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Synthesis and characteristics of zirconia fine powders from organic zirconium complexes

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An organic zirconium complex was synthesized from concentrated $ZrOCl_2$ solution and an organic complex which was a mixture of β-glycosyl urea (Schiff's base) and urea. Homogeneous hydrolysis and controlled polymerization of zirconium-tetramers was accomplished by heating the solution to boiling. Fine ZrO_2 and yttrium- or magnesium-stabilized ZrO_2 powders were prepared by dehydration and pyrolisis in air. The powders obtained are composed of 0.1 μm particles and were sintered to an above 98% density ceramic with 0.25–0.30 μm grain size.

1. Introduction

The prerequisites for high-performance engineering ceramics are high density and homogeneous structure with small grain size. The achievement of these goals largely depends on the starting powders, which must have adequate morphology, sintering activity and purity. Homogeneous microstructure with small grain size is particularly important in TZP (tetragonal zirconia polycrystal)-based ceramics, to stabilize the metastable tetragonal modification [1]. Formidable mechanical properties have been reported for > 98% dense TZP ceramics with average grain sizes of > 0.2 μm [2, 3]. The manufacture of such ceramics requires a fine powder without hard agglomerates. Such powders may be synthesized by the alkoxide route [4], or by special treatment to remove the agglomerates [3]. Several processes for preparation of fine ZrO_2 powders are reviewed in [5], and the importance of interparticle bond strength on the homogeneity of sintered density and microstructure has been pointed out.

The tendency of formation of hard agglomerates may be reduced by washing with organic liquids [6]; however, the results are still not satisfactory. Obviously, all the steps in the formation of crystallites (nucleation, nucleus growth and the agglomeration of nuclei in larger units) must be optimized by adjusting the controlling parameters, such as pH, concentration, temperature and time of heat treatment, variety and concentration of foreign anions. By careful control of the above parameters, sol particles of uniform size and shape may be obtained [7]; agglomerates are formed during the gelation and calcination steps.

This paper describes preparation of ZrO_2 and Y_2O_3- or MgO-stabilized ZrO_2 powders by pyrolisis of an organic zirconium complex compound formed during the reaction of $ZrOCl_2$ and β-glycosyl urea (Schiff's base). The advantage of this inexpensive method is that hydrolysis and polymerization of precipitates takes place in a homogeneous environment. Uniform, highly dispersed fine powders are obtained which may be sintered to high-density, fine-grained ceramics.

2. Experimental procedure

2.1. Sample preparation

Chemicals for preparation of ZrO_2 and stabilized ZrO_2 powders were reagent grade $ZrOCl_2 \cdot 4H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $C_6H_{12}O_6$ and CON_2H_4. Schiff's base (β-glycosyl urea) was synthesized by mixing urea and glucose in a molar ratio of 2:1 and heating the mixture at 150° C until melting was complete. A brown, viscous, honey-like syrup resulted. The reaction was considered to be complete when urea started to decompose giving ammonia vapours. The Schiff's base synthesized contained excess urea, as predetermined by the initial mixture composition.

The organic zirconium complex was formed by adding the Schiff's base with excess urea to concentrated (2–3 M) $ZrOCl_2$-H_2O solution. The composition of the solution corresponded to a molar ratio of $ZrOCl_2$: urea : glucose of 1 : 2 : 1, respectively. The clear, light-brown solution was boiled for 1 h and then spray-dried, or simply dried by evaporating the water. In both cases a fine powder resulted. This organic zirconium complex was decomposed by stepwise heating in air up to 850° C. By stepwise heating, any sudden increase in temperature of the powder due to carbon combustion was avoided.

Appropriate amounts of $Y(NO_3)_3$ or $Mg(NO_3)_2$ were added to the solution when stabilized ZrO_2 was prepared.

2.2. Characterization

Powder particle size and morphology were examined by a scanning electron microscope (SEM; Leitz AMP 1600 T). The same instrument was used to analyse the microstructure of the sintered ceramic. Crystallite size,

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shape and orientation were examined by transmission electron microscope (TEM; Jeol 2000 F). Phase composition and crystallite size were estimated from X-ray diffractograms using nickel-filtered CuK_α radiation (Philips). Average crystallite sizes were calculated from the breadth of the half peak height using the Schaerrer relationship [8] with a K value of 0.9. Correction for instrumental broadening was made using Warren's formula [8] and a crystalline quartz standard.

The structural characteristics of the organic zirconium complex were examined by an infrared apparatus (Perkin Elmer 783). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) data were collected on a Linseis apparatus in air at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. For the sinterability study, ZrO_2 – 2 mol % Y_2O_3 calcined powder was attrition milled with TZP balls in isopropanol. Pellets (diameter 7 mm, height 5–8 mm) were precompacted at 25 MPa and finally compacted isostatically at 680 MPa. The density of sintered samples was determined by mercury pycnometry.

3. Results and discussion

3.1. Genesis and properties of ZrO_2 and Y-, Mg-ZrO_2 powders

The fact that urea decomposes into carbon dioxide and ammonia when its solution is heated has been exploited for the homogeneous precipitation of various hydrated precipitates [9, 10]. The advantage of using urea is the uniform rise of pH, which is in contrast to the situation during the rapid addition of a base, where local supersaturation is very high. Slow, controlled increase of pH enables controlled nucleation, and the growth of precipitate particles and their agglomeration.

The role of large steric molecules of the organic base, introduced simultaneously with excess urea, was to further control nucleation and, above all, to control the polymerization of zirconium tetramers. It was expected that the large molecules of Schiff's base, when incorporated into the zirconium polymer structures, would after thermal treatment provide a zirconia product with particles of equiaxial dimensions, which would be more uniformly dispersed and finer than a zirconia product prepared without Schiff's base.

Some conclusions on the nature of the organic zirconium complex were drawn on the basis of IR analysis. Figure 1a shows the IR spectrum of the organic complex synthesized from urea and glucose in a molar ratio of 2 : 1. Characteristic absorption bands at $1455\,\mathrm{cm^{-1}}$ and at $1600\text{–}1700\,\mathrm{cm^{-1}}$ prove the formation of an azomethin group. The absorption band at $1755\,\mathrm{cm^{-1}}$ probably belongs to a carbonyl group, and disappears after reaction with $ZrOCl_2(H_2O)$ (Fig. 1b and c). It may be supposed by analogy with the reaction of $ZrCl_4$ with amides [11–13] that the carbonyl oxygen donates electrons to form bonds with the metallic cation. The absorption band at $1400\,\mathrm{cm^{-1}}$ belongs to ammonium chloride; Fig. 1b–e.

Chemical analysis of the organic zirconium complex, heat treated at 200° C for 10 h, gave the following

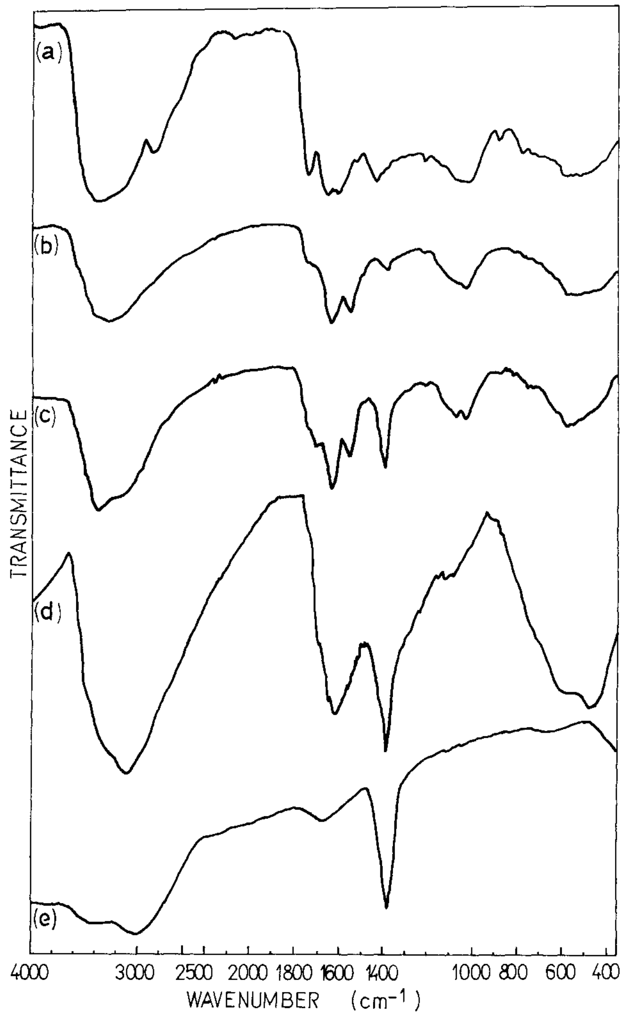


Figure 1 IR spectra of (a) organic complex (Schiff's base with excess urea); (b) spray-dried organic zirconium complex; (c) evaporation–dried organic zirconium complex; (d) organic zirconium complex heat treated at 450° C for 60 min in air; (e) ammonium chloride.

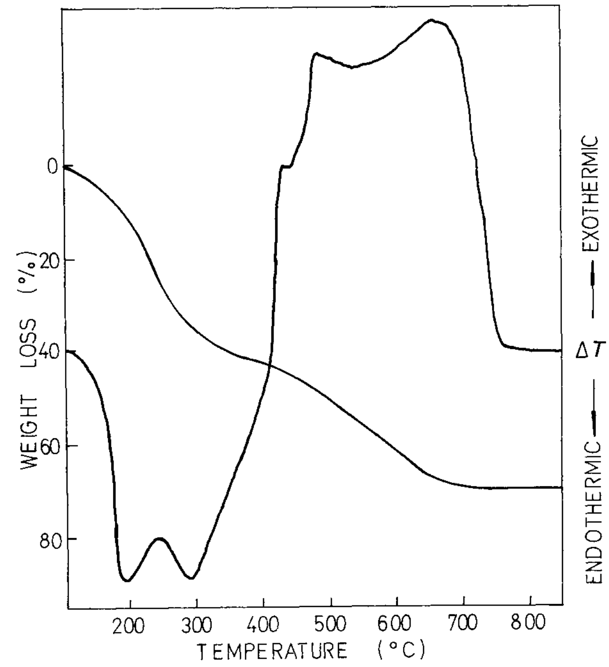


Figure 2 DTA and TGA curves of organic zirconium complex (in air, heating rate $10^\circ\mathrm{C\,min^{-1}}$).

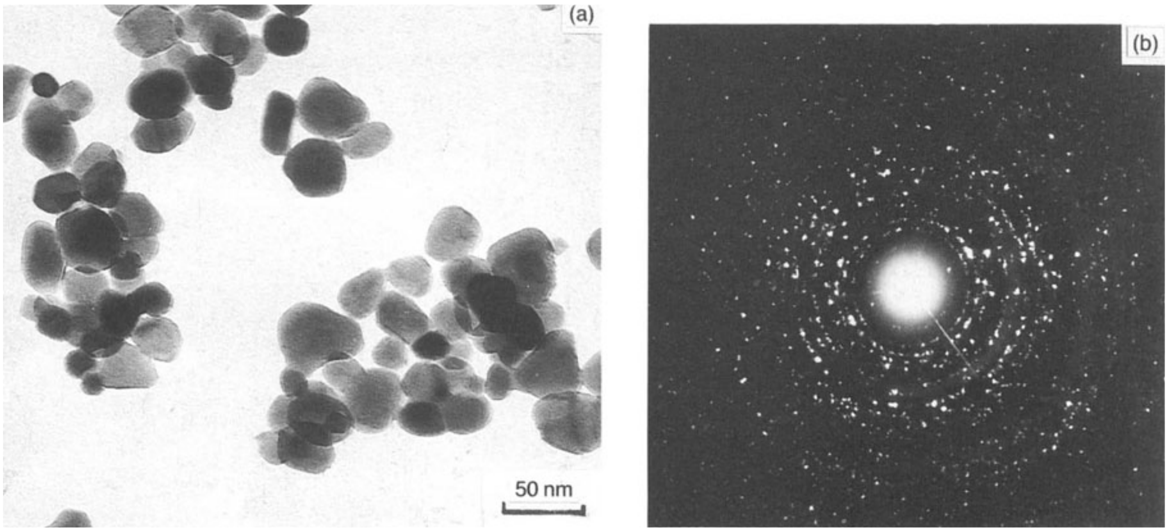


Figure 3 (a) TEM micrograph of ZrO_2 powders from an organic zirconium complex pyrolized at 650° C for 60 min; (b) diffraction pattern of (a).

composition (in wt %): zirconium 17%, carbon 17%, nitrogen 9.75% and chlorine 13.27%.

DTA and TGA curves of the spray-dried organic zirconium complex in air are shown in Fig. 2. The heating rate was 10° C min^{-1}. The TGA curve shows 73% loss of the initial weight up to 680° C. The DTA curve shows an endothermic reaction at ~200° C, which is ascribed to loss of the remaining adsorbed water and partial decomposition of the organic ligand. At this temperature, decomposition of organic matter is visually confirmed by the black colour of the sample. The endothermic reaction at 300° C corresponds to sublimation of NH_4Cl, which is an important characteristic of this powder synthesis method. Sublimation of NH_4Cl was directly proved by collecting and analysing the sublimated material. NH_4Cl was also detected by X-ray analysis of the organic zirconium complex after calcination at 200° C for 10 h. A strong exothermic peak above 350° C indicates the oxidation of organic matter. Amorphous ZrO_2 which is formed above this temperature crystallizes to tetragonal ZrO_2. Tetragonal ZrO_2 was confirmed by X-ray analysis in samples calcined at 450° C. Heat effects which accompany amorphous–tetragonal or tetragonal–monoclinic transformations are not detectable on the DTA curve. The first heat effect, the so-called, 'glow effect' [14, 15], is perhaps masked by heat evolved by carbon combustion smeared over a wide temperature range. However, the absence of the effect even in a protective nitrogen atmosphere indicates that it may be due to other reasons. Absence of a glow effect in some ZrO_2 samples was already noted [15]. This phenomenon needs further clarification.

After heating at 650° C for 1 h, the sample consisted of ~90% monoclinic and 10% tetragonal phase, as estimated from X-ray diffraction peak intensities. In yttrium-stabilized ZrO_2, only the tetragonal phase was observed after heating to 850° C. The carbon content of samples heated above 650° C was less than 300 p.p.m., and the chlorine was less than 0.5 wt %.

TEM examination confirmed the uniform size and spherical shape of the crystallites (Figs 3 and 4). Crystallites within agglomerates are randomly oriented as seen in the electron diffraction photograph of Fig. 3b. Domain structure, observed in aggregates

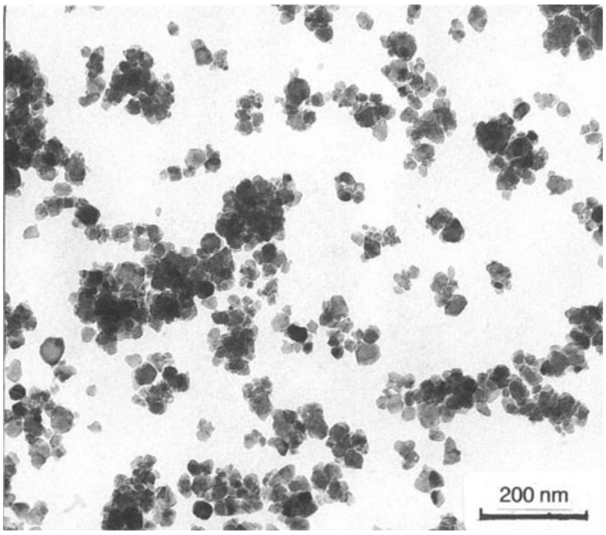


Figure 4 TEM micrograph of ZrO_2 (2 mol % Y_2O_3) powder from an organic zirconium complex after spray drying and pyrolisis at 800° C for 60 min.

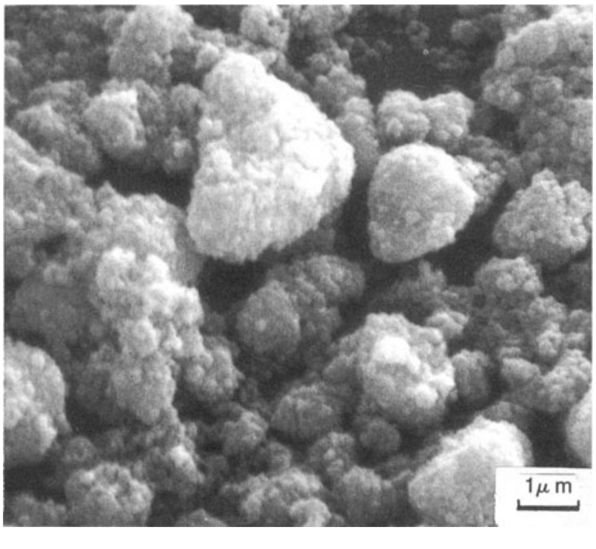
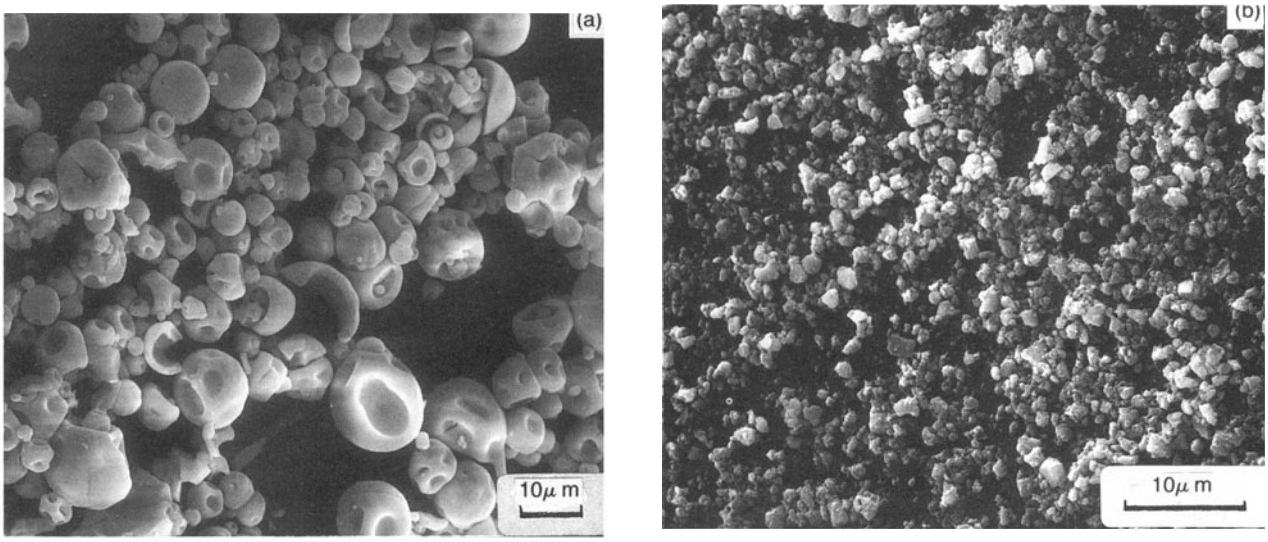


Figure 5 SEM micrograph of ZrO_2 powder from organic zirconium complex dried by evaporation and pyrolized at 700° C for 60 min.



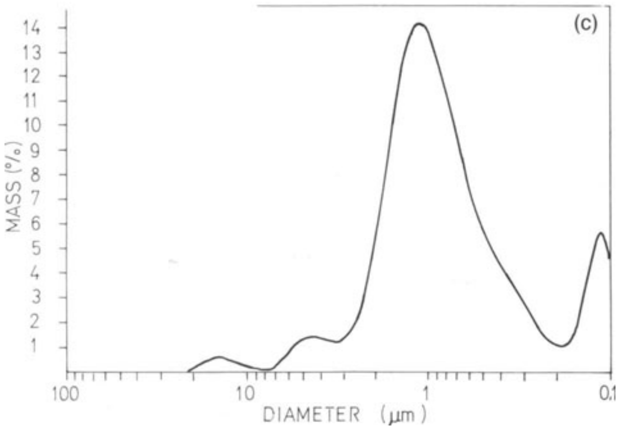


Figure 6 SEM micrographs of ZrO_2 (2 mol % Y_2O_3) from organic zirconium-complex precursor, spray-dried and pyrolized at 840° C for 60 min, (a) before milling; (b) after attrition milling (3 h). (c) particle size distribution of milled powder.

composed of oriented crystallites [16], is absent. From X-ray broadening, the crystallite size was estimated to be ~21 nm, Fig. 3a. SEM micrography shows that the powder consists of agglomerates containing individual ~0.1 μm particles (Fig. 5). The powder, prepared by spray drying of the organic zirconium complex and pyrolized at 840° C for 1 h, is composed of hollow balloons up to 10 μm in diameter (Fig. 6a). The balloons are made of particles less than 0.1 μm in size. After attrition milling for 3 h, the balloons disintegrated into uniform particles with an average size of ~1 μm (Fig. 6b). The size distribution of the milled powder indicates a large proportion of finer particles, ~0.1–0.2 μm (Fig. 6c).

It is believed that the uniform crystallite size in the powders synthesized by the method described is a consequence of homogeneous hydrolysis and polymerization of zirconium tetramers. The reaction sequence which leads to morphological characteristics of powders such as spherical shape and random orientation of crystallites is schematically shown in Fig. 7. Large organic molecule ligands control polymer growth and prevent the interaction of polymers, so that the end product is composed of small monodispersed particles. The experimental observations are in accordance with the proposed scheme. It is also suggested that fine carbon inclusions interfere with structure development during calcination, so that crystals develop independently with weak interparticle bonds.

3.2. Powder sinterability

Precipitated and calcined (at 840° C for 1 h), attrition milled, yttrium-stabilized (2 mol %) ZrO_2 powder was isostatically pressed at 680 MPa to 66% of theoretical density. Compacts started to densify at ~900° C and were sintered at 1400–1500° C in 2 h to 98% of theoretical density (ϱ_{theor} 6.07 g cm^{-3}). Typical dense microstructure (Fig. 8) shows a homogeneous grain-size distribution with average intercept length of 0.25–0.30 μm.

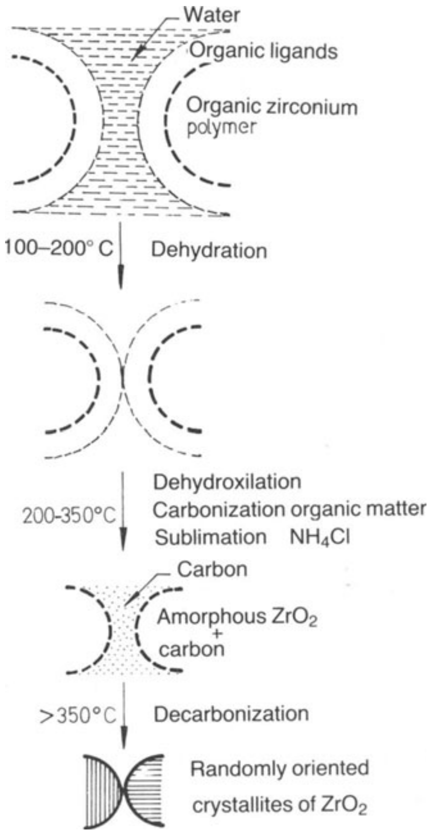


Figure 7 Formation of randomly oriented ZrO_2 crystallites from organic zirconium complex (schematic).

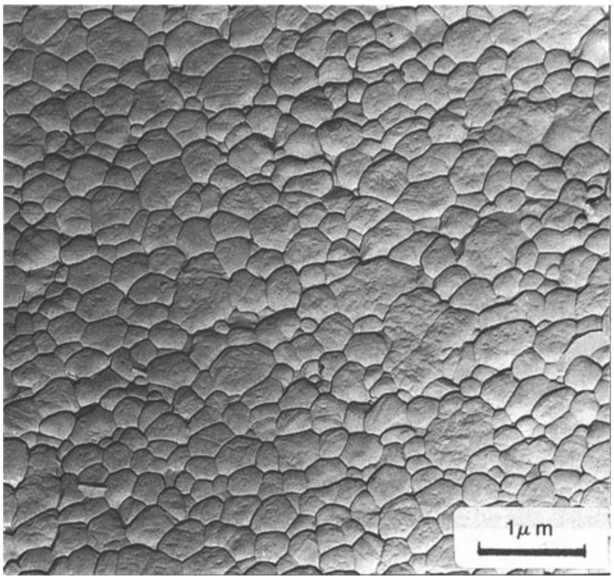


Figure 8 TEM micrograph of TZP ceramics sintered at 1250° C for 120 min and 1400° C for 60 min.

Summary

An organic zirconium complex was precipitated from $ZrOCl_2$ solution and Schiff's base under controlled conditions. During calcination in air, the organic material is removed by oxidation and chlorine is removed by sublimation of ammonium chloride. The method described offers several advantages: it is simple and could be scaled up; the chemicals are inexpensive; the resulting ZrO_2 or yttrium-stabilized ZrO_2 powder consists of weakly agglomerated uniform spherical particles with a size of $\sim 0.1\,\mu$m. High purity may be achieved with a carbon content below 300 p.p.m. and chlorine below 0.5 wt %. The powder could be compacted to high green density (66% of theoretical) and sintered to 98% of theoretical density. The microstructure of the sintered ceramics is uniform and with an average intercept length of $\sim 0.25\,\mu$m.

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