Development of large-scale nanopowder synthesis method using modulated inductively coupled thermal plasma and visualization of reaction fields in the torch

DOCTORAL THESIS

DEVELOPMENT OF
LARGE-SCALE NANOPOWDER SYNTHESIS METHOD USING
MODULATED INDUCTIVELY COUPLED THERMAL PLASMA AND
VISUALIZATION OF REACTION FIELD IN THE TORCH

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Abstract

The method for large-scale synthesis of Al^{3+}-doped TiO_2 nanopowder was developed using pulse-modulated induction thermal plasma with time-controlled feedstock feeding method (PMITP+TCFF method). In this method, feedstock was synchronously and intermittently injected into the PMITP torch with coil-current modulation. As a result, Al^{3+}-doped TiO_2 was successfully synthesized with the production rate of about 400 g/h at the input power of 20 kW. In addition, mean particle diameter was also successfully controlled by coil-current modulation.

Furthermore, two-dimensional optical emission spectroscopy (2D-OES) was carried out to investigate spatiotemporal distribution of Ti and TiO vapor during TiO_2 nanopowder synthesis using conventional ICTP or PMITP+TCFF method. In addition, spatiotemporal distribution of Ti excitation temperature ($T_{\mathrm{ex}}^{\mathrm{Ti}}$) was also estimated from 2D-OES results. Investigation results suggest that injected Ti feedstock was evaporated to form high concentration of Ti vapor at on- and off-axis region, while TiO vapor was almost simultaneously generated around low-temperature on-axis region. In addition, it was also confirmed that PMITP+TCFF method is effective for efficient feedstock evaporation and precursor TiO formation.

Furthermore, Ti vapor admixture ratio (X_{Ti}) was also estimated with $T_{\mathrm{ex}}^{\mathrm{Ti}}$ during Ti nanopowder synthesis to investigate Ti vapor admixing effect on plasma temperature. The X_{Ti} was estimated from 2D-OES results and calculated emission coefficients. These estimation results revealed much higher X_{Ti} and temperature at off-axis region compared with that at on-axis region.

Chapter 1

Abstract of each chapters

1.1 Large-scale synthesis of Al^{3+}doped TiO_2 nanopowder

A new and original nanopowder synthesis method was developed for large-scale Al^{3+} doped TiO_2 nanopowder synthesis using pulse-modulated induction thermal plasma (PMITP) with time-controlled feedstock feeding (TCFF) method. In this method, the feedstock was injected into the torch intermittently and synchronously with coil-current modulation of PMITP as shown in Fig. 1.1. The PMITP and synchronized feedstock injection enables heavy-load feeding of feedstock powder and their complete evaporation. Synthesized nanopowder was analyzed using different methods including FE-SEM, XRD, BF-TEM with TEM/EDX mapping. XPS and spectrophotometry. Results showed that Al^{3+} element was doped in TiO_2 structure. In addition, particle diameter of synthesized nanopowder was varied depend on shimmer current level of modulated coil current as shown in Fig. 1.2. The production rate of Al^{3+} doped TiO_2 nanopowder was estimated to be about 400 g h^{-1}. This production rate is 10 to 20 times higher production rate compared with conventional non-modulated ICTP method.

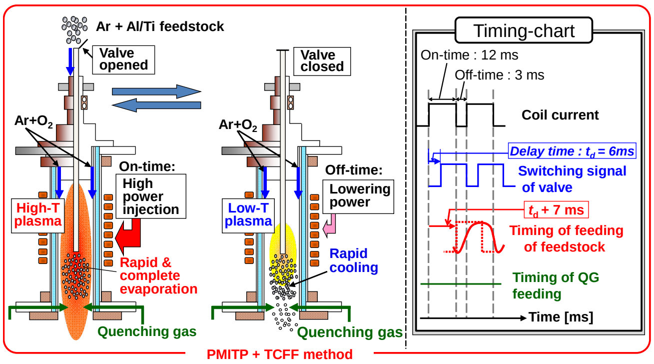

Fig. 1.1: Methodology of PMITP+TCFF method

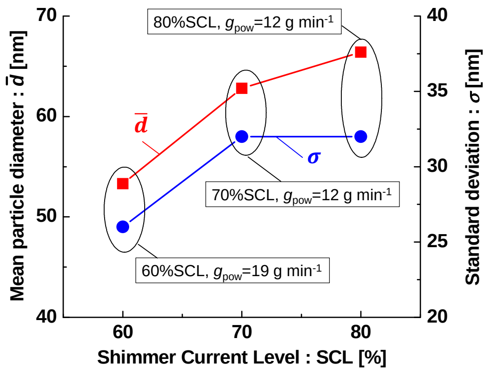

Fig. 1.2: The SCL dependence of mean particle size

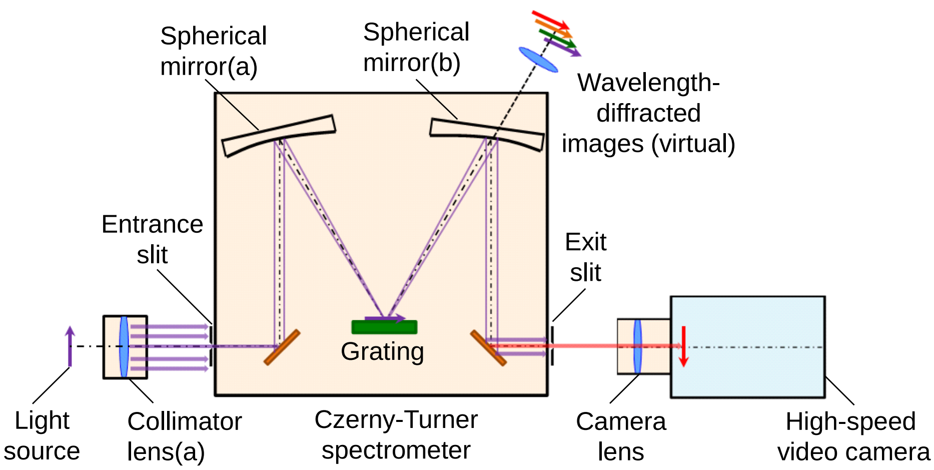

Fig. 1.3: Principle of 2D OES system.

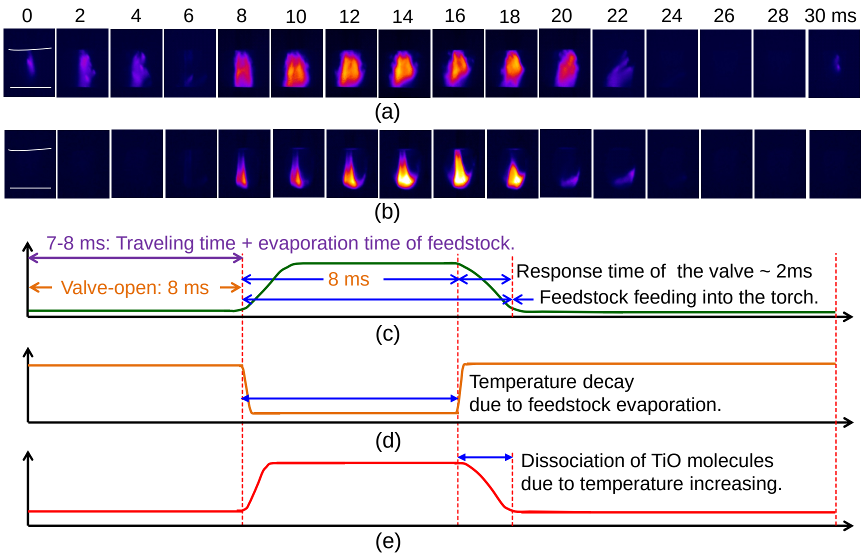

Fig. 1.4: 2D OES result during single shot Ti feedstock injection into ICTP. (a) Ti I@453.32 nm, (b) TiO@621.00 nm, (c) actual timing of feedstock injection into the ICTP torch, (d) change in temperature due to feedstock injection, and (e) change in TiO molecular density.

1.2 Fundamental investigation of Ti feedstock evaporation in the ICTP torch

Two-dimensional optical emission spectroscopy (2D OES) measurements were conducted for an ICTP torch during TiO_2 nanopowder synthesis. The single powder injection was performed into the Ar-O_2 non-modulated ICTP torch to fundamentally investigate the Ti feedstock evaporation and precursor TiO formation processes. Spatiotemporal distribution of Ti I and TiO radiation intensities were simultaneously observed inside the plasma torch using developed 2D OES system shown in Fig. 1.3. The observation results showed that the injected Ti feedstock was evaporated to form high density Ti atomic vapor in the ICTP torch. The generated Ti vapor is transported and diffused by gas flow and density gradient. In addition, TiO molecular vapor was generated almost simultaneously with Ti evaporation around only on-axis region in the ICTP torch. In this experiment, low temperature Ar carrier gas was injected with Ti feedstock into the torch. Consequently, on-axis temperature may cooled down by carrier gas injection and energy consumption due to feedstock evaporation. TiO molecules were formed inside this cooled down region as shown in Fig. 1.4.

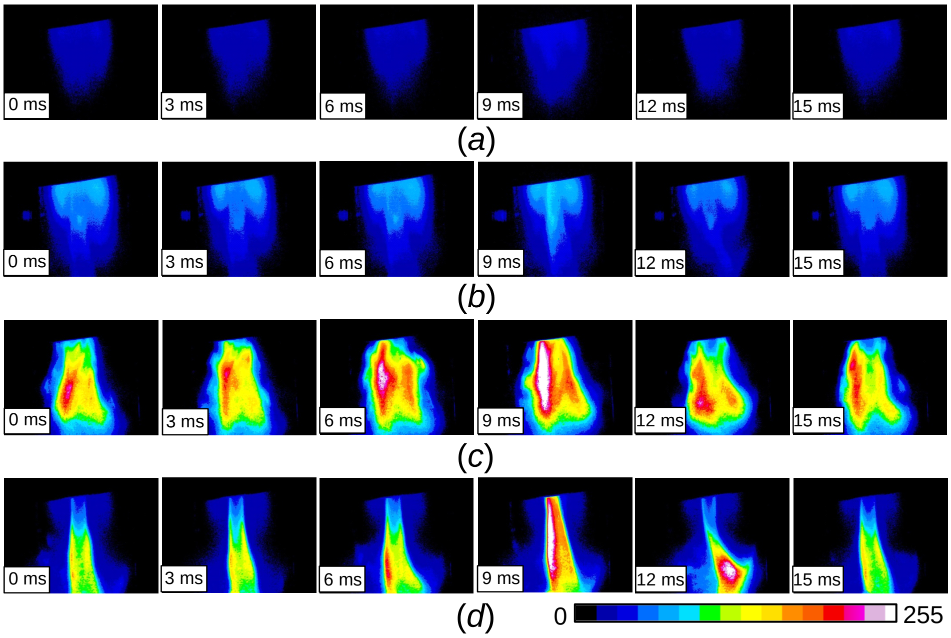

Fig. 1.5: Two-dimensional distribution of radiation intensities during TiO_2 nanopowder synthesis using PMITP+TCFF method. (a) Ar I@811.53 nm, (b) O I@777.54 nm, (c) Ti I@453.32 nm, and (d) TiO@615.91 nm.

1.3 Effect of coil-current modulation on feedstock evaporation and precursor TiO formation

Effect of coil-current modulation on Ti feedstock evaporation and precursor TiO formation were fundamentally investigated from 2D OES measurement results during TiO_2 nanopowder synthesis using conventional ICTP method or PMITP+TCFF method. In addition, an interpretation was suggested from the 2-D OES results for Ti feedstock evaporation and TiO formation in nanoparticle synthesis using a PMITP+TCFF method. As a observation result, high Ti I radiation intensity was detected at on-time, while high TiO radiation intensity was detected at off-time during nanopowder synthesis using PMITP+TCFF method as shown in Fig. 1.5. Results showed that coil-current modulation and intermittent feedstock injection may enable efficient feedstock injection and precursor TiO formation in the PMITP torch.

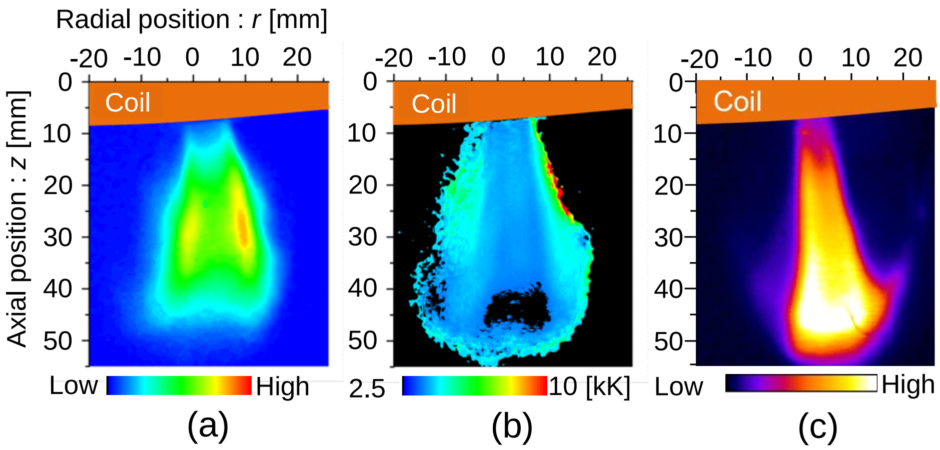

Fig. 1.6: Spatial distribution of Ti excitation temperature with TiO molecular spectra. (a) Ti I@453.32 nm, (b) Ti excitation temperature, and (c) TiO radiation intensity.

1.4 Spatial estimation of Ti excitation temperature in the ICTP

Spatiotemporal distribution of Ti excitation temperature ($T_{\mathrm{ex}}^{\mathrm{Ti}}$) was determined from 2-D OES during TiO_2 nanopowder synthesis using conventional ICTP torch with single-feedstock injection. The temperature is one of the fundamental information to discuss feedstock evaporation and nucleation of nanoparticle. The spectroscopic observation results revealed that $T_{\mathrm{ex}}^{\mathrm{Ti}}$ was estimated as 2500–4000 K around the central axis of the ICTP torch, and as more than 4500 K in the off-axis region. In the on-axis region, TiO was detected with high radiation intensity in the lower temperature region. These results showed that TiO molecules are formed only in low temperature region around the central axis of the ICTP torch. In addition, TiO molecular density could be high especially in downstream region at central axis of the ICTP torch. Based on estimated temperature, nucleation possibility was also investigated from determination result of saturation vapor pressure of TiO_2 vapor. As a result, TiO_2 nuclei can be formed inside the ICTP torch during nanopowder synthesis using ICTP with single feedstock injection.

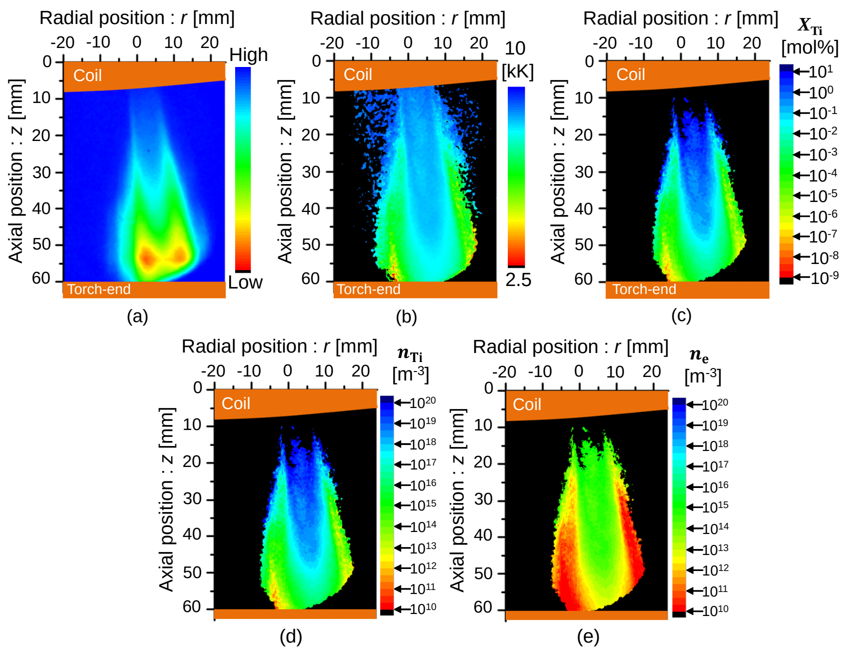

Fig. 1.7: 2D OES result for (a) Ti I@453.32 nm and spatial estimation results of (b) Ti excitation temperature, (c) Ti vapor admixture ratio, (d) Ti number density and (e) electron density.

1.5 Spatial estimation of Ti vapor admixture ratio

The spatial distribution of the Ti vapor admixture ratio (X_{Ti}) was determined together with $T_{\mathrm{ex}}^{\mathrm{Ti}}$ from 2-D OES during Ti feedstock injection into the Ar ICTP torch for Ti nanopowder synthesis. The X_{Ti} is one important parameter affecting ICTP properties such as its electrical conductivity. The value of X_{Ti} was estimated from the radiation intensity ratio of the Ar atomic line to the Ti atomic line, and $T_{\mathrm{ex}}^{\mathrm{Ti}}$ obtained from 2D OES observation. Furthermore the neutral Ti atomic density (n_{Ti}) and electron density (n_{e}) were also determined from the estimated results of $T_{\mathrm{ex}}^{\mathrm{Ti}}$ and X_{Ti} through the equilibrium composition. Fig. **??** illustrates estimation results of $T_{\mathrm{ex}}^{\mathrm{Ti}}$, X_{Ti}, n_{Ti}, and n_{e}, respectively. These 2D OES results revealed $T_{\mathrm{ex}}^{\mathrm{Ti}}$ as 2500–4000 K at around the central axis of the ICTP torch, although it was higher than 4000 K in the off-axis region. In the off-axis region, X_{Ti}, n_{Ti} and n_{e} were estimated much higher than in the on-axis region. These estimated results indicate that injected Ti feedstock was efficiently evaporated at high temperature off-axis region, and then off-axis high temperature was maintained due to joule heating.

1.6 Conclusions

In summary, large amount of Al^{3+} ion doped TiO_2 nanopowder was successfully synthesized using pulse-modulated induction thermal plasma with time-controlled feedstock feeding method. In addition, feedstock evaporation and precursor processes were investigated from spatiotemporal distribution of Ti and TiO radiation intensities obtained from 2D OES measurement during TiO_2 nanopowder synthesis. As a result, injected Ti feedstock was injected in the plasma to form high density Ti vapor in the torch. TiO molecular vapor was simultaneously formed with Ti feedstock evaporation in the torch due to temperature decay caused by feedstock evaporation and low temperature Ar carrier gas injection. Coil-current modulation and intermittent feedstock injection are very effective for high efficiency Ti feedstock evaporation and precursor TiO formation. From the 2D OES measurement during Ti nanopowder synthesis using Ar ICTP torch, spatial distribution of Ti vapor admixture ratio and particle number densities were successfully estimated. As a result, Ti vapor admixture ratio was successfully estimated to higher at off-axis region with high temperature and high electron density.

平成３０年　１月３１日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Development of large-scale nanopowder synthesis method using inductively coupled thermal plasma and visualization of reaction field in the torch

変調型

（誘導熱プラズマを用いたナノ粒子の大量生成法の開発とトーチ内反応場の可視化）

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３．審査結果の要旨（600～650 字）

平成 30 年 1 月 31 日に第 1 回学位論文審査委員会，同日に口頭発表，第 2 回審査委員会を開催し，慎重審議の結果，以下のとおり判定した。なお，口頭発表における質疑を最終試験に代えるものとした。

本論文は，ガス温度が 10000K に達する「誘導熱プラズマ」を用いて，ナノ粒子の大量生成法「PMITP+TCFF 法」を考案し，金属ドープ酸化物ナノ粒子の大量生成に適用したものである。さらにナノ粒子生成中の原料粉体の蒸発過程の一端を分光学的に解明している。従来の誘導熱プラズマを用いたナノ粒子生成法では，熱プラズマへの入力電力を一定定常とし，原料も連続投入していた。一方，本論文で用いる「PMITP+TCFF 法」は当該研究室の開発手法であり，熱プラズマへの入力電力を制御して大きく周期変動させ (PMITP 法)，さらにこの入力電力が大きい時刻にのみ原料粉体を導入するのが時間制御型原料投入法（TCFF 法）である。この PMITP＋TCFF 法により，入力電力が大きい時刻で原料を効率的に蒸発・原子化し，入力電力が小さい時刻で熱プラズマ温度を急激に低下させることで，蒸発原料が過飽和状態を経由して核生成することで，効率的にナノ粒子が生成される。本論文ではこの「PMITP+TCFF 法」を，Al^{3+}-doped TiO_2 ナノ粒子生成に適用し，それが 400 g/h の極めて高生成レートで生成できることを明らかにした。さらに二次元分光手法を用いてこの原料の蒸発過程における温度分布，原料蒸気の混合輸送状態を明らかにし，本 PMITP+TCFF 法の優秀さの一端を示した。

以上，本研究は新規の誘導熱プラズマによるナノ粒子生成の開発とその物理プロセス解明に対して大きく貢献するものであり，本論文は，博士（工学）に値すると判定した。

４．審査結果　(1) 判　定（いずれかに○印）　○合　格　・　不合格

(2) 授与学位　博　士（工学）