

Preparation of Yttrium Carbonate by Hydrothermal
Precipitation Method

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Abstract

Fine yttrium carbonate (hydrate and hydroxide) powders were prepared by hydrothermal precipitation from the mixed solution of yttrium chloride and urea. The mixed solutions were treated under various hydrothermal conditions in a zirconium-lined autoclave. Under the hydrothermal condition, urea acts as a precipitation agent by decomposing into CO_2 and NH_3 .

The products were washed with distilled water and ethanol by centrifugation to remove Cl^- and NH_4^+ ions. The products obtained were crystalline yttrium carbonate powders involved water. The water content were depended on the hydrothermal temperatures. Some unknown phases were obtained by hydrothermal precipitation at 220°C .

Observation under SEM indicated that the plate-like or foliated powders. The particle morphology was depended on the hydrothermal conditions. The crystalline yttrium carbonate was transformed to amorphous by calcination at 500°C and yttrium oxide above 700°C .

1. Introduction

Yttrium has played an important role as a fluorescent substance and a ceramic raw material so far. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has recently gained attention as a high-temperature superconductor¹⁾ and accordingly yttrium compounds have increasingly become the object of public attention. Considering the background of the yttrium compounds, the authors have tried to synthesize yttrium carbonate by the hydrothermal precipitation method.

Although yttrium is generally used as oxide, the demands of chloride, nitrate and carbonate have been increasing as the range of use of yttrium has increased. Yttrium carbonate is produced by adding ammonium hydrogencarbonate to a water-soluble yttrium salt solution. Long time aging or hydrothermal treatment is, however, required to prepare crystalline yttrium carbonate powder.

Crystalline yttrium carbonate is known as hydrate (tengerite) and hydroxide (ancylite). Perttunen²⁾ and Tareen et al.³⁾ presented X-ray diffraction data.

Nagashima et al.⁴⁾ prepared yttrium carbonate hydrate in such a way that trichloroacetic acid was added to an yttrium chloride aqueous solution, which was neutralized with ammonia water, and the heated solution was aged for a long time. Beall⁵⁾ and Tareen et al.³⁾ prepared yttrium hydroxide carbonate by the hydrothermal process. Beall et al. synthesized it by the hydrothermal treatment of commercially available yttrium carbonate at 360°C for 168 hours under 76 MPa in an ammonium chloride solution saturation with carbon dioxide. Tareen et al. prepared it by the hydrothermal treatment of yttrium hydroxide gel using formic acid as the mineralizer at 220 to 260°C for 80 to 90 hours under 35.3 MPa.

The authors previously prepared fine crystalline zirconia powder by the hydrothermal treatment of a zirconium oxychloride

solution containing urea at approximately 200°C^{6,7)}. Urea was hydrolyzed in the hydrothermal process into ammonia and carbon dioxide. While most of ammonia was consumed in the neutralization reaction, carbon dioxide remained unchanged in an autoclave, keeping the partial pressure considerably high. Just as it was estimated that yttrium carbonate would be also prepared in the same way as that, yttrium carbonate was successfully synthesized by this hydrothermal process.

2. Experimental method

Fig.1 illustrates the flow sheet of the experiment. An yttrium chloride aqueous solution was obtained by dissolving 99.9 %-yttrium oxide^{*1)} in 4N-hydrochloric acid at 70°C. The aqueous solution was diluted to 0.25, 0.5 and 1.0 mol/L with pure water and these diluted solutions were used as the starting solutions. Urea 1.2 times as much as the amount required for neutralization was added to each solution and the solution was hydrothermally treated at a temperature of 140 to 220°C for one to five hours. The solution was heated up to the specified temperature at the rate of 100°C/h and stirred at 500 rpm during the hydrothermal treatment process. A 1L-zirconium-lined autoclave with a stirrer was used for the hydrothermal treatment and 600mL of the solution was charged into it.

The reaction products were washed in a centrifugal separator until neither chlorine nor ammonium ions were detected and dried at 120°C for 24 hours in an air bath.

The reaction products were analyzed by the powder X-ray diffractometry (XRD; RU-200, Rigaku Electric Co., Ltd., Tokyo,

*1) Made by Nippon Yttrium Co., Ltd.

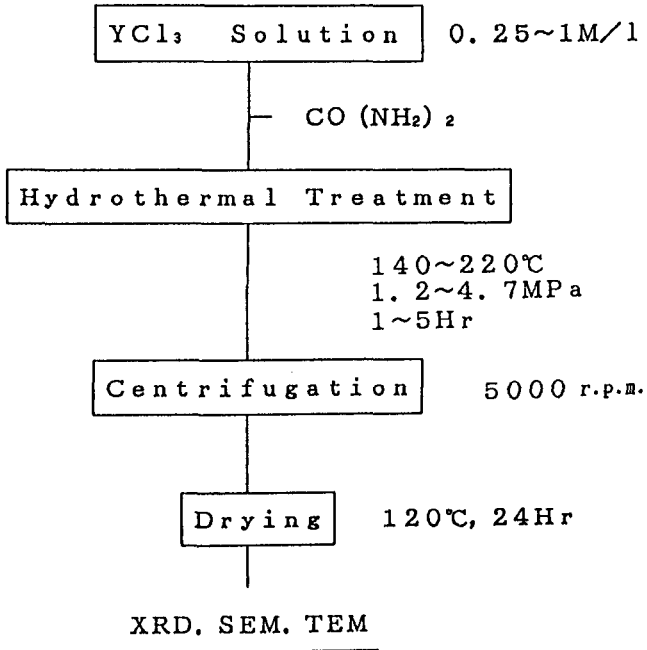


Fig. 1 Processing flow sheet of hydrothermal treatment.

Japan). As occasion demands, the reaction products were analyzed by the thermogravimetry and differential thermal analysis (TG and DTA; TG/DTA 300, Seiko Instruments & Electronics Ltd., Tokyo, Japan), and the particle shape was determined by the scanning electron microscopy (SEM; JSM-255, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM; JEM-2000EX, JEOL Ltd., Tokyo, Japan).

3. Results and Discussion

The pressure during the hydrothermal treatment process depended upon the temperature and concentration of solution and it was increased up to the pressure higher than the saturated vapor pressure by the production of carbon dioxide and ammonia. For instance, the pressure of an 1 mol/L-solution was 1.2 MPa at 140°C and 4.7 MPa at 220°C. Precipitable white powders were produced under all the hydrothermal treatment conditions in the experiments and the dried powders were bulky.

Figs 2 and 3 illustrate the powder X-ray diffraction patterns. Fig. 2 shows the X-ray diffraction patterns of the products obtained by the hydrothermal treatments of 1mol/L-solutions at various temperatures for 5 hours. Considerably crystalline yttrium carbonate hydrate [$Y_2(CO_3)_3 \cdot nH_2O$ ($n = 2$ or 3)], YI, was produced at 140°C. Yttrium hydroxide carbonate [$Y(OH)CO_3$], YII, was mixed in the hydrate with the increase of temperature and the mixture of YII and an unknown phase, XI, was produced at 220°C.

Another unknown phase, XII, was produced from a 0.25 mol/L-solution hydrothermally treated at 220°C for 5 hours as shown in Fig.3. The diffraction pattern of XII is sharp and the highest peak is observed at a position of 2θ of 12.04 ($d = 7.3$) on a lower angle side in Fig.3. The peak cannot be, therefore, identified by the

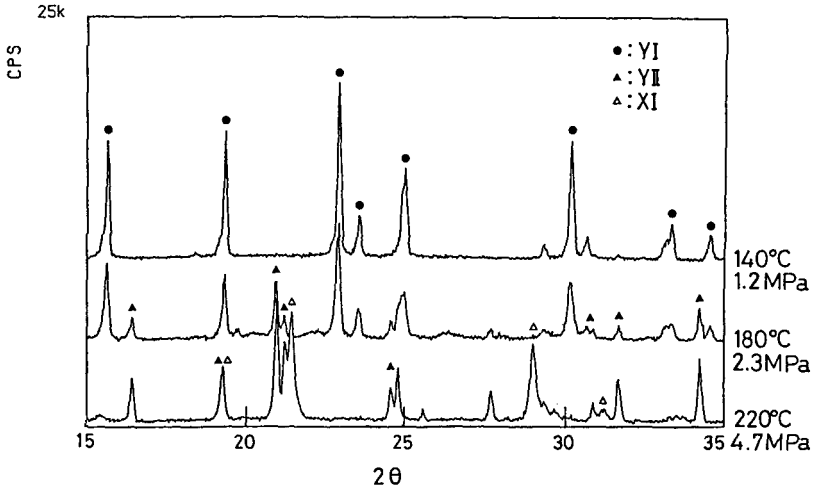


Fig.2 X-ray diffraction patterns of products by hydrothermal precipitation at various temperatures (1M/1,5Hr).

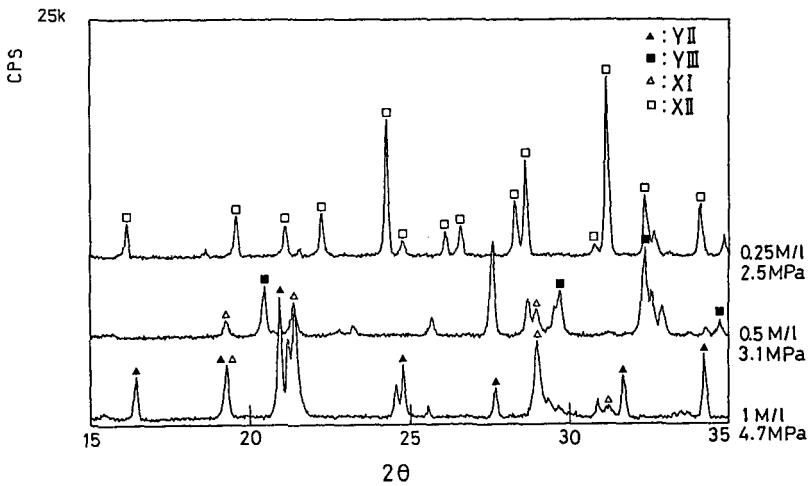


Fig.3 X-ray diffraction patterns of products by hydrothermal precipitation at various concentrations (220°C,5Hr).

JCPDS card. The chemical composition of the unknown phase, XII, was $Y : CO_2 = 1 : 0.24$. The reaction product from a 0.5 mol/L-solution was composed of YII, XI and yttrium hydroxide $[Y(OH)_3]$, YIII. It is considered that such a variety of phases are produced because the amount of urea added and consequently the partial pressure of carbon dioxide vary according to the concentration of solution.

The results of powder X-ray diffractometry of the reaction products obtained under various hydrothermal treatment conditions are shown in Table 1. Only YI was produced from the 0.5 and 1.0 mol/L-solutions at 140 and 180°C, and YII and XI were produced at 220°C. YII was produced even at 180°C for a long reaction time.

Fig.4 shows SEM photographs of the reaction products obtained by hydrothermal treatment of 1 mol/L-solutions at various temperatures for 5 hours. Photo A showing the products at 140°C reveals anisotropic plate particles 5 μm long and 1 μm wide each. Photo B showing the product at 180°C reveals hexagonal plate particles and Photo C showing the product at 220°C reveals flaky particles approximately 1 μm in size. It is known that hexagonal plate particles are produced by hydrothermally treating the orthorhombic hydrate and hydroxide^{3,8,9}). Chai et al.⁹⁾ produced yttrium carbonate $[Y_2O_2CO_3$ and $Y_2O(OH)_2CO_3]$ by the hydrothermal process though X-ray diffraction data were not disclosed. Although they mentioned that the crystal of $Y_2O_2CO_3$ is hexagonal and it forms also hexagonal plate particles, it is considered difficult to estimate the product from the shape of particle.

The thermal decomposition process of yttrium carbonate has been investigated by several researchers. A study by Nagashima et al.⁴⁾ reveals that large adsorption peaks are observed at 360°C

Table. 1 Products prepared by hydrothermal precipitation under various conditions

1Hr

Conc. (M/l) \ Temp. (°C)	140	180	220
0.25	YI	YII	YII
0.5	YI	YI	YI+YII+XI
1.0	YI	YI	YI+YII+XI

5Hr

Conc. (M/l) \ Temp. (°C)	140	180	220
0.25	YI	YII+XII	XII
0.5	YI	YII	YIII+XI
1.0	YI	YI+YII+XI	YII+XI

YI: $Y_2(CO_3)_3 \cdot 3H_2O$

YII: $Y(OH)CO_3$

YIII: $Y(OH)_3$

XI: ? Unknown

XII: ? Unknown

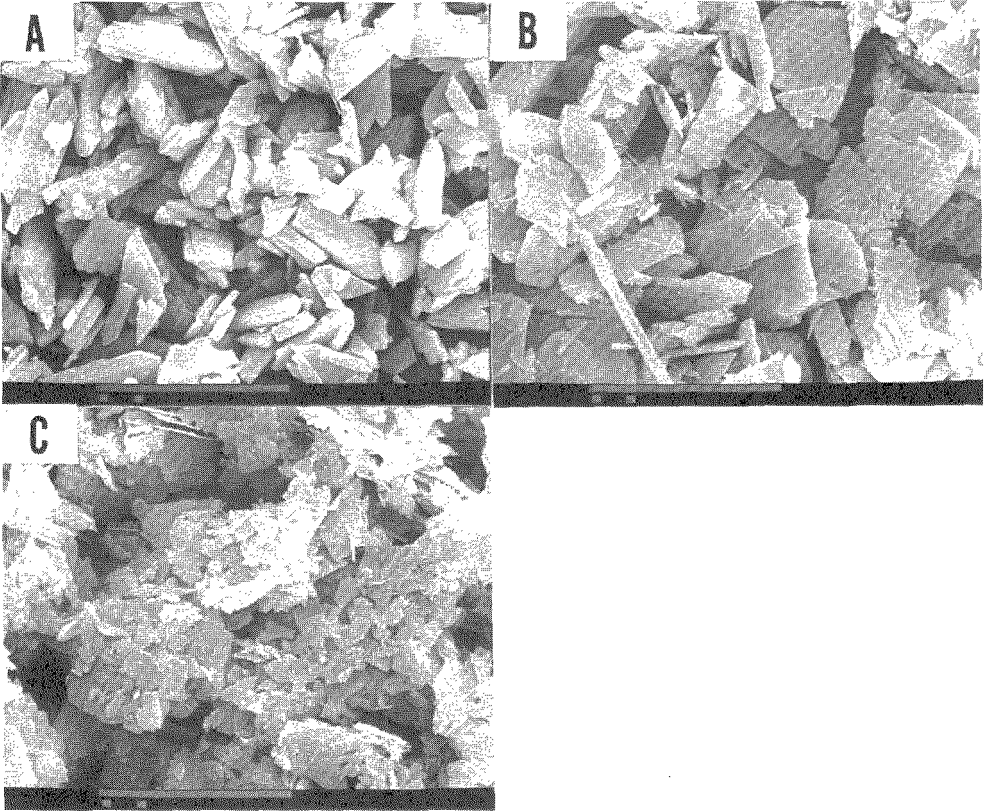


Fig.4 SEM photographs of the products by hydrothermal precipitation at various temperaturea (1M/L, 5Hr).

(A) 140°C, 1.2MPa (B) 180°C, 2.3MPa

(C) 220°C, 4.7MPa (bar=10um)

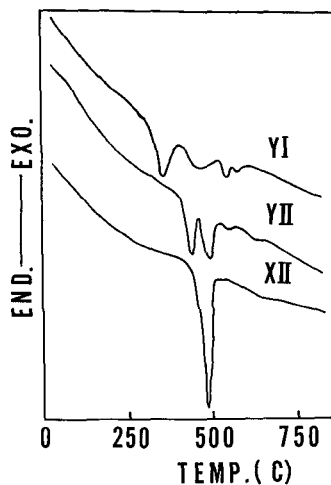
*2) and 560 and 610°C on the DTA curve of synthesized yttrium carbonate hydrate, corresponding to the dehydration and decarbonation reactions, respectively. D'assunção¹⁰⁾ reported that water of crystallization in yttrium hydroxide carbonate is released at 220°C and the dehydroxylation and decarbonation reactions of it take place at 520 to 640°C.

Fig.5 illustrated the DTA curves of reaction products obtained in the experiment. The figure reveals that an adsorption peak corresponding to the dehydration and those corresponding to the decarbonation are observed at 361°C and 466, 546 and 574°C, respectively, on the DTA curve of yttrium carbonate hydrate, and that no absorption peak corresponding to the dehydration is observed and absorption peaks corresponding to the dehydroxylation and decarbonation are observed at 443, 496, 550 and 631°C on the DTA curve of yttrium carbonate hydroxide. These curves are almost equivalent to the past experimental data. As mentioned above, two or more absorption peaks corresponding to the decarbonation are observed in the DTA curves. Maybe this is because oxo-carbonate was produced on the way of the reaction. Only an absorption peak is observed at 488°C on the DTA curve of unknown phase, XII. This is different from the above-mentioned DTA curves. It was found, therefore, that XII is decarbonated in an one-step process.

Fig.6 shows powder X-ray diffraction patterns of the products obtained by calcining yttrium carbonate hydrate. Amorphous product was formed at 500°C and yttria was produced at 700°C. All the products including unknown phases obtained by the hydrothermal treatment were transformed into yttrium oxide by calcining at 700°C

*2) Value from DTA curve

The paper describes that the value is 260°C



Y I : $Y_2 (CO_3)_3 \cdot 3H_2O$ XII : ? Unknown
 Y II : $Y (OH) CO_3$

Fig.5 DTA curves of the products prepared by hydrothermal precipitation.

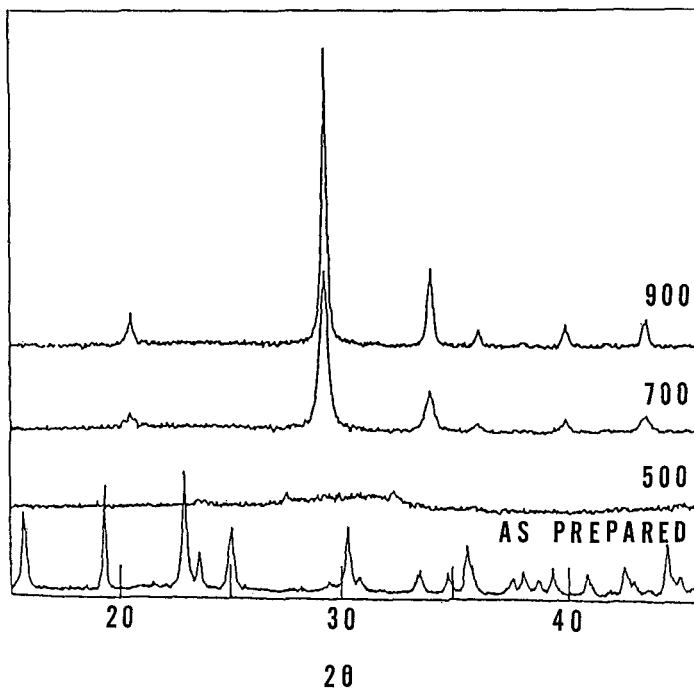


Fig.6 X-ray diffraction patterns of the products calcined at various temperatures.

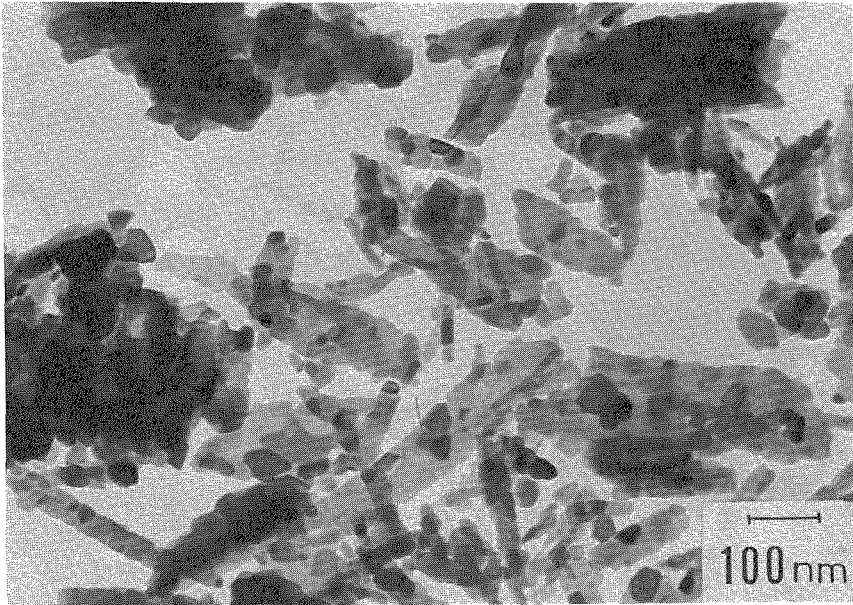


Fig.7 TEM photograph of the polycrystalline yttrium oxide by calcined at 900°C.

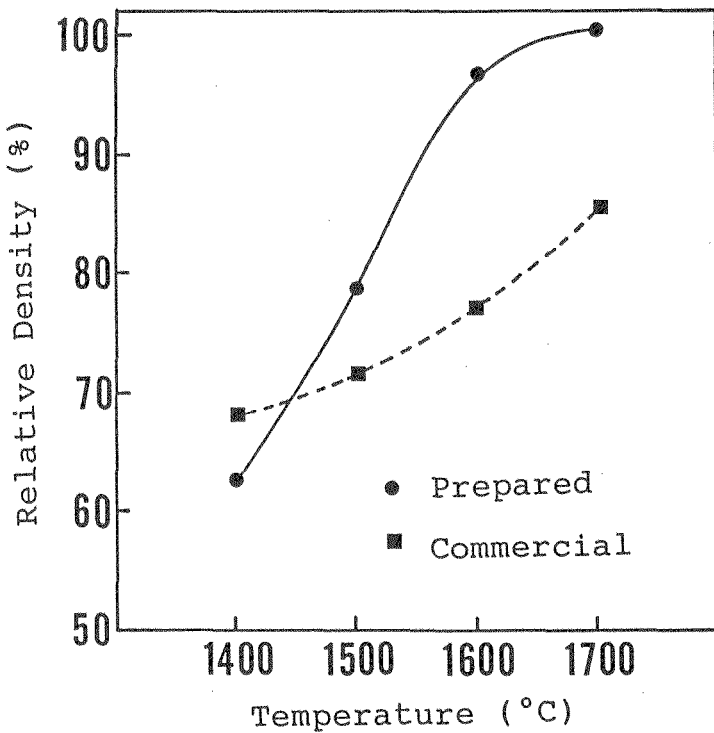


Fig.8 Effect of temperature on sintered density.

for one hour. Fig.7 shows a TEM photograph of yttrium oxide obtained by calcining yttrium carbonate hydrate at 900°C for one hour. Skeletal powder was prepared by calcining yttrium carbonate hydrate and the diameter of crystallite was approximately 30 nm. The skeletal powder can be easily pulverized. After calcining yttrium carbonate hydrate at 900°C for one hour, the skeletal powder was milled in a wet ball mill for three hours and then molded under 198 MPa in a pelletized. The sintering curves of the pellet are shown in Fig.8. Yttrium oxide produced in the experiment has superior sintering characteristics to those of commercially available one, and the density of yttrium oxide sintered at 1700°C for two hours reached nearly the theoretical density^{*3)}.

The identification of the unknown phases and investigation of sintering characteristics will be further made.

4. Conclusions

It became possible to produce crystalline yttrium carbonate by the hydrothermal precipitation method in a short time. The water content varied according to the hydrothermal treatment conditions. Hydrate was produced at low temperatures, while hydroxide was produced at high temperature. Moreover, it was found that unknown phases were produced under certain hydrothermal precipitation conditions. Those reaction products were transformed into yttrium oxide by the calcination at 700°C or higher. The yttrium oxide produced by calcining yttrium carbonate hydrate has excellent sintering characteristics and the density of yttrium oxide produced by sintering at 1700°C reached nearly the theoretical value.

*3) 5.031 g/cm³

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