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# Zirconium oxides formed by hydrolytic condensation of alkoxides and parameters that affect their morphology

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When zirconium oxides are formed via hydrolytic condensation of zirconium alkoxides, the particle size and morphology of the resultant zirconia is strongly affected by certain parameters during the condensation. These parameters include: the type of alkyl group in the alkoxide, water/alkoxide ratio, molecular separation of species, and the reaction temperature. The particle size and the morphology in turn affect the sintering behaviour and crystalline transformation of $ZrO_2$. In this work the parameters that affect the formation of $ZrO_2$ from zirconium alkoxides are investigated. It has been shown that the alkyl groups and molecular separations during the hydrolytic polycondensation have particular significance in the modification of monoclinic → tetragonal transformation of the resultant $ZrO_2$. Tetragonal phase can also be stabilized by copolymerization of $ZrO_2$ with $SiO_2$ producing tough ceramic materials.

## 1. Introduction

Zirconium alkoxides were synthesized and investigated in detail by Bradley and co-workers [1–3]. Later Mazdiyazni *et al.* investigated the formation of $ZrO_2$ from these compounds [4, 5].

The hydrolytic condensation of zirconium alkoxides differs fundamentally from that of silicon, aluminium, titanium etc. The hydrolysis reactions in this system lead to the formation of oxo-groups and aqua-groups rather than true hydroxides. This is reflected in the fact that, while the equivalent oxide content of hydrolytic polymer condensation products of titanium, silicon and aluminium alkoxides vary in a broad range of values, depending, for example, on the water/alkoxide ratio, the oxide content of hydrolytic polycondensation products of zirconium alkoxides remains constant [6].

Hydrolytic polycondensation reactions are complex multiple reactions. Bradley and Carter observed that the hydrolysis of some primary zirconium alkoxides are polymeric oxide-alkoxides [7, 8] $[ZrO_x(OR)_{4-2x}]_n$. A simplified form of hydrolysis of zirconium isopropoxide has been expressed at least in two steps [4]:

$$\mathrm{Zr(OR)_4 + H_2O \rightarrow ZrO(OR)_2 + 2\,R(OH)} \quad (1)$$

$$\mathrm{2\,ZrO(OR)_2 \rightarrow ZrO_2 + Zr(OR)_4} \quad (2)$$

Even though these reactions differ from the hydrolysis polymerization reactions described for silicon [9], it is clear that any hydrolytic condensation reaction involves multiple reactions. Initially water must alter some of the bonds of the alkoxide molecules, and these altered species must react with each other or with unaltered species to form large molecules. In these reactions diffusion and statistical interactions play significant roles in determining molecular-weight distributions [10], particle and surface morphologies (see Fig. 1) and even in modifying certain material properties [11, 12]. In a previous work [6] it was shown that the water/alkoxide ratio in the hydrolysis medium, even beyond the chemical requirements, strongly influences the sintering and crystallization behaviour of zirconia. In this work the effects of ester groups, molecular separation during the hydrolysis, and hydrolysis water temperature on the resultant zirconia are investigated. These parameters are in addition to, and somewhat more basic than, the processing parameters involved in the production of mono-size particles from metal alkoxides [13].

## 2. Effect of alkyl groups

### 2.1. Effect on the morphology

To check the effect of alkyl groups, R, in the zirconium alkoxides, $Zr(OR)_4$, 0.2 M solutions of zirconium alkoxides were prepared by dissolving 1 mol each of $Zr(OC_2H_5)_4$, $Zr(OC_3H_7)^i_4$, $Zr(OC_3H_7)^n_4$, $Zr(OC_4Hg)^n_4$ in 5 litres of alcohol of the same alkyl group. The first two compounds are solids and their dissolution in certain alcohols required the addition of acids, e.g., acetic acid. In these cases a reaction takes place between alkoxide and acetic acid forming alkoxide–acetic acid complexes:

$$\mathrm{{\equiv}M{-}OR + CH_3COOH \rightarrow {\equiv}M{-}O{-}COCH_3 + R(OH)} \quad (3)$$

Apparently a very small portion of the bonds must be reacted to render the compound soluble in alcohols. These solutions were then combined with mixtures containing 10 mol of water in 5 litres of the same

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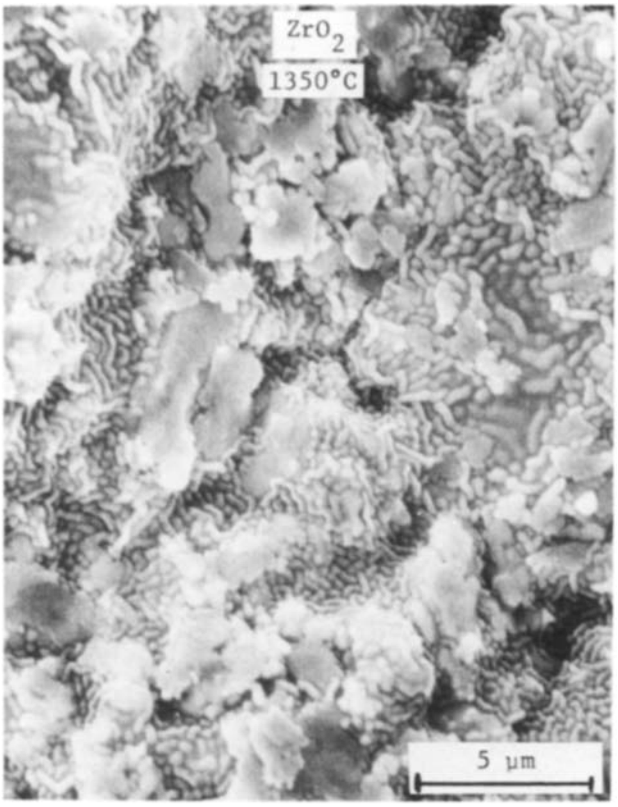

*Figure 1* Surface morphology of a $ZrO_2$ sample produced via hydrolytic polycondensation of $Zr(OC_4H_9)_4^n$.

alcohol. Thus, in effect, 1 mol of each alkoxide was hydrolytically condensed with 10 mol of water in its alcohol in a total volume of 10 litres.

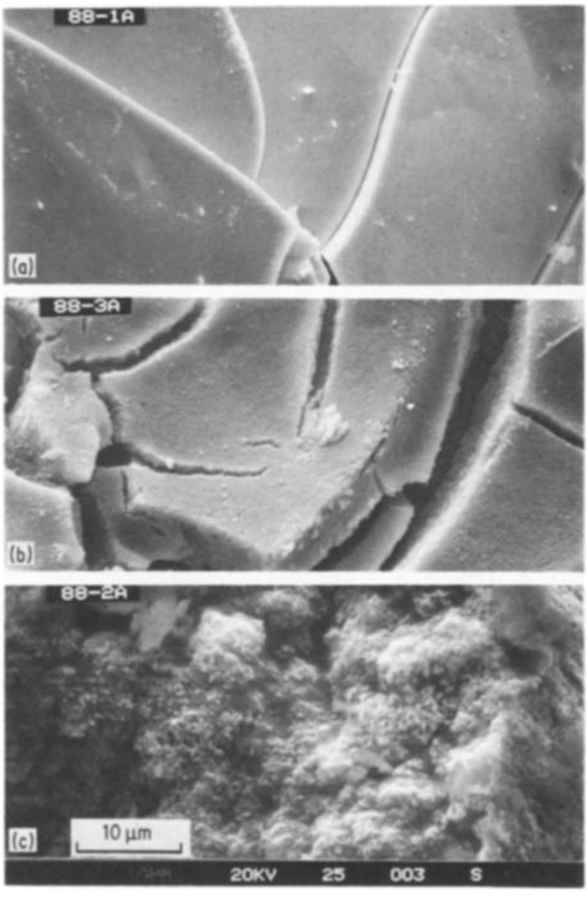

*Figure 2* Textures of dried gels obtained via 10 mol water hydrolysis of (a) $Zr(OC_2H_5)_4$, (b) $Zr(OC_3H_7)_4^n$, (c) $Zr(OC_4H_9)_4^n$ in their alcohols (10 litre volume).

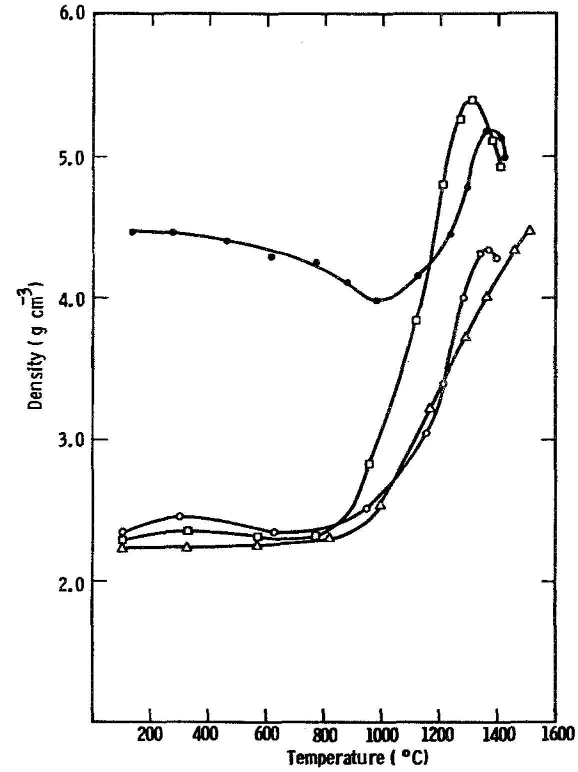

*Figure 3* Densification behaviour of $ZrO_2$ samples produced via hydrolysis of four different zirconium alkoxides. (Note that the temperature of the peak density varies and one of the samples does not exhibit the peak in the density curve.) $ZrO_2$ hot pressed at 280 kg cm$^{-2}$, $ZrO_2$ precursors, ● $Zr(OC_2H_5)_4$, □ $Zr(OC_3H_7)_4^i$, △ $Zr(OC_3H_7)_4^n$, ○ $Zr(OC_4H_9)_4$.

Fig. 2 shows scanning electron micrographs of the condensed materials after they were dried at 100° C. As is seen from Fig. 2, the higher the alkyl group of the alkoxide the coarser the texture of the material tends to be. Zirconium ethoxide, $Zr(OC_2H_5)_4$, produced yellow transparent grains or films having no discernible texture (Fig. 2a), whereas the texture of material produced from $Zr(OC_4H_9)_4^n$ is clearly visible (Fig. 2c). The fine texture and continuous nature of material produced from $Zr(OC_2H_5)_4$ remains unchanged when the hydrolysis of the alkoxide was carried out in higher alcohols. Apparently the ester exchange between the $Zr(OC_2H_5)_4$ and higher alcohols within the short experimental time, e.g., 15 to 20 min, is not extensive enough to make a significant difference. However, when $Zr(OC_2H_5)_4$ was used, with higher alcohols, it was necessary to add acetic acid for dissolution, so the effect of acetic acid on the microstructure remains undetermined. Nevertheless, the gradual coarsening of the matrix from $Zr(OC_3H_7)_4^n$ to $Zr(OC_3H_7)_4^i$ to $Zr(OC_4H_9)_4^n$ must be attributed to the alkyl groups, since all other factors were similar in these cases.

## 2.2. Effects on sintering and crystallization

Fig. 3 shows the sintering behaviour of $ZrO_2$ obtained by hydrolysis of the four alkoxides mentioned in the previous section. The hydrolytic condensation products were calcined to 500° C and then hot pressed under 280 kg cm$^{-2}$ (4000 p.s.i.) pressure. The resultant particle size and morphology were considered part of the process, and no attempts were made to control or alter them. Fig. 3 has several noteworthy features: First, it appears that a significant rate of sintering in

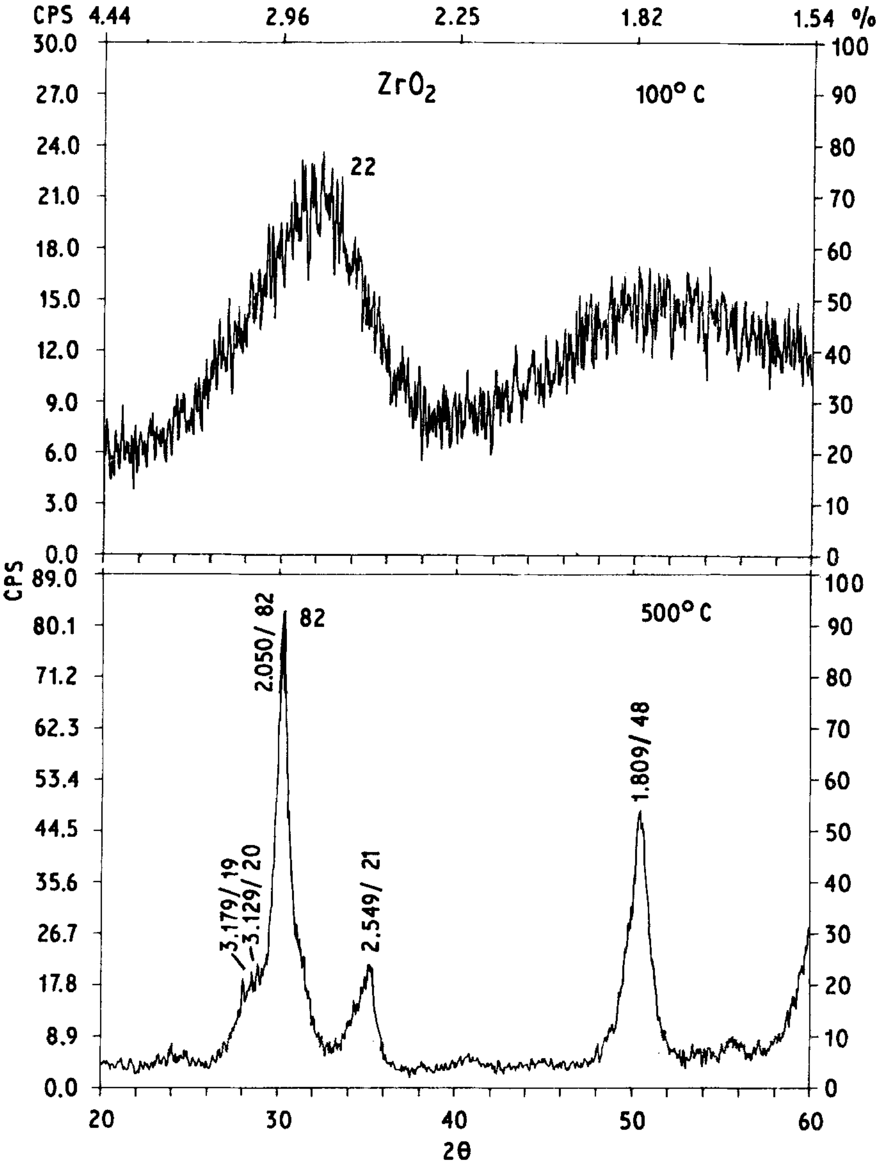

*Figure 4* Diffuse X-ray diffraction pattern of hydrolytic condensation product of $Zr(OC_3H_7)_4^n$ at 100° C indicates cubic phase structure (top); the same material develops traces of monoclinic structure when heated to 500° C (bottom).

these zirconias begins ~800° C. Second, the unsintered compaction density of zirconia obtained from $Zr(OC_2H_5)_4$ is twice as high as that observed for others. When pressed under 280 $kg\,cm^{-2}$ pressure, other zirconias had a compaction density of around 2.25 $g\,cm^{-3}$, whereas that of zirconia obtained from $Zr(OC_2H_5)_4$ was around 4.5 $g\,cm^{-3}$. This is clearly due to the different condensation characteristics of this alkoxide under acidic conditions giving a nonparticulate, continuous, and apparently rather dense matrix as shown in Fig. 2.

Probably the most important feature of the densification curves shown in Fig. 3 is that, in three out of four materials, the density first increases, obtains a peak value at somewhere around 1300 to 1400° C and then decreases with increasing temperature. This behaviour has been observed by Gupta in non-alkoxide derived $ZrO_2$'s and has been attributed to crystalline transformation [14].

In our investigations it has been shown that this behaviour is due to the monoclinic-to-tetragonal transformation. When $ZrO_2$ is produced by hydrolytic polycondensation of zirconium alkoxides, the initial phase is cubic [6, 15]. This initial cubic phase starts to convert to the monoclinic phase upon heating: trace amounts of the monoclinic phase are observed (Fig. 4) at a temperature as low as 500° C. The amount of monoclinic phase becomes as high as 87% at 1000° C [6] and the phase may be considered entirely monoclinic just below the temperatures at which the peak in the density curves occurs. As the temperature is increased, the monoclinic phase becomes unstable and converts to the tetragonal phase around 1300 to 1400° C. This conversion involves a volume change [16]: thus the peaks in the density curves are observed. It is interesting that not only do these peaks occur at somewhat different temperatures for zirconas derived from different alkoxides, but also that one of them, the $ZrO_2$ derived from $Zr(OC_3H_7)_4^n$ in Fig. 3, does not go through this density reversal within the temperature range to 1400° C. This indicates that the alkyl groups sufficiently alter the particle size and morphology during the hydrolytic condensation which in turn affects the transformation behaviour of the resultant zirconias. The effect of size on the transformation has been discussed previously by other workers [17–19]. In the next section it is shown that molecular spacing during the hydrolytic polycondensation also affects the transformation. These results indicate that a degree of stabilization can occur in $ZrO_2$ without any alloying agents.

## 3. Effect of molecular separation during hydrolytic condensation

The size of condensed particles in various systems ranges from 1.0 nm up to 1 μm involving thousands of atoms. The size, i.e., extent of polymerization, is determined by the nucleation and diffusion rates of these species in the reaction medium.

Under diluted conditions, larger molecular separations result. The mobilities of those species that comprise the higher-molecular units become more important. Prediction of the effect of solution concentration on particle size is not a simple task, however, and although higher concentration favours larger molecules, it also causes more extensive nucleation, which restricts the growth. This effect of molecular separation is addressed in another paper for silica [10]. Altering the molecular separation during the condensation has been found to modify the sintering and monoclinic–tetragonal transformation of the resultant $ZrO_2$. The degree of polymerization in zirconium alkoxides largely depends on alkyl radicals. It has been reported that alkoxides of straight-chain alkyl radicals, $Zr(OC_2H_5)_4$ and $Zr(OC_3H_7)^n$ and lower molecular weight branched-chain alkyls, $Zr(OC_3H_7)^i$, are trimers and tetramers, and form dimers in the parent alcohol [20–22]. Molecular separation of these units, even though they are not monomers, by a solvent still modifies the condensation process.

When the $ZrO_2$ derived from $Zr(OC_3H_7)_4^n$ was formed under more concentrated conditions (both the alkoxide and water were diluted in 0.7 litres of alcohol before mixing instead of 5 litres each as in the previous case), this did not affect the absence of the peak in the density curve exhibited previously (Fig. 5). It appears that among the zirconium alkoxides studied, hydrolytic condensation of zirconium n-propoxide, $Zr(OC_3H_7)_4^n$, results in oxides with a high degree of resistance to monoclinic–tetragonal transformation. The tetragonal–monoclinic transformation in zirconia is martensitic in nature [23, 24] and shows dependence on particle size [25–27], as well as on internal strain energy, etc. Martensite is considered to grow from pre-existing precursor embryos whose structure is thought to be intermediate of the two phases [28, 29], and whose growth dependence is on strain energy and particle size. It is reasonable to expect, therefore, that the alkyl groups, by affecting polycondensation reactions, can influence and modify both the population and growth environment of the precursor embryos.

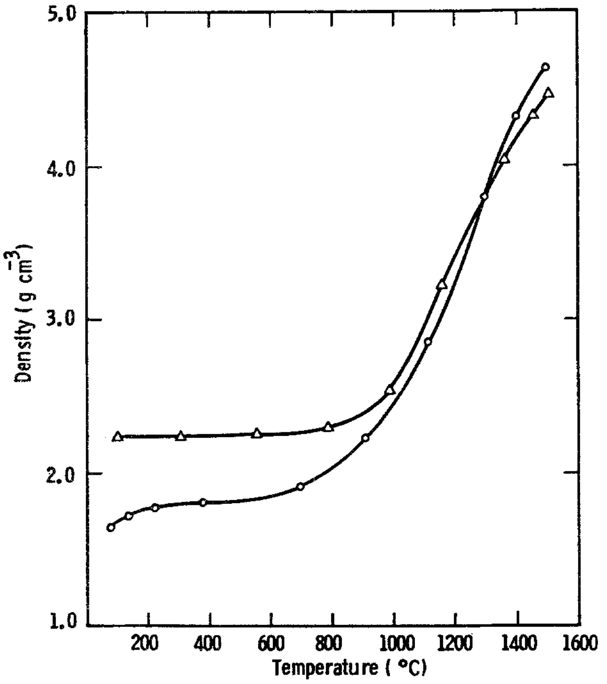

*Figure 5* The absence of a peak in the density curve is not affected when $ZrO_2$ is formed via hydrolytic polycondensation of $Zr(OC_3H_7)_4^n$ at two different solution concentrations. $ZrO_2$ hot pressed at 280 kg cm$^{-2}$. Solution concentration; △ dilute 10 litres mol$^{-1}$, ○ concentrated 1.4 litres mol$^{-1}$.

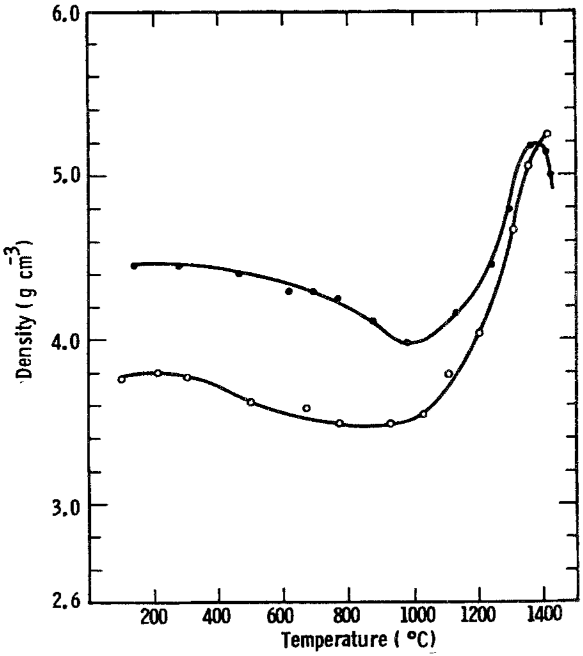

*Figure 6* Changing the molecular spacing, *ms*, of water during the hydrolytic polycondensation of $Zr(OC_2H_5)_4$ affects the compaction rate and the monoclinic–tetragonal transformation, as indicated by the peak in the density curve. (Spacing of water molecules in undiluted water is taken as unity, and separation of water molecules when diluted by ethanol is expressed as a multiple of that unit.) $ZrO_2$ hot pressed at 280 kg cm$^{-2}$. ● *ms* ($H_2O$) = 3, ○ *ms* ($H_2O$) = 1.

In another experiment the density reversal associated with the transformation was eliminated within the temperature range studied by changing the molecular spacing of hydrolysis water in alcohol. In this experiment, instead of reacting a 0.2 M solution of $Zr(OC_2H_5)_4$ (1 mol $Zr(OC_2H_5)_4$ in 5 litres of ethanol) with alcohol diluted water as described in Section 1, it was reacted with undiluted water

TABLE I Effect of silica doping on the crystalline structure of $ZrO_2$*

| wt % $SiO_2$ | 1100° C for 2 h | |
|---|---|---|
| | Monoclinic (~ %) | Tetragonal (~ %) |
| 0 | 100 | 0 |
| 5 | 88 | 12 |
| 10 | 68 | 32 |
| 15 | 42 | 58 |
| 20 | 13 | 87 |
| 22 | ~0 | ~100 |

*Prepared from zirconium *n*-propoxide and partially hydrolysed tetraethoxysilane in butyl alcohol.

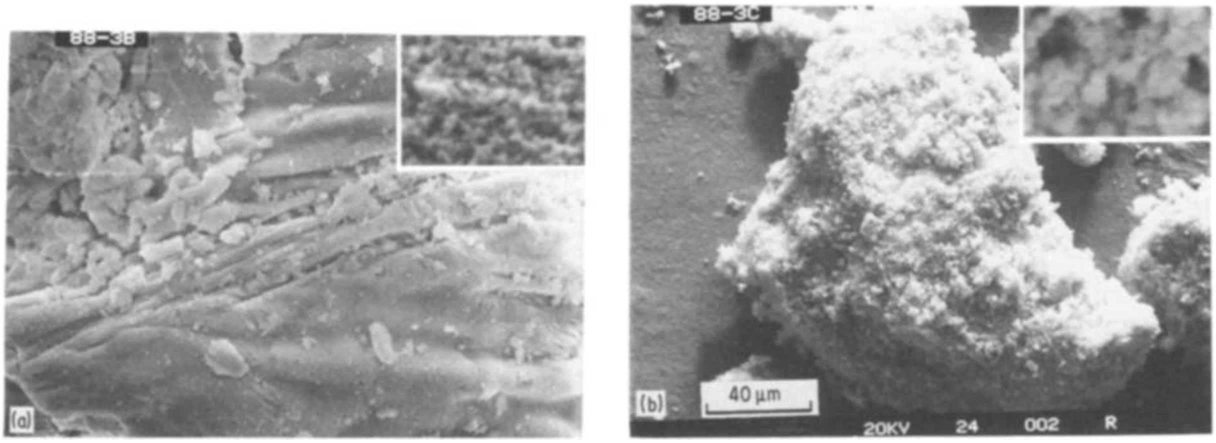

*Figure 7* Changing the water/alkoxide ratio from (a) 10 to (b) 2 affects the morphology of the condensate. In the experiment 1 mol of $Zr(OC_3H_7)_4^n$ was hydrolysed with 10 and 2 mol of $H_2O$ in 1.4 l of n-propanol.

(the molecular spacing, *ms*, of water in the diluted mixtures was three times that in pure water: thus *ms* = 1 against *ms* = 3 for water). The zirconia obtained under this hydrolytic polycondensation of $Zr(OC_2H_5)_4$ did not show a peak in the densification curve within the temperature range (Fig. 6).

Formation of zirconias from metal–organic compounds also permits room temperature doping or alloying of these oxides at the molecular level leading to the stabilization of cubic or tetragonal phases circumventing high temperature heat treatment requirements. Table I shows the result of an experiment where zirconia was doped with various amounts of silica by reacting zirconium n-propoxide with partially hydrolysed tetraethoxysilane in butanol. The silica doping stabilizes the tetragonal phase: near 100% stabilization seems to require about 22% $SiO_2$ doping by weight (approximately 1 Si for 2 Zr). These materials are extremely tough in both glass and crystalline forms.

## 4. Effect of water/alkoxide ratio and prevention of particulate condensation

The effect of the water/alkoxide ratio during the hydrolytic condensation of metal alkoxides on the behaviour of the resultant oxides is considerable. For example, Fig. 7 shows the effect of water on the morphology of the condensate when $Zr(OC_3H_7)_4^n$ is hydrolysed in 1.4 l of isopropanol with 2 and 10 mol of water. These morphologies are also modified by solution concentration.

Use of higher water/alkoxide ratios generally results in the formation of materials having superior sintering properties due to stoichiometry and particle morphology [6]. Sintering studies on zirconia samples produced at different water/alkoxide ratios show that the higher the hydrolysis water, the finer the texture of the matrix (see Fig. 8). Samples produced with less than 2 mol of hydrolysis water consist of large angular particles showing no consolidation after 2 h of heat treatment at 1350° C (Fig. 8a), whereas the 15 mol water-hydrolysed sample was sintered to a relatively high density of 5.4 g cm$^{-3}$.

This brings us to another aspect of the hydrolysis. Under certain hydrolysis conditions, localized condensations of the particles can be prevented, resulting in clear solutions. When these clear solutions are gelled by evaporation and thermally decomposed, they yield transparent $ZrO_2$ granulars. These solutions may also be used to deposit thin films. Generally when the water/alkoxide ratio exceeds a critical concentration, localized condensation occurs. The solution turns milky, reflecting the fact that it has become a two-phase suspension. When these materials are dried and thermally decomposed, they yield the

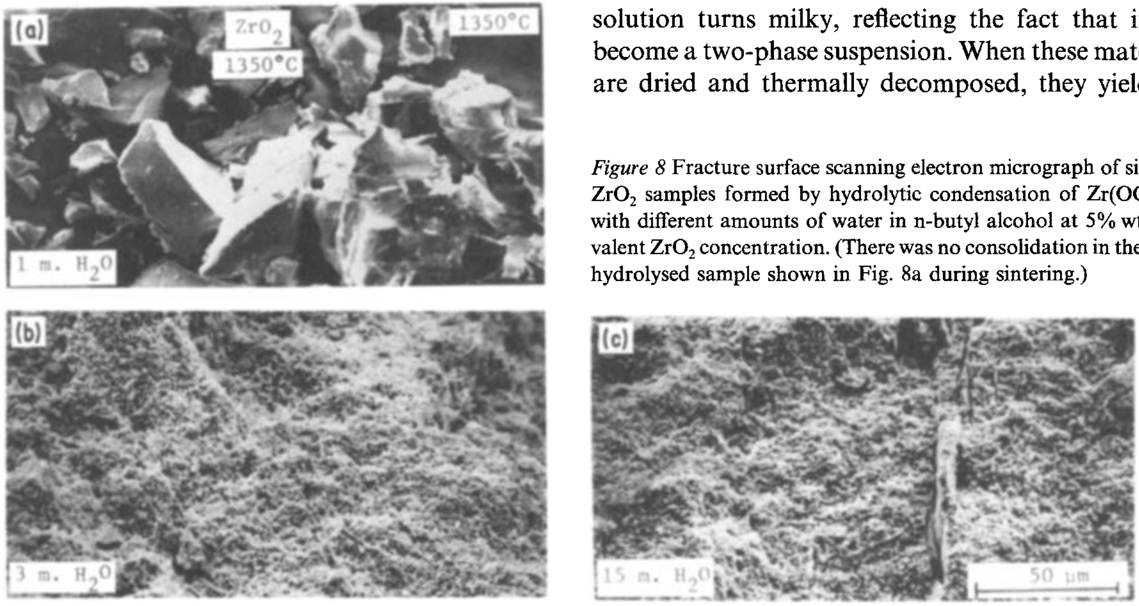

*Figure 8* Fracture surface scanning electron micrograph of sintered $ZrO_2$ samples formed by hydrolytic condensation of $Zr(OC_4H_9)_4^n$ with different amounts of water in n-butyl alcohol at 5% wt equivalent $ZrO_2$ concentration. (There was no consolidation in the 1 mol hydrolysed sample shown in Fig. 8a during sintering.)

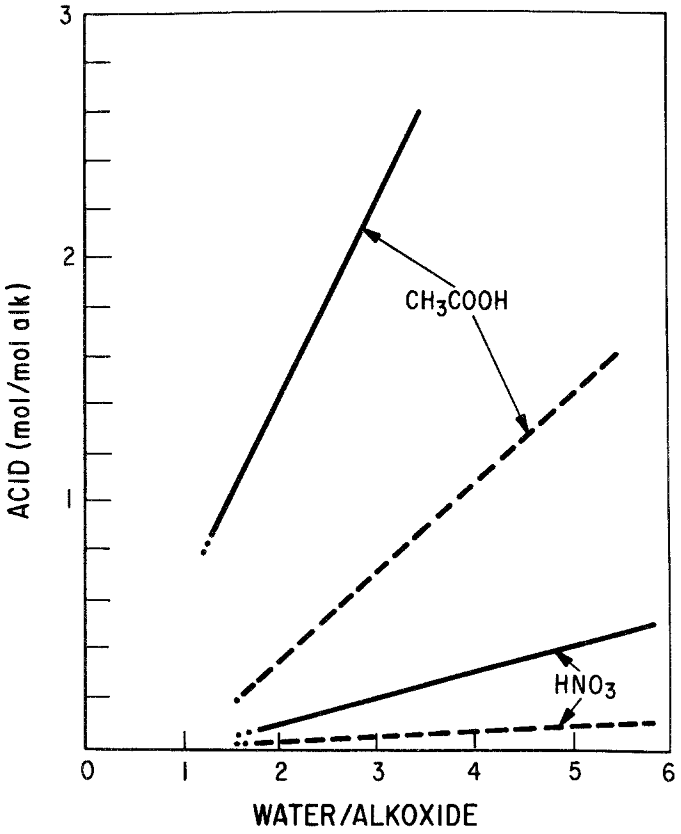

*Figure 9* Acid requirement for the formation of clear zirconia solutions as a function of water/alkoxide ratio at two different solution concentrations when $\mathrm{Zr(OC_3H_7)_4^n}$ is hydrolysed in 2-propanol. (Solution concentrations are expressed in terms of weight equivalent $\mathrm{ZrO_2}$.) (—) 5%, (– – –) 2.5%.

$\mathrm{ZrO_2}$ powders whose sintering and crystalline transformation has been discussed here. One of the reasons for the condensation of particulates in these systems is the near-complete removal of "OR" groups from the molecular structure. The presence of a small critical concentration of "OR" groups in the molecular structure is required for these molecules to be soluble in alcohols [30].

It is possible to maintain the clarity of these solutions under near complete hydrolysis by introducing acids into the system. The amount of acid required to prevent localized condensation is a function of the solution concentration and the water/alkoxide ratio. Fig. 9 shows the acetic acid and nitric acid requirements as a function of water/alkoxide ratio when $\mathrm{Zr(OC_3H_7)_4^n}$ is hydrolysed at concentrations corresponding to 2.5 and 5% equivalent $\mathrm{ZrO_2}$ by weight in 2-propanol. It appears that the effect of acid is both chemical in nature (Equation 3), and electrolytic.

Finally, the hydrolysis temperature has a bearing on the morphology and the particle size. Fig. 10 shows the effect of hydrolysis water temperature on the morphology of the condensation. In this experiment a portion of 0.2 M $\mathrm{Zr(OC_3H_7)_4^n}$ in n-propanol was poured into water at 20° C: another portion was poured into water at 65° C. The coarse granular appearance of the cold-water-hydrolysed material (Fig. 10a) is clearly different from the fine and fluffy structure of the hot-water-hydrolysed material (Fig. 10b) even though the magnifications are somewhat different.

## 5. Summary

In the hydrolytic condensation of zirconium alkoxides, the alkyl groups of the alkoxides play an important role, affecting the morphology and particle size of the resultant materials. These in turn affect the sintering and monoclinic → tetragonal transformation of the

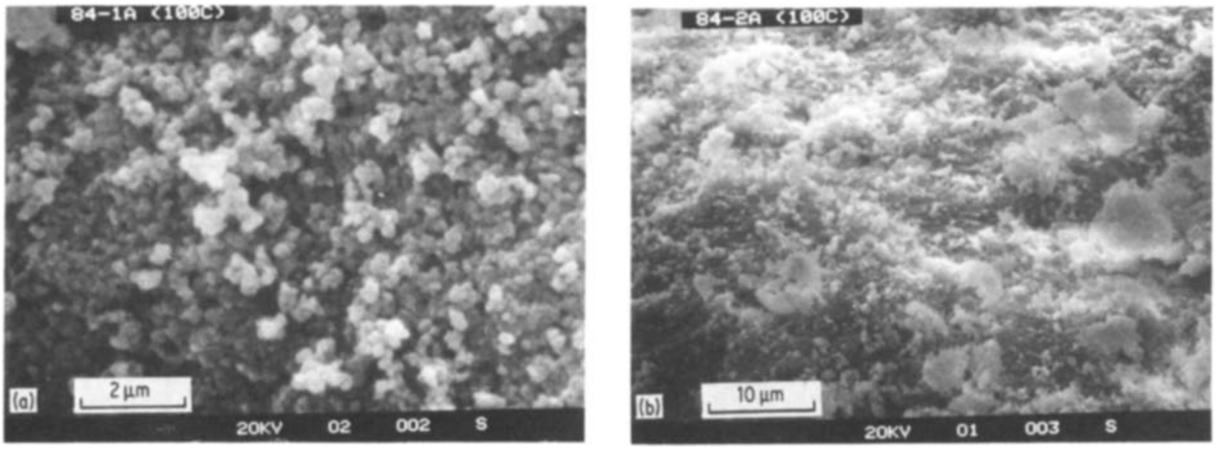

*Figure 10* Effect of hydrolysis water temperature on the particle morphology. Top photograph shows $\mathrm{Zr(OC_3H_7)_4^n}$ hydrolysed with water at 20° C and the bottom photograph shows the hydrolysis with a water temperature of 65° C.

$ZrO_2$ derived from these materials. Zirconium ethoxide, $Zr(OC_2H_5)_4$, tends to give the finest texture and highest compaction density before sintering. Zirconium n-propoxide $Zr(OC_3H_7)''$, on the other hand, gives an oxide morphology that is more resistant to the monoclinic → tetragonal transformation.

It has also been shown that the water/alkoxide ratio, the molecular separation of the reacting species, the reaction medium and the hydrolysis temperature all play important roles in determining the morphological make-up of the condensed materials. These morphological differences affect the thermal properties of the resultant $ZrO_2$ by modifying sintering behaviours and the phase transformation temperatures. Copolymerization of zirconia with silica produces tough glass and ceramic materials. Incorporation of approximately 22 wt % silica results in $\sim 100\%$ stabilization of tetragonal phase in these systems.

Localized condensation occurring at higher water concentrations can also be prevented by the introduction of acid. The acid requirement is found to be a function of the molecular spacing and the water/alkoxide ratio.

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## References

1. D. C. BRADLEY, R. C. MEHROTA and D. P. GAUR, "Metal Alkoxides" (Academic Press, New York, 1978) p. 30.
2. D. C. BRADLEY and W. WARDLAW, *J. Chem. Soc.* **73** (1951) 280.
3. D. C. BRADLEY, in "Metal-Organic Compounds" Advances in Chemistry, Series 23 (American Chemical Society, Washington, DC, 1959) pp. 10–36.
4. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *J. Amer. Ceram. Soc.* **48** (7) (1965) 372.
5. *Idem, ibid.* **50** (10) (1967) 532.
6. B. E. YOLDAS, *ibid.* **65** (8) (1982) 387.
7. D. C. BRADLEY and D. G. CARTER, *Can. J. Chem.* **39** (1961) 1434.
8. *Idem, ibid.* **40** (1962) 15.
9. B. E. YOLDAS, *J. Non-Cryst. Solids* **51** (1982) 105.
10. *Idem, ibid.* in press.
11. *Idem, ibid.* **63** (1984) 145.
12. *Idem,* Material Research Society Symposium Proceedings (Elsevier Science, New York, 1984) Vol. 24, p. 291.
13. E. A. BARRINGER, N. JUBB, B. FEGLEY, R. L. POBER and H. K. BROWN, in "Ultrastructure Processing of Ceramics, Glasses, and Composites" edited by L. Hench and D. Ulrich (Wiley, New York, 1984) pp. 315–333.
14. T. K. GUPTA, *Sci. Sinter.* **10** (1978) 205.
15. K. S. MAZDIYASNI, in "Reactivity of Solids" Proceedings of the VI International Symposium on the Reactivity of Solids, Schenectady, January, 1969, edited by J. W. Mitchell (Wiley-Interscience, New York) pp. 115–25.
16. E. C. SABBARAO, H. S. MAITI and K. K. SRIVASTAVA, *Phys. Status Solidi* **21** (1974) 9.
17. T. K. GUPTA, F. F. LANGE and J. H. BECHTOLD, *J. Mater. Sci.* **13** (1978) 1464.
18. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 225.
19. D. L. PORTER and A. H. HEUER, *J. Amer. Ceram. Soc.* **62** (1979) 295.
20. D. C. BRADLEY, *Nature* **182** (1958) 1211.
21. D. C. BRADLEY, R. C. MEHROTA, J. D. SWANWICK and W. WARDLAW, *J. Chem. Soc.* **73** (1953) 2025.
22. W. WARDLAW, *ibid.* (1956) 4004.
23. E. C. SABBARAO, H. S. MAITI and K. K. SRIVASTAVA, *Phys. Status Solidi* **A21** (1974) 9.
24. G. K. BANSAL and A. H. HEUER, *Acta Metall.* **20** (11) (1972) 1281.
25. R. C. GARVIE, R. H. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
26. D. L. PORTER and A. H. HEUER, *J. Amer. Ceram. Soc.* **60** (6–3) (1977) 183.
27. T. MITSUHASHI, M. ICHIHARA and U. TATSUKE, *J. Amer. Ceram. Soc.* **57** (2) (1974) 97.
28. H. KNAPP and V. DEHLINGER, *Acta Metall.* **4** (1956) 289.
29. G. B. OLSON and M. COHEN, *Met. Trans.* **7A** (1976) 1897.
30. B. E. YOLDAS, *J. Mater. Sci.* **4** (1979) 1843.

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