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THERMAL TRANSFORMATION OF YTTRIUM HYDROXIDES TO YTTRIUM OXIDES

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ABSTRACT

The reaction between aqueous solutions of yttrium salts (chloride and nitrate) at constant concentration and alkaline solutions (sodium and ammonium hydroxides) were investigated under different conditions. As a result, amorphous and hexagonal yttrium hydroxides, $Y(OH)_3$, were formed and in addition monoclinic yttrium hydroxide, α-$Y(OH)_3$, was prepared hydrothermally from amorphous yttrium hydroxide. The materials so obtained were examined by thermogravimetry and differential thermal analysis (TG and DTA), and yttrium hydroxides and their thermal decomposition products by X-ray diffraction study and infrared spectrophotometry. The sequence for the thermal decomposition of those materials is proposed on the basis of the results obtained.

INTRODUCTION

Recently yttrium oxide was found to be not only important as a raw material for electronics and ceramics, but it attracts many researches' attention as a component of superconductors. Accordingly the formation of yttrium oxide by thermal decomposition of yttrium hydroxide has been investigated in the present work. However, since the literature on the preparation of the hydroxide and oxide of yttrium is limited [1-5] , it is preferred to survey the preparation of yttrium hydroxides first and then their thermal decompositions.

EXPERIMENTAL

The reaction between aqueous solutions of yttrium salts (chloride and nitrate) at constant concentration and alkaline solu-

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tions (sodium and ammonium hydroxides) have been investigated under different conditions such as molar ratio [OH]/[Y], alkaline concentration, ageing period and temperature, etc. The resulting precipitates were washed with distilled water as free as possible from alkali and anions, and then dried with air.

Consequently, amorphous and hexagonal yttrium hydroxides, $Y(OH)_3$, were obtained, and then monoclinic yttrium hydroxide, α-$Y(OH)_3$, was prepared hydrothermally from amorphous yttrium hydroxide for 20 h at 300°C.

The materials so obtained were examined by thermogravimetry and differential thermal analysis (TG and DTA) [6], and yttrium hydroxides and their thermal decomposition products by X-ray diffraction study and infrared spectrophotometry [7]. The decomposition products were prepared by heating the samples at the stated temperature for 1 h after heating up to the temperature at the rate of 5°C min^{-1} under **atmospheric pressure.**

RESULTS AND DISCUSSION

Preparation of yttrium hydroxides

Although the composition of the precipitates does not depend on the kind of the yttrium salt, the basic yttrium salt is precipitated when the amount of alkali is not enough in comparison with the concentration of yttrium salt. Amorphous yttrium hydroxide, $Y(OH)_3 \cdot xH_2O$, is formed in the presence of excess alkali. By ageing for 9 days at 80°C in sodium hydroxide solutions at $[NaOH] > 6$ mol dm^{-3}, amorphous yttrium hydroxide **transforms into hexagonal yttrium hydroxide.** From these some representative samples are chosen (Table 1), and mono-

Table 1 $Y(OH)_3$ used as samples

Specimen No.	Conditions of preparation				Molar ratio $[H_2O]/[Y]$	Crystallographic composition[b)]
	[NaOH], mol dm^{-3}	Y salt added[a)]	Temp., °C	Ageing time, h		
1	1	YCl_3	50	1	5.19	A
2	1	$Y(NO_3)_3$	50	1	5.40	A
3	20	YCl_3	80	216	2.88	H
4	20	$Y(NO_3)_3$	80	216	2.93	H

a) Aqueous solutions of yttrium salts are in 0.1 mol dm^{-3}, and the rate of addition of those to alkaline solutions is 50 cm^3 min^{-1}.

b) A and H represent amorphous and hexagonal, respectively.

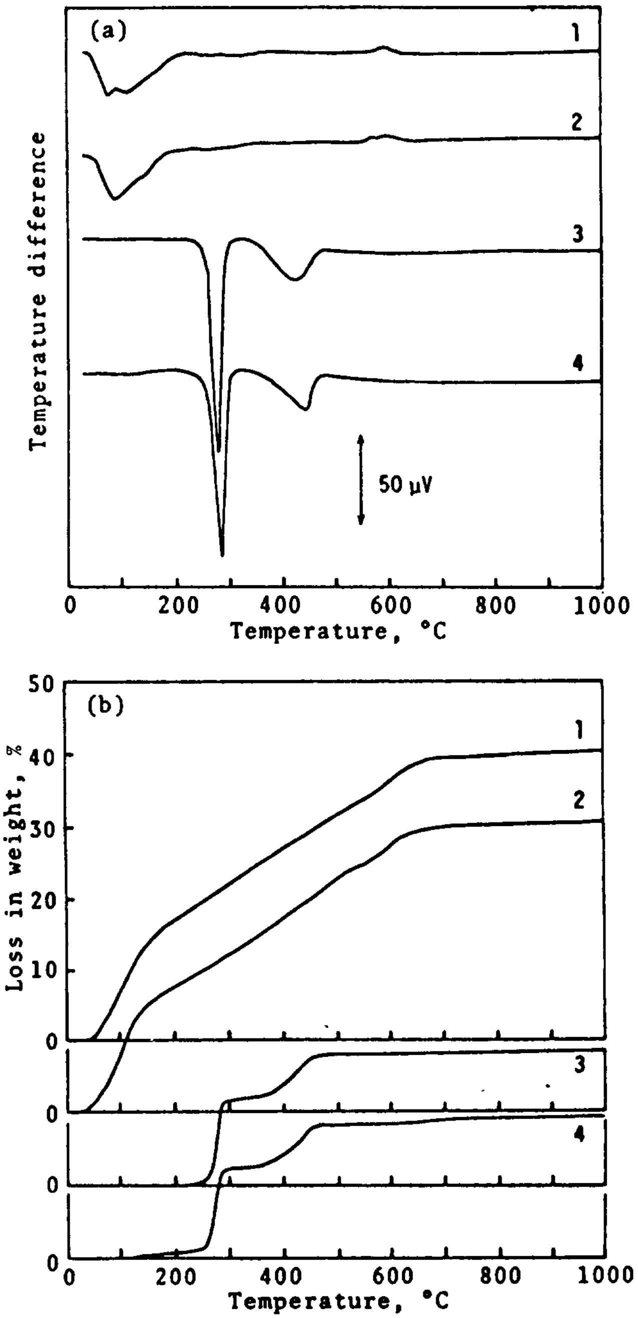

Fig. 1. DTA(a) and TG(b) curves of $Y(OH)_3$.

clinic yttrium hydroxide is prepared by hydrothermal treatment of the specimens Nos.1 and 2.

Thermal decomposition of yttrium hydroxides

The DTA curves of the amorphous yttrium hydroxides show a broad endothermic reaction centred around about 100°C and an endothermic peak at 500°C (Fig. 1(a)). The TG curves reveal that the weight-loss starts at 50°C but becomes more slowly at about 130°C. Weight-loss continues up to 600°C, when the sample attains constant small loss in weight. (Fig. 1(b)). The weight-loss at 1000°C suggests the molar ratio of $[H_2O]/[Y_2O_3] \approx 5 - 5.5$ in the composition $Y(OH)_3 \cdot xH_2O$ where x = 2 2.5. The X-ray diffraction results indicate that these reactions arise from the fact that the amorphous yttrium hydroxide decomposes thermally to amorphphous yttrium oxide until 500°C and transformes to cubic yttrium oxide at about 600°C. The infrared spectrum of amorphous yttrium hydroxide shows the OH stretching broad band with a maximum at 3300 cm^{-1}, the OH bending band at 1630, 1510 and 1390 cm^{-1}, the Y-OH bending absorption band at 980 and 720 cm^{-1}, and the broad band centred around about 540 and 365 cm^{-1}, assigned to the Y-O stretching frequency. Those absorptions become weak in intensity with increasing the temperature on heating, and the Y-O stretching bands appear at 560, 465, 375, 335 and 305 cm^{-1}, corresponding to the X-ray results.

The DTA curves of the hexagonal yttrium hydroxides reveal a sharp endothermic peak at 280°C and an endotherm at 330°C (Fig.1(a)). Those reactions occur at the points near the changes in shape of the TG curves (Fig.1(b)). The weight-losses of the first and second steps are about 12 and 7 %, respectively, and additionally the loss in weight at 1000°C indicates the molar ratio of $[H_2O]/[Y_2O_3] \approx 3$ in the composition of $Y(OH)_3$. It is thus expected that those weight-losses correspond to the respective thermal decompositions of $Y(OH)_3 \rightarrow YOOH$ and $YOOH \rightarrow Y_2O_3$. X-ray diffraction results for the thermally decomposed products exhibit the patterns of monoclinic YOOH at 300°C and cubic Y_2O_3 at 400°C, respectively. The infrared spectrum of hexagonal yttrium hydroxide gives the sharp absorption at 3600 cm^{-1} and the broad band until around 2800 cm^{-1}, due to the OH stretching vibration, the weak band due to the OH bending frequencies at 1630, 1510 and 1390 cm^{-1}, the broad band due to the Y-OH bending vibrations at 980 and 720 cm^{-1}, and the Y-O stretching absorption centred around about 550 and 365 cm^{-1}. These OH vibrations are hardly change on heating to 200°C, but at 300°C the intensities of the bands except the absorption at 3600 cm^{-1} decrease and the Y-O absorption appears at 475 and 350 cm^{-1}. At 400°C the Y-O absorption band is observed at 560, 465, 375, 335 and 305 cm^{-1}. As the infrared results support the X-ray diffraction ones, it is inferred that hexagonal yttrium hydroxide dehydrates to a monoclinic YOOH at 300 °C and decomposes thermally to cubic yttrium oxide at 450°C.

Accordingly the following schematic process is given for the thermal decomposition of amorphous and hexagonal yttrium hydroxides :

$$\begin{tikzcd}
Y(OH)_3 \cdot xH_2O(\text{amorphous}) \arrow[r, "500^\circ C"'] & Y_2O_3 \ (\text{amorphous}) \arrow[dr, "600^\circ C"] & \\
 & & Y_2O_3 \ (\text{cubic}) \\
Y(OH)_3(\text{hexagonal}) \arrow[r, "300^\circ C"] & YOOH \ (\text{monoclinic}) \arrow[ur, "450^\circ C"'] &
\end{tikzcd}$$

In contrast, the DTA curve of α-$Y(OH)_3$ denotes the endothermic reaction at 430°C, and the broad endotherm centred around 680°C (Fig.2). These reactions occur at points near the change in shape of the TG curve, corresponding to the respective weight-losses of about 9 and 4 % (Fig.2). The weight-loss at 1000°C gives the molar ratio of $[H_2O]/[Y_2O_3] \approx 2.6$ in the composition of $Y(OH)_3$. In the X-ray diffraction diagram of monoclinic α-$Y(OH)_3$, the peaks change little on heating below 300°C, and the intensity of those lines decreases at 400°C. On heating at 500°C, the new diffraction peaks appear, and these peaks become more intense at 600°C. From the loss in weight of TG curve, it is deduced that this phenomenon corresponds to the formation of YOOH which transforms to cubic yttrium oxide at 700°C. The infrared spectrum of α-$Y(OH)_3$ reveals the OH stretching band at 3600, 3500 and 3410 cm^{-1}, the OH bending band at 1520, 1420 and 1390 cm^{-1}, the Y-OH bending absorption at 800 and 675 cm^{-1}, and the broad absorption band centered around about 580, 440, 382, 370 and 340 cm^{-1}. In accordance with X-ray results, those absorptions point out little change on heating below 300°C, and decrease in intensity at 400°C; at 500°C, the OH bending band at 1560 , 1500 and 1400 cm^{-1} and the broad band centred around about 450 cm^{-1} due to the Y-O stretching vibration appear.

Hence it is found that the thermal decomposition of monoclinic α-$Y(OH)_3$ proceeds in

$$\alpha\text{-}Y(OH)_3 \xrightarrow[\sim 450^\circ C]{} YOOH \xrightarrow[\sim 700^\circ C]{} Y_2O_3 \ (\text{cubic}).$$

CONCLUSIONS

By the reaction between aqueous solutions of yttrium salts and alkaline solutions, amorphous yttrium hydroxide is precipitated as

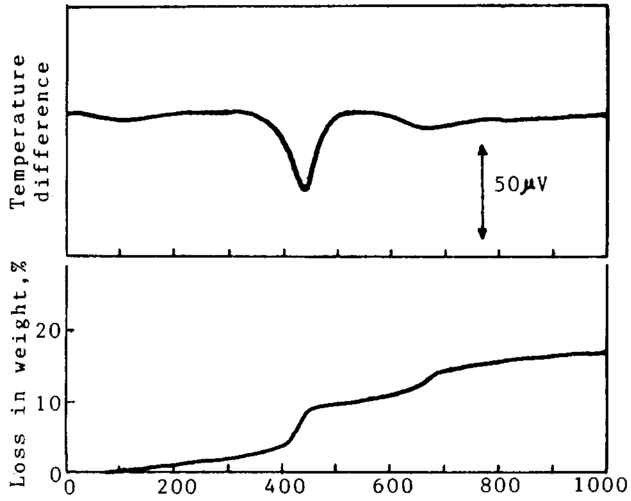

Fig. 2. DTA and TG curves of α-$Y(OH)_3$

the composition of $Y(OH)_3$ xH_2O. Hexagonal yttrium hydroxide is formed by ageing of amorphous yttrium hydroxide in alkaline solutions. Monoclinic yttrium hydroxide, α-$Y(OH)_3$, is prepared by hydrothermal treatment of amorphous yttrium hydroxide.

The thermal decomposition of those yttrium hydroxides proceeds in the following sequence:

$$\begin{tikzcd}
Y(OH)_3 \cdot xH_2O \text{ (amorphous)} \arrow[r, "500°C"'] & Y_2O_3 \text{ (amorphous)} \arrow[dr, "600°C"] & \\
Y(OH)_3 \text{ (hexagonal)} \arrow[r, "300°C"] & YOOH \text{ (monoclinic)} \arrow[r, "450°C"] & Y_2O_3\text{(cubic)} \\
\alpha\text{-}Y(OH)_3 \text{ (monoclinic)} \arrow[r, "\sim 450°C"'] & YOOH \arrow[ur, "\sim 700°C"'] &
\end{tikzcd}$$

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