Spectroscopic study on evaporation of Ti feedstock intermittently supplied and formation of precursor TiO in TiO2 nanopowder synthesis in the induction thermal plasma torch

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Abstract: The two-dimensional spectroscopic observation was carried out for the induction thermal plasma torch for the TiO2 nanopowder synthesis. The Ti solid powder feedstock is intermittently supplied for fundamental study on its evaporation process and formation of precursor molecules. As a result, we found the evaporation of Ti feedstock, efficient formation of TiO molecules and its convective transport to the downstream around central axis in the torch.

Keywords: thermal plasma, nanoparticle, nanopowder, TiO2, titanium dioxide

1. Introduction

Nanoparticles/nanopowders are expected as promising next generation materials used in various kind of field such as electronics, energy, environmental and biomedical field. For example, titanium dioxide (TiO2) nanopowder is used as photocatalyst material, photonic crystals, photovoltaic cells, and pigment. However, TiO2 works as photocatalyst only under ultraviolet light because of its wide energy band gap. Attention has thus been received to metallic-ion doped TiO2 nanopowder. Metallic-ion doped TiO2 nanopowder works as photocatalyst under visible light because the impurity energy levels can improve band gap. Another application of metallic-ion doped TiO2 nanopowder is in biomedical field. It has been reported that Al-doped TiO2 nanopowder has an inflammatory protein adsorption ability effective to skincare for atopic dermatitis. These applications require pure nanoparticles with no contamination because that contamination may influence human body and it also may change the characteristics of nanoparticles.

Various kinds of nanopowder synthesis method have been developed so far. Among them, the inductively-coupled thermal plasma (ICTP) method provides several important advantages for nanopowder synthesis. For example, it can provide high temperature and chemical activity fields, and thus one step process with short processing time. The most important feature of this method is that it can offer no contamination reaction field, which provide nanopowder with high purity. However, the conventional ICP method also has some disadvantages such as the difficulty in controlling the synthesized particle size, and the scale-up of the process for high production rate of nanopowder synthesis.

In order to improve these issues, the authors have developed a new nanopowder synthesis method using pulse-modulated induction thermal plasmas (PMITP) with time-controlled feedstock feeding (TCFF). The PMITP was developed in our group to control the temperature and chemical activity field in the thermal plasma by coil current modulation. In addition to this, our group developed a method for feedstock feeding, in which feedstock is intermittently and synchronously injected into the PMITP torch. We have adopted this PMITP-TCFF method to Al-doped TiO2 nanopowder synthesis with high production rate. Results showed that this method using 20 kW PMITP supported an extremely high production rate of about 400 g/h with a mean particle diameter of about 67 nm [1].

The developed PMITP-TCFF method for nanopowder synthesis with high production rate has several key points: one of them is efficient evaporation of solid feedstock, the other is efficient formation of molecules and precursor in gas phase before nucleation. This paper studies Ti feedstock evaporation and TiO molecules formation in the ICTP method. Non-modulated ICTP was used but solid Ti feedstock powder is intermittently supplied with a cycle of 30 ms to the ICTP torch. The two-dimensional spectroscopic observation was carried out using the image-spectrometer and highspeed video camera. The temporal and spatial variations were observed in radiation intensities from Ti spectral line and TiO molecular spectra. This could be used to discussion on the feedstock evaporation and precursor formation process.

2. Methodology of PMITP-TCFF method

Fig. 1 illustrates the methodology of PMITP-TCFF method we developed. Modulated coil current for PMITP has higher current level (HCL) during on-time, and lower current level (LCL) during off time. The PMITP can repetitively produce higher temperature and high chemical activity fields during on-time, and a lower temperature field during off-time. Feedstock was injected...
into the PMITP torch intermittently with a high-speed solenoid valve. The high-speed valve has an inherent response time of 2 ms to open and close. The feedstock injection to the PMITP is synchronized with the coil current modulation by controlling a valve open/close signal. The injected feedstock to the PMITP was effectively and completely evaporated due to high temperature field during on-time. Injection of feedstock is stopped during off-time by closing the solenoid valve. During off-time, the evaporated feedstock material is cooled down rapidly because of lower temperature field. This rapid cooling promotes formation of TiO molecule from a mixture of Ti vapor and O atoms. TiO₂ nanoparticle nucleation arises from condensation of TiO molecules and reaction of O atoms. After that, TiO₂ nanoparticle with a diameter of 50 nm grows due to condensation and agglomeration of TiO₂ clusters.

3. Particle composition in Ar-O-Ti gas phase system

It is important to understand dominant species in wide temperature range 3000 - 15000 K to study the evaporation of Ti in Ar-O₂ thermal plasma. From this reason, the equilibrium compositions of Ar-O-Ti system in gas phase were calculated by minimization of Gibbs’ free energy to consider the molecules formation in gas phase. Considering the isothermal and isobaric process, Gibbs’ free energy is shown as follow equation:

$$ G = \sum_{i=1}^{N} n_i \left( \mu_i^0 + RT \ln \frac{n_i}{\sum_{j=1}^{N} n_j} \right) + RT \ln \left( \frac{P}{P_0} \right) $$

(1)

$$ \mu_i^0 = -RT \ln \left( \frac{Z^{\nu,i}_i - Z^{\mu,i}_i}{Z^{\nu,i}_i + \epsilon_i^0} \right) $$

(2)

$$ Z^{\nu,i}_i = \frac{RT}{P_0} \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} $$

(3)

where $G$ is Gibbs’ free energy, $n_i$ is particle number density, $N$ is total number in the mixture gas, $T$ is the temperature, $P$ is the pressure, $R$ is the gas constant, $\mu_i^0$ is the chemical potential, $Z^{\nu,i}_i$ and $Z^{\mu,i}_i$ are partition function for translational motion and internal state, $P_0$ is standard atmosphere, $\epsilon_i^0$ is standard enthalpy of formation, $k$ is Boltzmann’s constant, and $h$ is Planck constant.

The calculated result for 89%Ar - 10%O - 1%Ti system in gas phase at 300 Torr is drawn in Fig. 2. In temperature range of over 15000 K, all the particles are ionized. From 15000 to 10000 K, atomic species Ar and O are formed from their ions. The recombination of Ti+ and electron to form Ti atom from 8000 to 5000 K. In temperature range of 10000 – 4000 K, Ar, O and Ti are dominant. A further decrease in temperature from 6000 to 3000 K produce TiO(g). On the other hand, TiO₂(g) and O₂ are formed with decreasing temperature from 3000 K.

4. Experimental

4.1. Experimental conditions for non-modulated induction plasma with intermittent feedstock feeding

This work adopted a non-modulated ICTP from the reason of fundamental study. On the other hand, the powder feedstock was intermittently supplied. TiO₂ nanopowder synthesis conditions were summarized in Table 1. Time-averaged input power was fixed at 20 kW. Sheath gas was a mixture of 90 mol% of Ar and 10 mol% of O₂, and its flow rate was set at 100 L/min. Pressure in the plasma torch was controlled at 300 Torr. Quenching gas was not injected because this study is a fundamental investigation on evaporation of Ti feedstock and formation of TiO molecules. From the same reason, the coil current was not modulated, which leads to the ICTP in steady state. Micro-size Ti powder with a mean diameter of 27 µm was used as feedstock. The feedstock feed rate was set to 4 - 7 g/min. This feed rate is lower than that of 12 g/min for our large-amount synthesis condition [1]. The open/close cycle of the solenoid valve was set at 30 ms, and the open-time and close-time of the valve were 6 ms and 24 ms, respectively. This valve open-time of 6 ms is shorter than that in our previous work. This is because to prevent from interaction between each single powder feeding in intermittent feeding.
4.2. Spectroscopic observation conditions

To study evaporation of Ti feedstock and formation of molecules in the plasma torch, spectroscopic observation was carried out from the plasma (Table 2). The left panel in Fig. 3 shows observation region. The observation region was set to $57 \times 52$ mm$^2$ region below the coil end. The light from the observation region is transmitted through a camera lens, and then it is separated into two optical paths with a beam splitter. The two split light are measured simultaneously with two imaging spectroscopic systems (System A and System B) having imaging spectrometers with high-speed video cameras. The imaging spectrometer has a diffraction grating of 1200 grooves/mm. The wavelength resolutions of the two system were 0.8 nm for Sys.A and 0.4 nm for Sys.B, respectively. Each of the systems measures a two-dimensional image at a specified wavelength. The right panel in Fig. 3 indicates an example of observed images using the two imaging systems (Sys.A and Sys.B). The focused image with Sys.A is smaller than that with Sys.B because the two system has different optical path lengths. If the specified wavelength is 453 nm, we can measure an image of Ti I spectral line from the plasma. TiO molecular spectra can be measured with the specified wavelength of 621 nm.

![Fig. 3. Spectroscopic observation region and example for observed radiation intensities.](image-url)

5. Results and discussion for non-modulated induction plasma with intermittent feedstock feeding

5.1. Two-dimensional distribution of radiation intensities

Fig. 4 illustrates variations in the two-dimensional distribution of radiation intensities for (a) Ti I from evaporated Ti feedstock and (b) TiO from by chemical reaction of Ti and O. In this figure, open/close signal of the solenoid valve for powder feeding was also denoted as (c). The signal of the solenoid valve is in high level to

![Fig. 4. Time variation in two-dimensional distribution of radiation intensities. (a) Ti I: 453.32 nm observed with Sys.B; (b) TiO: 621 nm observed with Sys.B; and (c) open/close signal for solenoid valve.](image-url)
open the valve at \( t = 0 \) ms, and it is in low level to close the valve at \( t = 6 \) ms. In panel (a) and (b), Ti I and TiO spectral intensities were low enough undetectable just after the solenoid valve for powder feeding was opened around \( t = 0 - 2 \) ms. On the other hand, strong Ti I radiation intensity was measured from \( t = 8 \) ms. This indicates that it needs time about 8 ms to open the valve from the timing of the opening signal received, to transport the Ti feedstock actually from the solenoid valve inlet to the outlet of the feeding tube, and then for the feedstock to begin its evaporation. The figure also implies that Ti feedstock evaporation occurred in millisecond time scale. Furthermore, this strong Ti I radiation intensity continues to be detected in longer time scale of \( t = 8 - 20 \) ms than the valve open time of 6 ms. This result implies that Ti feedstock feeding continues after solenoid valve received close-signal. In addition, Ti I radiation intensity was observed not only on the axis but also around off-axis region. This is attributed to Ti atoms from Ti solid particles injected in off-axis in the plasma, and also Ti atoms diffused in the radial direction by high gradient of Ti density. According to Fig. 2, Ti atom is present in temperature range of 4500 - 6000 K. Thus, the high intensity region of Ti atom may have this temperature range of 4500 - 6000 K with high Ti atomic density. Furthermore, the presence of high density Ti atom produces high intensity region of Ti in the thermal plasma. That region could have an enhanced electrical conductivity around the center axis to receive joule heating from electromagnetic field. This may also increase the temperature, and then Ti radiation intensity.

On the other hand, TiO radiation intensity was detected only around the central axis region in the plasma torch from \( t = 10 \) ms to 18 ms. This clearly indicates that TiO molecules are formed around the central axis in the plasma torch by mixing evaporated Ti atom and O atom in gas phase. The radial transport flux of TiO do not seems as high as that of Ti atom. In addition, TiO molecules were transported to downstream by the carrier gas flow convection from the powder feeding tube. According to Fig. 2, TiO is formed in temperature range of 3500 - 4500 K. Thus, the high intensity region of TiO may have this temperature range of 3500 - 4500 K with high TiO density present on the axis.

### 5.2. Temporal variation in radiation intensities below the coil end

Fig. 5 shows the temporal variation in the radiation intensities of Ti I and TiO observed at \( z = 5 \) mm, 10 mm and 20 mm below the coil end on the central axis of the plasma torch. Here the axial position \( z = 0 \) mm corresponds to the coil end position. Panel (a) is the time variation in Ti I radiation intensity and panel (b) depicts that in TiO radiation intensity. The open/close signal for the solenoid valve was specified in panel (b) as a green solid line. According to another consideration, Ti solid powder is actually injected from \( t = 7 \) ms to 15 ms.

![Fig. 5. Two-dimensional distribution of radiation intensities.](image)

- (a) Ti I: 453.32 nm observed at Sys.B; (b) TiO: 621 nm observed at Sys.B.

Ti I radiation intensity becomes high from \( t = 7 \) ms as described in the previous section, as seen in panel (a). Generally speaking, the radiation intensity of Ti I strongly depends on Ti atomic density and the excitation temperature. Injection of cold solid powder decreases the plasma temperature but increases evaporated Ti atomic density from evaporation. Thus, this measured increase in Ti I intensity results from the Ti atomic density increase. From an axial position of \( z = 5 \) mm to \( z = 20 \) mm, detectable timing of Ti I is almost the same. The Ti intensity gradually increases with time from \( t = 7 \) ms to 15 ms because of an Ti atomic density increase by Ti feedstock evaporation. This means that Ti solid feedstock is gradually heated and evaporated during their traveling in the plasma to downstream. From \( t = 15 \) ms, the Ti I radiation intensity decreases with time rapidly. This may be due to the fact that the Ti powder feeding is stopped to decrease Ti atomic density. The Ti I is detected up to around \( t = 23 \) ms, implying that Ti feedstock continues to injection until \( t = 23 \) ms.

On the other hand, TiO radiation intensity was detected around \( t = 7 \) ms, similarly to Ti I. This suggests that TiO molecules was formed rapidly just after Ti feedstock was evaporated. TiO radiation intensity was significantly decreased between \( t = 15 \) ms and 18 ms. Furthermore, TiO was not detected in spite of Ti I was detected after \( t = 18 \) ms. This result means that the gas temperature in the torch increased after the feedstock feeding was finished at \( t = 15 \) ms. TiO molecules were dissociated due to this increased temperature, and density of TiO molecule was decayed.

### 5.3. Conclusion

The two-dimensional spectroscopic observation was carried out from the specified spectra from the ICTP torch with intermittent feedstock feeding using two imaging spectrometry systems. The spatial and temporal variation in the radiation intensity of Ti I atomic spectral line and that of TiO molecule were measured simultaneously in the plasma torch. The observation results provides spatial and temporal information of Ti feedstock evaporation,
TiO molecules formation, and their transport to downstream in the torch.

6. References