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Growth of whiskered ZrO_2 crystals by hydrothermal decomposition of zirconium oxide sulphate pseudo-crystals

E. KATO, A. NAGAI, M. HIRANO, Y. KOBAYASHI
Department of Applied Chemistry, Aichi Institute of Technology, Yachigusa, Yakusa, Toyota, 470-03 Japan

Several kinds of metastable compounds, pseudo zirconium oxide sulphates (PZOS) with a chemical composition of $Zr_3O_5SO_4 \cdot nH_2O$, were previously synthesized by the thermal hydrolysis of solutions containing zirconium sulphate at 200 or 240 °C. The obtained PZOS samples were again hydrothermally treated in different sulphuric acid solutions (< 1.0 mol l^{-1}) at 240 °C, and their hydrothermal decomposition behaviour was investigated by TEM observation. The PZOS samples mostly crystallized to plate-like zirconium oxide sulphate (ZOS) in the concentrated sulphuric acid solution (> 0.5 mol l^{-1}), but long-whiskered monoclinic ZrO_2 crystals grew with decomposition of the PZOS samples obtained from the starting mixtures with added $Zr(OH)_4$ when rapidly heated to the hydrothermal treatment temperatures. It was found that many ultrafine monoclinic ZrO_2 crystals were simultaneously formed during the hydrothermal preparation of the PZOS samples, and during the following hydrothermal decomposition of the PZOS samples, the whiskered crystals of monoclinic ZrO_2 grew with the consumption of PZOS from the coexisting ultrafine monoclinic ZrO_2 particles which act as seed crystals.

1. Introduction

Thin, plate-like crystals with a chemical composition of $Zr_3O_5SO_4 \cdot nH_2O$ or zirconium oxide sulphate (ZOS), pseudo zirconium oxide sulphate (PZOS) and anisotropic monoclinic ZrO_2 particles elongated in the direction of the *c*-axis are hydrothermally obtained at 200–250 °C from aqueous solutions of zirconium salts with sulphuric acid, depending on the concentration of the solutions and the reaction time [1–3]. The kinds and properties of these obtained zirconium compounds largely depend on the concentration of SO_4^{2-} ions in the solutions. The plate-like hexagonal ZOS crystals were formed from highly concentrated solutions of SO_4^{2-} ions. As the solutions became dilute, PZOS were formed, and monoclinic ZrO_2 particles with anisotropic morphologies were crystallized from the more dilute solutions [3, 4].

From solutions containing more than 0.5 mol l^{-1} SO_4^{2-} ions, small amounts of PZOS were initially formed, then the nuclei of the ZOS crystals were formed, and they gradually grew [5]. On the other hand, two types of anisotropic monoclinic ZrO_2 particles, which were thin, flaky, single crystals and fibrous twin crystals, both of which were about 1.0–1.5 μm in length, were formed in solutions containing 0.2–0.4 mol l^{-1} SO_4^{2-} ions [3]. Anisotropic crystal growth of monoclinic ZrO_2 took place by decomposition of the previously formed metastable PZOS in the solutions which supplied zirconium for nucleation and crystal growth of monoclinic ZrO_2 by gradually releasing SO_4^{2-} ions [6].

In a previous report [7], only thin, flaky, relatively large single crystals of monoclinic ZrO_2 could be successfully crystallized in dilute sulphuric acid solutions by the hydrothermal decomposition of ZOS fine crystals with good hexagonal crystallinity previously produced from $ZrOSO_4$ solutions with relatively high concentrations of SO_4^{2-} ions. Although it has been reported [8] that anisotropic monoclinic ZrO_2 was formed by the hydrothermal treatment of $ZrOCl_2$ solution containing sulphuric acid at 250–650 °C, until recently, there were few reports, except for our own, relating to the crystal growth of monoclinic ZrO_2 in sulphuric acid solutions.

In the present study, PZOS particles hydrothermally prepared according to a previous report [4] were again hydrothermally treated in the solutions with different concentrations of sulphuric acid, and their decomposition behaviour and the morphology of decomposition products were examined using transmission electron microscope (TEM) observations. It was found that many whiskered monoclinic ZrO_2 crystals were grown from fine, monoclinic ZrO_2 particles by the decomposition of some PZOS. Because the result was somewhat different from that of the hydrothermal decomposition of ZOS and hydrothermal treatment of aqueous solutions of zirconium salts, we studied and clarified the formation conditions and mechanisms of these whiskered monoclinic ZrO_2 crystals.

2. Experimental procedure

Thin, plate-like hexagonal crystals with a chemical composition of $Zr_3O_5SO_4 \cdot H_2O$, ZOS, have sufficient crystallinity, whereas PZOS hydrothermally formed in dilute sulphuric acid solution at a relatively low temperature is metastable with insufficient crystallinity. Because the properties of PZOS, such as crystallinity, depend on the preparation conditions, several kinds of PZOS synthesized under different conditions were used for this study.

The sample preparation was performed in the following manner, which was similar to that in an earlier report. Zirconyl carbonate ($ZrO(OH)(CO_3)_{1/2} \cdot nH_2O$, Magnesium Electron Ltd) was dissolved in a 6 N sulphuric acid solution, maintaining the Zr^{4+}/SO_4^{2-} ratio at 1/2. To the prepared solution, zirconium hydroxide ($Zr(OH)_4 \cdot nH_2O$) and distilled water were added to give a final concentration of 0.4 $mol\,l^{-1}$ SO_4^{2-} ions and 1.0 $mol\,l^{-1}$ Zr. The starting composition was represented by ZS(0.2 +0.8/0.4), the same as in the previous report [4]. A given quantity (20 ml) of the mixture thus produced was poured into a Teflon vessel with an inner volume of 25 ml held in a stainless-steel vessel. After the vessel had been sealed, it was placed in a thermostatted oven and heated by rotating to 200 or 240 °C for 90 min and then continued heating for 3 h. The synthesized PZOS samples were then washed with distilled water.

Another PZOS sample was synthesized from the 0.4 $mol\,l^{-1}$ solution with a Zr^{4+}/SO_4^{2-} ratio at 1/1 (this was represented by ZS(0.4/0.4), the same as in a previous report [4]) in the same manner for comparison with the above synthesized PZOS samples. As it was found that the properties of the synthesized PZOS depended on the heating rate, another starting ZS(0.2 +0.8/0.4) sample was rapidly heated by directly placing it in a thermostatted oven at 200 or 240 °C and then continued heating for 3 h. The obtained PZOS samples from ZS(0.2 +0.8/0.4), rapidly heated ZS(0.2 +0.8/0.4) and ZS(0.4/0.4) are represented by PA, PA′ and PB, respectively. The synthesized temperatures of the PZOS samples are represented, for example, by PA 200 when PA was synthesized at 200 °C.

These synthesized PZOS samples were soaked in distilled water or different sulphuric acid solutions and the PZOS content was adjusted so as to correspond to 0.1–1.0 $mol\,l^{-1}$ Zr. The condition of the starting mixtures for hydrothermal decomposition was represented, for example, by PA(0.4)–HS(0.2) when the concentrations of PZOS and sulphuric acid were 0.4 and 0.2 $mol\,l^{-1}$, respectively. The starting mixtures were then hydrothermally treated again at 240 °C for different periods of time by the method mentioned above. The morphology of the solid products obtained by the treatment was examined by TEM observation (JEOL, JEM-200CX; acceleration voltage 200 kV). Crystalline phases of the products were identified by powder X-ray diffractometry with CuK_α radiation.

3. Results and discussion

3.1. Characteristics of PZOS and solid products

Fig. 1 shows the transmission electron micrographs of the solid products obtained from different kinds of PZOS (PA200, PA240, PA′200, PA′240, PB200 and PB240) hydrothermally treated at 240 °C for 7 days under the conditions of P(0.4)–HS(0.8) in comparison with the starting PZOS. XRD profiles of the starting PZOS are shown in Fig. 2. In the transmission electron micrographs of the PZOS samples, PA′200 and PA′240 prepared by rapid heating, small amounts of very fine monoclinic ZrO_2 crystals coexisting with the PZOS particles are observed. There are few apparent differences among these starting PZOS samples in the transmission electron micrographs and XRD profiles except for the one mentioned observation. In the XRD profiles of Fig. 2, the coexisting small amount of monoclinic ZrO_2 with PZOS was confirmed in only the PA′240 sample. As a result of the hydrothermal decomposition of these PZOS under the same conditions of P(0.4–HS(0.8) at 240 °C for 7 days, few differences in the morphology of the anisotropic monoclinic ZrO_2 particles were confirmed, depending on the starting PZOS.

Except for PA′200 and PA′240, which coexist with monoclinic ZrO_2 from the start, the samples PA200, PA240 and PB had relatively small amounts of anisotropic monoclinic ZrO_2 particles with large amounts of ZOS or PZOS remaining. The solid products formed from the PB sample showed a similar result as for the products formed by the hydrothermal treatment of ZS(0.4/0.4) solution at 240 °C for 7 days in a previous report [7]. The morphology of the many thin, flaky monoclinic ZrO_2 crystals formed from the PB sample are wide in width, whereas considerably narrower or thin, flaky crystals were observed in the case of PA200 and PA240. These results may be related to the two-dimensional regularity of the layer structure of PZOS, associated with the reported fact [7] that the widest flaky monoclinic ZrO_2 was crystallized by hydrothermal decomposition of ZOS particles with the highest crystallinity.

In a previous report [4], by comparing the $Zr(OH)_4$ added mixtures (ZS(0.2 +0.8/0.4), ZS(0.5 +0.8/1.0) and ZS(0.75 +0.8/1.5)) with those of $Zr(SO_4)_2$ solutions (ZS(0.2/0.4), ZS(0.5/1.0) and ZS(0.75/1.5)), the crystallites of the PZOS or ZOS synthesized from the former compositions were reduced in size, that is, the tendency of reducing the size of the layered crystal of PZOS or ZOS with an increase in the Zr/SO_4^{2-} ratio was recognized. The layered crystals of PZOS in the PA system were inferior to those of the PB system in two-dimensional regularity. It may be considered that the width of the flaky nuclei of the monoclinic ZrO_2 crystallized from these PZOS depends on the two-dimensional regularity of the layered structure and the crystallinity of the initial PZOS particles.

In the PA′ system, fine monoclinic ZrO_2 particles apparently coexist before treatment; however, long-whiskered monoclinic ZrO_2 crystals grew from fine monoclinic ZrO_2 particles and no particles of ZOS or PZOS could be observed. The morphology of the

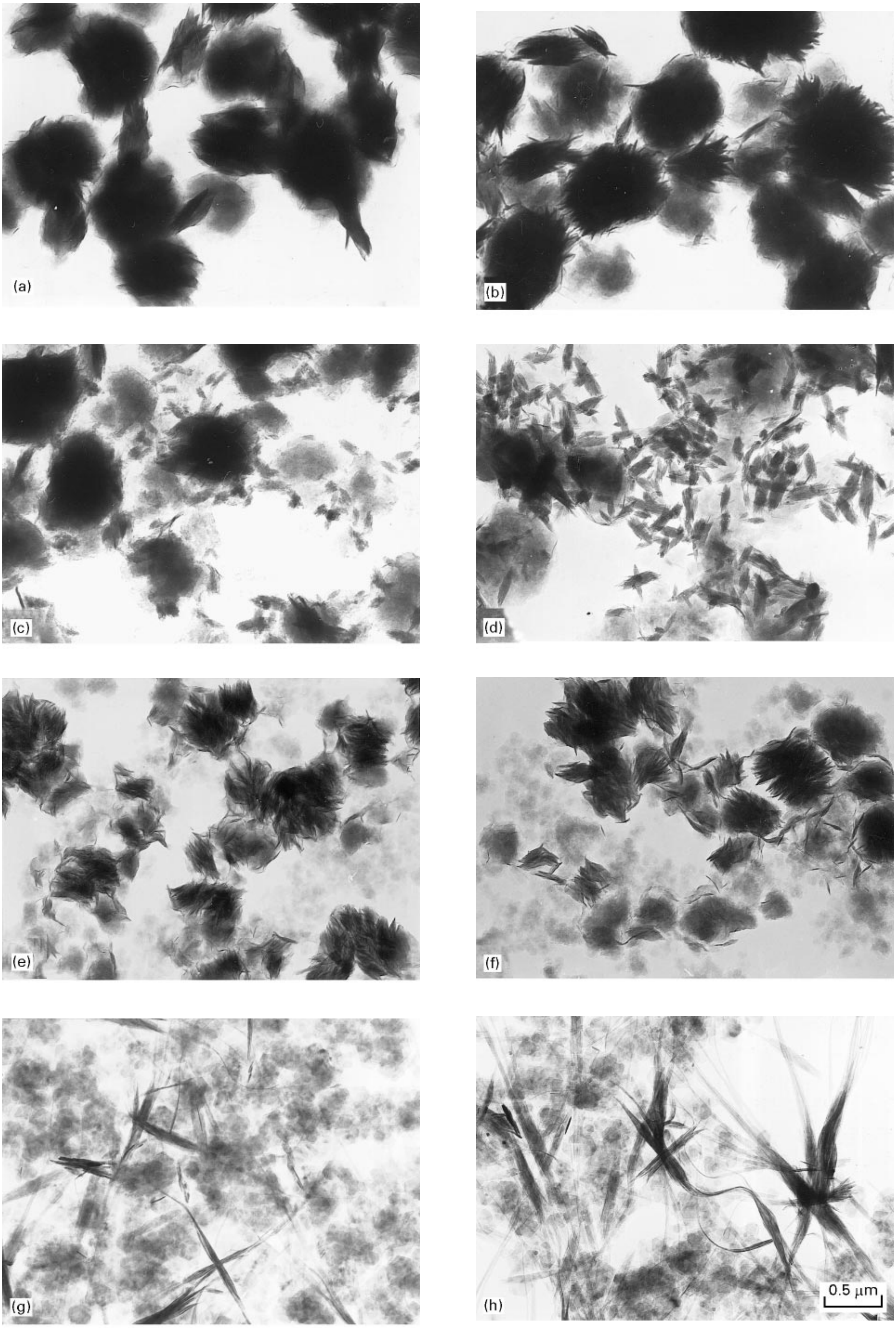
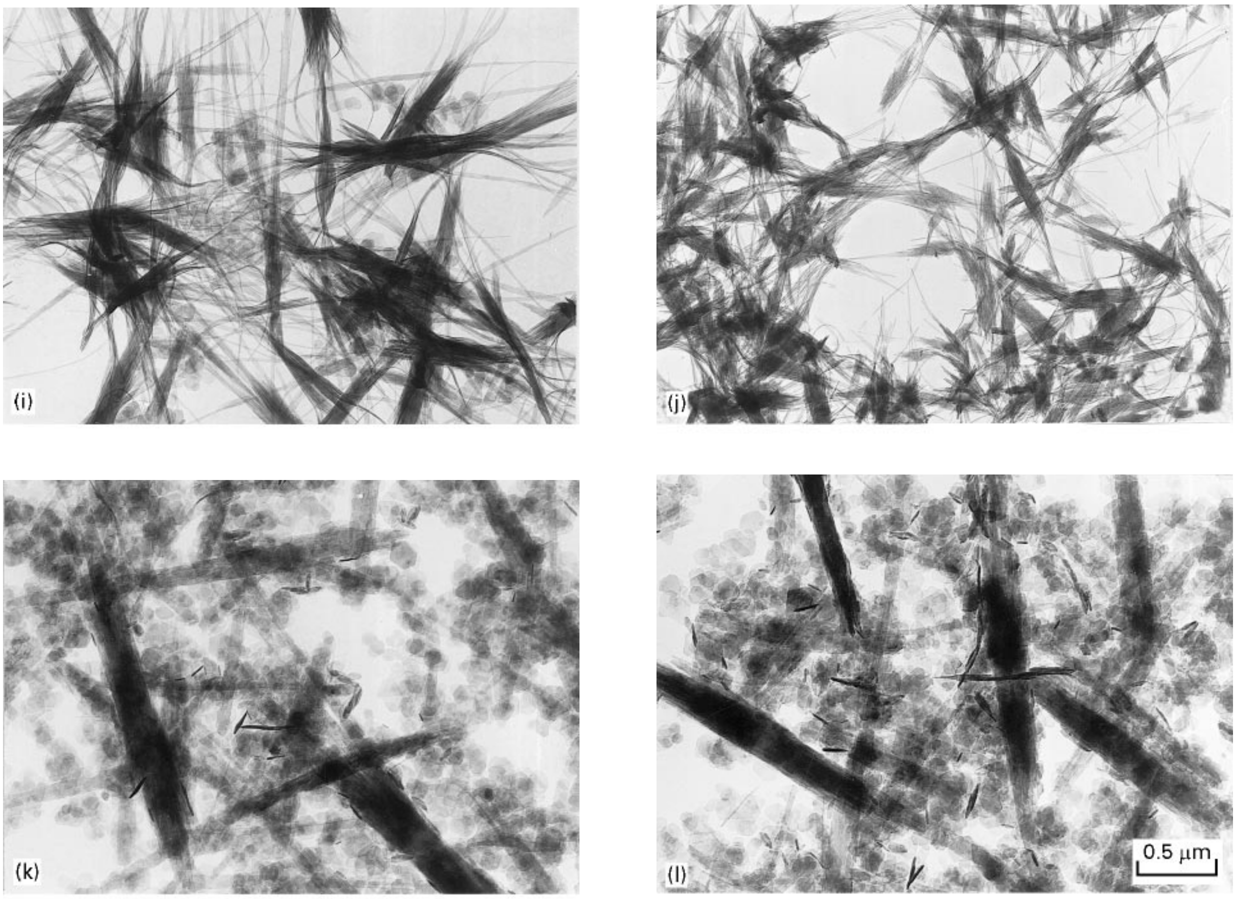


Figure 1 Transmission electron micrographs of different PZOS and their hydrothermal decomposition products under the condition of P(0.4)–HS(0.8) at 240 °C for 7 days; (a-f) PZOS, and (g-l) products (g) PA200, (h) PA240, (i) PA′200, (j)PA′240, (k) PB200, (l) PB240.



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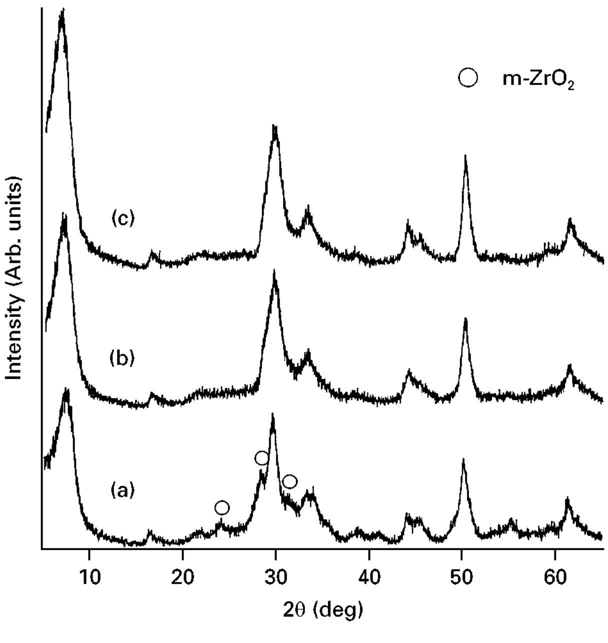

Figure 2 XRD profiles for (a) PA′240, (b) PA240, and (c) PB240 sample.

whiskered monoclinic ZrO_2 particles were quite different from the results in the cases of the PA system, the PB system and the solution previously reported. In highly concentrated solutions of SO_4^{2-} ions containing more SO_4^{2-} than in the case ZS(0.5/0.5), ZOS was crystallized but monoclinic ZrO_2 was not, even after treatment for 7 days, as had been reported in a previous study [5]. In the solution of PA′, however, the zirconium solute is consumed by the growing monoclinic ZrO_2 crystal during the hydrothermal reprocessing, so that the formation of ZOS crystal nuclei may be suppressed even in these solutions.

We discussed the formation process of PZOS and the crystallization mechanism of monoclinic ZrO_2 from aqueous solutions of zirconium salts with sulphuric acid, in a previous report [4], and showed monoclinic ZrO_2 tended to crystallize in a shorter treatment time from the starting mixture of ZS(0.2 +0.8/0.4) than that of ZS(0.2/0.4). From the results of the formation of PZOS in this study, it is apparent that monoclinic ZrO_2 further tended to crystallize rapidly by rapid heating in the mixture of ZS(0.2 +0.8/0.4). It may be considered that $Zr(OH)_4 \cdot nH_2O$ in the ZS(0.2 +0.8/0.4) mixture brought about nucleation or direct crystallization of monoclinic ZrO_2 with hydrothermal formation of PZOS without entirely soluting $Zr(OH)_4 \cdot nH_2O$ during rapid heating.

Small amounts of crystallized monoclinic ZrO_2 were also observed in the PA and PB samples after hydrothermal treatment under the conditions of sulphuric acid of HS(0.8), which is the formation area of ZOS. This result suggests that a few nuclei or fine crystals of monoclinic ZrO_2 were contained in these starting PZOS mixtures before hydrothermal reprocessing. It is supposed that the causes for the nucleation of the local decomposition of PZOS are (1) the PZOS formation in a relatively diluted solution of sulphuric acid, HS(0.4), and (2) the washing treatment after PZOS formation. As there are few nuclei of monoclinic ZrO_2 existing in the starting mixture compared with the PA′ system, it is considered that the zirconium solute sufficiently contributes to the nucleation and crystal growth of ZOS except for the crystal growth of monoclinic ZrO_2.

3.2. Concentration of sulphuric acid and solid products

Fig. 3 shows the transmission electron micrographs of the products formed by the hydrothermal treatment of PA′240 in distilled water and dilute sulphuric acid solution at 240 °C for 24 h. Because the decomposition of PZOS proceeds by releasing SO_4^{2-} ions, in general, decomposition of PZOS is accelerated by reducing the sulphuric acid concentration of the solution. In distilled water and a solution containing 0.1 mol l^{-1} sulphuric acid, PZOS was entirely decomposed and disappeared after hydrothermal treatment of only 1 day; crystallization of fine monoclinic ZrO_2 was observed. These results proved that the rapid formation of monoclinic ZrO_2 nuclei took place at the same time as decomposition. In the case of PA′(1.2)–HS(0.3), which contains a little sulphuric acid, SO_4^{2-} ions released from the PZOS crystals are rapidly reduced, and the decomposition hardly proceeded by the hydrothermal treatment for 1 day. On the other hand, the decomposition of PZOS was completed by the same treatment for 7 days at the same temperature, and the crystal growth of nearly the same whiskered monoclinic ZrO_2 as PA′(0.4)–HS(0.8), was observed.

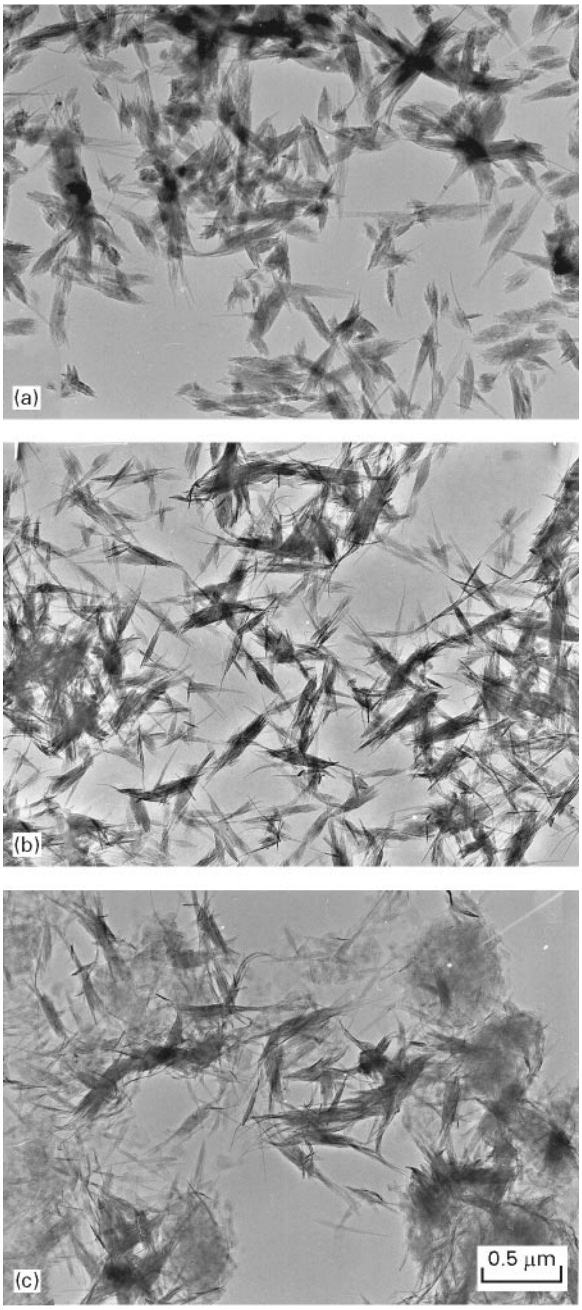

Figure 3 Transmission electron micrographs of hydrothermal decomposition products of PA240 in different concentrations of sulphuric acid at 240 °C for 1 day: (a) PA′(1.2)–HS(0.0), (b) PA′(1.2)–HS(0.1), and (c) PA′(1.2)–HS(0.3).

In a subsequent experiment, the amount of PZOS added to the reaction vessel was adjusted in order to fix the concentration of sulphuric acid of the solution at a value of 1.0 mol l^{-1} for the end of the reaction, because the sulphuric acid concentration in the solution increased as the decomposition of PZOS and crystallization of monoclinic ZrO_2 proceeded. Some of the results after hydrothermal treatment for 7 days at 240 °C are shown in Fig. 4. Although no significant difference in crystal growth of the whiskered monoclinic ZrO_2 between each sample could be recognized, it could be found that thin whiskered crystals grew with a decrease in the initial sulphuric acid concentration by comparison with PA′(0.4)–HS(0.86),PA′(1.2)–HS (0.6) and PA′(2.4)–HS(0.2).

In a previous report [5, 6], it was found that ultrafine particles of a metastable compound, PZOS, were formed from a $ZrOSO_4$ solution ZS(0.5/0.5) during the early stage of a hydrothermal process, and then PZOS gradually decomposed to crystallize as two types of anisotropic monoclinic ZrO_2 particles: thin, flaky, single crystals and fibrous twin crystals, both of which have an acicular morphology of about 1.0 μm in length and about 0.2–0.3 μm in width [5]. In concentrated solutions of about 1.0 mol l^{-1} of SO_4^{2-} ions ZS(1.0/1.0), ZOS was gradually crystallized by nucleation and growth after the formation of small amounts of PZOS particles [6]. In the present study, it was found that the crystal growth of monoclinic ZrO_2 proceeded according to the decomposition of PZOS from a solution above 0.5 mol l^{-1} SO_4^{2-} ions in the case of the existence of nuclei or seed crystals of monoclinic ZrO_2 in the solution. In the solution above 0.5 mol l^{-1} SO_4^{2-} ions, the free energy of PZOS, ZOS and monoclinic ZrO_2 at 240 °C must decrease according to the order PZOS > ZOS >monoclinic ZrO_2 and their solubility must also decrease in the same order. As the concentration of the sulphuric acid in the solution decreases, the difference between the free energy value of ZOS and monoclinic ZrO_2 increases and the concentration of zirconium in the solution further decreases.

Therefore, the above experimental results are accounted for as follows. The growth of the whiskered monoclinic ZrO_2 crystal and its width versus the

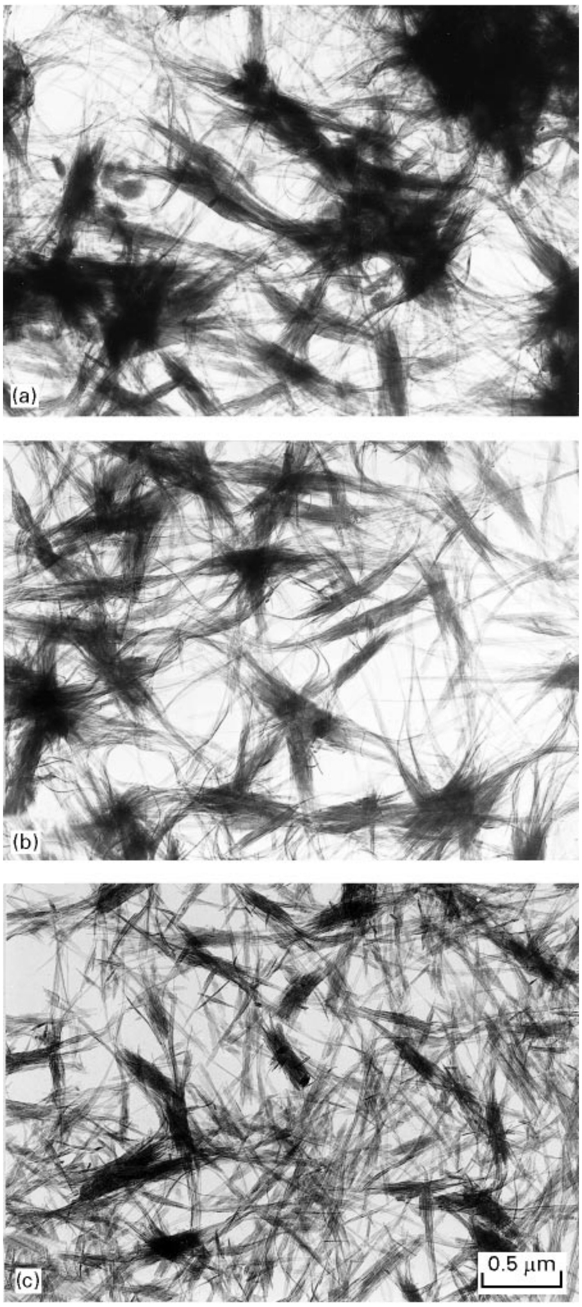

Figure 4 Transmission electron micrographs of hydrothermal decomposition products of PA in different concentrations of sulphuric acid at 240 °C for 7 days: (a) PA′(0.4)–HS(0.86), (b) PA′(1.2)–HS(0.6), and (c) PA′(2.4)–HS(0.2).

direction of elongation were both related to its growth rate and the concentration of zirconium solute in the solution, i.e. the balance of its consumption and supply. It may be considered that the whiskered crystals becomes narrower with increasing amount of nuclei or seed crystals of monoclinic ZrO_2 in the solution, with decreasing PZOS or ZOS remaining by its consumption, and with decreasing concentration of sulphuric acid and zirconium in the solution. Upon detailed inspection of the experimental results available at this time, whisker-like monoclinic ZrO_2 crystals are observable at the end of the formation of monoclinic ZrO_2 crystals from rapidly decomposed PA′(1.2)–HS (0.0) or PA′(1.2)–HS(0.2) in Fig. 3, and at the end of the thin, flaky single crystals and fibrous twin crystals from the $ZrOSO_4$ solutions. These whiskered monoclinic ZrO_2 crystals at the end of its crystallization are also explained by the same mechanism.

4. Conclusions

1. The hydrothermal decomposition behaviour of several kinds of PZOS samples, previously synthesized by the hydrolysis of solutions containing 1.0 $\mathrm{mol\,l^{-1}}$ Zr^{4+} and 0.4 $\mathrm{mol\,l^{-1}}$ SO_4^{2-} under different conditions, and the morphology of monoclinic ZrO_2 crystals grown by the decomposition of PZOS, were investigated by TEM observation.

2. In dilute sulphuric acid solutions, the decomposition of PZOS and the nucleation and growth morphology of monoclinic ZrO_2 crystals depended on the concentration of SO_4^{2-} ions in the solution, and were influenced by the crystallinity and two-dimensional regularity of the layered structure of PZOS as precursor.

3. In the concentrated sulphuric acid solutions, the PZOS crystallized to ZOS particles, but the PZOS samples, coexisting with fine monoclinic ZrO_2 crystals, decomposed to crystallize whiskered monoclinic ZrO_2 particles.

4. The morphology of the whiskered monoclinic ZrO_2 crystals was related to the amount of fine monoclinic ZrO_2 particles coexisting with PZOS, the concentration of zirconium solute and the sulphuric acid in the solution.

References

1. C. -T. LI, E. KATO, K. DAIMON and Y. MURASE, *Yogyo Kyokaishi* (*J. Ceram. Soc. Jpn*) **95** (1987) 509.
2. C. -T. LI, I. YAMAI and E. KATO, *Seramikkusu Ronbunshi* (*J. Ceram. Soc. Jpn*) **97** (1989) 113.
3. C. -T. LI, I. YAMAI, Y. MURASE and E. KATO, *J. Am. Ceram. Soc.* **72** (1989) 1479.
4. A. NAGAI, Y. MURASE, Y. KOBAYASHI and E. KATO, *Seramikkusu Ronbunshi* (*J. Ceram. Soc. Jpn*) **102** (1994) 844.
5. A. NAGAI, M. HIRANO, Y. KOBAYASHI, E. KATO and Y. MURASE, *J. Mater. Sci.* **30** (1995) 3333.
6. A. NAGAI, Y. MURASE, M. HIRANO, Y. KOBAYASHI and E. KATO, *J. Ceram. Soc. Jpn* **103** (1995) 610.
7. E. KATO, M. HIRANO and A. NAGAI, *J. Am. Ceram. Soc.* **78** (1995) 2259.
8. B. MOTTET, M. PICHAVANT, J-M. BENY and J-A. ALARY, *ibid.* **75** (1992) 2515.

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