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DISSOLUTION AND CRYSTAL GROWTH OF CERIUM OXIDE UNDER HYDROTHERMAL CONDITIONS

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Abstract

Using CeO_2 bulk sample dissolution experiment was carried out at temperatures of 100~500℃ and pressures of 4~90 MPa over pH=4.7~13.7 for 2 h. On the basis of this result CeO_2 powder sample was treated under hydrothermal condition: temperature of 500℃ and pressure of 90 MPa over pH=5.4~13.7 for 2 h. CeO_2 sample after hydrothermal treatment was examined by TEM. At all pH, the size of the CeO_2 powder after hydrothermal treatment was larger than that before the treatment. Although at pH=14 the dissolution of CeO_2 was the highest, the particle size was not large. Crystal growth of CeO_2 during hydrothermal treatment was influenced primarily by the pH rather than the mineralizer.

Key words: cerium oxide, hydrothermal condition, pH, dissolution, crystal growth

1. INTRODUCTION

The studies of CeO_2 and CeO_2 solid solutions with hydrothermal synthesis technique have been conducted by several groups of researchers [1-5]. Tani et al. [1] have studied crystal growth during hydrothermal treatment of CeO_2 and ZrO_2-CeO_2. They used many mineralizers such as KF, Li_2SO_4, NaOH, $LiNO_3$, K_2CO_3, LiBr, and LiCl, and hydrothermally treated CeO_2 at the temperatures of 500 and 600℃ and the pressure of 100 MPa for 24h. They did not fix the concentration of mineralizer. They concluded that crystal growth of CeO_2 depended on the kind of mineralizer. The mineralizer which had influenced crystal growth of CeO_2 most was KF and Li_2SO_4. Hydrothermal treatment of ZrO_2-CeO_2 was also carried out at the temperature of 600℃ and the pressure of 100 MPa for 24 h. The mineralizers which had influenced crystal growth of ZrO_2-CeO_2 were Li_2SO_4, LiCl, and LiBr. The crystalline size of ZrO_2-CeO_2 after hydrothermal treatment was generally smaller than that of CeO_2 except for the case in which LiBr was used as mineralizer. Although the same mineralizers were used for the hydrothermal treatment of CeO_2 and ZrO_2-CeO_2, the mineralizers had different effect on crystal growth of these oxides. From these results, they concluded that the mineralizers have different effects on hydrothermally-treated materials.

Following the initial sintering theory, it is easy to find that fine powder must be used to obtain high density sintered body. Hirano et al. [2] and Rahman et al. [4] used hydrothermal technique to make ultra fine powder of undoped CeO_2 and CeO_2 solid solutions which have uniform particle size. These researchers actually obtained ultra fine powders by hydrothermal synthesis technique. However

they did not study in detail the factors which control the size of powder during hydrothermal treatment. The purpose of present work is to investigate the effect of pH on hydrothermal crystal growth of CeO_2.

2. EXPERIMENTAL PROCEDURE

2.1. Dissolution experiment

Hydrothermal process involves three stages. First stage is the dissolution of the solid particle into a solution. Second stage is the migration of dissolved materials to the surface of another particle in the solution. Finally, third stage is the precipitation of the dissolved materials onto another particle in the solution. In order to have effective hydrothermal treatment, it is important to dissolve the solid particle into solution. Therefore, to investigate hydrothermal crystal growth of CeO_2, the dissolution experiments of CeO_2 were performed at first in temperature range from 100℃ to 500℃ and at pressures of 4~90 MPa for 2 h by using two types of apparatus. To study the hydrothermal process at temperatures from 100℃ to 200℃ and at pressure of 4 MPa, an autoclave was used. To study the hydrothermal process at 500℃ and at 90 MPa, the test tube type hydrothermal synthesis apparatus was used. For all experiments performed on these two types of apparatus, the pH of the solution was changed from 4.7 to 13.7.

All the dissolution experiments were performed on CeO_2 bulk sample. The bulk sample was formed by sintering the CeO_2 powder prepared by a homogeneous precipitation method [6]. The powder was pressed into discs and sintered at 1400℃ for 1 h in air. The relative density of the samples was about 98 % of theoretical. The sintered sample was cut into a rectangular parallelepiped, $2 \times 2.5 \times 6$ mm^3 in size to be used in the autoclave, or cut into spherical shape about 2 mm in diameter to be used in the test tube type apparatus.

2.2. Hydrothermal treatment

On the basis of the result obtained from section 2.1, hydrothermal treatment of CeO_2 powder was carried out. CeO_2 powder was prepared by adding NH_4OH to a cerium nitrate solution. The precipitate was washed with distilled water, and then dried at 85℃ over night. The prepared CeO_2 powder was ground in an alumina mortar. CeO_2 powder of about 0.2 g prepared in this way was placed in an Au one-end-closed tube with an aqueous solution of a mineralizer such as $Mg(NO_3)_2$, KOH, LiOH, and NaOH. The pH of the solution was varied by changing the concentration of mineralizer. The pH was measured at room temperature. After closing the other end of the Au tube, it was placed in the test tube apparatus. At the condition of 500℃ and 90 MPa, hydrothermal treatment was carried out for 2 h. CeO_2 sample after hydrothermal treatment was collected and subjected to TEM observation of shape and size of the powder.

3. RESULTS AND DISCUSSION

3.1. Dissolution experiment

To investigate the dissolution of the CeO_2 sample, the bulk sample weight was measured by an electronic balance before and after the hydrothermal treatment. During the hydrothermal treatment in the temperature range from 100℃ to 200℃ and at the pressure of 4 MPa, the sample did not dissolve at all for 2 h at pH=5.2 and pH=13.7. The result did not depend upon the mineralizer. Consequently, the temperature of hydrothermal treatment was increased to 500℃. At 500℃, weight loss of CeO_2 bulk sample was observed and was the largest at pH=13.7. Changing pH from 4.7 to 13.7, dissolution experiment was carried out at 500℃ and 90 MPa for 2 h. As the results are

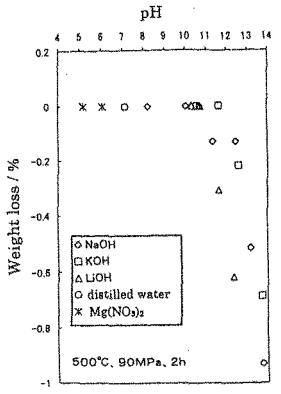

Fig. 1. The weight change of CeO_2 bulk sample after hydrothermal treatment at 500℃ and 90 MPa for 2 h plotted as a function of pH.

plotted in Fig. 1, dissolution of CeO_2 takes place at the pH greater than 11. The weight loss became more significant with increasing pH. The results predict that CeO_2 powder may grew larger during hydrothermal process in solution with high pH because the dissolution is one of the important processes in the hydrothermal treatment.

3.2. Hydrothermal treatment

Hydrothermal treatment of CeO_2 powder was carried out at 500℃ and 90 MPa for 2 h. CeO_2 powder after hydrothermal treatment was examined by TEM. The powder was all equiaxed and were very closed to spherical in shape. The maximum diameter of each particle of CeO_2 powder was measured from transmission electron micrographs. More than 50 particles were measured for each sample. The average value was plotted in Fig. 2 as a function of pH of the solution. All the particle sizes of CeO_2 powder after hydrothermal treatment were bigger than that before hydrothermal treatment. The particle size of CeO_2 powders treated at pH below 11 was also bigger than that before hydrothermal treatment, although at low pH range no weight loss was observed in the dissolution experiment. The largest particle size of CeO_2 powder was found in the sample that was treated at pH=11. At pH=12～14, large weight loss was observed in the dissolution experiment. Consequently, significant increase in particle size was expected during

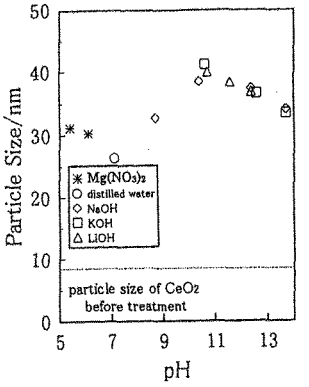

Fig. 2. The particle sizes of CeO_2 after hydrothermal treatment plotted as a function pH.

hydrothermal treatment at high pH. On the contrary, the particle size of the powder treated at pH=12～14 was smaller than that at pH=11.

The transmission electron micrographs of these particles are shown in Fig. 3. The shape of the CeO_2 powder changed from cubic to spherical with increasing pH of hydrothermal treatment. In addition, the kind of mineralizers used to make pH=9～14 did not have an effect on the shape of CeO_2 and, therefore, did not influence crystal growth of CeO_2 powder. Since the size and shape of CeO_2 powder prepared at pH=9～14 did not depend on the mineralizer used in this experiment, it may be concluded that crystal growth of CeO_2 was influenced by the pH of solution rather than mineralizer. When the sample was treated in the pH range lower than 11, the particle size of the CeO_2 powder after hydrothermal treatment was not uniform. However, when the sample was treated in the pH range over 12, the particle size and shape of CeO_2 powder were uniform.

To confirm that the samples after hydrothermal treatment were CeO_2, these samples were subjected to X-ray diffraction analysis. All the samples were exactly CeO_2 before and after the hydrothermal treatment. X-ray diffraction patterns of CeO_2 powder before

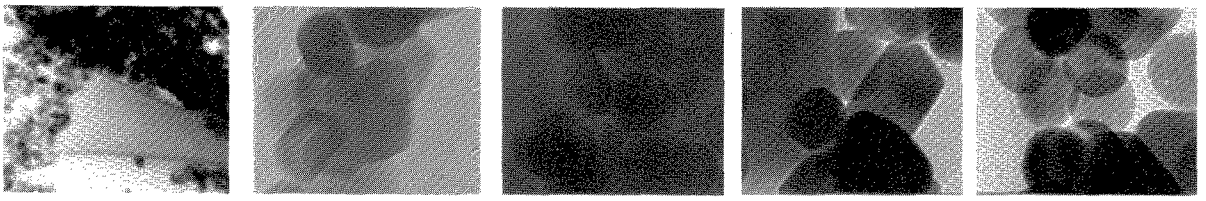

Fig. 3. Transmission electron micrographs of CeO_2 before and after hydrothermal treatment; (a) before hydrothermal treatment (b) $Mg(NO_3)_2$ pH=5.4 (c) distilled water pH=7.2 (d) NaOH pH=10.4 (e) NaOH pH=13.7.

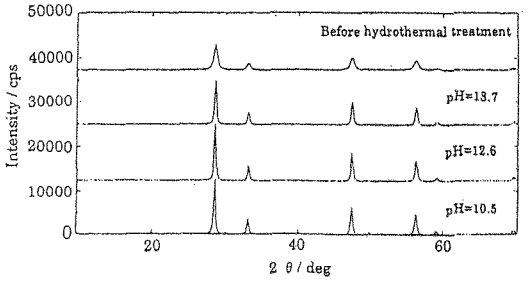

Fig. 4. X-ray diffraction diagrams of CeO_2 before and after hydrothermal treatment using NaOH as a mineralizer.

and after hydrothermal treatment using NaOH as a mineralizer are shown in Fig. 4. All these peaks were assigned to CeO_2. X-ray diffraction peaks of CeO_2 before hydrothermal treatment were weak in intensity and broad. After hydrothermal treatment, the peaks became strong in intensity and became sharp. At about pH=11 and 13, the intensity of peaks was the same. However, at about pH=14 the intensity of peaks became slightly weaker than pH=11 and 13. The sample exhibiting weak X-ray peaks is the powder with small particle size. The fact that at pH=14 the particle size was not the biggest can be explained if the growth mechanism at pH=14 was different from the mechanism at pH=11. This difference in mechanism has resulted in the difference in weight change of CeO_2 in dissolution experiment (Fig. 1) and the difference in the particle shape (Fig. 3).

4. CONCLUSIONS

Dissolution experiment of CeO_2 bulk sample was carried out at temperatures ranging from 100 to 500℃ and at the pressures of 4~90 MPa for 2h over pH=4.7~13.7. The weight change was observed only at 500℃. Consequently, hydrothermal treatment of CeO_2 powder was carried out at 500℃ and 90 MPa for 2 h using mineralizers such as $Mg(NO_3)_2$, LiOH, NaOH, and KOH. The pH was changed from 5 to 14. After hydrothermal treatment, CeO_2 powder was examined by X-ray diffraction and TEM. From the results it was found :

1. At any pH, CeO_2 powder after hydrothermal treatment was bigger than that before treatment. The shape of CeO_2 powder changed from cubic to spherical with increasing pH.
2. Crystal growth of CeO_2 during hydrothermal treatment was influenced by the pH rather than mineralizer.

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