

Continuous Hydrothermal Synthesis of Nano Copper Particles

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Abstract

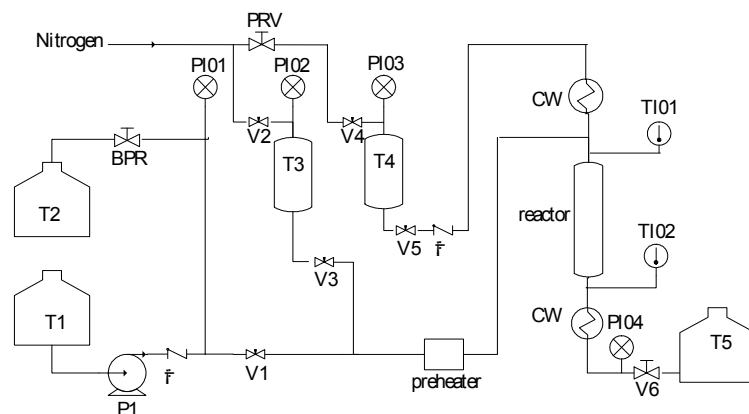
In this study the formation of copper particles by reacting $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 with $\text{C}_6\text{H}_{13}\text{SH}$ was conducted in a continuous hydrothermal reactor. The investigated pressure was 200 and 250 bar, and the temperature ranged from 310 ~ 385 °C. It is found that the reaction rate constant for CuSO_4 is higher than that of $\text{Cu}(\text{NO}_3)_2$. Also, the activation energy at compressed liquid is much lower than that at compressed gas. For CuSO_4 , three different morphology of metal particles are obtained; nanoparticles, agglomerated nanoparticles, and dendritic particles. However, no dendritic structure is obtained if $\text{Cu}(\text{NO}_3)_2$ is used. It is found that samples with dendritic structure are observed in the conditions of compressed liquid and high concentration of the precursor's solution. It is presumed that the formation of dendrite is due to the fast crystal growth. This need fast decomposition of the precursor and moderately rapid crystal growth. However, the organic alkanethiol ion can cap on the surface of growing particles and provide diffusion barrier to the hydrogen ion in the supercritical state. This would reduce the crystal growth rate. The mechanism for producing dendritic particles in the hydrothermal condition is proposed, and the effects of temperature and pressure and the precursor's concentration on the particle size are also discussed in this paper.

INTRODUCTION

Metal oxide prepared by hydrothermal synthesis is a well known process. In the past decade, researchers from Tohoku university promoted the continuous hydrothermal crystallization into the supercritical state. Many oxides were produced in the supercritical state [1-4]. Ziegler et al. used a batch reactor to synthesize and to stabilize the copper particles by organic alkanethiol in supercritical water [5]. In this work, we employed a modified continuous flow system to study the effects of the temperature and pressure and the concentration of the precursor's solution on the particle size and the morphology of the produced copper.

In a batch reactor, the aqueous solution of reactants is loaded into an auto clave and the pressure increases after heating up the reactor. This is an isochoric process. The reaction initiates as the activation energy of the reaction is overcome. Therefore, it is difficult to investigate the nucleation and crystal growth of the precipitation of produced particles, because

the initiated temperature is not available for this isochoric hydrothermal process and the state of the reacting environment is unclear. For safety reason, particles produced by a batch reactor were mostly formed in saturated liquid or in superheated gas state. In a continuous hydrothermal process, the reaction is conducted at constant pressure. The reaction also initiates at the temperature roughly as that in the batch reactor. In a continuous flow system, it is normally observed that the precipitated particles plugged the flow system at the inlet of the reactor. This implies that the reaction occurs at temperature lower than the setting temperature of the reactor. Researchers from Tohoku university used a cooling jacket for the stream of the precursor's solution right before the reactor to prevent plugging. However, the existence of temperature gradient will still gradually plug the flow system if the flow rate is low. We employed a high pressure gas head to inject the precursor's solution into the reactor, where the reactor is preheated and pressurized into the desired conditions. With this high pressure gas head, the aqueous solution is periodically injected into the reactor. This can prevent plugging and introduce small amount of aqueous solution directly into the supercritical state without quenching the temperature of the reactor.



T1: water T2: recycling T3: buffer tank T4: aqueous solution
P1: pump CW: cooling water V1~V5: hand valve V6: metering valve
BPR: back pressure regulator PRV: pressure reducing valve

Figure 1 Illustration of the hydrothermal flow system

THE FLOW SYSTEM AND EXPERIMENTS

The flow system used in this study is illustrated in **Figure 1**. The pressure is maintained by continuously pumping water, P1, into the reactor and regulated by a buffer gas tank, T3. The water flow rate is adjusted by a metering valve, V6, installed at down stream. The precursor's solution is preloaded into T4, and regulated high pressure nitrogen is introduced into T4 to pressurize the solution. The flow rate of the precursor's solution is adjusted by the pressure difference between PI01 and PI03 indicated in **Figure 1**. A correlation between the pressure difference and the water flow rate through the nozzle is pre-calibrated to realize the flow rate of precursor's solution. In order to obtain good atomization, it is recommended that the Weber

number for the nozzle should be larger than 10. The preheater provides required energy to heat up the reactor to the designed temperature. The temperature of the reactor roughly equals to the average of the inlet temperature, TI01, and the outlet, TI02.

$\text{Cu}(\text{NO}_3)_2$ and CuSO_4 are used as the reactants. 1-hexanthiol is employed as the reductant. The concentration of the reactants is measured by UV absorbance at 800 nm. Since the concentration of 1-hexanthiol is excess in this study, a first order reaction kinetics is assumed. The reaction temperature is calculated as the average temperature of the inlet and outlet. The produced particles are collected in T5 and sprayed in a glass for SEM analysis.

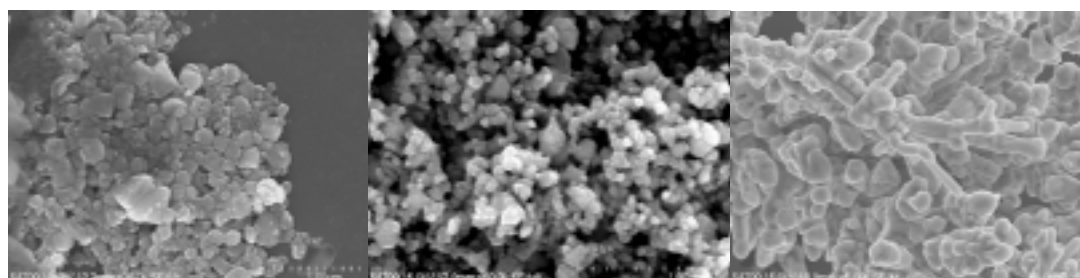


Figure 2 Metal particles produced from CuSO_4 .

Table 1 The particles morphology produced from CuSO_4

	310 °C	330 °C	345 °C	360 °C	385 °C
0.10M, 200 bar	dendrite	dendrite	Dendrite	dendrite	nanoparticles
0.10M, 250 bar	dendrite	dendrite	dendrite	dendrite	agglm.
0.05M, 200 bar	dendrite	dendrite	dendrite	agglm.	nanoparticles
0.05M, 250 bar	dendrite	dendrite	dendrite	agglm.	nanoparticles
0.01M, 200 bar	dendrite	agglm.	agglm.	agglm.	mod. agglm.
0.01M, 250 bar	agglm.	mod. agglm.	Mod. agglm.	mod. agglm.	mod. agglm.

agglm.: agglomerated nanoparicles

mod. agglm.: moderately agglomerated nanoparticles.

RESULTS AND DISCUSSION

I. The effects of temperature and pressure on the particle size and morphology

For CuSO_4 , three different morphology of metal copper were obtained; nanoparticle, agglomerated particles, and dendritic particles. **Figure 2** is the SEM for the metal copper produced in different conditions, and **Table 1** lists the morphology of metal particles produced from CuSO_4 in this study. The dendrite is mostly produced when the reaction is conducted in the conditions of compressed liquid and moderately high concentration of the precursor solution. If $\text{Cu}(\text{NO}_3)_2$ was used, we obtained only agglomerated nanoparticles with different size of the primary particle. This implied that the nucleation and crystal growth for the formation of metal copper from CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ solution differs from each other. Counter-ions may play an important role in the nucleation and crystal growth. In general, the size of the primary particle significantly decreases with temperature and slightly decreases

with increasing pressure. **Figures 3** and **4** illustrate the change of the mean diameter of the primary particle or the size of the coarse grain of the dendrite to the temperature produced from CuSO_4 and $\text{Cu}(\text{NO}_3)_2$, respectively. In **Figures 3** and **4**, solid blue and red lines represent 0.1 M of precursor's concentration operated at 20 and at 25 MPa respectively, dashed blue and red lines are 0.05 M at 20 and at 25 MPa, and dot blue and red lines are 0.01 M at 20 and at 25 MPa.

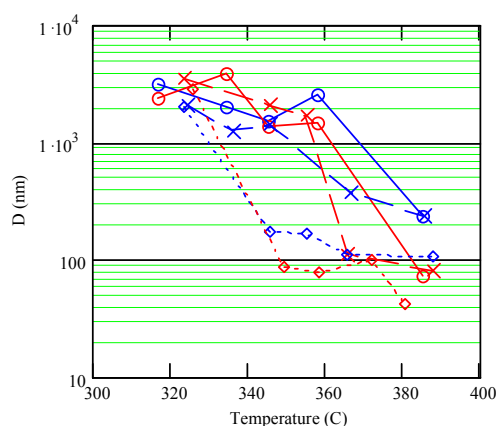


Figure 3 The change of particles, reacted from CuSO_4 with temperature, at different pressure and concentration.

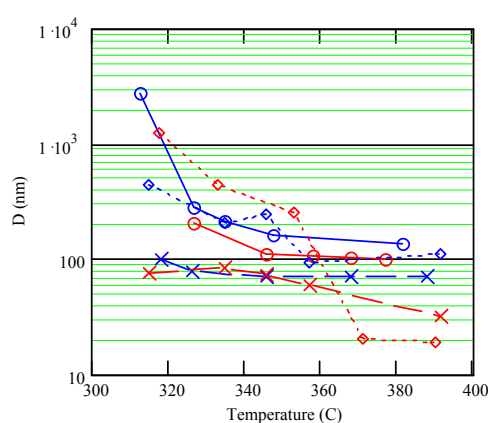


Figure 4 The change of particles, reacted from $\text{Cu}(\text{NO}_3)_2$ with temperature, at different pressure and concentration.

II. The reaction kinetics and the mechanisms of particle formation

Since the organic alkanethiol is excess, the reaction is assumed as a first order reaction and the reaction rate constant is calculated. Arrhenius' plots for the decomposition of CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ are illustrated in **Figures 5** and **6**. A dotted vertical line is also shown in the figure to represent the saturated temperature of 20 MPa. It is observed that the reaction rate constant increased with temperature and pressure. An abrupt change of the slope near the saturated temperature is also observed. While the temperature is higher than the saturated temperature, it is the compressed gas state. It is the compressed liquid state as the temperature is lower than the saturated temperature. The abrupt change of the activation energy gradually disappears while the operating pressure is increased up to 25 MPa. It is also observed that the reaction rate constant for CuSO_4 is larger than that of $\text{Cu}(\text{NO}_3)_2$ at the same temperature and pressure. Since the slope in **Figures 5** and **6** directly relates to the activation energy of the determinate reaction, it is observed that the activation energy in the state of compressed liquid is much lower than that in the compressed gas. This implies that the reaction mechanism is different from each other. Because the metal copper is nearly not soluble in water, it is assumed that the nucleation occurs once the reduction completes. Therefore, the determinate step for the formation of copper particle should be the step of forming the hydroxyl or the oxide. The structure of this

intermediate product and the counter ions on its surface will dominate the crystal growth and the particle's morphology.

The polar surface of the hydroxyl and oxide will be attached by counter ions, and it will further react with hydrogen ion to form the metal particle. In the polar compressed liquid, the intermediate is mostly capped by polar counter ions. While the reaction takes place in the supercritical state, it will be capped by nonpolar counter ions. For CuSO_4 and organic alkanethiol, the intermediate is expected to be surrounded by SO_4^{-2} at compressed liquid state. Since the rate constant is large, the rate of crystal growth is also rapid. Dendrite is formed due to the fast growth of crystal. If the temperature is increased up to the supercritical state, the reaction rate increases and the polarity of the water also changes. The change of water's polarity will also change the capped ions. It is expected that organic alkanethiol ions will attach to the intermediate in the supercritical state. This will increase the diffusion length to the hydrogen ions. Therefore, the crystal growth rate is largely depressed. Accordingly no dendrite is formed in the supercritical state. The crystal growth rate can also be deduced by lowering the concentration of the precursor solution. Therefore, few samples with dendritic structure are observed at low concentration even in the state of compressed liquid. The detached SO_4^{-2} ions from the intermediate in the supercritical state may react with other cations to form salt precipitated in the reactor or decompose to gases.

For $\text{Cu}(\text{NO}_3)_2$, no dendritic structure is observed. It is assumed that the reaction rate constant is low such that the crystal growth is slow. Increasing reaction rate by increasing temperature will also change the polarity of the water. The capped alkanethiol ions at high temperature will create diffusion barrier to the hydrogen ions. It will reduce the crystal growth rate. Therefore, no dendrite can be formed. However, the particles derived from $\text{Cu}(\text{NO}_3)_2$ are always agglomerated even in the state of supercritical and superheated. It implies that the capped ions do not provide electric charge on the growing particle. It is assumed that the electric charge is neutralized by other ions derived from the decomposition of NO_3^- .

On increasing temperature, the water density also decreases. The residence time of the dispersed intermediate or nucleus in the reactor is also shortened. Therefore, the particles size derived from $\text{Cu}(\text{NO}_3)_2$ is reduced because of short residence time for the crystal growth. However, the particle produced from CuSO_4 is mainly determined by the water's polarity. Therefore the temperature dependence of the particle size is different between CuSO_4 and from $\text{Cu}(\text{NO}_3)_2$. Although the particles size is affected by the temperature, the pressure, and the concentration, the influence is not always consistent with those derived from CuSO_4 and from $\text{Cu}(\text{NO}_3)_2$. It is assumed that the atomization of the liquid jet may moderately affect the particle size, and it needs

further studies.

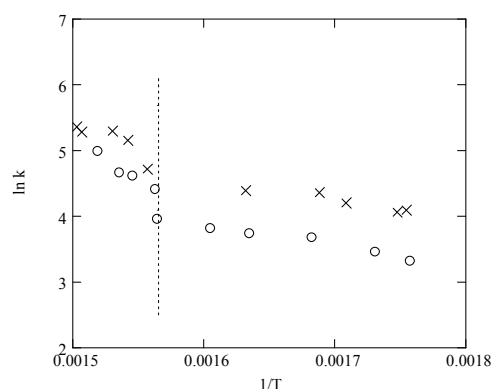


Figure 5 Arrhenius' plot for CuSO_4 . Circles and crosses represent that reacted in 20 and 25 MPa.

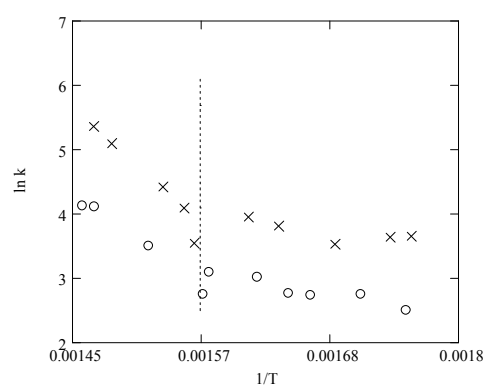


Figure 6 Arrhenius' plot for $\text{Cu}(\text{NO}_3)_2$. Circles and crosses represent that reacted in 20 and 25 MPa.

CONCLUSION

This work investigates the reduction reaction of CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ with organic alkanethiol to produce metal copper in the hydrothermal conditions. A pseudo-first order reaction is also assumed to calculate the reaction rate constant and to realize its effect on the crystal growth rate. The mechanism to form dendritic structure in hydrothermal condition is proposed. It is presumed that the water's properties play an important role to affect the species of the capped ions on the surface of the hydroxyl or the oxide. The effect of temperature and pressure, and the precursor's concentration on the particle size and morphology are also investigated and discussed.

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