

Crystallizability and sinterability of a precursor prepared by oxalate method in ethanol solution

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A precursor of yttria-stabilized zirconia (YSZ) powder was prepared by the oxalate method in ethanol solution. The crystallizability and sinterability of the precursor were studied. The crystallizability of the precursor depends on preparation conditions, especially acidity. The final acidity of the solution from which the precursor is produced and the temperature at which the precursor is calcined can strongly influence the crystalline phase composition of the resultant powder, and can, in turn, limit the ability of a sintering compact to reach high density. The YSZ powder which results from calcining the precursor without milling the calcined powder for a long time, may be a less-agglomerated powder with a crystallite size of about 9 nm and a specific surface area of $46.3 \text{ m}^2 \text{ g}^{-1}$. A full tetragonal zirconia polycrystal with 99% theoretical density can be obtained from the highly reactive powder by simple cold-pressing followed by pressureless sintering in air at temperatures as low as 1300°C .

1. Introduction

Tetragonal zirconia polycrystal (TZP) is gaining popularity as a potential engineering ceramic because of its excellent mechanical and thermal properties. However, the tetragonal phase appears as a metastable phase at room temperature. The retention of the tetragonal phase at room temperature must satisfy particular conditions. Among them the grain size is a very important condition. It is essential to make the material with an extremely fine grain size ($< 1 \mu\text{m}$). Consequently, it is necessary that the starting powder for TZP has a particle size of $0.5 \mu\text{m}$ or less and can be sintered to nearly full theoretical density at temperatures as low as 1400°C .

Much literature [1-5] exists on the preparation and properties of such material; nevertheless, an extensive number of programmes are underway worldwide aimed at understanding and improving both the synthesis and behaviour of YSZ powders. We reported recently that YSZ ultrafine powders with three crystalline phases could be prepared by the oxalate method in ethanol solution [6]. The present paper gives details describing the crystallizability and sinterability of the precursor prepared by this method, and of the preparation of a YSZ ultrafine powder without monoclinic phase and of a fully tetragonal zirconia sintered body.

2. Experimental procedure

We have reported that the YSZ ultrafine powders with three crystalline phases may be prepared from zirconium oxychloride and yttria by the oxalate method in ethanol solution [6]. However, in order to obtain the monoclinic-phase-free powder sinterable at a relatively low temperature, particular attention must be paid to both the chemical preparation conditions, such as the final acidity of the solution from which the precursor of the powder was produced, and to the subsequent handling, such as ageing the precursor gel in alcohol and calcination temperature.

The calcined powder with or without the addition of 1 wt % polyvinyl alcohol was milled in a mortar for 0.25 h and cold-pressed using a uniaxial press in a steel die to form a $30 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$ bar. The resulting compact was heated in air from room temperature to 1300°C at 160°C h^{-1} and held at 1300°C for 6 h.

The precursors were examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with DuPont thermal analyser. These experiments were conducted up to 1000°C with a heating rate of $10^\circ\text{C min}^{-1}$. The sample size was about 20 mg.

The samples for infrared analysis were prepared by the KBr pellet method, i.e. the calcined powder was mixed with KBr and pressed into a thin disc, and then

infrared spectra of the calcined powders were recorded with a Perkin-Elmer 983 spectrometer in the 400–4000 cm^{-1} region.

X-ray diffraction patterns of the precursor, powder and sintered body were recorded using a Shimadzu XD-3A diffractometer and nickel-filtered $\text{CuK}\alpha$ radiation. A scanning rate of 4°min^{-1} was used to obtain the patterns for phase identification, and 2°min^{-1} for crystallite size estimation. The amount of tetragonal phase (T) present in a powder is estimated from

$$T = \frac{1/4 I_{t(200)}}{1/4 I_{t(200)} + 1/6 I_{c(200)}} \quad (1)$$

where $I_{t(200)}$ is the intensity of the tetragonal peak (200) and $I_{c(200)}$ indicates the intensity of the cubic peak (200). The amount of monoclinic phase (M) present in a powder is calculated from

$$M = \frac{I_{m(111)}}{I_{m(111)} + I_{t(111)} + 1/8 I_{c(111)}} \quad (2)$$

where $I_{m(111)}$ is the intensity of the monoclinic peak (111), $I_{t(111)}$ is the intensity of the tetragonal peak (111) and $I_{c(111)}$ is the intensity of the cubic peak (111). It should be indicated that the amounts of tetragonal phase and cubic phase in YSZ powders could not be quantitatively estimated because most of the peaks from the tetragonal and cubic phases overlapped (7, 8). Therefore, in this paper the term “powder without monoclinic phase” refers to the powder with both tetragonal phase and cubic phase, in which the tetragonal phase is the prevailing one.

The crystallite sizes of the powders calcined at different temperatures are calculated from Scherrer's relationship

$$D = \frac{K\lambda}{B \cos \theta} \quad (3)$$

where D is the average crystallite size, λ is the X-ray wavelength, B is the corrected line width at half maximum of the peak, K is the crystallite shape factor and is chosen as unity in this study, θ is the Bragg angle. Transmission electron microscopy (TEM) was also used to estimate the crystallite size and observe the agglomeration state of the powder.

Particle size distribution analysis was performed for the powder according to Stokes' Law sedimentation technique. The specific surface area measurement of the powder was made by the BET method using nitrogen adsorption at -193°C .

The Archimedes technique performed in water was applied to measure the density of the sintered bodies. The green density was determined from the geometry and weight of a compact. Relative density was calculated by dividing the bulk density by an appropriate theoretical density. The theoretical density for about 3 mol % $\text{Y}_2\text{O}_3\text{-ZrO}_2$ was assumed to be 6.076 g cm^{-3} [9].

3. Results and discussion

It has been realized that TZP may be obtained by sintering very fine reactive starting powders within a tetragonal phase field at relatively low temperatures,

e.g. 1400°C , as indicated in the phase diagram for the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ system [10]. Therefore, it is important to obtain highly reactive powders sinterable at a relatively low temperature. The powder prepared by the present method may be characterized by thermal analysis, X-ray diffraction, infrared spectra, particle size distribution measurement, and transmission electron microscopy.

3.1. Thermal behaviour

Figs 1 and 2 show the DTA and TGA curves of the precursors (nos 25 and 26) prepared at different acidities. The following information can be derived from these curves.

1. In the DTA curves there is no endotherm peak evident which is responsible for the vaporization of water, suggesting that water may be substantially removed during powder processing and that the resulting powder will be loose and less-agglomerated.

2. In the DTA curves only an endotherm peak appears, which can be attributed to the decomposition of excess oxalic acid. The endotherm peak for precursor no. 26 has an onset at 282°C and a maximum at 318.7°C , and the corresponding weight loss obtained from the TGA curve is 29.85%, while the endotherm peak for precursor no. 25 has an onset at 295°C and a maximum at 345.8°C and the weight loss obtained from TGA curve amounts to 40.82%, showing that greater excess of oxalic acid in the preparation of precursor no. 25.

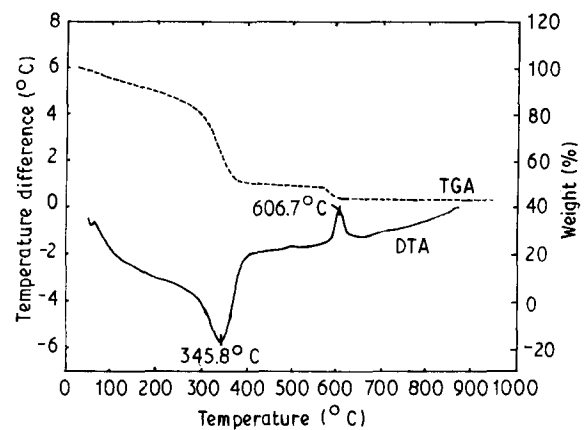


Figure 1 DTA and TGA curves of precursor no. 25.

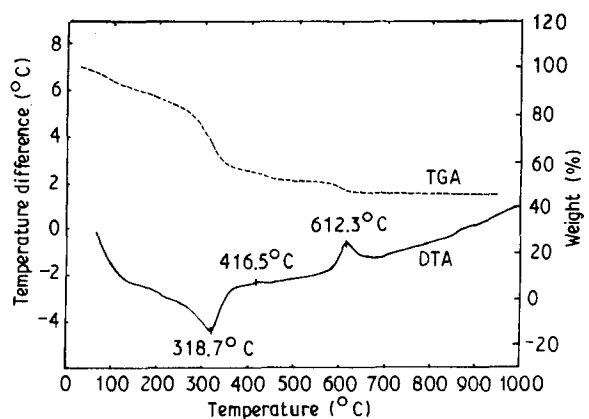


Figure 2 DTA and TGA curves of precursor no. 26.

3. In the DTA curves the exotherm peaks at about 600 °C result from the crystallization of yttria-stabilized zirconia. It may be noted that the exotherm peak for precursor no. 25 is sharper than that for precursor no. 26, implying that precursor no. 25 will be well crystallized.

4. No significant change is observed above 610 °C, indicating that the temperature should be sufficient for the calcination of the precursors.

3.2. Crystallinity

Mechanical properties of ceramic materials are defined by fine microstructural features. Their properties are very sensitive to slight changes in phase fraction, grain size, chemical composition, etc. The phase identification and phase fraction determination are of great importance.

Generally, the precursors prepared by various methods such as conventional coprecipitation in aqueous solution or metal alkoxide hydrolysis are found to be amorphous by XRD analysis. However, the precursors produced by the present method, depending on the final acidity of the solution in contact with precipitate, may be amorphous or crystalline, as shown in Fig. 3. It is well known that the relative concentrations of $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$ are strongly affected by pH value. The $\text{C}_2\text{O}_4^{2-}$ ions would dominate at $\text{pH} > 6$, but HC_2O_4^- dominates at $\text{pH} \leq 1$. Therefore, precipitation pH value will influence the nature of the resulting precipitate, i.e. precursor. In addition, because the precursor gel may be positively or negatively charged, the interaction between the precursor gel and impurity ions occurs in the precipitation solution, suggesting that the crystallographic nature of the precursor gel is also related to the nature and content of the remaining impurities in the solution, which often depend on the pH value of the precipitation solution.

The powder without monoclinic phase could be obtained by calcining precursor no. 25 at 500 °C, whereas a small amount (9%) of monoclinic phase was found as the calcination temperature rose to 650 °C, as shown in Fig. 4. However, the powder without monoclinic phase could not be produced by calcining precursor no. 26 at 500 °C. In addition, the prevailing phase present in the powder prepared by calcining precursor no. 26 at 600 °C, was monoclinic phase, as shown in Fig. 5. These differences may be ascribed to the different natures of the precursors which were prepared at different acidities, as stated above.

X-ray analysis of a sintered body which had been prepared from the powder without monoclinic phase

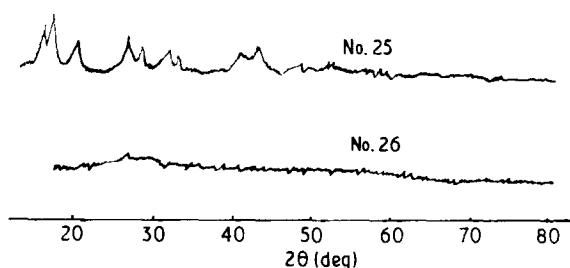


Figure 3 X-ray diffraction pattern of precursors.

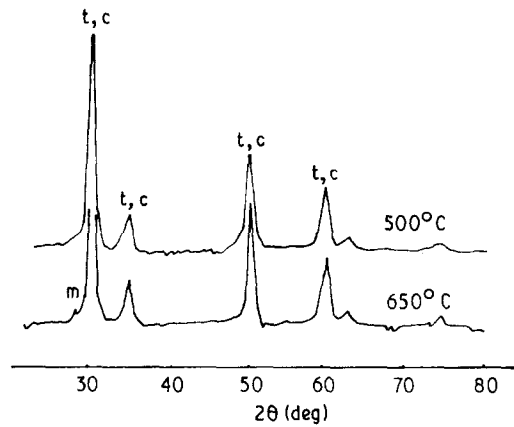


Figure 4 X-ray diffraction pattern of powders obtained by calcining precursor no. 25 at 500 and 650 °C. t = tetragonal, c = cubic, m = monoclinic.

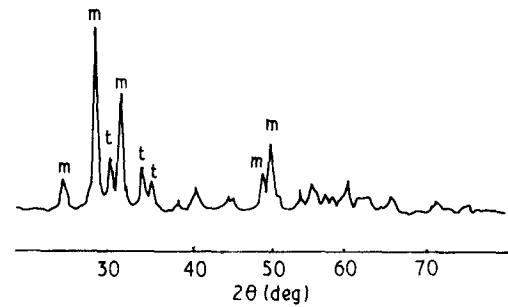


Figure 5 X-ray diffraction pattern of powder obtained by calcining precursor no. 26 at 600 °C.

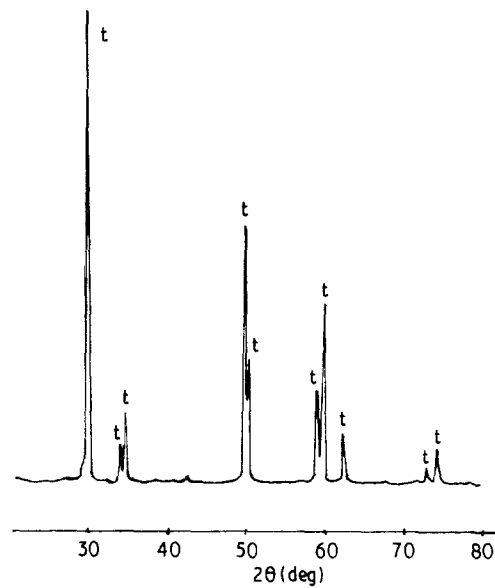


Figure 6 X-ray diffraction pattern of a sintered body.

or with a small amount of monoclinic phase revealed that the crystalline phase of the sintered body was a full tetragonal phase, as shown in Fig. 6. However, the presence of cubic or monoclinic phases was often found in 3 mol % Y_2O_3 -TZP ceramics fabricated by the conventional coprecipitation method, hydrothermal synthesis, etc. [11–13].

3.3. Infrared spectra

The infrared spectra of calcined powders are shown in Fig. 7. A broad band in the 3400 cm^{-1} region may

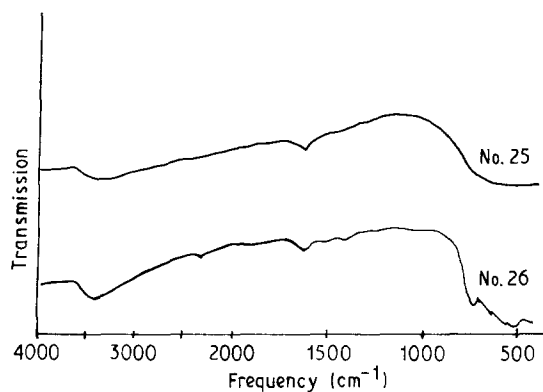


Figure 7 Infrared spectra of powders prepared by calcining precursors 25 and 26.

result from atmospheric moisture retained by the KBr pellets. Because a sharp band at 2340 cm^{-1} corresponds to the frequency for CO_2 , it could be inferred that the powder obtained by calcining precursor no. 26 contained more CO_2 . The presence of CO_2 is detrimental to the sintering of yttria-stabilized zirconia. Carbon dioxide increases the stability of the amorphous phase, as indicated in the X-ray diffraction pattern, Fig. 3. A band at 1620 cm^{-1} may be associated with adsorption of atmospheric constituents because powders, before being measured, were blended with KBr and ground.

Sharp bands at 1400 and 740 cm^{-1} are observed only for sample no. 26. Because the monoclinic spectra are distinguished by an increase in number and sharpness of the bands, and because the band at 740 cm^{-1} is distinctive for this phase [14], it is evident that the monoclinic phase is among the crystalline phases of sample no. 26. This result is in a good agreement with that obtained by XRD. The relatively broad bands at 580 and 520 cm^{-1} indicate the presence of a certain amount of tetragonal and cubic phases in sample no. 26.

In contrast to sample no. 26, no characteristic bands of monoclinic phase appear in the spectrum of sample no. 25, confirming the correct results from XRD. In addition, a very broad band from $420\text{--}620\text{ cm}^{-1}$ is found in the spectrum of sample no. 25. This represents the infrared spectra of cubic and tetragonal phases, further confirming the result from XRD.

3.4. Particle size

As mentioned previously, tetragonal zirconia polycrystal (TZP) has excellent mechanical properties, etc., whereas the amount of tetragonal phase retained at

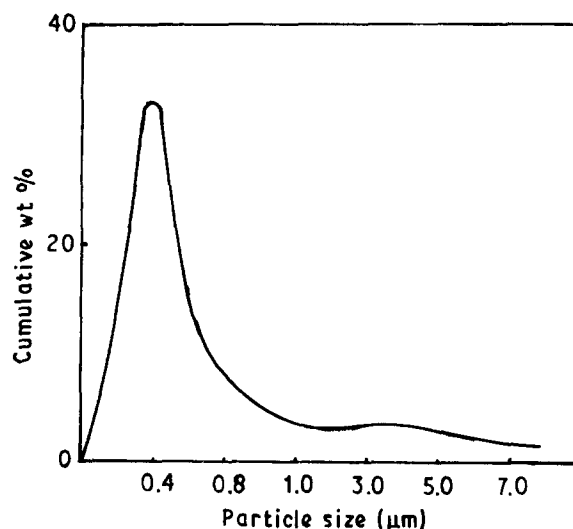


Figure 8 Particle size distribution of YSZ powder without monoclinic phase.

room temperature is related to many variables such as grain size, the kind and amount of stabilizing agents, etc. Among the most important variables is grain size. If grain size exceeds about $0.8\text{ }\mu\text{m}$, conversion to cubic phase occurs. The particle size of the starting powder for TZP must, therefore, be less than the ultimate grain size in a sintered body because the processes leading to sintering and densification also tend to enlarge the grain size. Generally, the starting powder is required to have a particle size of $0.5\text{ }\mu\text{m}$ or less. The powder produced by the present method had a mean particle size of $0.4\text{ }\mu\text{m}$ and a specific surface area of $46.3\text{ m}^2\text{ g}^{-1}$. 33.7% particles were of $0.4\text{ }\mu\text{m}$ diameter. A typical cumulative particle size distribution curve is shown in Fig. 8.

A powder calcined at 500°C is composed of cubic crystallites of $8\text{--}9\text{ nm}$ diameter and tetragonal crystallites of $7\text{--}7.9\text{ nm}$ diameter. It is observed that the crystallite size increases with increasing calcination temperature, as shown in Table I. The crystallite size calculated by Scherrer's relationship shows a good agreement with the following TEM estimation.

The microstructure of the powder calcined at 500°C was further examined by TEM, as shown in Fig. 9. The crystallite size is about 10 nm , which is comparable with that based on the X-ray data. In addition, it can be seen from the transmission electron micrograph that the powder produced by the present method is less agglomerated. It is well known that ceramic powders are apt to agglomerate, especially when they are very fine. The control of agglomerates in the powders

TABLE I Crystallite size of the powder calcined at different temperatures

Sample no.	Calcination temperature ($^\circ\text{C}$)	Monoclinic (nm)	Cubic (nm)	Tetragonal (nm)
1	500	0	8.984	7.035
2	500	0	8.169	7.891
3	600	9.502	10.479	11.050
4	700	12.922	13.457	11.700

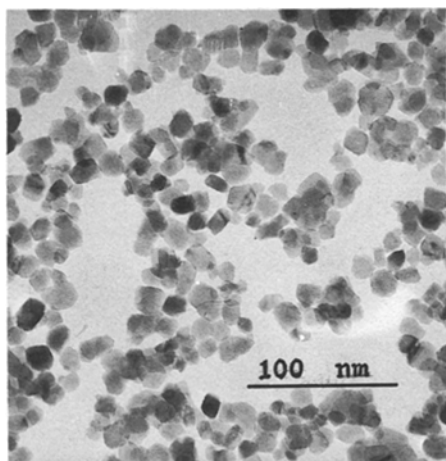


Figure 9 Transmission electron micrograph of YSZ powder.

is of utmost importance because the presence of relatively strong agglomeration in the powders would give rise to the occurrence of pores during compaction. As a result, sintering temperature increases and only relatively coarse-grained ceramics can be produced. Powders obtained from various preparation methods appear to be different in agglomeration degree, agglomerate strength and surface activity. By the present method the precursor is produced and aged from and in ethanol solution, and calcined at a relatively low temperature so that the calcined powder is soft and less agglomerated. This can also be demonstrated by the facts that the present method eliminates the need to mill the calcined powder for a long time to obtain the submicrometre-sized powder, and that a compact with a high green density can be produced from the powder and sintered to nearly theoretical density at a relatively low temperature, as described below.

3.5. Sinterability

The sintering behaviour provides the best indication of the potential utility of a ceramic powder. Sintered density gives an immediate indication of the overall success of a powder preparation method. Pressing the powder prepared by the present method can result in a compact with a mean green density of 3.48 g cm^{-3} . Firing the compact at 1300°C for 6 h can yield a sintered body with a maximum density of 6.02 g cm^{-3} with about 19% shrinkage.

It is generally accepted that it is probably not possible to achieve high green density without eliminating or markedly reducing agglomerates [15], and that the densification of stabilized zirconia ceramics at relatively low temperatures is only possible when a highly uniform packing of ultrafine crystallites is present in a green compact [16]. Experience with pressureless sintering of the powder prepared by the present method has shown that some processing parameters such as the preparation conditions and calcination temperature of precursors, and the consolidation pressure of calcined powders have a significant effect on the particle size, agglomeration state and crystalline phase composition of the powder, on the

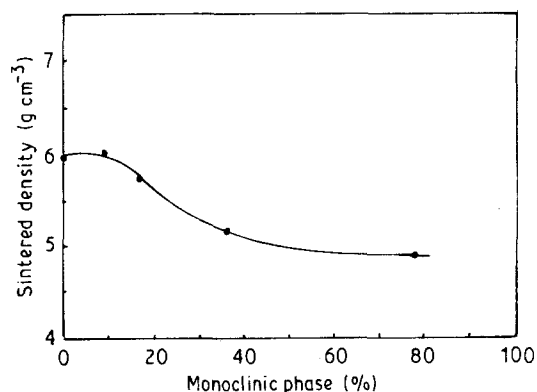


Figure 10 Variation of sintered density with monoclinic phase fraction of YSZ powder.

uniformity of powder packing, and on the green density of a compact. These will, in turn, result in different sintered densities. However, sinterability for the powders with similar particle sizes at an equal sintering temperature and time is mainly dependent on the monoclinic phase fractions of the powders. As shown in Fig. 10, the sintered density decreases with increasing monoclinic phase fraction of the powder. This result suggests that the crystallizability of the precursor will affect the sinterability of the powder. Control of crystalline phase composition of the powder is primarily important to the achievement of a high sintered density.

4. Conclusions

The characteristics of YSZ powders prepared by the oxalate method in ethanol solution have been examined by thermal analysis, XRD, infrared spectra, particle size distribution measurement and TEM observation. It has been demonstrated by these studies that this method, which differs from that of conventional coprecipitation, may result in a precursor with a certain crystallinity, and yield a YSZ powder without monoclinic phase. The acidity of the solution from which a precursor is produced plays a key role in determining the crystalline phase composition of the resultant powder. The calcination temperature of a precursor also controls the crystalline phase composition of the YSZ powder to a certain extent. Pressing the powder can form a compact having a mean green density of 3.48 g cm^{-3} . Firing the compact at 1300°C for 6 h can achieve a fully tetragonal zirconia polycrystal with a maximum density of 6.02 g cm^{-3} . The sintered density decreases with increasing monoclinic phase fraction of the YSZ powder, suggesting that the sinterability of the powder is closely associated with its crystalline phase composition.

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