24G14

TiO_2 and Ni Nanoparticle Synthesis using Pulse-Modulated Induction Thermal Plasmas
パルス変調誘導熱プラズマを用いた TiO_2 および Ni ナノ粒子生成

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Nanoparticles of titanium dioxide(TiO_2) and nickel(Ni) were synthesized by direct evaporation of titanium and nickel powders using Ar-O_2 or Ar-H_2pulse-modulated induction thermal plasma(PMITP). The PMITP has been developed to control temperature and gas flow fields of the thermal plasma in time domain. Effect of the pulse modulation was investigated on synthesized particles in terms of the mean particle diameter, the standard deviation, the morphology and the phase constituent. Fabricated particles were analyzed by FE-SEM, BET (Brunauer, Emmet and Teller's equation) and XRD.

1. Intorduction

Nowadays, various types of effective vapor-phase processing techniques are well known for nanoparticle syntheses [1]. The inductively coupled thermal plasma (ICTP) method is one of them to synthesize nanoparticles [2]. The ICTP method have great advantages for nanoparticle syntheses from their features of high enthalpy and radical density, and high temperature gradient. It is also characterized by little contamination because of no electrodes. These advantages allow highly-functional nanoparticles to be synthesized by direct evaporation of raw material powders. On the other hand, our group have developed a pulse modulated induction thermal plasma (PMITP) system, which is established by periodically modulated coil-current in a rectangular waveform [3]. Such a pulse modulation of the coil-current leads thermal plasmas to be under periodical transient states in milliseconds time scale. The rapid temperature variation in the PMITP can be expected to be utilized for effective nanoparticle synthesis.

In this study, the authors experimentally investigated the application of the PMITP to nanoparticle synthesis. The TiO_2 nanoparticles were selected as a target in this work because these materials are widely used as a photocatalyst for cleaning, water processing, etc. Additionally, we began to research Ni nanoparticles synthesis with the PMITP to study its usefulness for synthesis of different materials nanoparticles.

2. Experimental setup

2.1. *Experimental arrangements*

Fig.1 portrays the experimental arrangement used for this study. The plasma torch is configured identically to that used in our previous work [4]. Its details were described in our earlier papers. The plasma torch has two coaxial quartz tubes. The interior quartz tube has an inner diameter of 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 a water-cooled tube probe. The water-cooled tube probe was inserted from the top of the plasma torch head, as depicted in Fig.1. Downstream of the plasma torch, the water-cooled chambers were installed vertically and then horizontally, as depicted in Fig.1. The total length of the vertical chamber is 600 mm; its inner diameter is130 mm. Similarly, the total length of the horizontal chamber is 600 mm; its inner diameter is 130 mm. Further downstream of the horizontal chamber, a powder-collecting filter and the collecting chamber are set up. A vacuum pump is set up further downstream.

2.2. *Experimental conditions*

In TiO_2 nanoparticle synthesis, the total flow rate of Ar-O_2 sheath gas was fixed at 100.0 standard litres per minute (slpm). The O_2 gas admixture ratio to Ar was

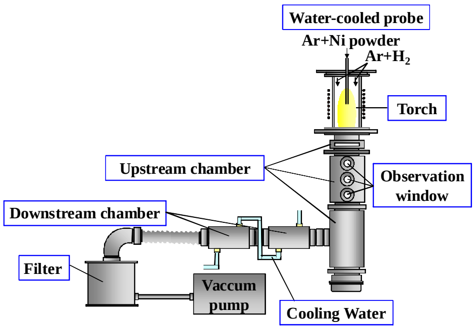

Fig. 1: Experimental setup for nanoparticle synthesis.

10% in the sheath gas in the gas flow rate. The gas flow rate of Ar carrier gas was 4 slpm. On the other hand, for Ni nanoparticle synthesis, the flow rate of Ar sheath gas was fixed at 90 slpm. The flow rate of H_2 sheath gas set up with 1, 2, 3, and 4 slpm. The gas flow rate of Ar carrier gas was 7 slpm. Ti or Ni powder with a mean diameter of 30 μm was used as raw material. The powder feed rate of these raw material was fixed around 3.0 to 4.0 g/min for both cases. The pressure inside the chamber was controlled to be fixed at 300 Torr (=40 kPa) with an automatic feedback controller. The time-averaged input power to the rf power supply was fixed at 20 kW. The PMITP was adopted for a reactive plasma field periodically disturbed by the modulated coil current. The on-time and the off-time for the modulated current were fixed respectively at 12 ms and 3 ms for the PMITP. The shimmer current level (SCL), which was defined as the ratio of the lower current level to the higher current level, was taken as a modulation parameter.

2.3. *TiO_2 nanoparticle synthesis with PMITP*

Fig. 2 presents the example of FE-SEM micrograph of synthesised TiO_2 nanoparticles. From the micrograph, the mean diameter $\bar{d}$ was subsequently estimated from observation of 200 randomly sampled particles. Such estimation was done for different modulation conditions. Fig. 3 shows the dependence of $\bar{d}$ on SCL and duty factor DF. As seen, $\bar{d}$ decreases with reducing SCL except for DF=60%, i.e. too small DF. In particular, around DF from 67% to 80%, $\bar{d}$ is declined by reducing SCL. The condition 80%DF-65%SCL provides the smaller nanoparticle synthesized in the present work. This result implies that the PMITP offers the effective rapid-cooling of evaporated material, which prevents a particle growing up.

2.4. *Ni nanoparticle synthesis with PMITP*

The Ar-H_2 PMITP was in trial used for Ni nanoparticle synthesis in this work. Fig. 4 presents the example of FE-SEM micrograph of synthesised Ni nanoparticles. These particles were collected in the upstream chamber wall. We can confirm that Ni nanoparticles

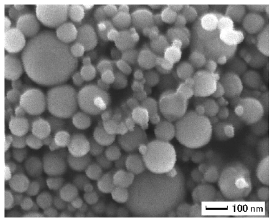

Fig. 2: SEM image of synthesized TiO_2 nanoparticles

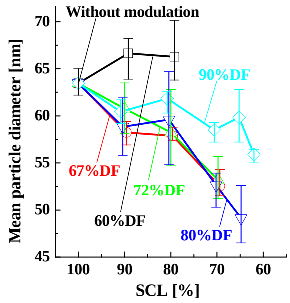

Fig. 3: Dependence of mean diameter of synthesized TiO_2 nanoparticles on SCL

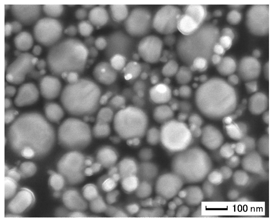

Fig. 4: SEM image of synthesized Ni nanoparticles

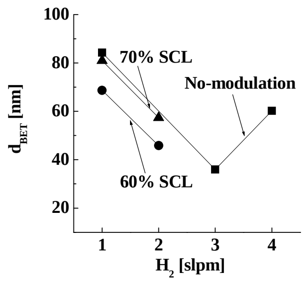

Fig. 5: Ni nanoparticles diameter estimeted by specific surface area

around 100 nm were synthesized in this case. The synthesized Ni nanoparticles were analyzed by BET method to measure specified surface area S_{BET}, and then mean particle diameter d_{BET}. Fig. 5 shows the dependence of d_{BET} on the H_2 gas flow rate, and also on the modulation condition with DF=80%. It was found from this figure that d_{BET} is decreased from 82 nm to 38 nm with H_2 gas flow rate from 1 to 3 slpm. Furthermore, the use of the PMITP decreases d_{BET} compared to the non-modulated plasmas. This means that the PMITP may provide a more rapid cooling effects also for Ni evaporated materials.

3. Conclusion

We have investigated the effects of use of the PMITP on nanoparticle synthesis. The TiO_2 and Ni nanoparticles were synthesized using the PMITP. Results showed that use of the pulse modulation provides smaller nanoparticles synthesized for both cases.

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