

TiO₂ Nanoparticle Production with Flame Synthesis Method by using Flash Boiling Spray - Relation between Injection Conditions and Nanoparticle Physical Properties -

M. Oshima^{*1}, M. Matsushita², H. Miyamoto², D. Fukushima², J. Senda³, K. Ishida⁴

1: Fukui University of Technology, 3-6-1, Gakuen, Fukui city 910-8505, Japan

2: Doshisha University Graduate School, 1-3, Miyakodani, Tatara, Kyotanabe city 610-0321, Japan

3: Doshisha University, 1-3, Miyakodani, Tatara, Kyotanabe city 610-0321, Japan

4: HORIBA, Ltd., 2 Miyano Higashi, Kissyoin, Minami-ku, Kyoto city 601-8510, Japan
m-oshima@fukui-ut.ac.jp, dtl0354@mail4.doshisha.ac.jp, dtk0337@mail4.doshisha.ac.jp,
jsenda@mail.doshisha.ac.jp and kozo.ishida@horiba.com

Abstract

The authors proposed a novel nano-sized particle production system called the Flashing Spray Flame Nanoparticle Synthesis Method, which uses flash boiling spray. In this method, the solution is directly injected into the low pressure ambient from the injector, which is installed in the bottom of the chamber. In addition, the injected solution rapidly evaporates and forms a homogeneous vapour through flash boiling. However, the vapour pressure of the precursors for TiO₂, ZnO₂ nanoparticles, and others is very low. In this study, the high boiling point precursor and low boiling point organic solvent mixed solution are used to improve the vaporization characteristics of the precursor. The nanoparticles are created from the homogeneous vapour by using the flame thermal energy from a burner flame. We investigated the relation between the TiO₂ nanoparticle physical properties and the injection frequency for this paper. Tetraisopropoxytitanium was used as the precursor and isopropyl alcohol and cyclohexane were used as the low boiling point organic solvent. The TiO₂ nanoparticle was created by using the mixed solutions in the system. The TiO₂ nanoparticles were also investigated using a particle size distribution analyzer (PSD), SEM, and XRD. As a result, the anatase TiO₂ particle agglomerated when increasing the injection frequency because the vapor concentration increased when the injection frequency was increased.

Introduction

TiO₂ nanoparticles are used in electronic devices, optical devices, cosmetics, chemicals, and ceramics [1]. The diameter of the particles is decreasing from the micron order to lower than 100 nm for energy saving reasons. TiO₂ particles are produced by using the liquid phase method or a vapor phase method such as plasma CVD and the sol-gel method [2], [3]. The production of these nanoparticles using flame combustion energy (flame synthesis) is generally used in the liquid and vapor phase methods. The flame synthesis is the most important particle production method because it has advantages such as simplicity, continuous production, and ease of temperature control [4], [5]. However, the diameter of a particle depends on the liquid diameter in the liquid phase method, such as in the sol-gel method. In addition, it is difficult to control the chemical composition because decomposition temperatures often differ in the vapor phase when producing multi component particles.

The authors propose a novel nanoparticle production method in this study that contains a flame synthesis that uses flashing spray. In the previous study, homogeneous SiO₂, Nb₂O₅, and HfO₂ films were formed on an 8-inch (200 mm) wafer by using a Flashing Spray CVD (FS-CVD) method [6]. The novel nanoparticle production method applies the FS-CVD method to the flame synthesis. Figure 1 shows a schematic image of the nanoparticle production with flame synthesis when using flash boiling spray. The solution is directly supplied to the low pressure ambient in the chamber through the injector, which is set at the bottom of the chamber as an intermittent spray. The injected solution evaporates and forms a homogeneous vapor through flash boiling. The nanoparticles are produced from the homogeneous vapor at the flame combustion temperature. We propose using the precursor and the low boiling point organic solvent mixed solution to improve the characteristics of the precursor when the high boiling point precursor is used.

The TiO₂ nanoparticle was produced by using this method for this paper. In addition, we investigated the relation between the injection frequency and the physical properties. Tetraisopropoxytitanium is used as the precursor and cyclohexane and isopropylalcohol are used as the organic solvent, respectively. We researched the TiO₂ nanoparticles by using SEM, XRD, and a particle distribution analyzer. As a result, it is expected to create

* Corresponding author: m-oshima@fukui-ut.ac.jp

any nanoparticle diameter and any crystal structure by controlling the injection frequency. The particle diameter distribution has two peaks at 0.1µm and 2µm. Furthermore, the mass fraction of anatase phase is increased by increasing the injection frequency.

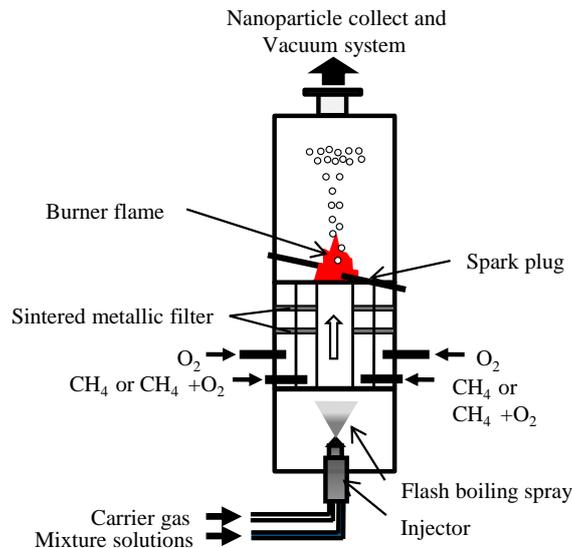


Figure 1 Schematic image of nanoparticle production with flame synthesis by using flash boiling spray

Characteristics of Nanoparticle Production using Flame Synthesis Method Intermittent Supply of Precursor by Using Injector

The precursor is directly intermittently sprayed into the chamber. The diameter and composition can be controlled by changing the injection quantities and injection frequency. The composite nanoparticle can also be formed based on the injection position.

Evaporation of Precursor by Flash Boiling

Figure 2 is a schematic image of the flash boiling on a pressure-temperature diagram. When the pressure of the solution reaches the vapour pressure of the solution temperature, flash boiling occurs. The spray angle remarkably increases and rapidly forms vapour when increasing the pressure between the vapour and the ambient pressures ΔP_v [7]. The use of flash boiling spray forms a more homogeneous vapour than without using flash boiling spray. As a result, we promptly create vaporization when using flashing spray.

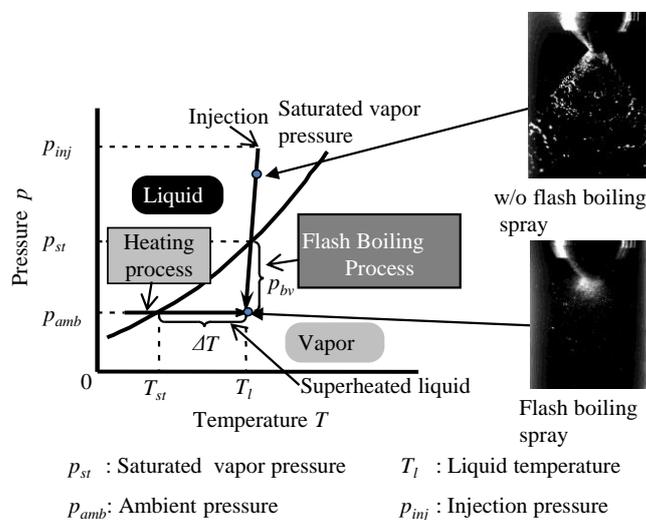


Figure 2 Flash boiling mechanism on pressure-temperature diagram

Improvement of Evaporation Characteristics of Precursor by Mixing Low Boiling Organic Solvent

The boiling point of the precursor is very low. In this study, the evaporation characteristics of the precursor are improved by mixing the low boiling point solvent. The vapour pressure of a solution with two components that have different saturated pressures forms a two phase region, as shown on pressure-temperature diagram in Figure 3. The vapour pressure with a high boiling point precursor moved to the lower temperature higher pressure side and the vapour pressure with a low boiling point organic solvent moved to the higher temperature and lower pressure side. Both vapour pressures are connected at the critical point [8]. Thus, it is possible to reform the evaporation characteristics of the precursor by mixing the low boiling point organic solvent.

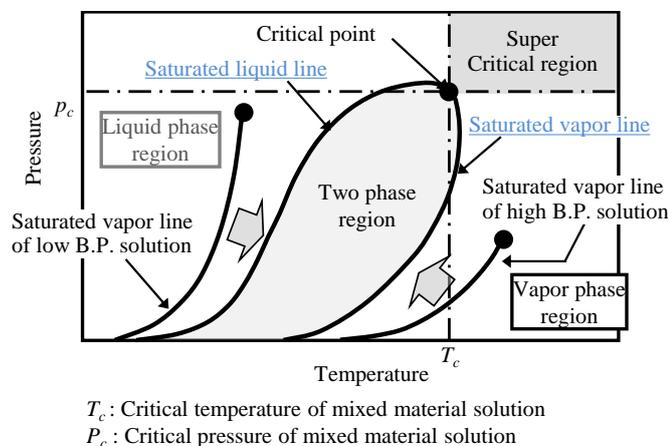


Figure 3 Schematic image of two phase region on pressure-temperature diagram

Using of triple annular burner

A triple annular burner is used in this study. The diffusion, premixed, and premixed diffusion flames can be formed by supplying methane and oxygen from the outer and middle of the annular burner. In addition, the shape of the flame and combustion temperature can be controlled by changing the equivalence ratio. Thus, this system can be used to control the diameter and composition among other characteristics.

Experimental Apparatus and Conditions

Nanoparticle Production Apparatus

Figure 4 illustrates the nanoparticle production system. This system consists of a reaction and collection division, a burner division, and a fuel and mixed solution supply division. The mixed solution is pressurized by using nitrogen and supplied to the injector at the bottom of the system. The solution injected from the injector is evaporated by flash boiling and moved to the burner division by nitrogen carrier gas. The nanoparticles are pro-

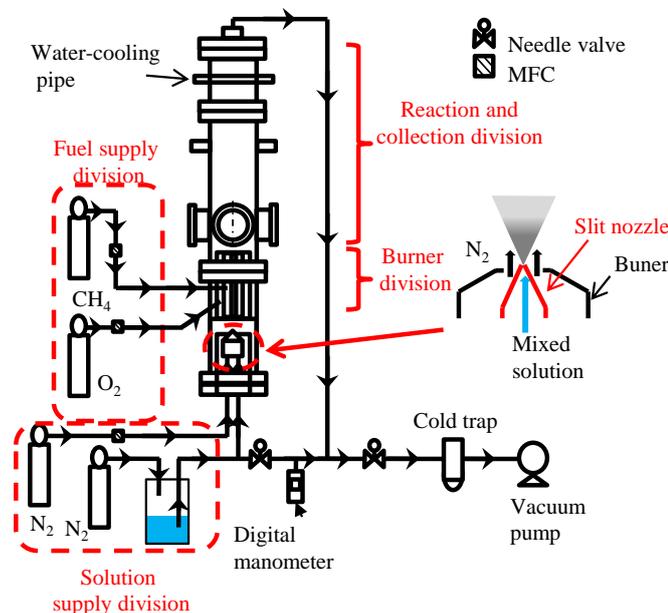


Figure 4 Nanoparticle production apparatus with flame synthesis using flash boiling spray

duced by burner flame combustion. The diffusion flame is formed by using an annular burner. In addition, the particle is collected by using thermophoresis in the reaction and collection divisions, which are installed at the top of the chamber. The ambient is vacuumed up by using a vacuum pump with a cold trap.

Experimental Conditions

Table 1 lists the experimental conditions. Tetraisopropoxytitanium (TTIP, Ti[OCH(CH₃)₂]₄, 308 K/at 13.3 Pa) was used as the precursor. Isopropyl alcohol (IPA, CH₃CH(OH)CH₃, 355 K) and cyclo-hexane(C₆H₁₂, 354 K) were used as the low boiling point organic solvents. The molar fraction of the low boiling point solvent is 0.9. The mixed solution is pressured at 0.42 MPa by using nitrogen and injected at 3.8 ms to the ambient. The ambient pressure and temperature are 5 kPa and 380 K. The injection frequency was set at 2, 4, 6, 8, and 10 Hz. The CH₄ flow rate, Q_{CH_4} is 2.1 L/min and the O₂ flow rate, Q_{O_2} is 14.3 L/min due to set the equivalent ration equal to 0.3. The adiabatic flame temperature is 2393 K. The N₂ carrier gas flow rate, Q_{N_2} is 3.0 L/min. Figure 5 shows the experimental condition points on a pressure-temperature diagram. Both solution vapour pressures improve the TTIP characteristics when mixed with the low boiling point organic solvent. The vapour pressure of the TTIP

Table 1 Experimental conditions

Mixture material	TTIP+cyclohexane TTIP+isopropyl alcohol
Mole fraction of the low boiling point organic solvent X [-]	0.9
Nozzle type	Slit
Injection pressure P_{inj} [MPa]	0.42
Injection duration T_{inj} [ms]	3.8
Injection frequency F_{inj} [Hz]	2, 4, 6, 8, 10
Ambient pressure P_{amb} [kPa]	5
Ambient temperature T_{amb} [K]	380
Equivalent ratio ϕ [-]	0.3
CH ₄ flow rate Q_{CH_4} [L/min]	2.1
O ₂ flow rate Q_{O_2} [L/min]	14.3
N ₂ carrier gas flow rate Q_{N_2} [L/min]	3.0
Adiabatic flame temperature T_f [K]	2393

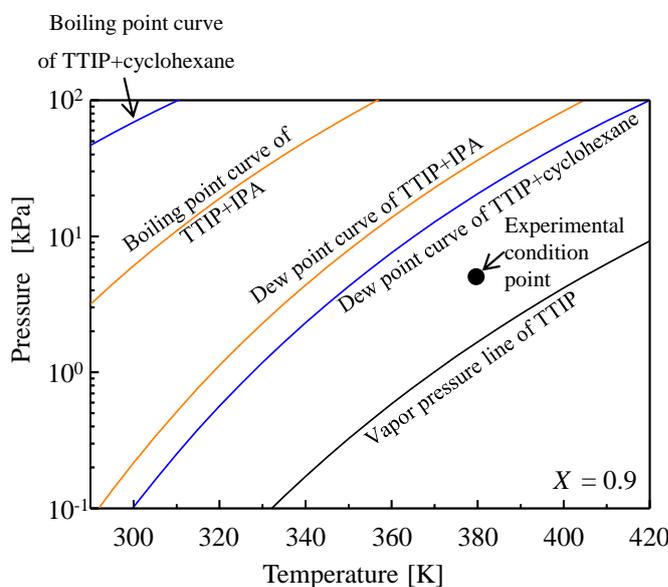


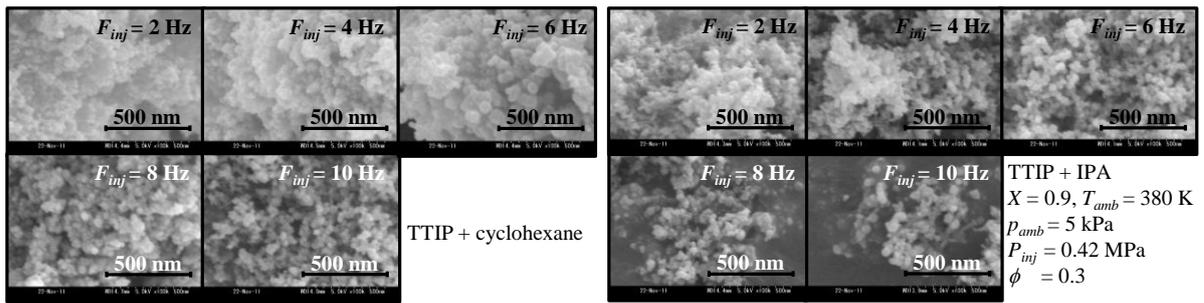
Figure 5 Relation between Two-phase region of TTIP+cyclohexane and TTIP+IPA mixed solutions and experimental conditions on pressure-temperature diagram

+ cyclohexane mixed solution is about 15 times higher than the TTIP, and the TTIP+IPA mixed solution vapour pressure is about 30 times higher than the TTIP. The solution is evaporated and forms homogeneous vapour by flash boiling for the TTIP + cyclohexane and TTIP + IPA solutions.

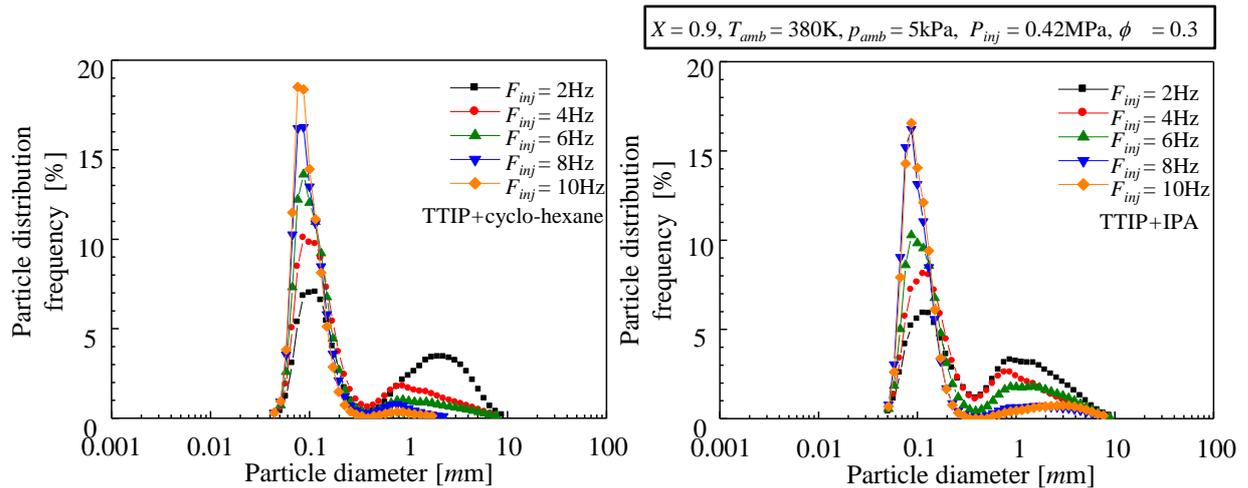
Results and Discussion

Physical property of the nanoparticle

We used SEM (HITACHI, S-4300N) to investigate the TiO₂ nanoparticle. The accelerating voltage was 5 kV. The magnifying power of the microscope was 100000. Figure 6 shows the TiO₂ nanoparticle SEM images for the TTIP+cyclohexane and TTIP + IPA mixed solutions. The diameter of the nanoparticle decreases when the injection frequency is increased. The particle is similarly dispersed at 8 and 10 Hz from the images. The vapour concentration is the same at 8 and 10 Hz because the evaporation is saturated at 10 Hz. Figure 7 shows the diameter distribution of TiO₂ nanoparticles when measured by a particle distribution analyser (HORIBA, Partica LA-950V2). The distribution has two peaks at about 0.1 and 2 μm. For the TTIP+IPA mixed solution, the distribution curve at 8 and 10 Hz has the same trend. The latent heat of the IPA is higher than the cyclohexane. When the injection frequency is high, the evaporation is saturated because the heat capacity for the evaporation is higher than the ambient heat capacity. For the TTIP+cyclohexane, the peak at 0.1 μm increased when the frequency increased.



(a) TTIP + cyclohexane mixed solution (b) TTIP + IPA mixed solution
Figure 6 TiO₂ nanoparticle SEM images when using TTIP + cyclohexane and TTIP + IPA mixed solutions



(a) TTIP + cyclohexane mixed solution (b) TTIP + IPA mixed solution

Figure 7 Diameter distribution of TiO₂ nanoparticle when using TTIP + cyclohexane and TTIP + IPA mixed solutions

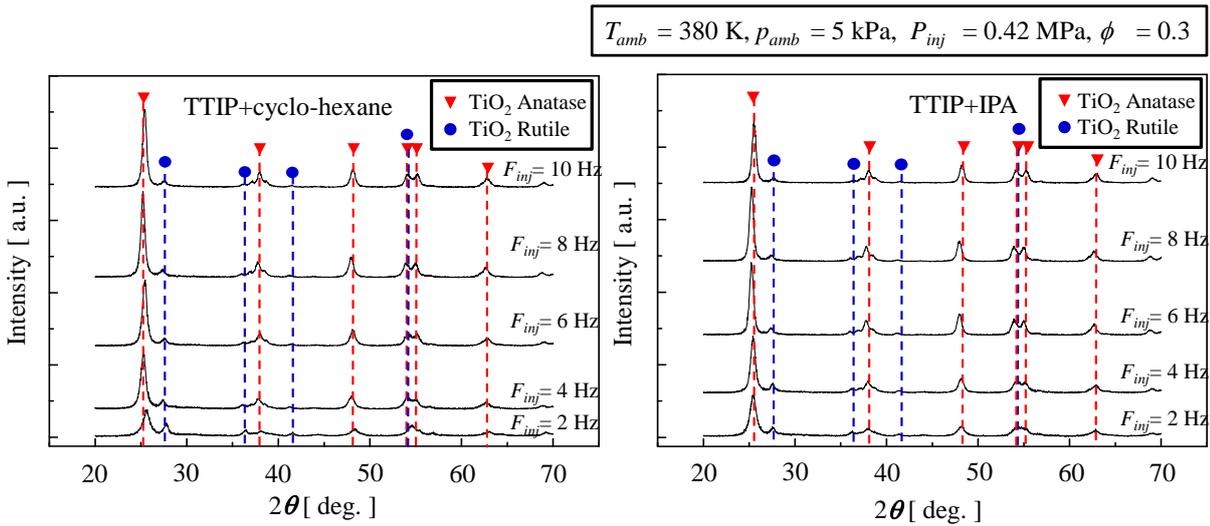
Chemical composition of nanoparticle

The chemical composition was measured by using XRD (Rigaku, MiniFlexII). Figure 8 show the XRD images of the TTIP+cyclohexane and TTIP+IPA mixed solutions. The blue circle points are the rutile phase and the red triangular points are the anatase phase. We can see from these images that the TiO₂ anatase phase nanoparticle can be produced by using this system. The anatase phase peak is increased by increasing the injection frequency in both mixed solution. The anatase clusters coagulate to form the anatase phase because the vapour concentration is increased by increasing the frequency. For the low frequency, only some of the anatase TiO₂ clus-

ters coagulate to form nanoparticles and the rest transform into rutile nanoparticles [9]. The anatase phase peak of TTIP+cyclohexane is lower than that of TTIP+IPA at 2 Hz. The reason for this is that TTIP+cyclohexane is not completely evaporated because the vapour pressure of TTIP+IPA is higher than TTIP+cyclohexane. As the result, the anatase phase and amorphous particle was produced by using TTIP+cyclohexane at 2 Hz. The rutile phase is a more stable phase than the anatase one. The anatase phase is changed to a rutile phase above 1188 K. However, when highly pure oxygen is used, the phase transition from anatase to rutile does not occur [10]. Thus, in the experiment, the anatase phase does not change to the rutile phase because of the use of highly pure oxygen. The anatase phase mass fraction, Y_A , was calculated by using the following equation to investigate the anatase phase nanoparticle [11].

$$Y_A = \frac{1}{1+1.26(I_R/I_A)} \quad (1)$$

The I_A in this equation is the X-ray diffraction intensity of the anatase phase at $2\theta = 27.5^\circ$ and the I_R is the X-ray diffraction intensity of the rutile phase at $2\theta = 25.3^\circ$. Figure 9 shows the effect of the injection frequency on the anatase phase mass fraction. The anatase phase mass fraction has the same trend for both mixed solutions from 4 to 10 Hz because the vapour concentration is increased when the injection frequency increases. At 2 Hz, the anatase phase of TTIP+IPA is higher than that of TTIP+cyclohexane. The evaporation character of TTIP+IPA is higher than that of TTIP+cyclohexane.



(a) TTIP + cyclohexane mixed solution

(b) TTIP + IPA mixed solution

Figure 8 XRD pattern when using TTIP + cyclohexane and TTIP + IPA mixed solutions

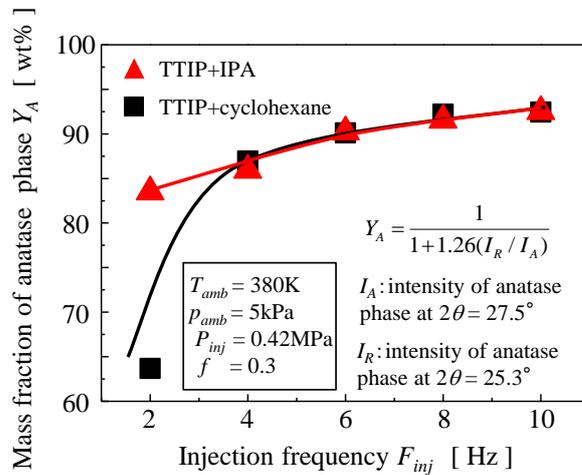


Figure 9 Effect of injection frequency on anatase phase mass fraction

Summary and Conclusions

The authors proposed a novel nanoparticle production system with flame synthesis using flash boiling spray. In this paper, we investigated the relation between the physical properties of a TiO₂ nanoparticle and the injection frequency. A Tetraisopropoxytitanium and cyclohexane mixed solution and tetraisopropoxytitanium and isopropyl alcohol mixed solution were used. The TiO₂ nanoparticles were investigated using a particle size distribution analyser, SEM, and XRD. As a result, the following conclusions were drawn from the experiments:

- (1) It is possible to create any nanoparticle diameter and any crystal structure by controlling the injection frequency.
- (2) The TiO₂ nanoparticles can be produced by using both TTIP+cyclohexane and TTIP+IPA mixed solutions.
- (3) The particle diameter distribution has two peaks at about 0.1 μ and 2 μm for both mixed solutions. The distribution peak at 0.1 μm increased and the peak at 2μm decreased by increasing the injection frequency.
- (4) The agglomeration of the nanoparticles is saturated by increasing the vapour concentration because the energy needed for evaporation is higher than the ambient thermal capacity at 8, 10 Hz by using TTIP+IPA.
- (5) The anatase phase mass fraction is increased by increasing the injection frequency for both mixed solutions. When the evaporation is not completed, the anatase phase mass fraction is decreased, and the amorphous particle is produced at 2 Hz when using TTIP+cyclohexane.

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