流通式超臨界水熱合成反応器内の
熱流動場の可視化

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Hydrothermal synthesis of metal oxide nanoparticles

\[
\begin{align*}
\text{M}^{n+} & \rightarrow \text{M(OH)}_n \rightarrow \text{MO}_{n/2} \\
\text{M(SO}_4\text{)}_{n/2} & + n \text{ H}_2\text{O} \\
\text{M(NO}_3\text{)}_n & - n/2 \text{ H}_2\text{O} \\
\text{Cheap precursors} & \text{can be used.} \\
\text{Water: solvent and reactant} & \\
\text{200~400°C} & \text{25~30 MPa}
\end{align*}
\]

Produced metal oxide nanoparticles

- CeO2
- TiO2
- ZrO2
- ZnO
- Fe2O3
- Fe3O4
- Cu2O
- NiO
- CuO
- RuO2
- MnO2
- MgFe2O4
- BaTiO3
- CoAl2O4
- LiCoO2
- LiMn2O4
- ITO, IZTO
- TiO2:Nb-Co
- AIOOH
- Gd(OH)3
- Cu
- Ni

~5 nm
5~10 nm
Synthesis with plug-flow reactors

Batch reactor

Plug-flow reactor

Heater

Heater

Cooler

mixing

Water

Metal ion solution

Metal oxide nanoparticles

Heater

~ 5 mL

2~3 min
Synthesis with plug-flow reactors

Size of products

Plugging

Mixing of supercritical water and reactants affects the products

Experimental approaches

Model fluid


View cell


Buoyancy force

Cascade down

Mixing in real apparatus is difficult to visualize.
Mixing of two water streams

Difference in water density can be visualized.

- **Plug-flow reactor**
- **Heater**
- **Cooler**
- **Pressure valve**
- **Water**
- **Metal ion solution**
- **Metal oxide nanoparticles**

300~400°C, 25 MPa

Density of water @ 25 MPa

Fe ~70%
Cr 16~18%
Ni 10~14%
Mo 2~3%

![Graph showing density of water with temperature and pressure]

Temperature (°C)

Density of water (g/cm³)
Experimental setup

High-pressure pumps

$Q_{SC}$ (g/min)

$Q_{RT}$ (g/min)

Neutron from nuclear chamber

Imaging area (3.3×3.3 cm$^2$)

SUS 316 1/8-inch tube

$^6$LiF/ZnS scintillator screen

Mirror

CCD camera with telephotographic lens

Jacket cooler

Back-pressure regulator

Luminescent light

Resolution: 1024×1024 dots
Bit depth: Gray scale 16 bits

@ B4 port of Kyoto University Research Reactor Institute

Experimental condition for 2D

Temperature: $T_{SC}$
Flow rate: $Q_{SC}$

Temperature: $T_{RT} = 21{^\circ}C$
Flow rate: $Q_{RT}$

Outer diameter: 1/8 inch
Inner diameter: 2.3 mm
$P = 25$ MPa

<table>
<thead>
<tr>
<th>$Q_{SC}$ (g/min)</th>
<th>$Q_{RT}$ (g/min)</th>
<th>$T_{SC}$ (°C)</th>
<th>$Re_{Sc}$</th>
<th>$T_{mix}$ (°C)</th>
<th>$Re_{mix}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1</td>
<td>385</td>
<td>2.5$\times 10^3$</td>
<td>360</td>
<td>1.2$\times 10^3$</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>385</td>
<td>2.5$\times 10^3$</td>
<td>341</td>
<td>1.2$\times 10^3$</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>385</td>
<td>2.5$\times 10^3$</td>
<td>303</td>
<td>1.1$\times 10^3$</td>
</tr>
<tr>
<td>12</td>
<td>1.5</td>
<td>393</td>
<td>4.8$\times 10^3$</td>
<td>380</td>
<td>2.4$\times 10^3$</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>393</td>
<td>4.8$\times 10^3$</td>
<td>377</td>
<td>2.3$\times 10^3$</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>393</td>
<td>4.8$\times 10^3$</td>
<td>338</td>
<td>2.0$\times 10^3$</td>
</tr>
</tbody>
</table>

30 s for 1 image
6 images for one condition
Averaged water density

\[ Q_{SC} : Q_{RT} = 8 : 1 \]

8.0 g/min
385°C

1.0 g/min

8.0 g/min
385°C

12.0 g/min
393°C

2.0 g/min

4.0 g/min

3.0 g/min

6.0 g/min

Water Density (g/cm³)

[Color scale from 0.0 to 1.0]
Experimental condition for tomography

<table>
<thead>
<tr>
<th>Q₁ (g/min)</th>
<th>T₁ (°C)</th>
<th>Q₂ (g/min)</th>
<th>T₂ (°C)</th>
<th>Tₘix (°C)</th>
<th>Reₘix</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>~385</td>
<td>6</td>
<td>30</td>
<td>335</td>
<td>2.0×10³</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>12</td>
<td>~391</td>
<td>355</td>
<td>2.3×10³</td>
</tr>
</tbody>
</table>

Flow rate: Q₁
Temperature: T₁
Flow rate: Q₂
Temperature: T₂

Outer diameter: 1/8 inch
Inner diameter: 2.3 mm
P = 25 MPa

Imaging area: 65×65 mm²

60 s for 1 image
200 images for one condition

OCTOPUS software was used for CT reconstruction.
Heated water from side

200 images were obtained
Comparison between mixing modes

Nanoparticles were produced using these mixer.
Experimental results

How these products were formed?
Flow dynamics simulation

- Navier-Stokes equations were solved considering buoyant force.
- Temperature-dependent properties of water were given as fit curves of NIST database.
- Temperature and flow rate of inlet streams were given.
- Parabolic flow velocity profile at the inlet was supposed.
- No control at outlet stream.
- FLUENT code was used to solve the equations.
- Non steady-state calculation was performed.
Validation of simulation

Numerical simulation reproduced experimental results.

Neutron radiography

- 8.0 g/min
- 1.0 g/min

Numerical simulation

- 374°C
- 300°C

Temperature of streams
Chemical reaction

\[ \text{Ce(NO}_3\text{)}_3 \rightarrow \text{CeO}_2 \]

Reaction rate

\[ r = k [\text{Ce(NO}_3\text{)}_3] = \frac{d [\text{CeO}_2]}{dt} \]

Simulation results

- Concentration of products
  - [kmol/m³]
  - Streamline
  - [m/s]

- Concentration of products
  - [kmol/m³]
  - Streamline
  - [m/s]

Unsteady-state vortex flow
Visualization of plugging

Radiography measurements with supplying metal ion solution

395.3°C 24.0 g/min

0.01 M Gd(NO₃)₃
6.0 g/min
28.1°C

Products: Gd(OH)₃

Other plugging behaviors
Summary

- Mixing behavior of water streams in a flow-type chemical reactor was visualized by neutron radiography.
- Mode of mixing affected the produced nanoparticles.
- Numerical simulation was checked by neutron radiography.
- In future, the combined use of radiography and simulation can design new mixer to produce better nanoparticles.

Acknowledgment

This work has been performed under the Visiting Researchers Program of Kyoto University Research Reactor Institute.