Effects of microwave irradiation heating in the homogeneous precipitation method using the reductant generated by hydrolysis of urea in an autoclave under high pressure

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In order to synthesize the fine composite oxide powder with uniform composition and good sinterability, reduce the alkaline effluent, and increase the process flexibility by shortening the precipitation time, improvement of the homogeneous precipitation method using the reductant generated by hydrolysis of urea is investigated. Yttria-stabilized zirconia (YSZ) fine powder, which is representative of complex oxide consisting of multiple metal ions, is synthesized by the homogeneous precipitation method under high pressure in an autoclave with the microwave irradiation heating. Effects of microwave irradiation heating on microstructure, size, composition uniformity, and sinterability of the powder particles are elucidated. By using the improved method, the hydroxide powder, which is a precursor of the YSZ powder, is generated quickly even when the amount of urea used is not large excess. The YSZ powder particle synthesized by this method is fine and has the uniform composition and good sinterability.

1. Introduction

Ceramics nano powder with weak agglomeration was synthesized by homogeneous precipitation method using the reductant generated by hydrolysis of urea in an autoclave at high temperature under high pressure. In general, nucleation rate is small when the urea concentration is low, because the required amount of ammonium ion for the precipitation is not generated in a short time. If the nucleation rate is low, it is difficult to synthesize the homogeneous fine powders and the process flexibility is low. Therefore, large excess urea was used even in the synthesis process reported by Xin et al. As a result, a large amount of strong alkaline effluent is generated, so the precipitation process using urea is high cost and environmental impact is large. Moreover, in the precipitation method using the reductant generated by hydrolysis of urea, pH increase in the solution happens with the raising the solution temperature is slow. All metallic ions have a peculiar pH range for precipitate generation. Thus, it is difficult, in principle, to precipitate different metallic ions at the same time. In order to precipitate different metallic ions while maintaining the homogeneity in the precursor solution, the pH adjustment should be conducted quickly. It follows that it is desirable to generate the amount of ammonium ions required by using a minimum amount of urea in a short period of time.

Homogeneous and rapid heating of water can be achieved by microwave irradiation. The authors infer that the total amount of urea in the solution is hydrolyzed in a short time if the heating process in the hydrothermal technique is performed by the microwave irradiation.

An autoclave suppresses the evaporation loss of ammonia generated by the hydrolysis of urea and enables the specimen synthesis at high temperature. When the solution temperature is high, the precipitation is generated quickly so that homogeneous fine powder is synthesized.

In this study, fine ceramic powder with high sinterability and uniform composition is synthesized by homogeneous precipitation method using the reductant quickly-generated by hydrolysis of urea in an autoclave under high pressure at rapidly-raised high temperature. Yttria stabilized zirconia (8 mol % Y2O3/92 mol % ZrO2; YSZ) electrolyte material for solid oxide fuel cells is synthesized under the condition not to generate the strong alkaline effluent, and the advantageous effect of the microwave heating in the hydrothermal method using urea as a precipitation reagent is investigated.

2. Experimental

2.1 Precursor solution

ZrOCl2·8H2O powder (Wako, special grade, 99.0%) was dissolved into deionized water. Y2O3 powder (Wako, reagent grade, 99.9%) was dissolved into a small amount of concentrated nitric acid (Wako, special grade, 60%). The Y3+/Zr4+ solution was mixed to the Zr6+ solution at a molar ratio of Y3+:Zr4+ = 4:23. The total concentration of the metal ions in the solution was adjusted by addition of deionized water to 0.3 mol/dm3.

2.2 Generation and calcination of hydroxide precipitation

A large excess amount of urea [Zr4+/urea = 1/10 (mol)] was added in the precursor solution while stirring. The solution...
temperature was raised on a hotplate up to 85°C or the boiling point of the solution. White powder was precipitated in the solution during the heat treatment. The powder was thoroughly washed with deionized water using a centrifuge, dried in an oven at 85°C for 10 h, pounded in an alumina mortar, and calcined at 500°C for 1 h in air. Hereafter, the powders, which are synthesized via the heat treatments of 85°C and the boiling point, are named powders A1 and A2, respectively. Urea [\(\text{Zr}^{4+}/\text{urea} = 1/1\) (mol)] was added into the \(\text{Zr}^{4+}\) solution while stirring. The solution was transferred into a Teflon\(^6\) cup and heated in an autoclave. Heating processes were performed by two different ways: the first one is using an oven or hotplate and the second one is by microwave irradiation with input power of 600 W at 2.45 GHz. The synthesized powders were washed, dried, pounded, and calcined in the same manner. Hereafter, the powders are named powders B and C, respectively.

### 2.3 Characterization

Crystal phase was identified by X-ray powder diffraction (XRD) with Cu K\(\alpha\) radiation (Bulker, D8 DISCOVER X-ray diffractometer). The crystallite diameters of the specimens were estimated by the whole-powder-pattern decomposition (WPPD) method. Heterogeneity of composition in the synthesized powder was evaluated by the slope of Williamson-Hall Plot of XRD peaks, which reflects the fluctuation range of lattice spacing. Microstructures of the specimens were analyzed by scanning electron microscopy (SEM) (HITACHI, S-4800). Crystallization temperatures of the specimens were measured by differential scanning calorimetry (DSC) (SHIMADZU, DSC-50). Sinterability of the specimens was evaluated by comparing the density of the sintered compact.

### 3. Results and discussion

#### 3.1 Precipitation time

The conditions and the required time for the precipitation are summarized in Table 1. When a large excess urea was added to the precursor solution, the cloudiness due to a precipitation of fine powder, which can be visually confirmed, has occurred by the thermal treatment at 85°C for 3 h at atmospheric pressure. The precipitation of the fine powder gradually increased during the heating at 85°C, and the whole metal ions were precipitated within 36 h (precursor for powder A1). Raising the temperature of the thermal treatment up to the boiling point accelerated the precipitation (precursor for powder A2), and the whole metal ions precipitated within 4.5 h. This short deposition time is a result of the rapid increase in pH with the hydrolysis of urea by the sharp temperature rise.

A large amount of alkaline effluent was generated in the synthesis process of the powders A1 and A2 because the large excess urea was used, and a large quantity of chemicals was also used to neutralize the effluent. Hence, the cost and environmental impact of this synthesis process is large. The precipitation was therefore prepared at the small molar ratio of urea-metal ion of 1/1 (precursor for powder B). The preparation for the powder B was performed in an autoclave, because Xin et al.\(^1\) reported that the precipitation conducted at high pressure in an autoclave requested only a short time of 1 h. Also, the treatment temperature was raised up to the boiling point in order to accelerate the hydrolysis of urea. Under this condition, although it was performed at high temperature and under high pressure, a long time of 5 h was needed to deposit all the metal ions. On the contrary, the fine powder was precipitated in a short time of 3 min, when the thermal treatment in the autoclave was conducted by microwave irradiation.

#### 3.2 Crystalline phase and microstructure

SEM images of the powders A1, A2, B and C are shown in Fig. 1. The powders had the almost same microstructure in spite of the different synthesis condition.

As Fig. 2 shows a DSC profile of the powder which was precipitated in the process to synthesize the powder A1, exothermic peaks were observed at temperatures of 270 and 450°C. Figure 3 shows the XRD profiles of the powders calcined for 1 h at 350 or 500°C which were higher or lower temperature than the peak temperature of around 450°C. Although the specimens were amorphous when the calcination temperature was 350°C, they crystallized by raising the temperature to 500°C. Therefore, the peak at around 270°C corresponds to the change from hydroxide to oxide by desorption of chemical adsorbed water, and the peak at around 450°C is a result of crystallization. Figure 4 compares the exact crystallization temperatures when the scanning temperature ratio was sufficiently slow, that was obtained by extrapolating the data obtained by the scanning rate of 10 and 15°C/min (Figure S1). The crystallization temperatures of the precursors prepared via the precipitation process for the powders A1, A2, B and C were 400, 407, 425 and 370°C, respectively. The lowest crystallization temperature of the precursor for powder C is due to the fine powder particle resulted by the huge amount of nucleation generated by the rapid increase in pH with the

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**Table 1. Conditions and required time to precipitate precursors**

<table>
<thead>
<tr>
<th>Heating</th>
<th>Pressure</th>
<th>Urea</th>
<th>Solution temperature</th>
<th>precipitation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Hot plate</td>
<td>Atmospheric pressure</td>
<td>Large excess</td>
<td>85°C</td>
</tr>
<tr>
<td>A2</td>
<td>Hot plate</td>
<td>Atmospheric pressure</td>
<td>Large excess</td>
<td>Boiling point</td>
</tr>
<tr>
<td>B</td>
<td>Oven</td>
<td>High pressure</td>
<td>Moderate amount</td>
<td>Boiling point</td>
</tr>
<tr>
<td>C</td>
<td>Microwave irradiation</td>
<td>High pressure</td>
<td>Moderate amount</td>
<td>Boiling point</td>
</tr>
</tbody>
</table>

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Fig. 1. Scanning electron microscopy images of powders synthesized via calcination at 500°C for 1 h in air.
hydrolysis of urea by the sharp temperature rise. Figure 5 shows the crystallite diameters of the powders A1, A2, B and C, which were estimated by WPPD method. The crystallite diameters of the powders A1, A2, B and C were 21.0, 18.2, 23.2 and 12.9 nm, respectively. The smaller and the smallest crystallite diameters of the powders A1, A2 and C are because of the small particle sizes of the hydroxide particles prepared by the precipitation.

All the peaks on Fig. 2 were assigned to YSZ of fluorite structure. Figure 6 is a Williamson-Hall plot of the XRD peaks for the powders A1, A2, B and C. The slope of the plot for the powder C was the smallest. The slope reflects the fluctuation range of lattice spacing, which is caused by heterogeneity of composition in the specimen. Therefore, the composition uniformity of the powder is improved by decreasing the period of precipitation time. Because the precipitation starting pH is different for each metal ion, one of the metal ions of Y$^{3+}$ and Zr$^{4+}$ selectively precipitated during the relatively low pH range in the synthesis process for the powder A1, in which the hydrolysis of urea happens slowly. In contrast, when the hydrolysis of urea was happened in the autoclave by the rapid heating to the boiling point by microwave irradiation, the composition uniformity of the powder was improved because the solution pH reached up to the enough value for the co-precipitation of Y$^{3+}$ and Zr$^{4+}$.

3.3 Sinterability
The densities of the pressed compact and the sintered compact of the powders A1, A2, B and C prepared at relatively low temperatures of 1000 and 1100°C for 1 h in air are compared in Fig. 7. The density by the low-temperature sintering reflects the sinterability of powder particles. Although all the powders were pressed into pellets and sintered under the same conditions, the sintered densities of the powders A1 and B were lower. In contrast, the sintered density of the powder C was higher than
those of the other powders. This higher sintered density is caused by the high green density and the better sinterability, both of which come from the powder particle size.

4. Conclusion

Through synthesis of the yttria-stabilized zirconia (YSZ) fine powder, which is representative of complex oxide consisting of multiple metal ions, the effect of the heating by microwave irradiation performed in the homogeneous precipitation method using the reductant generated by hydrolysis of urea in an autoclave under high pressure was elucidated. The hydroxide powder, which is a precursor of the YSZ powder, is generated quickly by the effect of the microwave heating even when the amount of urea used is not large excess. The YSZ powder particle synthesized by this method is fine and has the uniform composition and better sinterability.

References