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THERMAL DECOMPOSITION OF ZIRCONIUM HYDROXIDE

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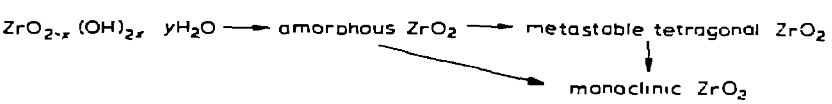
ABSTRACT

The thermal decomposition of zirconium hydroxides prepared from aqueous ammonium hydroxide solutions on the addition of potassium fluorozirconate, K_2ZrF_6, under various conditions has been examined by thermogravimetry, differential thermal analysis, X-ray diffraction study and infrared spectrophotometry. As a result, it is found that the thermal decomposition of zirconium hydroxide proceeds according to



In this process, the transformation of amorphous ZrO_2 to either the metastable tetragonal or monoclinic form depends on the composition of the original starting material as an hydrated oxyhydroxide, $ZrO_{2-x}(OH)_{2x} \cdot y\,H_2O$ where $x \leq 2$ and $y \geq 1$.

INTRODUCTION

The properties of zirconium oxide prepared by the thermal decomposition of zirconium hydroxide have been investigated by a number of researchers [1—10]. In particular, Cypries et al. [1] reported a curve for the differential thermal analysis (DTA) of zirconium hydroxide exhibiting a broad endothermic reaction at 175—300°C and a sharp exothermic peak at 405°C, and they have interpreted the latter reaction as being due to the transformation of amorphous zirconia to the tetragonal form. According to Livage et al [2], the somewhat explosive crystallization into tetragonal zirconia appears at about 430°C. In contrast, Selim et al. [3] have suggested that the transformation of zirconium oxyhydroxide to amorphous oxide, viz. $ZrO(OH)_2 \rightarrow ZrO_2 \cdot H_2O$ appears as a sharp exothermic effect at 460°C, and then part of the amorphous oxide which transforms to a metastable form gives rise to the exotherm at 540°C, although the former exothermic effect is believed by some to be due to the crystallization of amorphous zirconia into the monoclinic form. However, since some discrepancies still remain in the observations on the thermal decomposition of zirconium hydroxide, the present work has been undertaken to obtain further information on its thermal decomposition.

EXPERIMENTAL

A number of earlier investigators used hydrated amorphous precipitates from an aqueous zirconium oxychloride solution with ammonia. In this experiment, however, zirconium hydroxide was precipitated by pouring rapidly or slowly at the rate of 10 ml min^{-1} an aqueous solution containing 10 g l^{-1} of potassium fluorozirconate [11], K_2ZrF_6, into 1.5, 7.5 and 15 *M* ammonia at 20, 50 and 80°C; the resulting precipitates were aged in the mother liquors for 1 h at a selected temperature, centrifuged, washed with distilled water until as free as possible from alkali and anion, and then dried in air at room temperature. The zirconium concentration in aqueous solution was determined by EDTA titration using xylenol orange as an indicator [12].

The thermally decomposed products were prepared by heating the samples at the stated temperatures for 1 h after being heated to this temperature at a rate of 5°C min^{-1} on the basis of the results of thermal analysis.

The materials so obtained were examined by thermogravimetry and differential thermal analysis (TG and DTA), X-ray diffraction study and infrared spectrophotometry, according to the procedures described previously [13,14]. TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus made by the Agne Research Center, using platinum—platinum/rhodium thermocouple at a heating rate of 5°C min^{-1} in air [14] X-Ray powder diffraction diagrams were obtained on a Rigaku Denki diffractometer [14]. Infrared spectra were determined by a Nujol or Fluorube mull method on a Shimazu Model infrared spectrophotometer, equipped with a sodium chloride prism, using a Japan Spectroscopic Co Ltd. Model IRA-1 grating infrared spectrophotometer for measurements at 4000—650 cm^{-1}, and a JASCO Model IR-F (a grating model) for measurement at 700—200 cm^{-1}, using a capillary film between thallium halide plates or polyethylene.

RESULTS AND DISCUSSION

For the precipitates from ammonia on addition of aqueous potassium fluorozirconate solution, the condition of precipitation, the decomposition temperature, i.e. the peaks in the DTA curve, and the value of the molar ratio $[H_2O]/[ZrO_2]$, determined by the loss in weight on ignition above 100°C, are shown in Table 1. The TG and DTA curves for each specimen are illustrated in Fig. 1 and 2, respectively. Figures 3—8 and Table 2 give the infrared and X-ray results for the zirconium hydroxide specimens and their thermally decomposed products, but only representative X-ray diffraction diagrams and infrared spectra for the materials derived from a few specimens heated at various temperatures are shown in these figures.

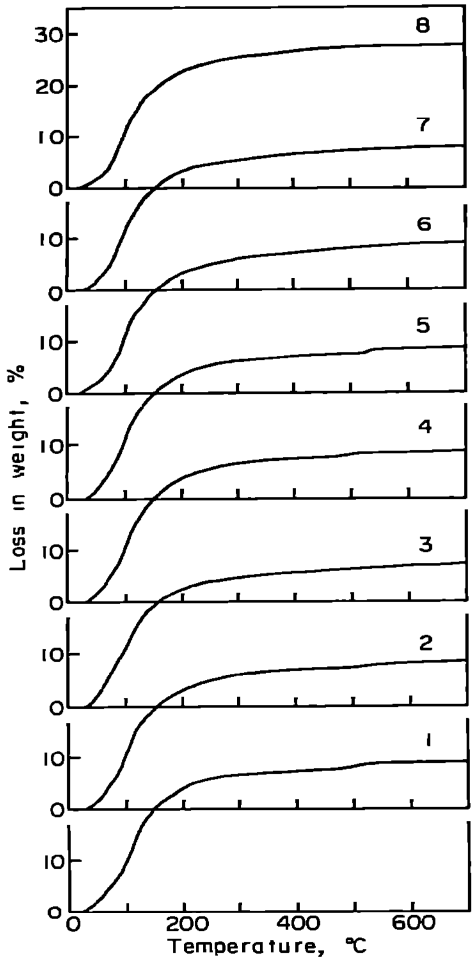
The results of the thermal analysis (Table 1 and Figs. 1—2) suggest that the thermal decomposition behaviour of zirconium hydroxide precipitates occurs in two ways. The DTA curve exhibits the broad endothermic reaction at about 140°C, accompanied by the endothermic one which

TABLE 1

Precipitates from aqueous ammonium hydroxide solutions on addition of aqueous K_2ZrF_6 solutions

Specimen no.	Condition of precipitation				Temp. of reaction in DTA curve [a] (°C)		Molar ratio $[H_2O]/[ZrO_2]$
	$[K_2ZrF_6]$ ($g\ l^{-1}$)	$[NH_4OH]$ (M)	Temp. (°C)	Rate of addition of K_2ZrF_6	Endo. [a]	Exo [a]	
1	10	1.5	20	Rapid	80, 139	462, 492	2.36
2	10	1.5	50	Rapid	80, 110	470, 483, 505	2.19
3	10	1.5	80	Rapid	80, 148	452	2.04
4	10	1.5	20	Dropwise	80, 143	468	2.33
5	10	7.5	20	Rapid	80, 141	468	2.30
6	10	7.5	50	Rapid	80, 140	459	2.30
7	10	7.5	20	Dropwise	80, 140	460	2.21
8	10	15	20	Rapid	80, 141	438	2.29

[a] Endo. and Exo. represent the endothermic and exothermic reaction, respectively



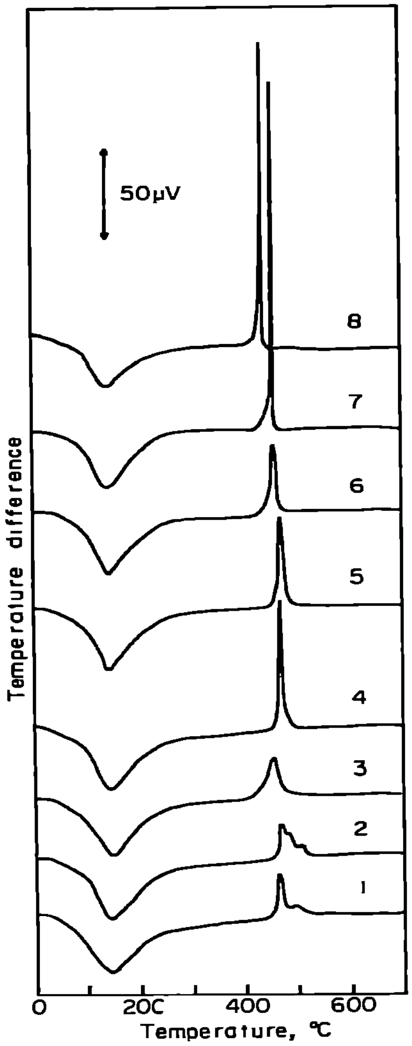


Fig. 1. TG curves for zirconium hydroxides. The figures on the curves represent the speciment numbers in Table 1.

Fig. 2. DTA curves for zirconium hydroxides. The figures on the curves represent the specimen numbers in Table 1.

appears as a shoulder centered around 80°C, and the exothermic reaction at about 450°C. The endotherm appears at the same temperature for all specimens, but the exotherm depends on the conditions of preparation of the specimen: No. 1, at 460 and 490°C, No. 2, at 470, 483 and 505°C, Nos. 3—7 at 452—468°C and No. 8 at 438°C. From this it can be deduced that the exotherm in the DTA curve of the specimen will appear as a sharp peak at a lower temperature between 400 and 500°C when the precipitate is formed from a highly concentrated aqueous ammonium hydroxide solution when potassium fluorozirconate is added slowly and precipitated at a higher temperature. These reactions occur at points near the change in shape of the TG curves. In Figs. 1—2, it is found that the loss in weight for the TG curve

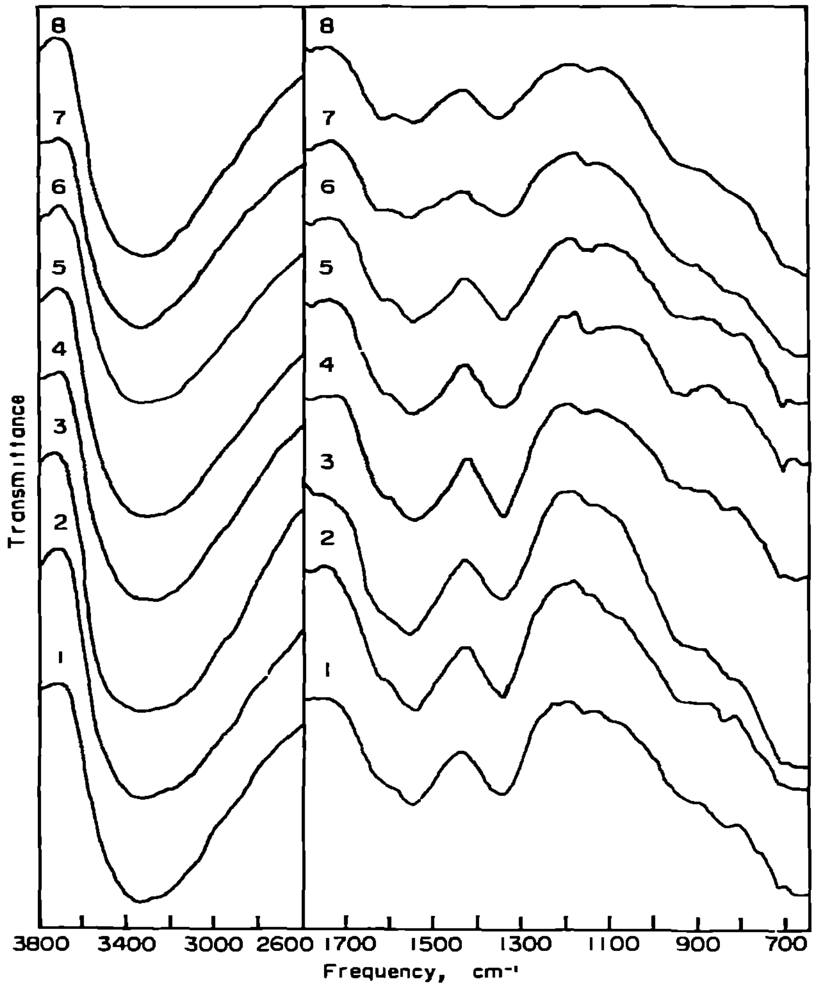


Fig 3. Infrared spectra for zirconium hydroxides. The figures on the curves represent the specimen numbers in Table 1.

TABLE 2

X-Ray diffraction results of the products derived from zirconium hydroxide heated at various temperatures

Temp (°C)	Specimen no.							
	1	2	3	4	5	6	7	8
400	Am	Am	Am	Am	Am	Am	Am	Am
500	T	T	T, M	T	T	T, (M)	T, M	M, T
600	T	T	T, M	T, (M)	T, (M)	T, M	T, M	M, (T)
700	T, M	T	T, M	T, (M)	T, M	T, M	M, T	M
800	T, M	T, M	T, M	T, M	T, M	T, M	M, T	M

Am, T and M represent amorphous, tetragonal and monoclinic ZrO_2, respectively.

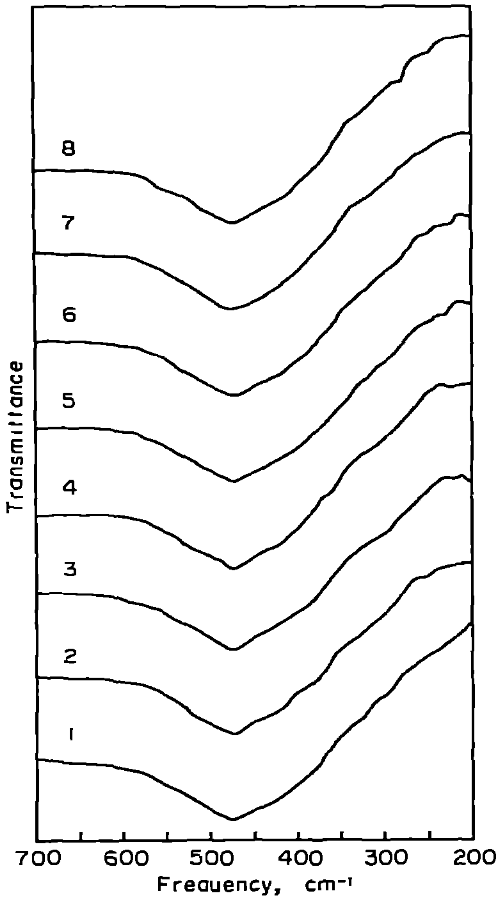


Fig. 4. Infrared spectra in the region of lower frequency for zirconium hydroxides The figures on the curves represent the specimen numbers in Table 1.

of the specimen below 100°C corresponds to the loss of a molecule of water, and above 100°C to the loss of two molecules of water, although the loss in weight of a few per cent is observed between 400 and 600°C. Figures 3—8 and Table 2 give the X-ray and infrared results for the zirconium hydroxide specimens and their thermally decomposed products. As represented in Figs. 7—8, the X-ray diffraction diagrams for the precipitates of all specimens show a typical pattern of the amorphous species, and the products heated at 200—400°C also give the amorphous form. In the infrared spectra (Figs. 3—6), however, the former exhibit the OH stretching band (broad) with a maximum at 3300 cm^{-1}, the OH bending bands at 1630, 1560 and 1340 cm^{-1}, and a broad absorption band centered around about 450 cm^{-1}, assigned to the Zr—O stretching frequency [10], while those of the latter show a very broad absorption band centered around 460 cm^{-1}, due to the Zr—O stretching vibration of amorphous ZrO_2, although the OH absorption bands still slightly remain. Additionally, for specimens 7 and 8, the intensity of the OH absorption band at 1620 cm^{-1} is similar to that at 1560 cm^{-1}, but for specimens 1—6, its relative intensity at 1620 cm^{-1} is lower

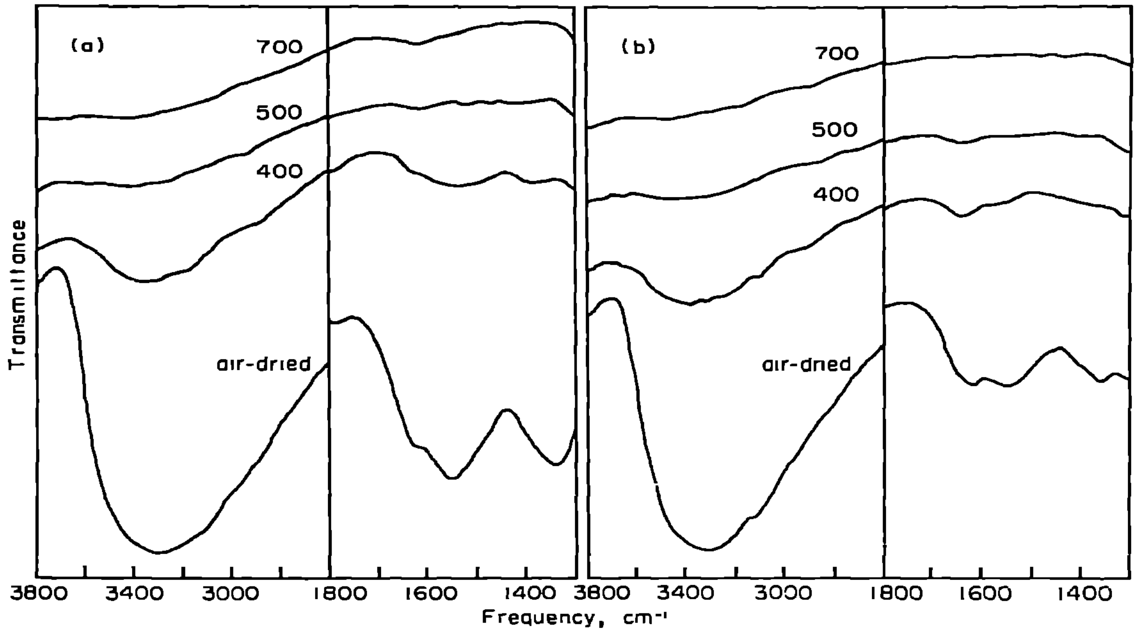


Fig 5 Infrared spectra for the materials derived from zirconium hydroxide heated at various temperatures. The figures on the curves represent the heating temperatures (°C). (a) From specimen 2 in Table 1; (b) from specimen 8 in Table 1.

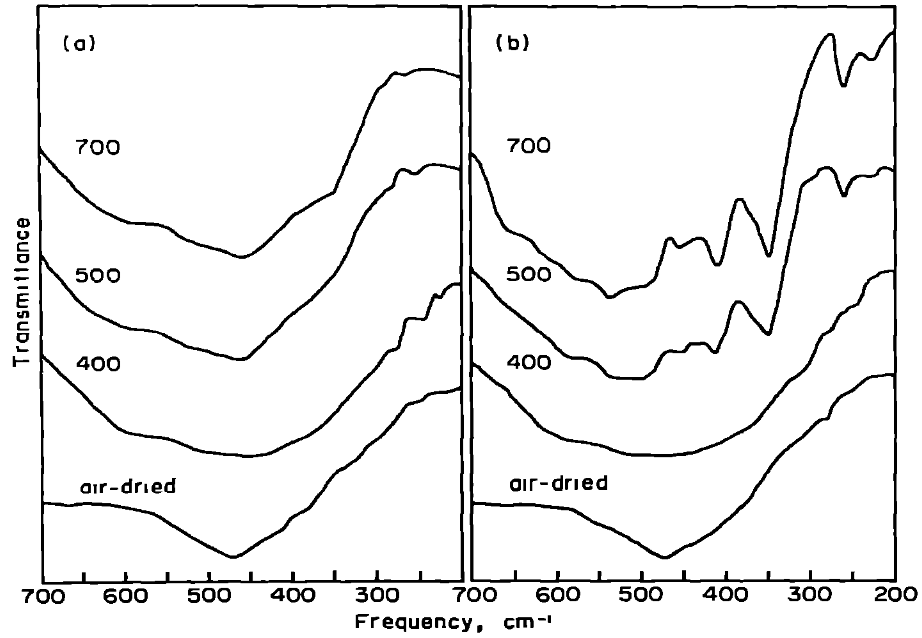


Fig. 6. Infrared spectra in the region of lower frequency for the materials derived from zirconium hydroxide heated at various temperatures. The figures on the curves represent the heating temperatures (°C) (a) From specimen 2 in Table 1; (b) from specimen 8 in Table 1.

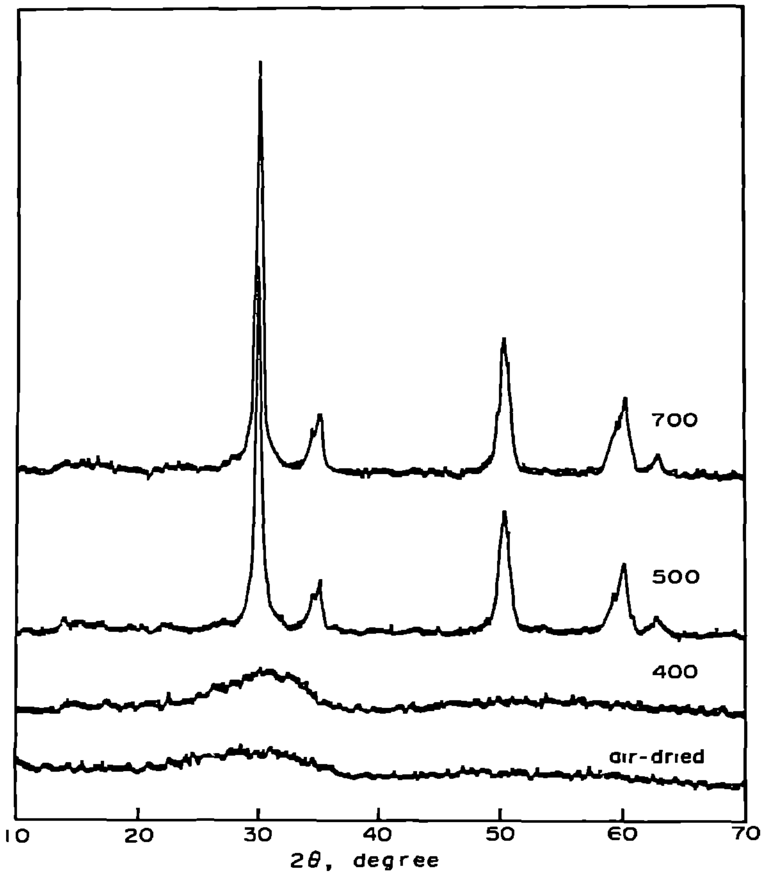


Fig. 7. X-Ray diffraction diagrams for the materials derived from zirconium hydroxide heated at various temperatures. The figures on the curves represent the heating temperatures (°C) of specimen 2 in Table 1

(Fig. 3). This implies that the combined effect of hydrogen bonding with hydroxyl groups for the former specimens is greater than for the latter ones. Accordingly, it is inferred that the composition of the precipitates is expressed as an amorphous hydrated oxyhydroxide, $ZrO_{2-x}(OH)_{2x} \cdot y\ H_2O$, where the value of $x \leqslant 2$ diminishes with the relation to the experimental condition to form the precipitate homogeneously from aqueous solution, and $y \simeq 1$ in this experiment. In addition, an amorphous zirconium oxide is produced by heating their precipitates at 200—400°C. At 500°C, the amorphous zirconium oxide crystallizes in a tetragonal or monoclinic phase, in which its formation is concerned with the kind of the specimen (Figs. 7—8 and Table 2). Only the tetragonal phase appears in the thermally decomposed products derived from specimens 1, 2, 4 and 5, and a mixture of the tetragonal phase and the monoclinic one from specimens 3, 6, 7 and 8. The major part of the material from specimen 8 is constituted from the monoclinic phase. A progressive increase in the intensities of both diffraction lines of the tetragonal and monoclinic phases is observed on heating at 600°C. With further heating, the decrease in the intensity of the tetragonal diffraction lines is accompanied by

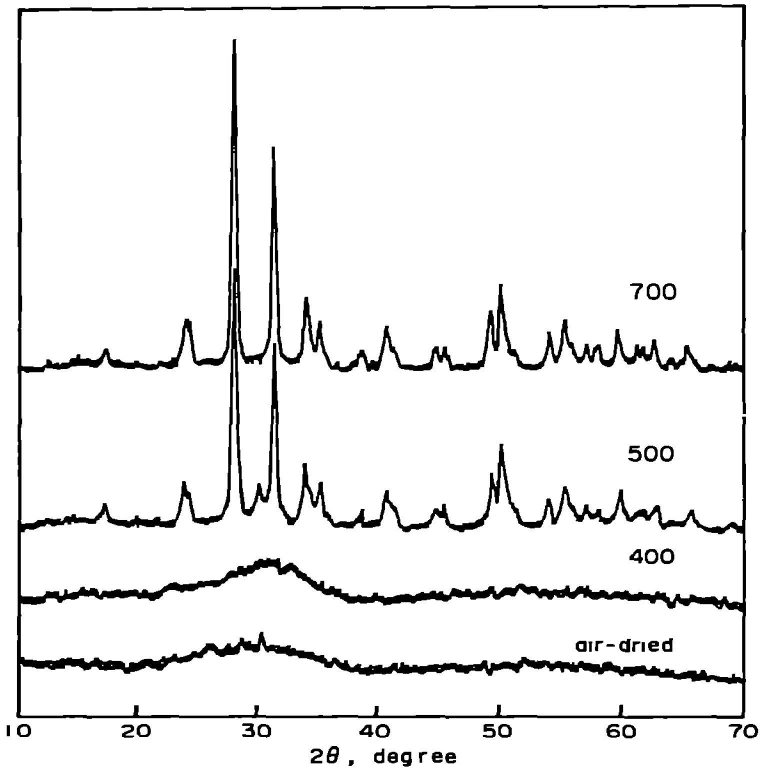


Fig. 8 X-Ray diffraction diagrams for the materials derived from zirconium hydroxide heated at various temperatures. The figures on the curves represent the heating temperatures (°C) of specimen 8 in Table 1.

the increase in that of the monoclinic ones. These facts imply that the tetragonal phase formed by heating at about 500° C at first exists in the metastable form [8,9] and then is transformed to the stable monoclinic phase with further heating. Moreover, the infrared spectra for the thermally decomposed products derived from the specimens heated at various temperatures (Figs. 5—6) show the characteristic absorptions [6,7,15] corresponding to the X-ray diffraction results. On heating at 500° C, the very broad bands centered around 460 and 350 cm^{-1}, due to the formation of the tetragonal phase, are observed for the materials derived from specimen 2, and the absorptions at 575—480, 453, 413, 348, 260 and 230 cm^{-1}, ascribed to the presence of the monoclinic phase, from that for specimen 8. Therefore the following interpretation may be given for the DTA curve. the first endothermic reaction at 80° C is due to the release of adhesive water, the second endothermic reaction at about 140° C arises from the dehydroxylation during the thermal decomposition of zirconium hydroxide to amorphous zirconium oxide, and the final exothermic reaction at about 450° C is attributed to the crystallization of the amorphous zirconium oxide into the tetragonal or monoclinic phase. This explanation is also supported by the result that the molar ratio $[H_2O]/[ZrO_2]$, obtained from the loss in weight of the TG curve corresponding to the endothermic reaction at ~140° C in the DTA curve, is nearly two, as indicated in Table 1, suggesting that the release of two molecules of water occurs in the thermal decomposition of zirconium hydroxide.

Hence it is concluded that the thermal decomposition of zirconium hydroxide proceeds according to

$$\begin{tikzcd} ZrO_{2-x}(OH)_{2x}\cdot yH_2O \arrow[r] & \text{amorphous } ZrO_2 \arrow[r] \arrow[dr] & \text{metastable tetragonal } ZrO_2 \arrow[d] \\ & & \text{monoclinic } ZrO_2 \end{tikzcd}$$

where $x \leqslant 2$, and $y \simeq 1$. In this process, the transformation of amorphous zirconium oxide to either the metastable tetragonal or monoclinic form depends on the composition of the original starting material When the precipitate is homogeneously prepared from aqueous solution, the amorphous zirconium oxide formed by heating its precipitate crystallizes in a monoclinic phase.

REFERENCES

1 R. Cypries, R. Wollat and J. Raucq, Ber Dtsch. Keram. Ges., 40 (1963) 527, and the references cited therein.
2 J. Livage, K Doi and C. Mazieres, J. Am. Ceram. Soc., 51 (1968) 349, and the references cited therein.
3 S A. Selim and T.M. El-Akkad, J. Appl Chem. Biotechnol., 27 (1977) 58, and the references cited therein.
4 G.L Clark and D.H. Reynolds, Ind Eng. Chem , 29 (1937) 711.
5 A Dietzel and H Tober, Ber Dtsch. Keram. Ges , 30 (1953) 47.
6 N T. McDevitt and W.L. Baum, J. Am. Ceram. Soc., 47 (1964) 622.
7 C.M. Phillippi and K.S. Mazdiyasni, J. Am. Ceram Soc., 54 (1971) 254
8 V.G Keramidas and W.B. White, J. Am. Ceram. Soc., 57 (1974) 22.
9 T. Mitsuhashi, M. Ichihara and U. Tatsuke, J. Am. Ceram. Soc., 57 (1974) 97
10 D Vivien, J. Livage and C. Mazieres, J Chim. Phys , 67 (1970) 199, and the references cited therein.
11 N.P. Sajin and E.A Pepelyyaeva, Proc Int Conf Peaceful Uses At. Energy, Geneva, 1955, Vol. 8, United Nations, 1956, p. 559.
12 J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 46 (1957) 92
13 T. Sato and H Watanabe, Thermochim Acta, 31 (1979) 159
14 T Sato, Y. Yamashita and F. Ozawa, Z. Anorg. Allg. Chem., 370 (1969) 202.
15 J.R. Ferraro, Low-Frequency Vibration of Inorganic and Coordination Compounds, Plenum Press, New York, 1971, p. 74.