Influence of some variables of the precipitation process on the structural characteristics of fine zirconia powders

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Abstract

Zirconia gels precipitated at pH 6, 10.4 and 13.5 from zirconyl chloride solutions have been investigated by thermogravitry and differential thermal analysis techniques. The total mass loss is 20% but increases for the lower pH studied. Oxide crystallization occurred at 447°C, and no clear relation appears between processing conditions and thermal effects. The calcined powders were investigated by X-ray diffraction and nitrogen adsorption techniques. X-ray powder patterns only exhibited the tetragonal reflections after precipitation performed at pH 13.5 at room temperature. However, for a slight increase in the precipitant temperature the diffraction profile shows a mixture of monoclinic and tetragonal phases. The order of addition of solutions during the precipitation process produces some differences concerning crystallite sizes. Specific surface area values are found to be independent of the pH of precipitation, but strongly affected by the washing media.

Keywords: Crystallite; pH; TGA; Washing; XRPD; Zirconia

1. Introduction

Zirconia ceramics have long been used as refractories. High ionic conductivity results when the cubic fluorite-type structure is stabilized by doping with aliovalent cations. These solid electrolytes can be used as oxygen sensors. When the cubic

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structure is partially stabilized high mechanical properties are obtained and these solid solutions are suitable for structural applications [1].

The difficulties of sintering a high melting point ceramic and the microstructural requests for these applications have stimulated the use of unconventional processes [2]. Among these, fine powder preparation methods via chemical routes have been emphasized. In this regard the precipitation of salts has been one of the oldest and most used techniques [3].

The precipitation technique involves a number of variables giving rise to a product with specific characteristics. In the case of zirconia, it has recently been shown [4] that the metastable tetragonal polymorph is primarily formed as a result of oxide crystallization. Its thermal stability, however, is strongly influenced by the pH [5] and rate of precipitation [6], additives [7] and the characteristics of the precipitant [8], among other variables.

In these studies precipitations were brought about by adding a given amount of precipitant to a solution containing the zirconium cations, the so-called "direct strike". Alternatively it can be done by inverting the order of solution addition, or "reverse strike". As already pointed out [9], the environment in which nucleation and growth of the precursor precipitate occur is not the same in both cases. As a result, ceramics with different structural characteristics might be expected. In addition, in the case of solid solution formation the reverse strike precipitation is preferred because it ensures a simultaneous precipitation of the desired cations.

The aim of the present work is to investigate the effect produced on the structural characteristics of zirconia powders when precipitations are performed in an inverted manner, i.e. by adding the cation solution to the precipitant solution. The influence of some washing media on the physical properties of the calcined powders is also studied.

2. Experimental

A zirconia gel was precipitated from a 0.6 M $ZrOCl_2 \cdot 8H_2O$ (99.5%, Riedel de Haën) aqueous solution. To effect precipitation, this solution was added dropwise at a rate of 50 ml min^{-1} to a previously determined amount of precipitant under vigorous stirring. 6 M NH_4OH or 4 M $NaOH$ solutions, or a mixture of NH_4OH and HCl precipitant were used in order to obtain specific pH values of 10.4, 13.5 and 6, respectively. These figures correspond to the pH of the supernatant liquid, and were kept constant throughout this step. Most of these precipitations were done at room temperature (RT). In one experiment, however, the NaOH solution was held at 40°C during the precipitation step. The reagents used were of analytical grade.

The resulting gelatinous precipitate was dispersed in distilled water (300 ml for each 50 ml of initial zirconyl chloride solution), and collected by vacuum filtration. This washing cycle was repeated four times. At this point, test for Cl$^-$ with a 1 M $AgNO_3$ solution was conducted in the usual manner. For precipitations at pH 6 two more cycles of washing and filtration were necessary.

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                        Precipitated gel
                          ( pH 10.4 )

        Washing with                    Washing with
        distilled water                 0.2 N NH4OH
            ( 4 x )                         ( 4 x )
              1                               2

                        Washing with          2
                           ethanol
                           ( 2 x )
                             1

                        Washing with
                            ATA
                             1

                           Drying
                        110 °C / 24 h
                             1   2

                         Calcination
                        600 °C / 30 min
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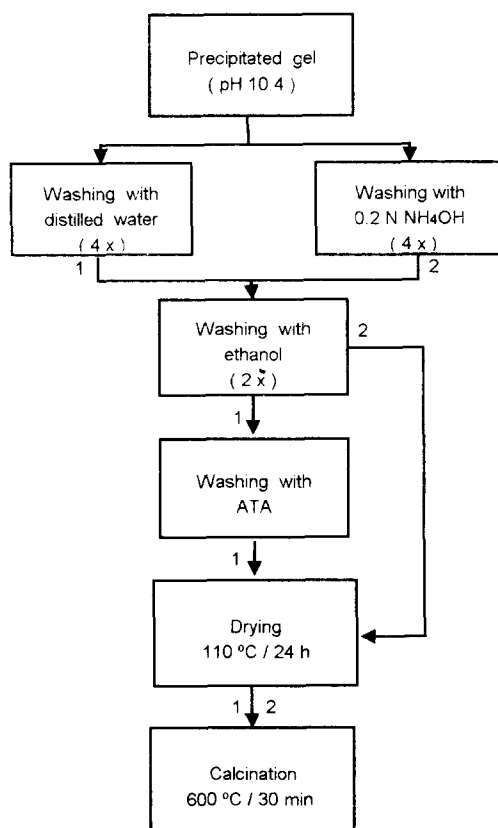
Fig. 1. Flow diagram showing the washing routes, drying and calcination procedures.

Some precipitated batches at pH 10.4 were washed differently in order to verify the effect of the washing media on the characteristics of the calcined powder. The sequence acetone–toluene–acetone (ATA) has proved [10] to be very efficient in producing highly sinterable oxide materials, and was used here as a reference washing media. Fig. 1 is a flow diagram showing the experimental sequence employed in this case.

Samples were dried at 110°C for 24 h. Calcinations were done at 600°C for 30 min in air. Drying and calcination steps were the same in all cases.

The chloride content was determined by pyrohydrolysis and the metallic impurities by spectrographic analysis. Thermogravimetric analysis (TGA), derivative thermogravimetry and differential thermal analysis (DTA) were performed with a DuPont TA 2000 analyzer with modules TGA 951 and DTA 1600, from room temperature to 900°C, with a heating rate of 10 K min^{-1}. Alumina was used as reference sample in DTA runs.

X-ray diffraction patterns of the powders were obtained with a Rigaku diffractometer, using a nickel filtered Cu Kα radiation. The volume fraction of each phase
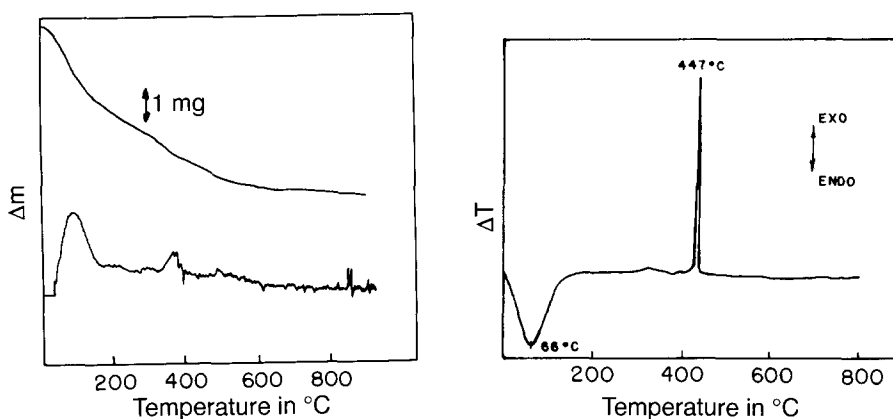
Fig. 2. TGA curve of hydrous zirconium oxide precipitated at pH 6.
Fig. 3. Typical DTA curve of hydrous zirconium oxide precipitated at pH 10.4

was estimated from the ratio of the corresponding peak intensities [11]. the crystallite sizes (D_c) of tetragonal (t) and monoclinic (m) zirconia were calculated using Scherrer's equation on the (11$\bar{1}$) m- and (111) t-ZrO_2 reflections, respectively.

Specific surface areas (S) of the calcined powders were determined by the Brunauer–Emmett–Teller (BET) method.

3. Results

Several samples were analyzed for Cl^- content giving an average value of 0.06%, indicating that more than four water cycles are needed to reduce chloride contamination to a trace level.

Thermogravimetric results show that the mass loss up to 200°C is approximately equivalent to the loss of one water molecule, and is independent of other precipitation variables. The total mass loss is about 20%, except when the precipitation was done at pH 6 (Figure 2). In this case, the total loss is 24.5%, showing an increase in the structurally bound water content with decreasing pH. The derivative thermogravimetry presents a second peak of mass loss between 350 and 400°C due to organic content. No differences were observed in TGA curves obtained in flowing air or nitrogen.

As general features, most mass loss occurred up to 200°C, and completion is reached at about 600°C.

All samples exhibited similar DTA curves. Figure 3 is a typical example showing an endothermic effect below 150°C, characteristic of water loss, and a sharp exothermic peak around 447°C due to oxide crystallization [4,6,7]. Apparently, there is no relation between processing conditions and temperatures of thermal effects.

Table 1
Metallic impurity content of zirconium oxide calcined powders determined by spectrographic analysis

Element	Content/ppm at pH 10.4	pH 13.5
Mg	130	5
Sr	350	70
Al	150	400
Cu	10	< 1
Na	60	> 590
Fe	20	—
Si	350	70

Table 2
Volume fraction of monoclinic phase V_m and average crystallite sizes D_c for t and m reflections of zirconia powders

pH	$V_m/\%$	D_c/nm	
		t	m
6	61	15.2	17.2
10.4	82	14.0	17.4
13.5 (RT)	≈ 0	28.6	—
13.5 (40°C)	62	12.3	12.3

Table 1 presents results obtained by spectrographic analysis, for powders precipitated at pH 10.4 and 13.5, both at room temperature. The metallic impurity content of the powders is relatively low, and is basically dependent upon the purity of the starting chemicals. The sodium content is considerably higher when the precipitant used was NaOH. It was shown [8] that when sodium contamination is of the order of 3% or higher, it can promote the stabilization of the cubic phase. In this study, the washing cycle was sufficient to keep the sodium content below that value. Thus, the cubic phase stabilization did not occur.

Diffractogram profiles of dried powders show that the precipitates were amorphous. After calcination the powder patterns exhibited a mixture of monoclinic and tetragonal reflections. The volume fraction of monoclinic phase (V_m) and the crystallite sizes for both t and m reflections are given in table 2. D_c values for powders precipitated at pH 6 and 10.4 do not differ significantly. The crystallite size for the m reflection is slightly higher than that for the t reflection. For precipitations at pH 13.5 and RT the crystallite size of the t reflection is relatively higher, and is near the critical size (about 30 nm) for the tetragonal to monoclinic phase transformation [12,13].

Powders precipitated at pH 13.5 at RT are almost 100% tetragonal, whereas those precipitated at the same pH but at 40°C contain approximately 62% of the
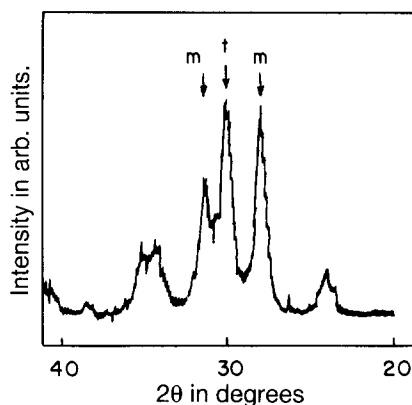
Fig. 4. X-ray diffractometry profile for zirconium oxide specimen precipitated pH 13.5 at 40°C, showing the main t and m reflections.

Table 3
Values of specific surface area S for different pH and washing media used for preparing ZrO_2 powders

Washing media[a]	pH	S $(m^2 \, g^{-1})$
w + e	13.5	50.5
w + e	10.4	49
w + e	6	48
w + e + ATA	10.4	72.5
a + e	10.4	73

[a] w, water; e, ethanol; ATA, acetone–toluene–acetone; a, 0.2 N NH_4OH solution.

monoclinic phase (Fig. 4). Hence, the effect of temperature is to allow for the formation of the monoclinic phase with a simultaneous reduction in crystallite sizes.

Comparing the above results and those obtained in direct strike precipitations [4–8], the content of bound water in the gel does not vary significantly. Also, in both cases of processing conditions, the temperature of oxide crystallization is independent, although it is strongly affected by the kind of precursor and zirconia content [14].

The main observed difference is related to crystallite sizes. Crystallite sizes shown in Table 2 are slightly higher than those obtained under similar experimental conditions in direct strike experiments. Moreover, the crystallite sizes for m and t reflections are slightly higher for low and intermediate pH values, and twice as large in the case of pH 13.5 [4]. Yet, for room temperature precipitations the fraction of monoclinic phase, in the studied pH range, is approximately the same as that obtained from direct strike experiments [5,6].

Values of specific surface area of the calcined powders are shown in Table 3. Assuming spherically shaped particles, their calculated diameters are in the 10 to 25

nm range. The surface area does not vary with the pH precipitation. In contrast, the washing media has a remarkable effect on this parameter. The role of ethanol washing in zirconia powders has recently been studied [15,16]. It promotes the formation of surface ethoxy groups that have a direct influence on the strength of the resulting agglomerates. The values in Table 3 for the same pH of 10.4 show a considerable increase in the specific surface area with the ATA washing sequence, after previous washing with water and ethanol. This improvement is a result of better water removal from the gel. The benefit of washing the precipitate with a diluted NH_4OH solution and ethanol seems to be equivalent. Therefore, in this case also, a powder free of "hard" agglomerates, and with higher sinterability might be expected.

4. Conclusions

For zirconia powders precipitated at pH 10.4 and 13.5 the mass loss is around 20%. There is an increase in the content of the structurally bound water with decreasing pH. The oxide crystallization temperature (447°C) is independent of processing variables. Precipitations performed at pH 13.5 and 40°C give rise to a powder with both m and t phases, and smaller crystallite sizes. The main observed difference between these results and those obtained in direct strike precipitation is related to crystallite size.

Washing with ethanol followed by ATA sequence or with a dilute NH_4OH solution, considerably increases the specific surface area of the calcined zirconium oxide powders.

Acknowledgements

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