

# CONTINUOUS HYDROTHERMAL SYNTHESIS OF NANO PARTICLES USING T-SHAPE MICRO MIXER

Shin-ichiro KAWASAKI\*<sup>a</sup>, Yuichiro WAKASHIMA<sup>a</sup>, Akira SUZUKI<sup>a</sup>, Kiwamu SUE<sup>b</sup>,  
Yukiya HAKUTA<sup>a</sup>, and Kunio ARAI<sup>a</sup>

<sup>a</sup> Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), Nigatake 4-2-1, Miyagino-ku, Sendai, Miyagi, 983-8551, JAPAN.

Fax +81-22-237-5224, E-mail shin-ichiro-kawasaki@aist.go.jp

<sup>b</sup> Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Izumi-cho 1-2-1, Narashino, Chiba, 275-8575, JAPAN.

The continuous hydrothermal synthesis by supercritical water (SCW) was investigated. The feature of this process is that the starting solution (e.g. nitrate salt solution) at room temperature was directly mixed with supercritical water, and it was heated to reaction temperature rapidly. The good mixing leads to the quick temperature changes and the quick changes of solubility of starting material, precursor, hydroxide and oxide. If the degree of supersaturation is large, particle size and size distribution will be small and sharp caused by the inhibition of particle growth.

We have developed the micro mixer for the supercritical water reaction. In this paper, we focused the effect of micro mixer configuration on nano particle characteristics (size, size distribution). The mixing performance of 2 kinds of commercialized T-shape mixers was estimated as an example of the ALOOH (boehmite) synthesis. One of mixer is a standard T-shape mixer (STD) with inner channel diameter of 1.3 mm. Other one is a low dead volume T-shape mixer (LDV) with inner channel diameter of 0.3 mm. As a result, the average particle size of STD was 52.4 nm and size distribution was broad. In contrast, the average particle size of LDV was 6.8 nm and this distribution was very sharp. We estimated to understand the flow condition in the micro mixer by the CFD simulation. The each heating rate of the metallic salt solution by the SCW mixing was much different, the LDV is higher than STD. The good mixing can synthesize the small size and sharp distribution nano particles.

## KEYWORDS

Nano particle, hydrothermal synthesis, micro mixer, supercritical water, turbulent mixing

## INTRDUCTION

Continuous hydrothermal syntheses of nano particles using the supercritical water were investigated. Typical reaction conditions are 400 - 500 °C, 30 - 50 MPa, a few seconds of residence time. This synthesis was known high reaction rate and high conversion by high temperature and high pressure conditions of supercritical water. Adschiri et al. reviewed the synthesis of nano particles using the continuous hydrothermal reaction [1], and Smith et al. reported the recovery of metals from the waste stream by hydrothermal reaction [2]. This research group have reported many kinds of nano particles such as electrode materials (LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, and Ni) [3-6], magnetic materials (BaO·6Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub>) [7,8], and phosphors (YAG: Tb) [9,10] by the subcritical and supercritical water conditions. Poliakoff et al. have reported the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> synthesis using subcritical water conditions, and it can control ratio x by varying the Ce:Zr ratio of the starting solution [11,12]. They reported the oxidation catalyst of La<sub>2</sub>CuO<sub>4</sub> synthesis using supercritical water, which has large surface area compared with

the conventional solid sintered method [13]. Sue et al. reported many kinds of nano particle synthesis based on the estimation technique of metal oxide solubility [14].

Many researchers have focused to find the suitable synthesis conditions for small particle synthesis. They have examined reaction temperature, pressure, residence time, starting solution concentration, pH, and additional materials. On the other hand, Adschiri et al. also reported about mixing by the CFD simulation of the T shape mixer [15]. Lester et al. have investigated many kinds of the mixer configuration (swirl flow, reversing flow type (nozzle reactor type)) [16,17]. These engineering studies of the mixing device are very important to optimize the hydrothermal synthesis process for the practical application development.

Authors have developed the continuous hydrothermal synthesis using the micro mixers and micro reactor under supercritical water conditions. In general, the conventional micro mixer was developed under the laminar flow condition and it was made by glass or plastic. The mixing theory of this mixer is to reduce the diffusion length. In contrast, authors have studied to apply the micro mixer for the high temperature and high pressure process under the turbulent flow condition and our mixer was made by the metal. Our mixing theory is to use the turbulent flow. We focused that the mixing device is a key technology not only for this hydrothermal reaction but also other continuous system, such as organic synthesis using supercritical water or supercritical CO<sub>2</sub> extraction. Now, authors have developed the several types of the micro mixer for the high temperature and high pressure process. In this paper, we will report the effect of the micro mixer configuration on nano particle characteristics such as particle size and size distribution using the commercialized T shape mixer.

## EXPERIMENTAL

### (1)REACTION AND MATERIALS

We selected the boehmite (AlOOH) synthesis for the model hydrothermal reaction to estimate the effect of the micro mixer configuration. The reaction equation was shown at Eq. (1) and (2).



Here, eq. (1) is the hydrolysis reaction and (2) is the dehydration reaction. The typical reaction conditions are 400 – 500 °C, 30 - 50 MPa, and a few seconds of residence time (in this study; 400 °C, 30 MPa, 2s). Distilled water was used for supercritical water and dilution water of metallic salt solution. Aluminum nitrate of the special grade chemicals (Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O; Wako Pure Chemical Industries, Ltd) was used to adjust the 0.02 mol/L as the solution tank concentration.

### (2)APPARATUS AND PROCEDURE

Experimental apparatus was shown in Figure 1. There are two feed tanks, distilled water and the metallic salt solution. Two high pressure plunger pumps (NIHON SEIMITSU KAGAKU Co. Ltd., NP-KX-540, Max. pressure; 50MPa, Max. flow rate; 40 g/min) were used to supply water and the metallic salt solution. Distilled water was heated to the SCW state by the pre-heater which was made by the long heating coil and the traditional electric heater. The metallic salt solution was supplied at room temperature. The metallic salt solution was heated to the reaction

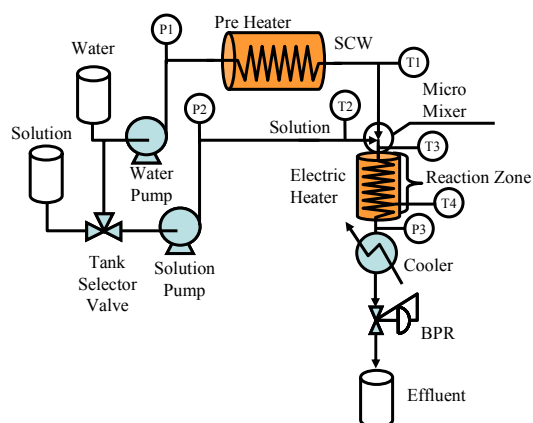


Figure 1 Experimental apparatus

temperature by the direct mixing with SCW at the micro mixer. Each flow line temperature (SCW T1 and the metallic salt solution T2) before mixing were measured. The temperature after mixing T3 was defined the reaction temperature. In this study, the reaction zone temperature T4 was same temperature with T3. The temperature measurements were used the K type thermocouples (SUS316, sheath diameter 1 mm) tied on the outer surface of the tubes. We can adjust the objective reaction temperature by the heat balance calculation, and we can check by the temperature measurement.

The residence time was adjusted to change the inner diameter and length of the reaction zone tube. The effluent was cooled by the cooler, and it was depressurized by the back pressure regulator (TESCOM, 26-1762-24). Pump supplying pressures P1, P2 and reaction pressure at the outlet point of the reaction zone were measured by the pressure transducers. The mixing performance of the 2 type micro mixers, the conventional standard T mixer (STD; Swagelok 1.6 mm TEE Union, SUS316, SS-100-3) and the low dead volume T mixer (LDV; Swagelok 1.6 mm TEE Union for the chromatography, SUS316, SS-1F0-3GC), were compared. Figure 2 showed the cutaway view of micro mixers. Figure 2 (a) is a STD and (b) is a LDV. The inner channels are different, STD is I.D. 1.3 mm, L. 9.2 mm and LDV is I.D. 0.3 mm., L. 1.3 mm. The STD was used for the mixer in previous studies. The connection tube (SUS316) of the each mixer is the O.D. 1.6 mm, I.D. 0.8 mm. The reaction zone tube (SUS316) was used the O.D. 3.2 mm, I. D. 1.8 mm. All parts (micro mixer, other connection union and tube, from the mixing point to the cooler outlet) were changed to new one at the every test to reduce the small contamination by nano particle. All of experimental conditions were same except for the micro mixer. The flow rates of SCW and the metallic salt solution were 33 and 12 g/min. The reaction temperature T3 and the reaction zone temperature T4 were same 400 °C. The reaction pressure was 30 MPa, and residence time of the reaction zone was 2 s, and the tank concentration based on Al was 0.02 mol/L.

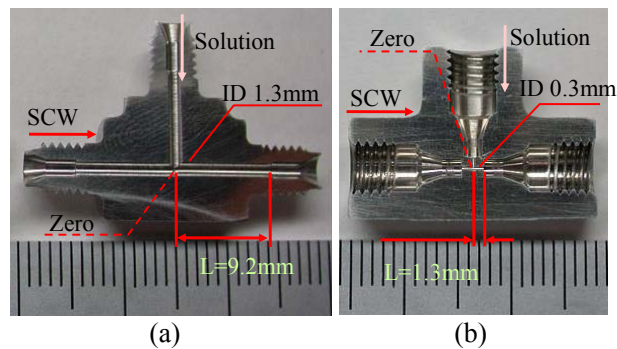


Figure 2 Cutaway view of the T shape mixer

(a) STD, (b) LDV

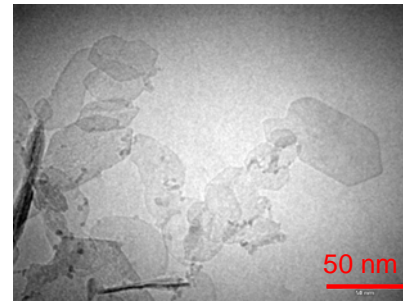
## ANALYSES

The nano particles were separated from the effluent by a membrane filter (MILLIPORE, nitrocellulose filter; pore size: 25 nm, filter size: 90 mm), and the particles were dried in an oven for 12 h. The residual aluminum ions in the recovered solution were measured to obtain the reaction conversion rate by an inductively coupled plasma atomic emission spectrometer (ICP–AES, Seiko Instruments Inc., SPS7800). The crystal structure of the dried particles was estimated by a powder X–ray diffractometer (XRD, Rigaku, RINT 2200VK/PC, 60 kV, 3 kW). The source of the X–radiation is Cu K $\alpha$ , and the scan rate was set to 2 °/min. The size of the particles and their morphology were measured by transmission electron microscopy (TEM, JEOL–2000EX2, 200 kV). In this study, the average particle size was evaluated based on the equivalent area diameter due to the length measurement of the long axis and short axis of a particle. The average particle size and size distribution were estimated to measure more than 200 – 300 particles.

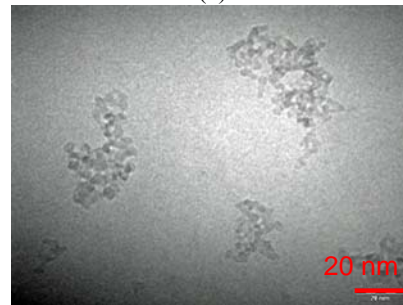
## RESULTS AND DISCUSSION

The particle photos by TEM were shown in figure 3. The particle of the STD is hexagonal shape. And a black slit at the bottom of the photo showed the risen particle and it indicated thin particle. In contrast, the particle of the LDV is circular shape and it is small and homogeneous. The graphs of the particle size distribution were shown in figure 4. In the case of the STD, the average particle size is 52.4 nm and the size distribution showed broad. In contrast, the average particle size of the LDV is 6.8 nm and its distribution is sharp. The standard deviation data of the STD and LDV are 13.9 and 2.0. The LDV is better than STD for synthesis of the small and homogeneous particle.

We estimated the CFD simulation (FLUENT, Fluent Asia Pacific Co.,Ltd) to understand the reason of this difference. We considered not only the fluid mixing but also the heat transfer from SCW flow channel to the mixer body in this calculation. The outside surface of the mixer body was defined the insulated wall to adapt to the experimental apparatus. In figure 2, the center of the mixing point was defined the zero point. The figure 5 showed the maximum and minimum fluid temperature in the cross section of the flow channel from zero point to mixer outlet. The starting temperature of SCW and the metallic salt solution at the zero point were 456 °C and 20 °C. The rhomboid symbol and triangle symbol was represented the metallic salt solution temperature of the STD and the LDV. The solution temperature of the STD gradually increased as it downs the stream of the mixed line, however, temperature difference still maintained 65 °C (max. 431 °C and min. 366 °C) at the 9 mm (STD mixer outlet). In contrast, the solution temperature of the LDV rapidly increased, the temperature difference dwindled to almost nothing at the 2 mm (17 °C). This CFD result indicated that the two fluids mixing conditions using the STD and LDV were much different. Here, the heating rates from 20 to 380 °C were compared with STD and LDV. The axial distances which the metallic salt solution achieved at 380 °C were 11 mm (STD) and 1.6 mm (LDV). The each inner volume required to heat to the 380 °C were 13  $\mu$ L (STD) and 0.3  $\mu$ L (LDV). The heating rates of the STD and LDV based on the average fluid temperature, 200 °C, were 23,000 °C/s and 1,200,000 °C/s. The required heating times to 380 °C were 15 ms and 0.3 ms, respectively. In this calculation, the heat loss was not considered, thus, the actual heating rate is not so large. We have understood that the particle grows under the subcritical water conditions by the large solubility of materials. If the temperature transitional region to supercritical water condition



(a)



(b)

Figure 3 TEM images of particles  
(a): STD, (b): LDV

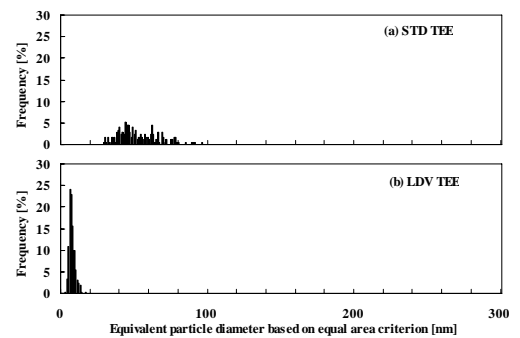


Figure 4 particle size distribution  
(a): STD, (b): LDV

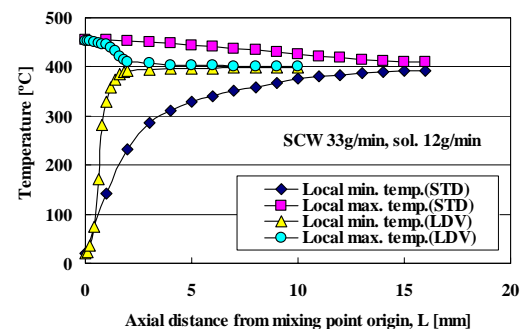


Figure 5 CFD result

was small, the large degree of supersaturation was given and particle growth will be inhibited. Therefore, the particle size of the LDV was small and size distribution was sharp. It is considered that this is one reason of the difference of the synthesized particle characteristics.

As a result of this study, authors do not conclude that the LDV is best micro mixer. When we carried out the long operation of the hydrothermal synthesis, the pump pressure gradually increased. It indicated that the 0.3 mm micro channel will be too small. Now, we have developed the novel micro mixers for the supercritical water reaction. There are the swirl flow type, the central collision type, corrosion resistant material lining type, and so on. Authors consider the good mixing device is expected to change the chemical reaction.

## CONCLUSION

The effect of the micro mixer configuration on the nano particle characteristic by the continuous hydrothermal synthesis was investigated. Under the conditions of 400 °C, 30 MPa, residence time 2s, the Standard T shape mixer with a large inner flow channel (STD, I.D. 1.3 mm) and the Low dead volume T shape mixer with a small inner flow channel (LDV, I.D. 0.3 mm) were compared under the same experimental conditions of AlOOH synthesis reaction. In the case of STD, the average particle size was 52.4 nm, and the size distribution was broad. In contrast, the particle size of the LDV was 6.8 nm and size distribution was sharp. The reason of results was considered the difference of the heating rate to reaction temperature. The STD needs a long time to achieve to the reaction temperature due to the mixing condition is not so good. Therefore, particle grows under the subcritical temperature condition. On the other hand, the LDV can achieve rapidly to homogeneous supercritical temperature condition. Hence, the particle size was small and size distribution was sharp.

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