

Preparation of Weakly Agglomerate Nanometer $ZrO_2(3 \text{ mol}\% Y_2O_3)$ Ceramic Powder

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Abstract

Yttria-doped zirconia powders (3 mol%) with an extremely small crystallite size (10–15 nm) and a narrow size distribution had been prepared by gel precipitation. Hydrothermal technique was used to suppress agglomerate formation, which occurs during the synthesis and processing of wet-chemical prepared powder. Precipitates aging under hydrothermal condition resulted in weaker agglomerates which were fractured during isostatic compaction. The homogeneous pore structure of compact provided a better indicator for densification during sintering. Agglomerate-free powders were sintered to 98.5% of theoretical density in constant heating rate sintering to 1220°C which was 300°C lower than necessary for a normal route prepared powders.

Zirkoniumdioxidpulver mit 3 mol% Yttriumdioxid-Dotierung und einer extrem geringen Kristallitgröße (10–15 nm) mit einer engen Größenverteilung wurden mittels Ausscheidung aus einem Gel hergestellt. Eine hydrothermische Methode wurde angewendet, um die Agglomeratbildung, die bei der Synthese und der Verarbeitung naßchemisch hergestellter Pulver auftritt, zu unterdrücken. Bei hydrothermischen Bedingungen führt das Wachsen der Ausscheidungen zu schwächeren Agglomeraten, die bei isostatischer Verdichtung des Pulvers zerfallen. Die homogene Porenstruktur kompakterter Teile zeigt ein besseres Verdichtungsverhalten beim Sintern. Agglomeratfreie Pulver wurden bis zu 98.5% theoretischer Dichte durch CHR Sintern bis zu 1220°C, also 300°C niedriger als bei der konventionellen Pulverherstellung, gesintert.

Des poudres de zircone dopées avec 3% en mole d'yttrium de taille très fine (10–15 nm) et de distribution granulométrique étroite, ont été préparées par précipitation de gel. Une technique hydrothermale a été utilisée pour éviter la formation d'agglomérats qui apparaissent pendant la synthèse et le traitement

par voie humide. Les précipités qui se forment dans les conditions du traitement hydrothermal sont en fait des agglomérats faiblement liés qui sont facilement fracturés lors du pressage isostatique. L'homogénéité de la structure des pores dans des échantillons compactés nous indique une bonne aptitude au frittage. Les poudres sans agglomérat ont été frittées à 98.5% de la densité théorique par frittage CHR à 1220°C, c'est-à-dire 300°C en dessous de la température nécessaire pour les voies mêmes poudres préparées par la voie chimique.

1 Introduction

In the process of preparing $ZrO_2(Y_2O_3)$ nanometer powder, the most difficult problems are how to prevent the formation of strong agglomerates and to obtain agglomerate-free powder.^{1–4} In the present work, special precautions were taken during the wet-chemical coprecipitation and the hydrothermal treatment of precipitate in the synthesis of $ZrO_2(Y_2O_3)$ powder. The interdependence among processing parameters, and properties of powder, compact as well as sintered body, will be discussed further.

2 Experimental Procedure

2.1 Powder preparation

The amorphous 3 mol% yttria-doped zirconia powder was synthesized by gel coprecipitation techniques. Precipitates were obtained from the aqueous solution of high purity $ZrOCl_2 \cdot 8H_2O$ and YCl_3 with ammonia. The processing flow sheet with experiment details are shown in Fig. 1. There were two factors which should be considered:

- (1) during hydrolysis the pH value remained about 11;
- (2) $[Cl^-]$ should be removed from the gel precipitate.

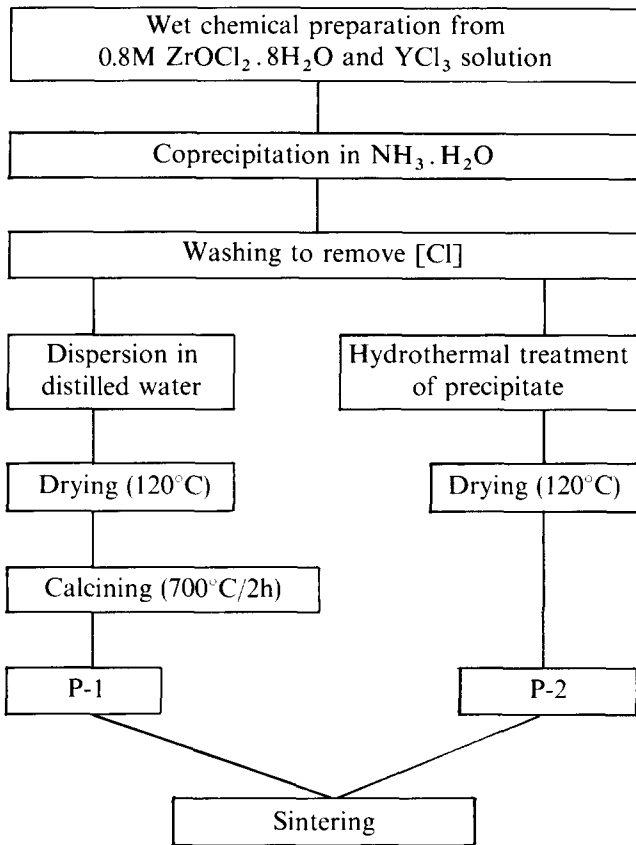
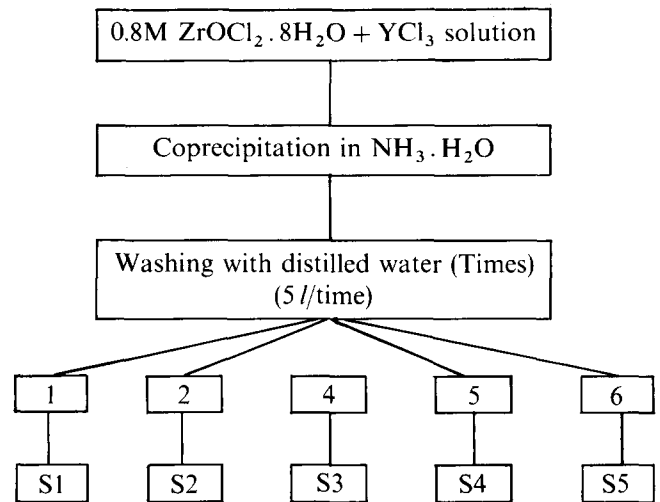


Fig. 1. Processing flow sheet.

Precipitates that contained different amounts of $[Cl^-]$ were prepared by washing the gel precipitates with distilled water. The processing flow sheet is shown in Fig. 2. In order to measure the amounts of $[Cl^-]$, first the precipitates were decomposed in hot H_2O , then the P[Cl] glass electrode was used to measure the amount of $[Cl^-]$ in the precipitates. The results are shown in Table 1. Sintering behavior as a function of $[Cl^-]$ in precipitates is shown in Fig. 3. It is clear that the amount of $[Cl^-]$ in precipitates influences the sintering properties, but as the amount of $[Cl^-]$ is lowered to a certain extent, such effects can be neglected.

2.2 Powder crystallization

The amorphous powder was divided into two portions. The first portion was crystallized by air calcination at $700^\circ C/2h$ (P-1), while the second portion was hydrothermally treated with distilled water in a stainless steel autoclave (P-2). A tempera-

Fig. 2. Preparation of precipitates contained different amount of $[Cl^-]$.Table 1. Different amounts of $[Cl^-]$ in precipitate

Sample	S1	S2	S3	S4	S5
$[Cl^-]$ (ppm)	8 600	417	1·63	1·33	1·07

ture of $200 \pm 10^\circ C$, a pressure of about 1·5 MPa and a soak time of 4 h were adopted.

2.3 Powder characterization

Crystalline size of powders was determined by means of X-ray line broadening measurement; particle size was measured by TEM. Specific surface area was analyzed by the Brunauer–Emmett–Teller (BET) method, and differential thermal analysis (DTA) was used to characterize the amorphous and hydrothermal treatment powders. The properties of the powders are shown in Table 2.

2.4 Green compact and sintered ceramics

The green compacts were obtained by pressing at 150 MPa, then pressing isostatically at 300 MPa. Green compacts were characterized by mercury porosimetry; the contact angle was 130° , while the surface tension was $4\cdot5 \times 10^7$ N/m. Sintering kinetics were determined by constant heating rate (CHR) dilatometry. The CHR experiments were conducted using a heating rate of $2^\circ C/min$ from 900 to $1500^\circ C$.

Table 2. Characteristics of powders after crystallization

Powder	S_{BET} (m^2/g)	d_{BET} (nm)	d_{50} (μm)	d_+ (nm)	AF (d_{50}/d_{BET})	Aggl. σ (MPa)
P-1	40·50	24	1·40	22	56·96	250
P-2	75	13	0·62	11	47·69	40

d_+ , Crystallite size (X-ray line broadening measurement).

AF = Agglomerate factor (reflects the agglomeration of powders).

Aggl. σ = Agglomerate strength (reflects the force necessary to damage the agglomerates).

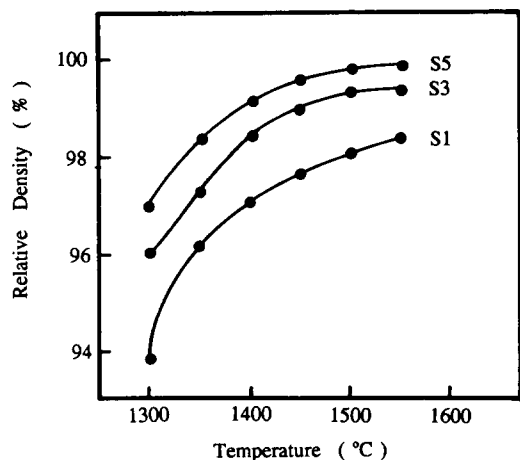


Fig. 3. Concentration of $[Cl^-]$ in precipitates as a function of sintering temperature.

3 Results and Discussion

3.1 Properties of nanometer powder

The characteristics of the powders are listed in Table 2, and the microstructures of the powders are demonstrated in Fig. 4. From these data, it is evident that P-1 powder shows a high degree of agglomeration while P-2 powder results in weaker agglomerates. Figure 5 shows the DTA curves for the powders before and after crystallization in the autoclave. The DTA curves show endothermic peaks in the range 100–200°C, corresponding to the

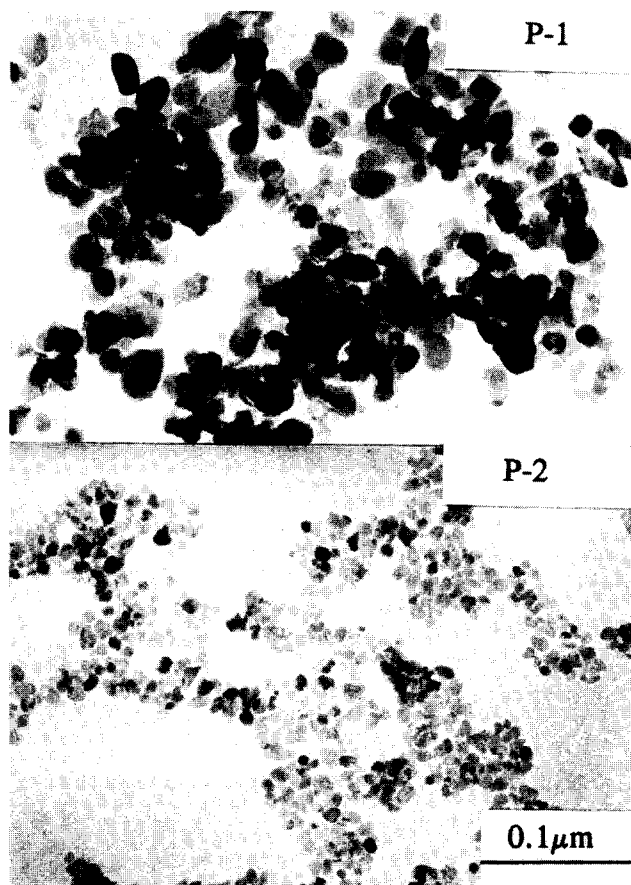


Fig. 4. Transmission electron micrograph of powders after crystallization.

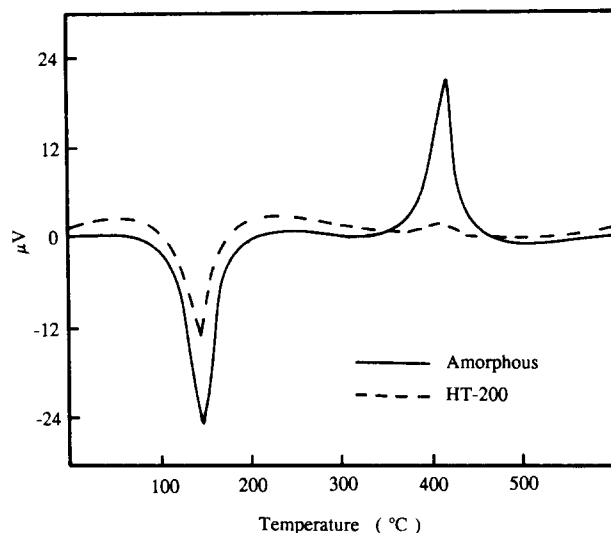


Fig. 5. Different analysis curves for the powders before and after hydrothermal crystallization.

loss of the physically adsorbed water, and an exothermic peak around 400–450°C, relating to the crystallization.⁵ The exothermic peak for P-2 powder is low, because the powder is already crystallized. This is also proved by the XRD lines in Fig. 6; from this result it is deduced that $Zr(OH)_4$ had transformed to $ZrO_2(t)$ after the hydrothermal treatment.

Pore size distribution in the powders and compacts seem to be an excellent indicator for sintering behavior. The pore size distribution in P-1, P-2 is shown in Fig. 7. In the distribution, the different peaks represent different sizes of pores, pores which are smaller than 0.1 μm are represented by the packing of primary crystallites; for 0.1–5 μm, pores have been formed by the packing of hard agglomerates formed during calcination; and the pore peak in 10 μm is regarded as the packing of weak agglomerates. The pore size distribution of P-2 powder showed clearly a bimodal pore structure. In addition to the pore size at 8 nm, 10 μm pore was formed by the weak agglomerates. After being pressed, the interagglomerate pores disappear, the primary particles are arranged and the pore of primary particles becomes narrower, smaller than before. A small pore size and a narrow distribution

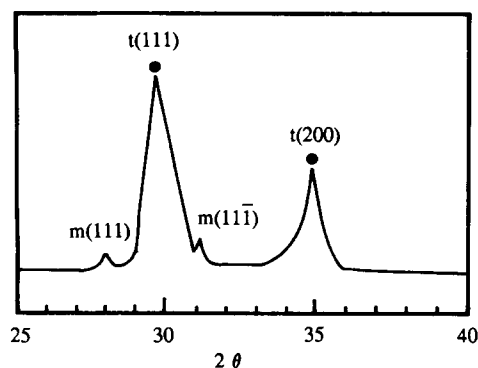


Fig. 6. X-ray diffraction pattern of powder after hydrothermal treatment.

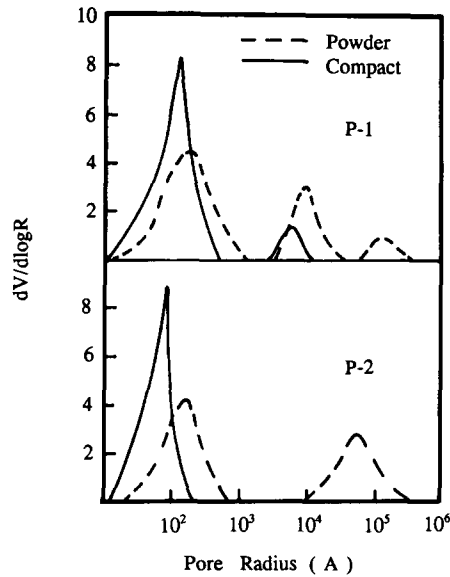


Fig. 7. Pore size distribution of powder; compact after isostatic pressing at 200 MPa.

in the green compact are believed to be the reasons for the lower densification temperature and higher shrinkage at a given temperature; this has been proved by the shrinkage curves obtained for P-1 and P-2 green compacts (Fig. 8). The sample made from hydrothermal treatment exhibits a large shrinkage at the same temperature and densifies to about 98% theoretical density at 1220°C, compared to 1500°C for the sample made by normal route.

3.2 The forming mechanism of agglomerates in nanometer powder

In all the processes of powder preparation—from wet-chemical coprecipitation to gel precipitate washing, dispersing, drying and calcining—every step will cause agglomerates. But what is the most critical step in the production of hard agglomerates? From the authors' experimental analysis, it is shown that it is the wet-gel washing and aging treatment. Figure 3 shows the relationship between $[Cl^-]$ in the precipitates and their sintering behavior. The

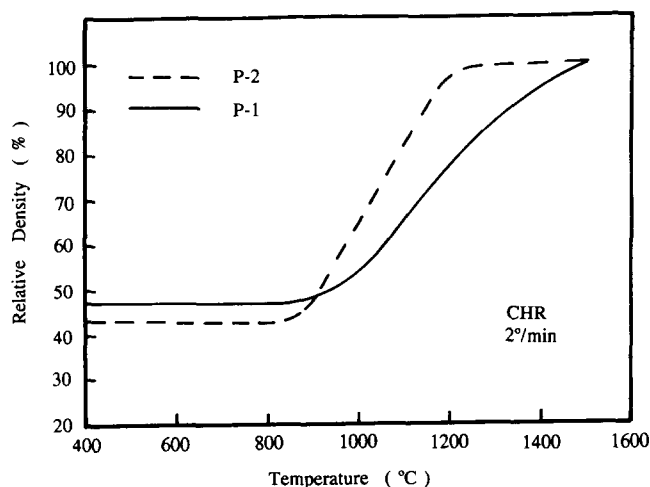


Fig. 8. Shrinkage curves obtained by dilatometry for compacts P-1 and P-2.

experimental results show that the amount of $[Cl^-]$ in the precipitates will influence their properties of sintering. This is because the $[Cl^-]$ in the powder cause the formation of solid bridges by crystallizing salts, and these solid bridges between the particles are the main reason for the production of hard agglomerates. Thus, it is necessary to control the amount of $[Cl^-]$ in the powders, by introducing washing procedures to remove the $[Cl^-]$. Furthermore, the powders which are prepared from coprecipitation are amorphous and should be crystallized in order to make monolithic ceramics; otherwise, cracking will occur during firing. The crystallization can be accomplished by calcination at a temperature $>400^\circ C$; during this process, the agglomerates become stronger and also cause coarsening of the powder. The strong interparticle forces between the amorphous $Zr(OH)_4$ results in close packing and the formation of dense agglomerates after drying and calcination. If the powder is prepared via hydrothermal routes, at a high pressure the $Zr(OH)_4$ begins to crystallize and is transformed into $ZrO_2(t)$ by hydrothermal treatment; thus, the calcining step is not necessary in this case. This can avoid the growth and coarsening of particles. Crystallites are formed with less tendency to agglomerate than that in the case of amorphous gel type particles. This is why the P-1 powder contained more agglomerates than the P-2 powder.

4 Conclusion

Powders prepared by controlling wet-gel structure and hydrothermal processing could obtain narrow size distribution and weakly agglomerate $ZrO_2(Y_2O_3)$ nanometer powder, which can be densified without pressure at a lower temperature. Comparing the various methods of characterization for powders and compacts, it is evident that the pore size distribution in the compact is an excellent indicator for sintering behavior.

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