chamber. First, three dimensional (3D) numerical simulation was conducted to obtain temperature field in the reaction chamber downstream of the ICTP torch with quenching gas injection. Two conditions were set of continuous injection and alternating injection of quenching gas with the same time-averaged flow rate of 50 L/min. Alternating quenching gas injection condition has a maximum instantaneous flow rate of 100 L/min, which results in rapid cooling by deeper peneration of quenching gas into the thermal plasma. Secondly, Fe^{3+}-doped TiO_2 nanoparticle synthesis was tested using non-modulated induction thermal plasma with and without alternating injction of quenching gas for a fundamental study. Results indicated that smaller nanoparticles can be synthesized with alternating quenching gas injection than with continuous quenching gas injection.

2. Numerical simulation of temperature field in the chamber with continuous or alternating quenching gas injection

2.1. Plasma torch and reaction chamber for numerical simulation

Figure 1 depicts the schematic of the ICTP torch and the reaction chamber for antiparticle synthesis used in our experiment. The ICTP torch consists of two coaxial quartz tubes (an inner tube and an outer tube) and an induction coil. The inner quartz tube has an inner diameter of 35 mm and a length of 350 mm. Between the inner and outer tubes, cooling water flows to keep the wall temperature around 300 K. The induction coil has a turn number of eight. To this coil, an rf power source is connected to supply rf coil current. The coil current generates rf axial magnetic field, and then azumuthal electric field inside the torch. This electric field creates a thermal plasma inside the torch. Downstream of the ICTP torch, a vertical reaction chamber, a horizontal chamber and a collection filter are installed. Quenching gas (QG) can be injected in radial

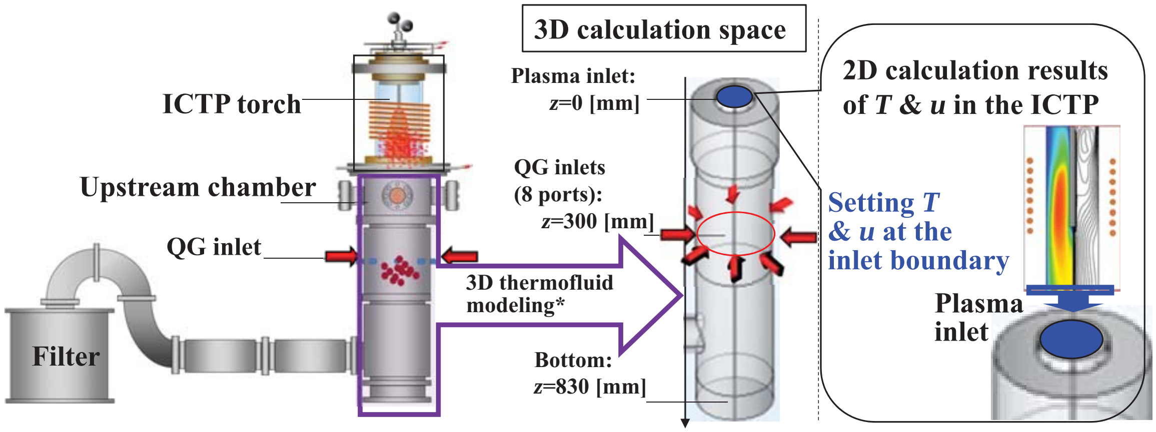

Fig. 1. Plasma torch with chamber for nonpolitical synthesis and the calculation space.

Table 1. Calculation conditions.

Input power	20 kW
Coil-current frequency	400 kHz
Sheath gas	Ar 90 L/min
Pressure	300 torr (≃ 40 kPa)
Carrier gas	Ar 4 L/min
Quenching gas (QG)	Ar 50 L/min in time-average

Table 2. Calculation conditions for quenching gas.

Quenching gas (QG)	Ar 50 L/min in time-average
Cond.-(1)	No-QG (0 L/min)
Cond.-(2)	Continuous QG
Cond.-(3)	Alternating QG with a cycle 30 ms

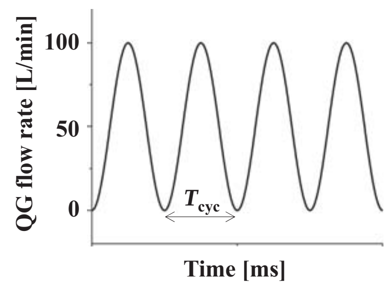

Fig. 2. Gas flow rate of quenching gas in case of alternating injection. In this report, a cycle T_{cyc} was set to 30 ms.

direction from eight ports located at the vertical chamber. The distance between the end of the ICTP torch and the QG ports were 300 mm.

2.2. Calculation condition

For numerical simulation, the ICTP torch and a vertical reaction chamber were set as a calculation space. The ICTP inside the torch was calculated by solving mass, momentum and energy conservation equations as well as the Maxwell equation for vector potential in two-dimensional (2D) cylindrical coordinate under local thermodynamic equilibrium assumption for steady state. For a vertical reaction chamber, three dimensional (3D) thermofluid simulation was conducted to obtain gas flow and temperature fields with quenching gas (QG) injection in a transient state by solving time-dependent mass, momentum and energy conservation equation. In this 3D simulation, the 2D simulation results on the gas flow velocity and temperature distributions were used at the boundary between the ICTP torch and the vertical chamber as boundary condition. 2D simulation was made for the ICTP torch by our original hand-made program, while 3D simulation was conducted by COMSOL Multiphysics Ver.5.3.

Table 1 summarizes the calculation condition. The input power to the thermal plasma was fixed at 20 kW. The coil current is not amplitude-modulated. Argon sheath gas was supplied at gas flow rate of 90 L/min. Argon quenching gas was supplied at total gas flow rate of 50 L/min in time-averaged value. Figure 2 indicates the waveform of instantaneous gas flow rate in case of alternating QG injection. The waveform was set to sinusoidal one with a cycle T_{cys} of 30 ms. For comparison, calculation was also done for no QG injection and continuous QG injection. The QG conditions were listed in Table 2. For thermodynamic and transport properties of thermal plasma, those of 100%Ar was used at a pressure of 300 torr as a function of temperature under thermal equilibrium state.

2.3. Numerical simulation results on the temperature distribution

Figure 3 shows the temperature distribution with (a) No-QG and (b) continuous QG injection. As seen in Fig. 3(a), at the plasma inlet boundary z=0 mm, the temperature is about 8000 K around the axis from the 2D simulation. According to this 2D simulation result, the gas flow velocity reaches to 30 m/s at the plasma inlet boundary z=0 mm. From Fig. 3(a), the high temperature region above 5000 K was found to be expanded from the plasma inlet position z=0 mm to z=700 mm for QG condition. This is mainly

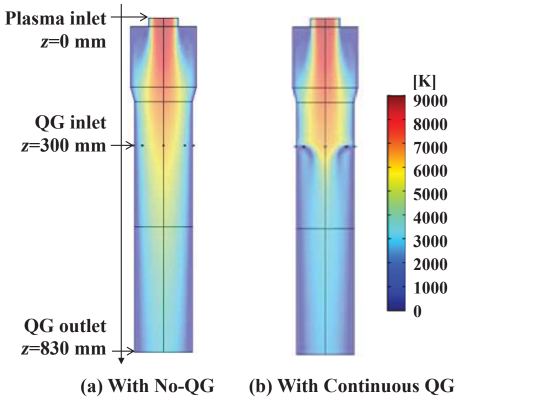

Fig. 3. Temperature distribution in the vertical chamber (a) with no quenching gas or (b) with continuous quenching gas injection.

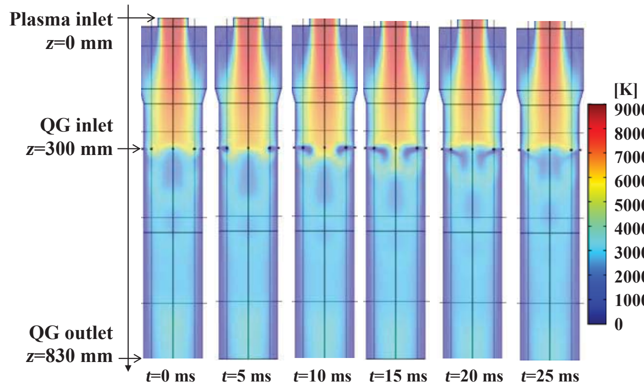

Fig. 4. Temperature distribution in the vertical chamber with alternating injection of quenching gas at a cycle of 30 ms.

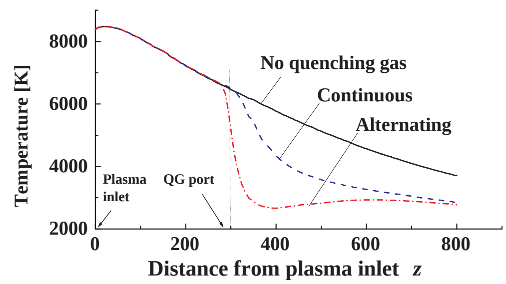

Fig. 5. Axial temperature distribution on the axis in the vertical chamber for different quenching gas injection.

because of the convection transport of the high temperature plasma by strong gas flow. With continuous QG injection as depicted in Fig. 3(b), the temperature near the chamber wall decreases in axial direction from the quenching gas port around z=300 mm to downstream. This indicates that cooling of thermal plasma jet by QG injection in radial direction. However, the temperature on the axis still have high temperature, and it is decreased gradually from 6800 K at z=300 mm to 4000 K at z=500 mm. On the other hand, Fig. 4 illustrates the time variation in the temperature distribution with alternating QG injection of T_{cyc}=30 ms from timing t=0 ms to t=25 ms. In this simulation, the flow rate of QG is 0 L/min at timing t=0 ms, while the QG flow rate reaches to 100 L/min at t=15 ms following a sinusoidal waveform. As seen, the QG flow rate increases with time from t=0 ms to 15 ms, leading to the penetration of QG more deeply into axial thermal plasma flow. As a result, the temperature even around the axis around z=300 mm decreases to lower value than 3000 K at t=20 ms. This penetrating QG injection effectively cools down the thermal plasma in the chamber. From this reason, the whole temperature below axial position z=300 mm in the chamber is decreased below the quenching gas ports.

Axial temperature distribution in time-averaged value can be seen for different QG conditions in Fig. 5 for comparison. From the chamber inlet z=0 mm to QG port z=300 mm, the temperature gradually decreased from 8200 K to 6800 K. From z=300 mm, the temperature keeps to decay gradually for condition of no QG condition. On the other hand, continuous QG injection was found to decrease the temperature rapidly from 6800 K to 4000 K up to axial position z=400 mm. Alternating QG injection furthermore declines the axial temperature in time-averaged value remarkably from 6800 K to 2500 K up to axial position z=400 mm. This suggests that alternating QG injection offers rapid temperature gradient of evaporated material for nanoparticle synthesis.

3. Experimentals for nanoparticle synthesis using alternating quenching gas injection

3.1. Experimental condition

Nanoparticle synthesis experiments were conducted using ICTP with continuous or alternating quenching gas (QG) injection. Table 3 shows the experimental condition. In this experiment, we synthesized Fe^{3+}-doped TiO_2 nanoparticles with $Ar+O_2$ sheath gas. The experimental condition was almost the same to the previous one expect QG condition. Three conditions for QG injection was set: (i) No QG, (ii) continuous QG and (iii) alternating QG injection conditions. To make alternating QG gas injection, an electromagnetic valve was installed between the QG port on the chamber wall and the gas supplying system. This electromagnetic valve can be opened and closed by a signal in a response time of 3 ms. The valve was controlled to be open for 15 ms and to be close for 15 ms with a duty factor of 50%.

3.2. Experimental results

Figure 6 represents (a) SEM images and (b) particle size distributions of synthesized nanoparticles for different conditions of QG injection. Panel (i) is a result for no QG, panel (ii) corresponds to a result for continuous QG injection, and panel (iii) indicates that for alternating QG injection. The particle size distributions were evaluated from

Table 3. Experimental condition

Input power	20 kW
Modulation	Non-modulation
Sheath gas	Ar: 90 L/min
	O_2: 10 L/min
Pressure	300 torr
Carrier gas	Ar 4 L/min
Feedstock	5wt%Fe+95wt%Ti
Feedstock feed rate	3.0 g/min
Feedstock feeding method	Continuous
Quenching gas (QG)	Ar: 50 L/min
	(Time-averaged value)
Duty factor for QG DF^{QG}_{valve}	50%
(open-time/ close time	15 ms / 15 ms)

400 particles randomly selected in several SEM images for each of conditions. From SEM images, synthesized particles under the three conditions were found to have all sphere shapes, indicating that nanoparticles were synthesized in gas phase. Among these conditions, no QG condition produces larger particles, which shows that particles grew up in gas phase in evaporated material in the thermal plasma. Thus, particles larger than 200 nm was obtained because the particles can be grown. From the SEM image in panel (ii), continuous QG injection can decrease the fraction of larger particles, and increase the percentage of smaller nanoparticles as presented in panel (ii). On the other hand, further smaller nanoparticles can be obtained in case of alternating QG injection apparently, having a mean diameter $\bar{d}$ of 71 nm. Figure 7 compares the mean particle diameter $\bar{d}$, the median diameter d_{50} and the standard deviation for $\bar{d}$ for different three QG conditions. This figure clearly shows that alternating QG injection produces smaller nanoparticles of $\bar{d}$=71 nm and d_{50}=65 nm. This may be attributable to the follwing facts: alternating QG injection has an instantaneous gas flow rate of 100 L/min in case of a time-averaged flow rate of 50 L/min. Therefore, the QG injection penerates thermal plasma more deeply, which results in more rapid cooling of evaporated material. This rapid cooling by deeper penetration of QG may provide smaller nanoparticles synthesized.

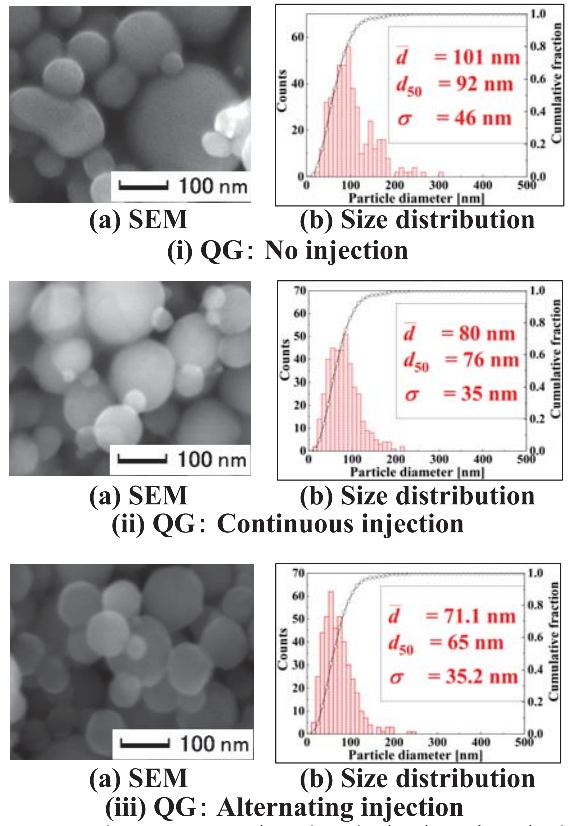

Fig. 6. SEM images and particle size distribution of synthesized particles for different conditions of quenching gas injection.

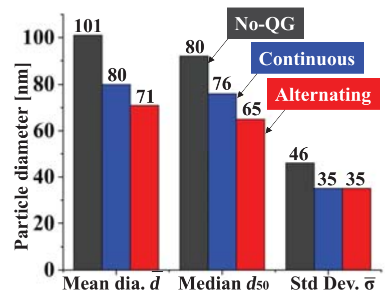

Fig. 7. Comparison in mean diameter and median diameter of synthesized particles for different conditions of quenching gas injection.

4. Conclusions

Alternating injection method of quenching gas was studied to control the cooling effect of thermal plasma for nanoparticle synthesis. First, three dimensional (3D) numerical simulation was conducted to obtain alternating effect of QG injection on the temperature fields. Results showed that alternating injection of quenching gas can penetrate thermal plasmas more deeply, which results in rapid cooling of the thermal plasma. Nanoparticle synthesis for Fe^{3+}-doped TiO_2 was tested with and without modulation of quenching gas. Results indicated that alternating QG injection condition provided smaller nanoparticles. This may be attributable to the more rapid cooling effect of evaporated material by more deep penetration of alternating QG compared to continuous QG injection. The alternating QG injection can be used combining PMITP+TCFF method for advanced nanoparticle synthesis.

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