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# Hydrolysis of zirconium alkoxide under an uncontrolled atmosphere

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The laboratory prepared zirconium *n*-butoxide was hydrolysed under an uncontrolled atmosphere by exposing it to air moisture (natural hydrolysis) or adding water solutions at various pH (accelerated hydrolysis) to the alkoxide solutions. Investigations were performed on the effects of the different processes and the pH of the water solutions on the products morphology, crystallinity and phase transformation. XRD, SEM, TEM and SAD were used for these investigations. A strong correlation between crystallite size, calculated with Scherrer formula, and phase transformation was observed in the present work.

## 1. Introduction

The wet chemical process for ceramic powder preparation has been widely investigated [1] due to its main advantage of achieving high-purity fine powders. Among the chemical processes, alkoxide hydrolysis seems to be the more interesting because of its possibility of producing monodispersed powders. Experimental work has been described for $Al_2O_3$, $TiO_2$, $SiO_2$ and $ZrO_2$, etc. [2, 3].

A number of discussions have focused on preparing $ZrO_2$ powders by means of alkoxide hydrolysis since the work reported by Mazdiyasni *et al.* [4]. Fegley *et al.* [5] prepared zirconia–alumina powder, as well as yttria-doped zirconia [6] by the hydrolysis process. Ikemoto *et al.* [7] prepared monodispersed zirconia powder by hydrolysis of zirconium *n*-butoxide. Yoldas [8] also prepared zirconia by the hydrolysis process and investigated the effect of the alkyl groups on powder morphology. Ogihara *et al.* [9] investigated the water/alkoxide ratio effect on the zirconia particle size and reported the most suitable concentration range for obtaining monodispersed particle size.

In spite of the advantage of alkoxide hydrolysis, an inconvenience in the processing was encountered due to the ease with which hydrolysis of the alkoxide occurred. It is strongly recommended that the hydrolysis process is carried out in a well protected enclosure [3, 6]. The present work describes a more convenient process for separating the synthesized zirconium alkoxide from ammonium chloride. The alkoxide obtained is hydrolysed under an uncontrolled atmosphere. It has been shown that the hydrolysis product of zirconium *n*-propoxide gives rise to cubic phase [8] which would transform to monoclinic phase upon heating. Yet, the present work observed tetragonal phase instead of cubic phase with zirconium *n*-butoxide being the precursor.

## 2. Experimental techniques

### 2.1. Preparation of zirconium *n*-butoxide

In the present work we tried to prepare zirconium alkoxide and to carry out the hydrolysis in a subsequent step, A schematic diagram of the apparatus used for alkoxide preparation is presented in Fig. 1. The ammonia generated from boiling the ammonium hydroxide solution is dried over calcium chloride before being introduced to react with the zirconium chloride–*n*-butanol solution in a three-neck reactor. The organic solvents were dried with magnesium *n*-butoxide prior to use.

During preparation of the alkoxide, 9.2 g (0.04 mol) of zirconium tetrachloride was dissolved in 85 ml *n*-butanol. The alkoxide formation reaction is exothermic. Ammonia gas was flushed until the bath felt cool, showing that reaction had ceased. At this point 150 ml dried benzene was introduced to eliminate the hydrolysing interference from the air moisture, because the alkoxide is known to be very easily hydrolysed. The idea of using benzene was derived from the fact that Mazdiyasni *et al.* [4] applied benzene in the preparation of zirconium propoxide.

### 2.2. The hydrolysis of zirconium *n*-butoxide

The hydrolysis experiment was carried out under an uncontrolled atmosphere by either exposing the alkoxide solution, covered with plastic foil containing pin holes, to the air (natural hydrolysis), or by adding water solutions to the alkoxide solution (accelerated hydrolysis). It takes about 20 days to completely dry 10 g alkoxide solution by the natural hydrolysis process. The resulting powder cake is shown in Fig. 2. The accelerated hydrolysis was carried out by adding 100 ml water solutions (0.04 ml $sec^{-1}$) of various pH (adjusted with $NH_4OH$ and HCl) to 100 ml magnetically stirred alkoxide solution. The double distilled water was found to have pH 5. This procedure gives rise to gel products. A Jeol JSM35 Microscope, and Hitachi 100H STEM were utilized to investigate product morphology.

### 2.3. The crystallinity and phase transformation of hydrolysed products

In order to study phase transformation, the gel products were ground in an agate motar to powders.

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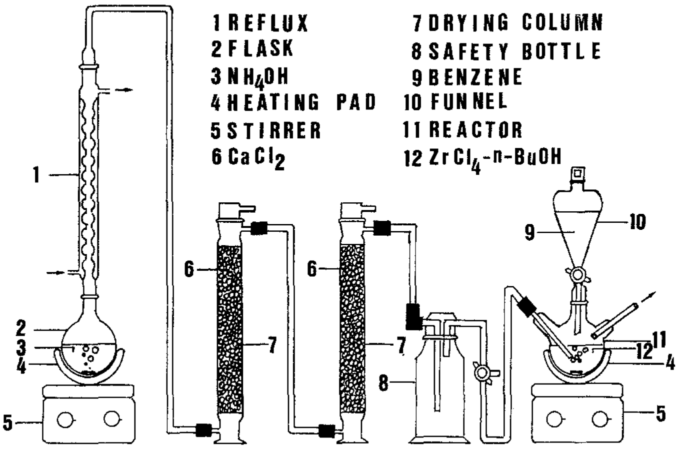

*Figure 1* Schematic diagram of the apparatus used for alkoxide synthesis. 1, Reflux; 2, flask; 3, $NH_4OH$; 4, heating pad; 5, stirrer; 6, $CaCl_2$; 7, drying column; 8, safety bottle; 9, benzene; 10, funnel; 11, reactor; 12, $ZrCl_4$-*n*-BuOH.

Heating was conducted at a rate of 15° C min$^{-1}$ and aged at the desired temperature for 24 h. The dark-field and selected-area diffraction (SAD) investigations were performed with the Hitach 100H STEM. The phase transformation was studied with a Rigaku X-ray diffractometer with Cu($K$) target and nickel filter. The crystallite size was calculated using the Scherrer formula applying the tetragonal (1 1 1) peak.

## 3. Results and discussion

### 3.1. Process effect on product type

In the present work it was observed that the natural hydrolysis gives rise to powder cake, Fig. 2. On the other hand, accelerated hydrolysis produces gel products, as shown in Fig. 3, for acetone-treated products. It was observed that acetone, in comparison with water, tends to induce powder agglomeration or gel aggregation, resulting in larger powder agglomerates or a rough surface appearance of the gel products. The effect of water quantity on the alkoxide hydrolysis has been reported previously [9]. The water/alkoxide ratio has been reported to be a critical factor in determining the particle size as well as the morphology of hydrolysed products [9]. The natural and accelerated hydrolysis processes of the present work are the two extreme cases of hydrolysis in terms of water contents and reaction rate. Natural hydrolysis receives the required water molecule gradually from the air. The release of solvent molecules to the air greatly depends on the coverage of the momentarily hydrolysis products on the solution surface which inhibits the subsequent hydrolysis reaction. Accordingly, the polycondensation of the hydrolysis reaction is very little restricted. The powders are thus formed without gel formation. On the other hand, the addition of water to the alkoxide solution enables the rapid formation of a large quantity of polymerization units which will polymerize to give gel products as observed in the accelerated hydrolysis process.

The flush of ammonia gas during the alkoxide preparation accelerates the reaction between zirconium chloride and *n*-butanol by precipitating the chloride in the form of ammonium chloride. In addition to filtration, a suitable process to separate the butoxide from ammonium chloride is reflux. Yet it is somewhat inconvenient. Direct filtration is also not appropriate unless the interference by hydrolysis from the atmospheric moisture can be avoided.

In the present work the alkoxide was dissolved in an *n*-butanol–benzene mixed solvent in the sense that the solubility of atmospheric water, for instance, in benzene is very low. The addition of benzene to the solution shrinks the surface area available for water absorption. It is observed in the present work that the application of benzene enables the filtration of ammonium chloride easily without interference from

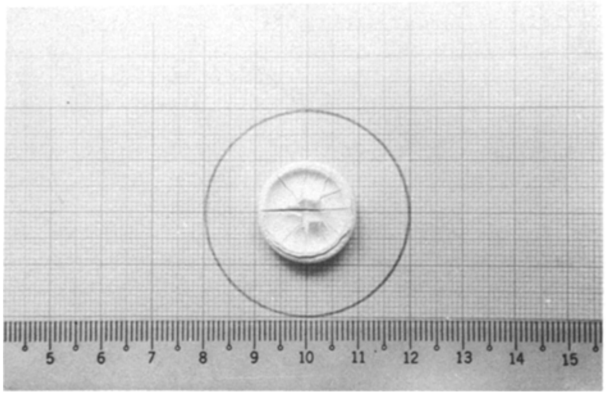

*Figure 2* The powder cake resulting from natural synthesis, the circle indicates the container size.

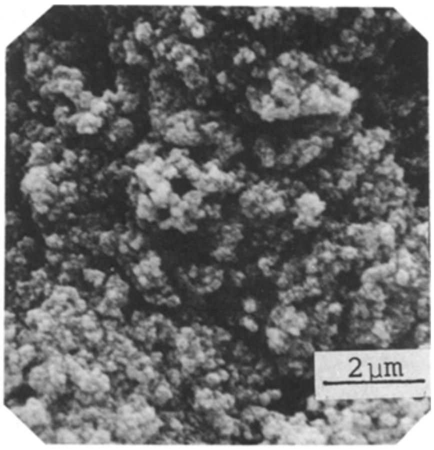

*Figure 3* The gel products of the accelerated hydrolysis process with pure water (pH 5), acetone-treated.

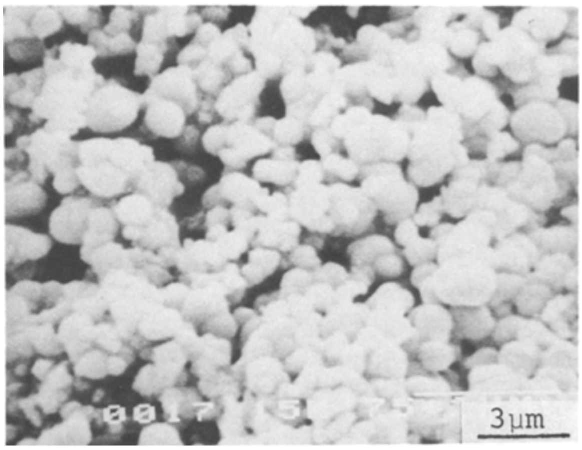

*Figure 4* The granular powdery products of the natural hydrolysis process, $NH_4Cl$-filtered.

TABLE I Process effect on crystallite size* variation of hydrolysed products

| $T$ (° C) | Crystallite size (nm) | |
|---|---|---|
| | Natural hydrolysis | Accelerated hydrolysis |
| 350 | 25.3 | 18.2 |
| 400 | 28.1 | 22.4 |
| 500 | | 23.7 |

*Calculated using XRD $(1\,1\,1)_t$ peak.

hydrolysis. In view of this, it may be appropriate to apply another organic solvent instead of benzene as long as the solvent has a low solubility of water.

It is also observed in this work that adequate separation of ammonium chloride from the solution is essential in controlling the morphology of the powder obtained through hydrolysis. Granular powders are obtained when the $NH_4Cl$-filtered solution is the precursor for natural hydrolysis, as shown in Fig. 4. Nevertheless, the unfiltered decant solution would give rise to powders of irregular shape as shown in Fig. 5. The difference in these observations may be due to the fine suspension of ammonium chloride which inhibits uniform growth of zirconia powders through surface absorption on to the zirconia powders.

## 3.2. The effect of the process on crystallinity and phase transformation

The effect of the hydrolysis process on the crystallite size and the phase transformation of the powders is presented in Tables I and II, respectively. The crystallite sizes presented in Table I clearly indicate the expected trend of larger crystallite size at higher temperatures. Additionally, the natural hydrolysis process gives rise to larger sizes. The latter observation seems to be due to the characteristics of the natural hydrolysis process in that it takes place slowly through the complete hydrolysis of the alkoxide solution. Consequently, it allows the crystal to grow to a certain extent.

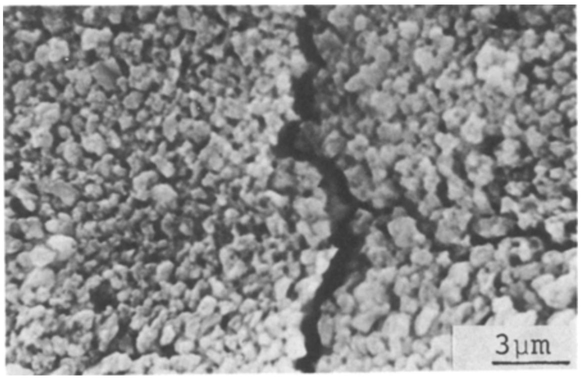

*Figure 5* The products of the natural hydrolysis process, incomplete separation of $NH_4Cl$.

The results of Table II are obtained from the XRD profiles. The comparative correlations show the relative peak height. It is seen that both hydrolysis processes produce amorphous powder which converts to tetragonal and then to monoclinic as the temperature is raised. The phase variation observed in the present work is different from that reported by Yoldas [8] who observed the cubic phase of hydrolysed powders. A comparison between the results of Tables I and II indicates that the natural hydrolysis powder exhibits a crystallite size of 28.1 nm at 400° C. The monoclinic phase was not observed until about 500° C. Furthermore, the monoclinic phase of the accelerated hydrolysis process produced powder does not appear until 600° C. The crystallite size of the latter case at 500° C is only 23.7 nm, much less than the critical crystallite size reported by Garvie [10]. In an earlier work, Garvie [10] proposed a critical crystallite size for the transformation of metastable tetragonal to monoclinic phase. The above mentioned experimental results seem to correspond to Gavie's conclusion.

## 3.3. Effect of pH on crystallinity and phase transformation

Table III shows the effect of pH on the crystallite size of the powders produced by the accelerated hydrolysis process. It was observed that the hydrolysed products obtained with the solution at pH 1 disappear after being present in the solution for a couple of days. The results further show a trend that a higher pH solution gives rise to smaller crystallite size. These observations are not explainable at present. The powder phase transformations are shown in Table IV. In all cases the powders are found to be amorphous at temperatures below 300° C from the XRD results. Nevertheless, further investigation of the powders by TEM and

TABLE II Process effect on phase transformation of hydrolysed products

| Hydrolysis process | $T$ (° C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 300 | 350 | 400 | 500 | 600 | 700 | 800 |
| Natural | A | T | T | T > M | M > T | M > T | M > T |
| Accelerated | A | T | T | T | T > M | T > M | M > T |

A = amorphous, M = monoclinic, T = tetragonal.

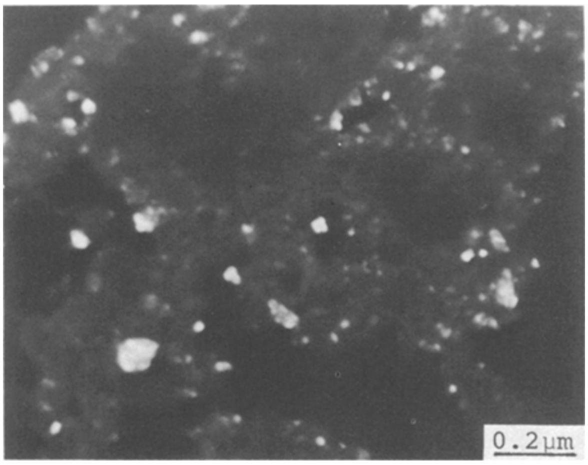

*Figure 6* Dark-field TEM spectroscopy of the gel products, hydrolysed with a pH 7 solution.

TABLE III pH effect on crystallite size of hydrolysed products

| $T$ (°C) | Crystallite size (nm) at pH: | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 3 | 5 | 7 | 9 | 11 |
| 350 | * | 24.7 | 18.2 | 18.2 | 17.8 | 17.8 |
| 400 | * | 24.7 | 22.4 | 20.1 | 17.8 | 20.6 |

*Precipitates disappear overnight.

SAD shows slightly different behaviour. Figs 6 and 7 show an example of the powders prepared by hydrolysis with a pH 7 solution, without heat treatment. The dark-field TEM observation (Fig. 6) as well as the SAD (Fig. 7) investigation on the bright spot of the dark-field TEM picture, show crystalline structure. Such a behaviour is observed for all the powders hydrolysed with water solutions except for that with pure water (pH 5). From the dark-field picture it is clear that the crystalline structure does exist in the powders but to a limited extent. The limiting quantity of the crystalline structure may be beyond the detection limit of XRD. The results of Table IV also show the relative ease with which the transformation of tetragonal to monoclinic phase occurs. It is seen that for the powders hydrolysed with pH 3 and 7 solutions the monoclinic phase appears in XRD spectroscopy at 500° C, the lowest temperature at which the monoclinic phase appears in all the investigations. On the other hand, for the powder hydrolysed with pure water (pH 5), the monoclinic phase exceeds the tetragonal phase only at temperatures as high as 800° C. Yet, it takes place at 600° C for pH 3 and 7, and at 700° C for pH 9 and 11. These observations in Table IV indicate that in addition to affecting the crystallite size, the appearance of ionic species may also be of importance in determining the powder phase transformation. The SAD results give a further indication of the effect of ionic species on powder phase transformation. The effect of the ionic species on the zirconia powder phase transformation has been mentioned previously [11–13]. Mitsuhashi *et al.* [12] indicated the presence of hydroxyl ions in the metastable tetragonal zirconia through infrared and NMR investigations. Clearfield [11] reported that the crystalline, hydrous zirconias are hydrated oxo-hydroxides. The experimental observations of the present work seems to emphasize further the definite influence of the ionic species on the phase transformation of zirconia powders.

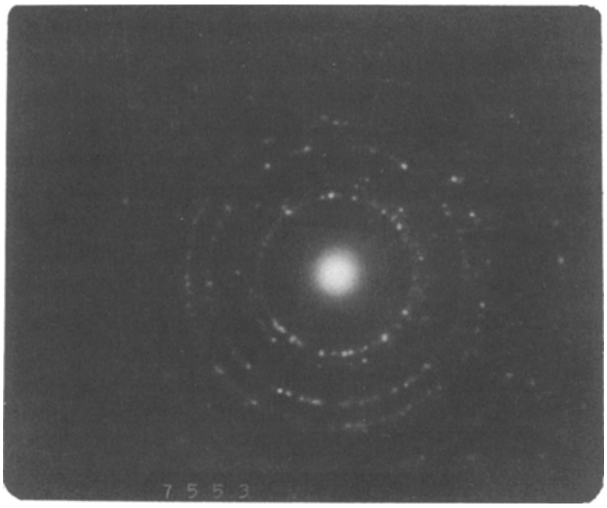

*Figure 7* SAD of the products, hydrolysed with pH 7 solution (the same sample as Fig. 6).

TABLE IV pH effect on phase transformation of hydrolysed products

| $T$ (°C) | pH | | | | |
|---|---|---|---|---|---|
| | 3 | 5 | 7 | 9 | 11 |
| 300 | A | A | A | A | A |
| 350 | T | T | T | T | T |
| 400 | T | T | T | T | T |
| 500 | T > M | T | T > M | T | T |
| 600 | M > T | T > M | M > T | T > M | T > M |
| 700 | M > T | T > M | M > T | M > T | M > T |
| 800 | M > T | M > T | M > T | M > T | M > T |

A = amorphous, M = monoclinic, T = tetragonal.

## 4. Conclusions

A convenient procedure for manipulating the alkoxide solution by modifying the solvent character is described. The natural hydrolysis of alkoxide exposed to atmospheric moisture gives rise to powders. Accelerated hydrolysis by adding water directly tends to yield gel products. Natural hydrolysis induces a greater crystallite size than the accelerated hydrolysis process. The decreasing pH value of the water solution of the accelerated hydrolysis process gives rise to greater crystallite size. In general, natural hydrolysis produces powders which are easier to transform to monoclinic phase upon heating than those produced by the accelerated hydrolysis process. Yet, the introduction of foreign ions into the water solution enhances the formation of monoclinic phase upon heating.

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