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Crystalline products and their formation mechanism in thermal hydrolysis of $ZrOSO_4$ solution

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Solid products were prepared from mixtures of zirconyl carbonate and sulphuric acid solution under thermal hydrolysis at 240 °C. These crystalline products and their formation mechanism were investigated by evaluating the amount of products, and by X-ray diffraction analysis and TEM observation. The solid products precipitated were zirconium oxide sulphates (ZOS, PZOS, $ZrOSO_4 \cdot H_2O$) and m-ZrO_2. The area and thickness of the fine plate-like crystals of ZOS increased with increasing concentration of the solution and hydrothermal treatment time. For thin starting solutions, the precipitation velocity and the amount of PZOS increased. For thick starting solutions, those of ZOS increased. For 0.5 mol/l^{-1} $ZrOSO_4$ solution (ZS0.5) from the thin solution, PZOS crystallized early and m-ZrO_2 crystallized by releasing sulphuric acid ions in PZOS with treatment time. For ZS2.5 from the thick solution, $ZrOSO_4 \cdot H_2O$ was crystallized by increasing the proportion of sulphuric acid ions to zirconium ions in the solution, which was caused by ZOS precipitation.

1. Introduction

Fine thin plate-like crystals of zirconium oxide sulphate (layer-like compounds with the chemical composition $Zr_3O_5SO_4 \cdot H_2O$) and fine fibrous crystals of monoclinic zirconia are formed in the sols state from $Zr(SO_4)_2$ solution under hydrothermal conditions at 200–250 °C, which depend on the concentration of the solution and the hydrothermal treatment time [1, 2]. These fine particles are dispersed homogeneously, show a high degree of orientation during the drying process, and are expected to be useful for many applications as ZrO_2 particles of anisotropic shape [3].

We have investigated the process of thermal hydrolysis and chemical reaction of $Zr(SO_4)_2$ solution and part of the $Zr(SO_4)_2$–$Zr(OH)_4$–H_2O system. We have already shown that the solid products depend on the concentration of sulphuric acid ions in the mother liquor and fine crystals of $ZrOSO_4 \cdot H_2O$ are prepared from a thick concentrated solution. As the concentration becomes more dilute, the fine plate-like crystals of zirconium oxide sulphate (ZOS) and their low crystalline form (PZOS) are prepared. We have also reported that fine fibrous monoclinic zirconia may be prepared from a thinner mother liquor, and their morphology and formation area were reported [1]. Moreover, we have indicated that the formation of these thin plate-like and fibrous fine crystals does not proceed in accordance with a single mechanism, that is, PZOS or the precursor of PZOS are formed first, and they are then converted into fine plate-like crystals of ZOS and fibrous monoclinic-ZrO_2, depending on the length of the treatment time. During these studies, the formation process and mechanism have not yet been sufficiently elucidated.

In the present study, the time dependence of the products formed from the $ZrOSO_4$ solution containing excess zirconium ions, on sulphuric acid ions content, was investigated by evaluating the amount of products and using X-ray diffraction (XRD) and TEM observation. One of the aims of this study was to clarify the formation process and mechanism of the fine crystals.

2. Experimental procedure

Zirconyl carbonate ($ZrOCO_3 \cdot H_2O$) was dissolved in sulphuric acid solution of equal molarity and distilled water was added to prepare a fixed molar concentration. These solutions are identified as in the following example: ZS1.5 represents Zr^{4+} 1.5 $mol\,l^{-1}$ and H_2SO_4 1.5 $mol\,l^{-1}$.

Starting solution of 18 ml was poured into a Teflon vessel, which was held in a stainless steel vessel. The vessel was placed in a thermostat with a rotary device and kept at 240 °C for various periods of time.

The products obtained were washed by repeated centrifugation and dispersion in distilled water and were dried at 60 °C. The ZrO_2 in the solutions separated out by centrifugation was precipitated as $Zr(OH)_4$ by the addition of excess NH_4OH, and was

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then thermally decomposed to ZrO_2 at 800 °C. The amount of solid products was calculated by subtracting the amount of ZrO_2 in the separated solutions from the amount of ZrO_2 in the starting solution.

The crystalline phases of the products were ZOS, PZOS, $ZrOSO_4 \cdot H_2O$ and m-ZrO_2. These were identified by powder X-ray diffractometry (XRD). The apparent crystallite size, layer spacing of the (0 0 1) plane and the peak intensity of the (1 1 1) plane were evaluated from XRD data. The morphology and size of the products were observed by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Solid products

The XRD patterns of the solid products from 0.3–2.5 $mol\,l^{-1}$ solution treated under hydrothermal conditions for 5 h and 168 h, are represented in Fig. 1. In this wide concentration area of the solution, the products were thin plate-like crystals of zirconium oxide sulphate, which were layer-like compounds with the chemical composition $Zr_3O_5SO_4 \cdot H_2O$(ZOS), their low crystalline form (PZOS), crystals of zirconyl sulphate ($ZrOSO_4 \cdot H_2O$) and monoclinic zirconia. These products were the same as previously reported [1, 4]. The time dependence of the products with increasing treatment time was as follows. As the treatment time became longer, zirconia began to crystallize in the diluted solution area, the crystallinity of zirconium oxide sulphate increased and PZOS was converted into ZOS in the medium concentration area, while zirconyl sulphate gradually began to precipitate from the thick solution. These results exhibited the same tendency as that already found in products from $Zr(SO_4)_2$ solution under hydrothermal conditions [1], though they differred in time and concentration to some degree.

3.2. Precipitation rate

At a high treatment temperature, 240 °C, the formation rate of the solid products remarkably increased in general. In all the specimens whose $ZrOSO_4$ concentration was higher than ZS1.0, the formation rate increased rapidly after an induction period of 5–24 h. However, the formation velocity in specimens with a low $ZrOSO_4$ concentration became higher than that of specimens with a high concentration in the early stage of the formation process. On the other hand, it was noticed that the formation rate in specimens with a high concentration increased markedly after the induction period, (Fig. 2).

Fig. 3 shows the formation rate of precipitated solid products as the amount of product precipitated from the starting solutions with concentrations ZS0.3 to ZS2.5 after hydrothermal treatment at 240 °C for 5–168 h. The difference in mechanism of the

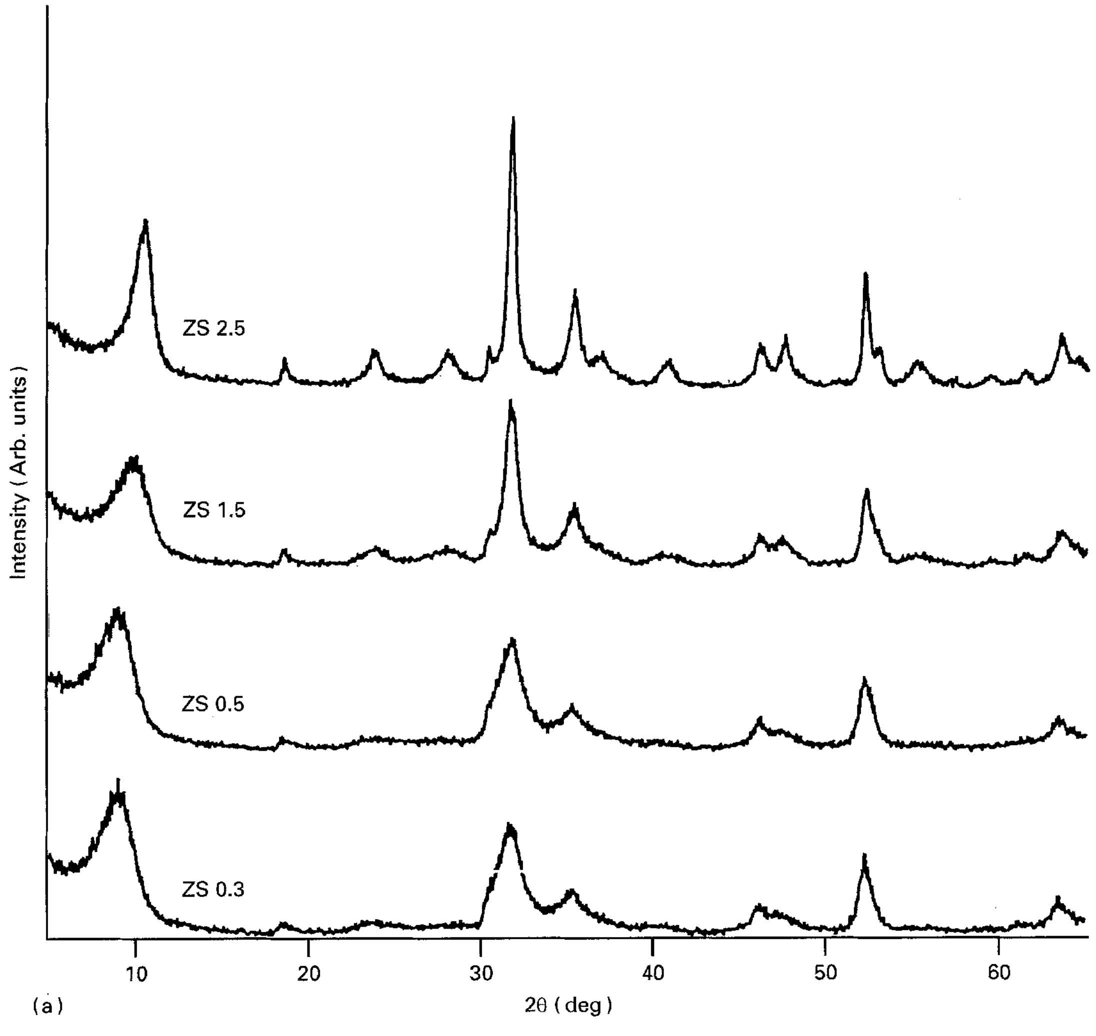
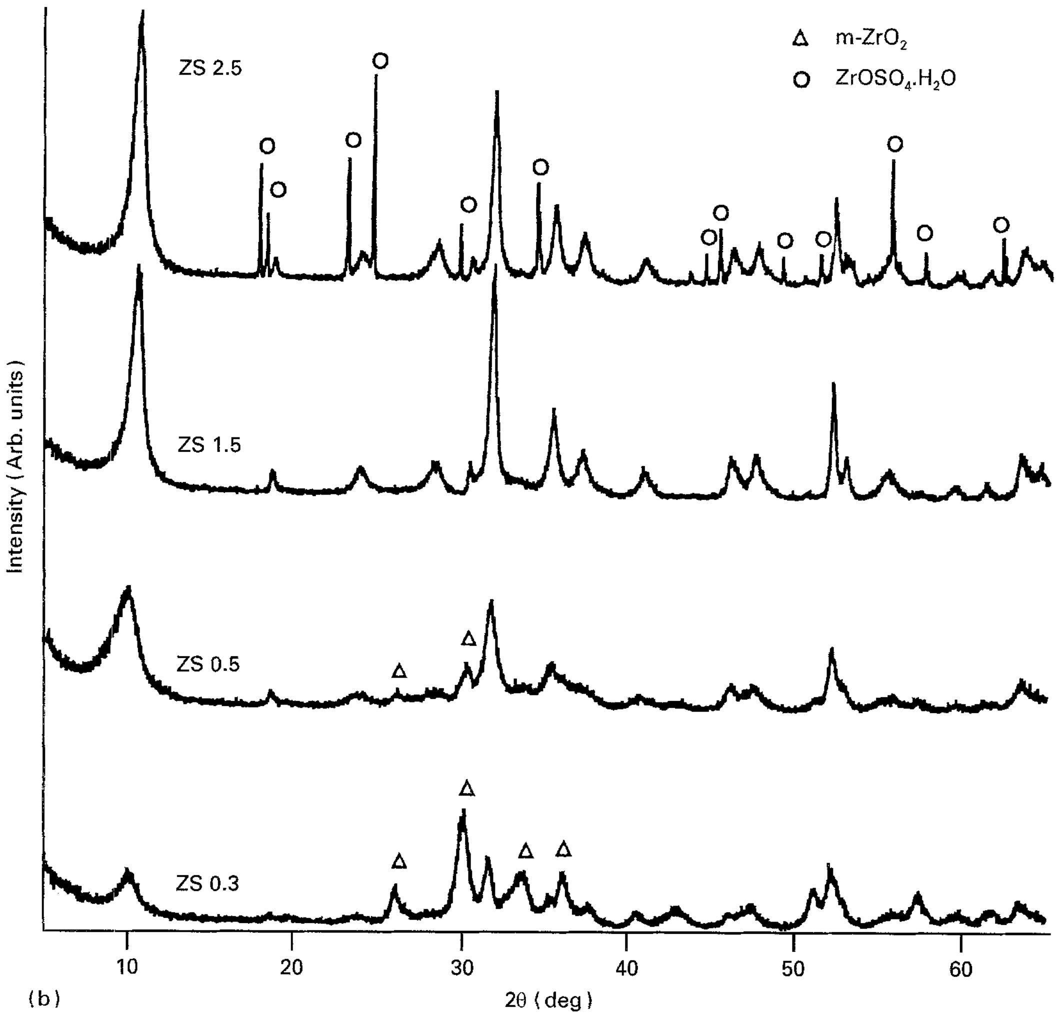


Figure 1 XRD patterns of solid products synthesized at 240 °C after (a) 5 h, and (b) 168 h.



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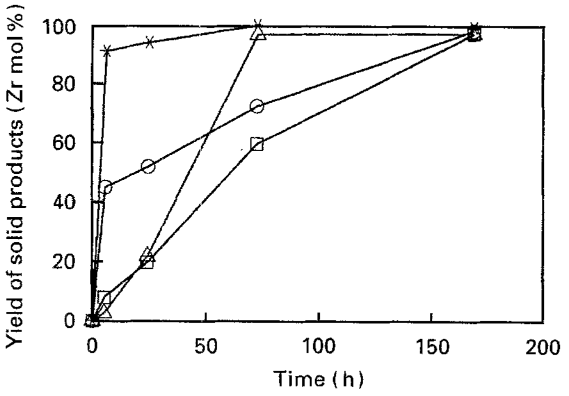

Figure 2 Yield of solid products synthesized at 240 °C from $ZrOSO_4$ solution. (×) ZS0.5, (○) ZS1.0, (□) ZS1.5, (△) ZS2.0.

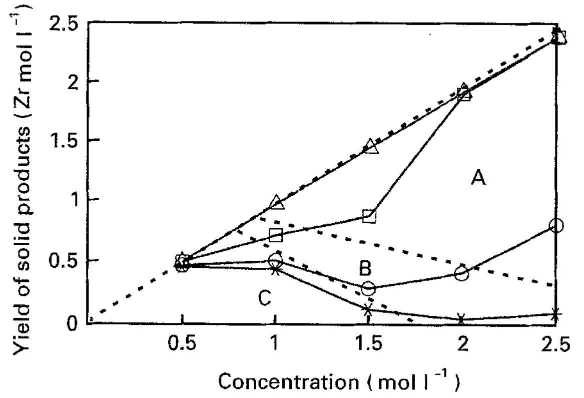

Figure 3 Yield of solid products at 240 °C with hydrothermal treatment time and crystalline phases. (×) 5 h, (○) 24 h, (□) 72 h, (△) 168 h. A, ZOS; B, ZOS + PZOS; C, PZOS.

precipitation between the low and high concentration areas is more easily seen. The rough areas of crystal phases precipitation obtained from the XRD patterns of the products, are shown by the dotted lines. The thinner the concentration of the starting solution the greater was the precipitation velocity and the amount of PZOS formed. By contrast, as the concentration of the starting solution became thicker, the precipitation velocity and the amount of ZOS formed increased. In the area of approximately middle concentration, these parameters were all decreased. The precipitation in the middle concentration area was PZOS in its early stage and this was converted into ZOS by mid-treatment time. However, this does not mean that all the precipitated ZOS was converted via PZOS, but it is proved that the PZOS did not precipitate from the solution on the way to completion, and these phenomena corresponded to changes in the outset of nucleation and growth of new ZOS crystals.

3.3. Crystallinity and morphology

The treatment time dependence of XRD data, i.e. crystallite size and layer spacing of the (0 0 1) plane and the peak intensity of the (1 1 1) plane, are exhibited in Fig. 4. The corresponding transmission electron micrographs of these specimens are shown in Fig. 5. The crystallinity of the precipitates was raised with treatment time. In the final stage of the precipitation, they all became hexagonal thin plate-like ZOS and the area and thickness increased with increasing concentration of the solution.

In the early stage of the precipitation, XRD patterns were all classified as PZOS, but it was found that there were some differences in its crystallinity and morphology. For the thin concentration solution (ZS0.5), the precipitation was completed in a comparatively short treatment time, the layer spacing of the precipitates was fairly open, and the precipitate consisted of fine flake-like substances. With increasing treatment time, they became distinct thin discs, with one part decomposed into m-ZrO$_2$ releasing SO$_4^{2-}$ ions, and the remainder of them crystallized to very fine hexagonal plate-like ZOS in the final stage.

As the concentration increased, the amount of precipitation decreased, but the crystallinity of the products was raised and they approached the structure of ZOS; also they grew a relatively small amount of

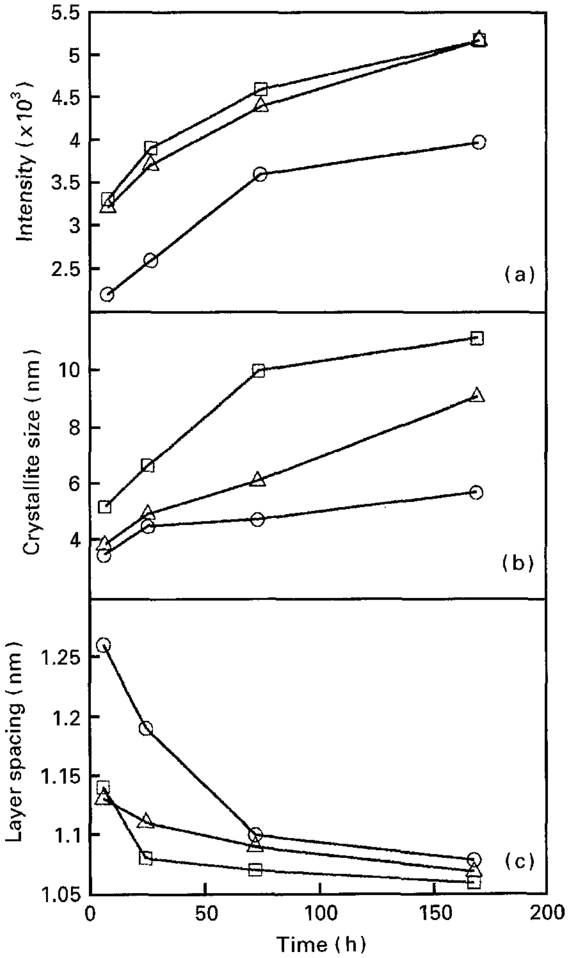

Figure 4 Change of (a) intensity (1 1 1), (b) apparent crystallite size (0 0 1), and (c) layer spacing of solid products synthesized at 240 °C: (○) ZS (1.0), (△) ZS (1.5), (□) ZS (2.0).

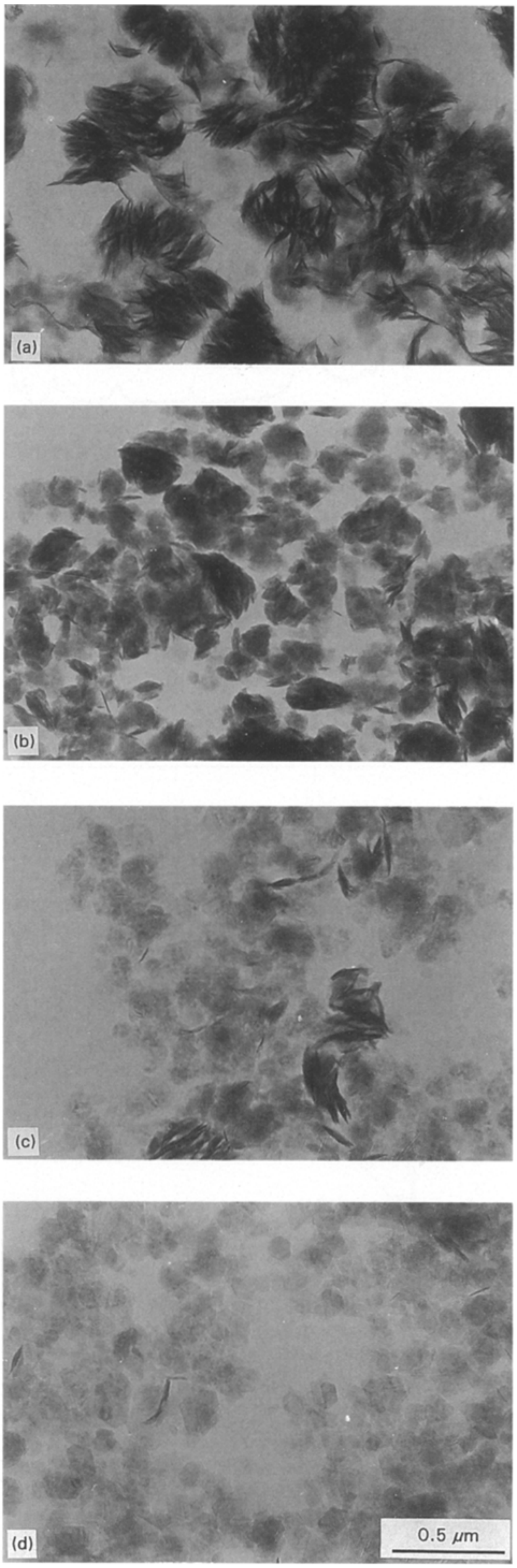

Figure 5 Transmission electron micrograph of solid products synthesized from (a–d) ZS1.0, (e–h) ZS1.5, and (i–l) ZS2.0, at 240 °C with hydrothermal treatment time: (a, e, i) 5 h, (b, f, j) 24 h, (c, g, k) 72 h, (d, h, l) 168 h.

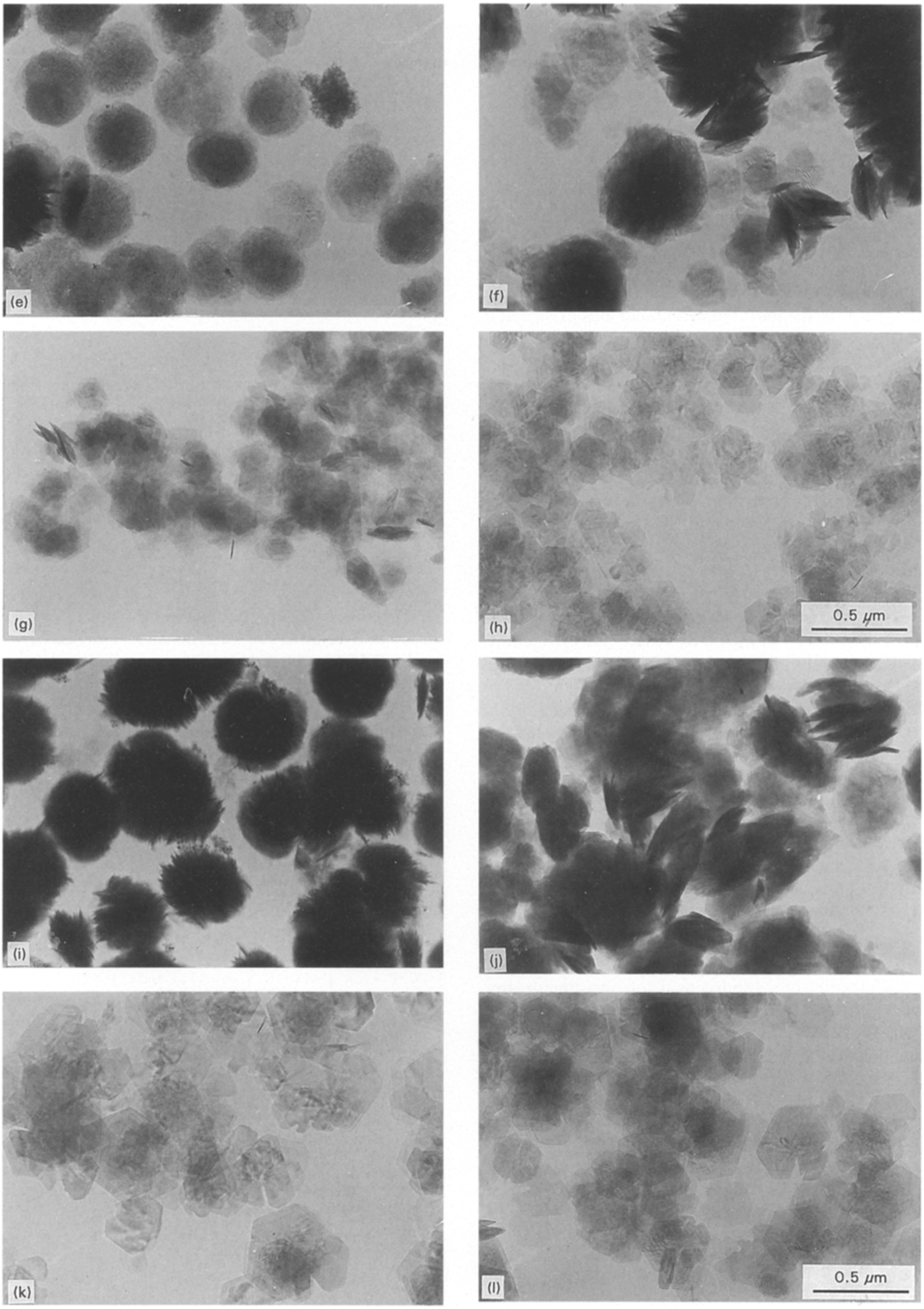

Figure 5 (Continued).

isolated spherulite. It appears that the products were converted into laminated aggregates of thin discs and that they were gradually peeled and separated into thin discs with treatment time. However, as mentioned above, it may be considered that most of the precipitated ZOS was formed without this process, judging from the precipitation velocity and the amount formed. As the concentration increased further (above

ZS2.0) PZOS was formed in the isolated state from the beginning, and this was precipitated into thin discs with almost near crystallinity of ZOS.

3.4. Crystallization mechanism

In the above experiment, the general tendency of the change in the amount of PZOS formed is a phenomenon common to many hydrolysis processes as the precipitation tendency of m-ZrO_2 in the hydrolysis process of zirconium salts [5–7]. It may be considered that the thicker the concentration of the starting solution became, the more sulphuric acid ions existed in it, so hydrolysis was prevented from occurring and the amount of precipitation decreased. It is possible that the lower the treatment temperature became, the greater was the solubility of PZOS in the acid solution, and lower was the amount of precipitation in equilibrium. For ZOS, the higher the treatment temperature became, the greater was the velocity of ZOS formation, which showed the same tendency as the formation of m-ZrO_2 and PZOS. However, with a thicker concentration of the solution, the velocity of precipitation increased, in striking contrast to the phenomenon in PZOS.

With increasing concentration of sulphuric acid ions, the stability of PZOS decreased and the stability of ZOS rapidly increased, which may be due to the difference in solubility in the sulphuric acid formed by the hydrolysis, and that solubility may depend on the difference in their crystallinity. The crystallization mechanism may be considered as follows. With a low concentration of sulphuric acid ions, the velocity of the hydrolysis was accelerated, so that crystallization into ZOS with a high crystallinity became insufficient and metastable PZOS was first crystallized. As the concentration of sulphuric acid ions was further decreased by the precipitation of PZOS from the solution with a thin concentration of sulphuric acid ions, metastable PZOS became unstable and crystallized into m-ZrO_2, releasing sulphuric acid ions. As the concentration of sulphuric acid ions became greater, the velocity of hydrolysis decreased and its solubility increased. Thus the degree of supersaturation decreased, and it became difficult for PZOS to nucleate gradually. However, ZOS with good crystallinity began to nucleate and grow, so its amount formed increased with increasing concentration. Therefore, it may be considered that PZOS formed was dissolved into the solution and that the nucleation and growth of ZOS proceeded simultaneously in the area of mid-concentration.

After long term treatment, $ZrOSO_4 \cdot H_2O$ began to crystallize from the high concentration specimen ZS2.5, and from a solution more concentrated than ZS2.5, $ZrOSO_4 \cdot H_2O$ was precipitated from the start. From these results, it may be considered that the crystallization of $ZrOSO_4 \cdot H_2O$ containing a high concentration of sulphuric acid ions became easier with treatment time, which may be due to the increasing proportion of sulphuric acid ions to zirconium ions in the solution caused by the precipitation of ZOS.

4. Conclusions

Solid products were prepared from $ZrOSO_4$ solutions of various concentrations under thermal hydrolysis. The formation process and mechanism of these crystalline products were investigated.

1. With increasing hydrothermal treatment time and concentration of the starting solutions, the area and thickness of fine plate-like crystals of ZOS increased.
2. For thin starting solutions, the precipitation velocity and the amount of PZOS increased. For thick starting solutions, those of ZOS increased.
3. For ZS0.5 from thin solutions, m-ZrO_2 crystallized by releasing sulphuric acid ions from PZOS, as the concentration of sulphuric acid ions was decreased by the PZOS precipitated.
4. For ZS2.5 from thick solutions, $ZrOSO_4 \cdot H_2O$ crystallized by increasing the proportion of sulphuric acid ions to ziconium ions in the solution by the ZOS precipitated.

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