

## ZrO<sub>2</sub> AND ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> PHASE STRUCTURE IN FILMS AND POWDERS

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### ABSTRACT

Zirconia and zirconia-yttria coating films and powders obtained by the sol-gel route using a zirconium alkoxide as starting material and acid and neutral catalytic were investigated by the Perturbed Angular Correlations method (PAC), XRD, DTA and TGA. The hyperfine interaction was measured either during heat treatments or after annealing the samples at increasing temperatures up to 1200°C. All samples have presented a high fraction of crystalline phases at low temperatures. The yttria doped cubic zirconia has not shown the phase transition to the monoclinic phase. Pure zirconia powders produced in neutral hydrolysis and zirconia coatings produced in acid catalysis stabilized the tetragonal phase in a high fraction and up to high temperatures.

### INTRODUCTION

During the preparation of ZrO<sub>2</sub> and ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> coatings and powders by sol-gel route, the obtained phases and their thermal evolution are strongly dependent on the synthesis process<sup>1,2</sup>. Yoldas<sup>1</sup> has found that in the hydrolytic condensation of zirconium alkoxides, the alkyl groups of an alkoxide play an important role, affecting the morphology and particle sizes of the resultant materials. Rivas et al.<sup>3</sup>, have shown that the amount of tetragonal zirconia retained at room temperature after heat treatments is greater at lower water/alkoxide ratios. Caruso et al.<sup>4</sup> have found that zirconia coatings retain a higher fraction of tetragonal phase than zirconia powders when both are prepared from the same precursor solution.

The aim of this work is to study the effect of Y<sub>2</sub>O<sub>3</sub> on the phase content and the thermal evolution in zirconia powders and films prepared by sol-gel route. The effect of the solvent and the catalytic agent in pure zirconia powders is also investigated.

### EXPERIMENTAL

#### Solution Preparation

The precursor solutions were prepared mixing n-propoxide of zirconium (ZNP) (70 % in propanol, Alfa), alcoholic solvent and HNO<sub>3</sub> as catalytic agent in an anhydrous nitrogen atmosphere under stirring. After six hours, the distilled water was aggregated. Ethylic (EtOH) and isopropyllic (iPrOH) alcohols were used as solvent. The ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> precursor solution was prepared by adding yttrium acetate dissolved in iPrOH with HNO<sub>3</sub> on the ZNP/H<sub>2</sub>O/EtOH/HNO<sub>3</sub> with stirring during 2 hours. The final [Y<sub>2</sub>O<sub>3</sub>] was 11,38 % molar. Table I lists the solution concentrations used.

TABLE I

Code	Y <sub>2</sub> O <sub>3</sub> (%)	Solv.(SiOH)	H <sub>2</sub> O/ZNP	SiOH/ZNP	HNO <sub>3</sub> /ZNP
Z1	0	EtOH	3,5	10,1	1,2
Z2	0	iPrOH	3,1	10,1	1,3
Z3	0	iPrOH	3,1	10,1	0
Y1	11.38	EtOH	5,4	13,3	0.9

### Coating and Powder Samples

Sheets and tubes of alumina were used as substrates for the coating. The liquid films were deposited by dip-coating of the substrates into the precursor solutions in an air atmosphere. The withdrawal rate was of 8 cm/min. The films were dried at 60°C during 90 minutes. Finally they were treated thermally at 500 and/or 1000°C during 1 hour. The coating thickness was measured with a Hommel Tester T2 profilometer. The thickness of densified monolayer coatings was 110 nm. Coatings with thickness of 0.95 μm were prepared by a multilayer process. The powders were obtained by gelificating and drying the solutions in an open flask at 100°C. The Y<sub>2</sub>O<sub>3</sub> doped zirconia powder was heated at 500°C after the drying.

### Phase Characterization and Thermal Analysis

XRD spectra of the as-prepared and annealed coatings and powders were obtained at room temperature. The low angle region ( $2\theta = 27^\circ$ - $32^\circ$ ) was used to estimate the monoclinic/(tetragonal+cubic) content intensity ratio and the high angle region ( $2\theta = 72^\circ$ - $76^\circ$ ) was recorded with the intention of deciding between the tetragonal and the cubic forms. A Philips PW 3710 diffractometer with a grazing beam was used for the coatings.

Differential thermal (DTA) and thermogravimetric (TG) analyses were accomplished on the obtained powders up to 1400°C in normal atmosphere. The heating rate was 10°C min<sup>-1</sup>.

A better qualitative and quantitative determination of phases and their thermal evolution was achieved using the PAC method<sup>4</sup>. PAC is a technique based on the fact that "pure" zirconium contains at least 1-3 % of hafnium impurities. Irradiation of zirconium compounds with thermal neutrons generates radioactive Hf nuclei which decay by β- emission to an excited state of <sup>181</sup>Ta and by emission of two gamma rays in cascade to the ground state of <sup>181</sup>Ta. In non magnetic materials such as ZrO<sub>2</sub>, the PAC technique consists of measuring the hyperfine interaction between the nuclear quadrupole moment Q of the <sup>181</sup>Ta intermediate level and the extra nuclear electric field gradient (EFG) produced by the charge distribution that surrounds it. It is usual to characterize the second order EFG tensor V<sub>ij</sub> by two quantities: the quadrupole frequency ω<sub>Q</sub> (proportional to the major component V<sub>zz</sub>) and the asymmetry parameter η = (V<sub>xx</sub>-V<sub>yy</sub>)/V<sub>zz</sub> valued between 0 (axially symmetric sites) and 1 (maximally non-symmetric sites). There is also a third quantity which can be derived from the experiment, the distribution frequency width δ introduced to take into account a Lorentzian distribution of the EFG's around the average value, caused by the existence of disorder, random impurities or defects in the lattice. The hyperfine interaction of all zirconia polymorphs, monoclinic, tetragonal and cubic, have been already reported. The PAC spectra of sol-gel derived ZrO<sub>2</sub> were obtained on the as-prepared samples and on samples with two hours of heat treatment at increasing temperatures up to 1200°C. The temperature uncertainty was ±5°C. The measurements on ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> samples were performed in situ at increasing temperatures. The powder samples were encapsulated in 0.5 cm sealed

quartz tubes and the coated substrates were alumina tubes of proper dimensions for the PAC measurements.

## RESULTS AND DISCUSSION

### A-Phases in Z1 Pure Zirconia Coatings and Powders.

Table II lists the mean values of the fitted quadrupole parameters. The observed evolution of

TABLE II. Average PAC quadrupole parameters

Microstructures	$\omega_Q(\text{Mrad s}^{-1})$	$\eta$	$\delta(\%)$
x	$215 \pm 15$	$0.65 \pm 5$	$13 \pm 3$
t'	$175 \pm 10$	$0.65 \pm 5$	$15 \pm 3$
c'	$110 \pm 10$	$0.75 \pm 10$	$5 \pm 3$
t	$190 \pm 5$	$0.15 \pm 5$	$5 \pm 3$
m	$124 \pm 3$	$0.34 \pm 2$	$3 \pm 2$

the relative fractions of the hyperfine interactions found in the Z1 samples over the whole temperature range is plotted in Fig. 1a for the powder and in 1b for the coating.

Only the (t'), t-ZrO<sub>2</sub> and m-ZrO<sub>2</sub> interactions are common to the coating and the powder.

While the interactions labeled (t') and (x) depict disordered structures ( $\delta \sim 15\%$ ), the (c') one, which appears exclusively in the coating, describe an unknown metastable phase probably of cubic symmetry which stabilizes at low temperatures and disappears simultaneously with the onset of the t  $\rightarrow$  m transformation.

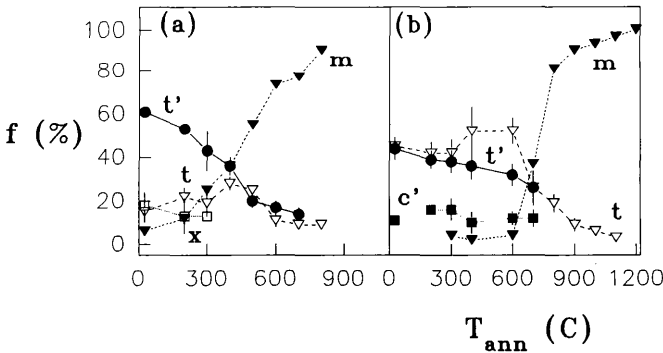


Figure 1: Thermal evolution of the phase content in Z1 powder (a) and coating (b).

distinguishable by XRD from t-ZrO<sub>2</sub>. It has been characterized as a disordered tetragonal structure from which the metastable ordered t-ZrO<sub>2</sub> phase would rise through a thermally activated process by which the additional groups are eliminated<sup>3</sup>. The non-zero but low value of the asymmetry parameter fitted for the (t)-interaction could indicate that the associated

crystalline tetragonal structure is slightly distorted. On the other hand, the (x)-interaction is present exclusively in the powder and disappears above 300°C. Both the coating and powder exhibit the monoclinic phase at higher annealing temperatures but differ in the initial phase content and in the thermal evolution towards the crystallization. The film proved to be more efficient than the powder in retaining (t') and stabilizing t-ZrO<sub>2</sub> and (c')-crystalline phases. It is also more resistant to the transformation to the monoclinic phase, probably due to the sintering constraints arising by the adherence of ZrO<sub>2</sub> to the alumina substrate.

### B-Phases in Y<sub>2</sub>O<sub>3</sub> Doped Zirconia Coatings and Powders

The in-situ PAC results of powder and coating (Figs. 2a and 2b) show that the as-prepared samples (500°C) possess 100 % of cubic structure (c1). However, at higher temperatures (700°C for the powder and 800°C for the coating) a new, sample dependent interaction (c2) appears. Between 600 and 900°C, the DTG curve of the powder (Fig. 2c) exhibits a weight profit that would indicate that c2 describes a high temperature structure less oxygen deficient than c1.

The irruption of the c2 interaction is delayed until 800°C are reached in the coating. Near 1000°C the powder possesses 70 % of c1 and 30 % of c2 while the coating contains 60 % of c1 and 40 % of c2. During the cooling, a partial inverse transformation from c2 to c1 was observed and no other interaction appeared. Moreover, the absence of an exothermic peak near 920°C in the DTA during the cooling would confirm that both samples retain just the two cubic

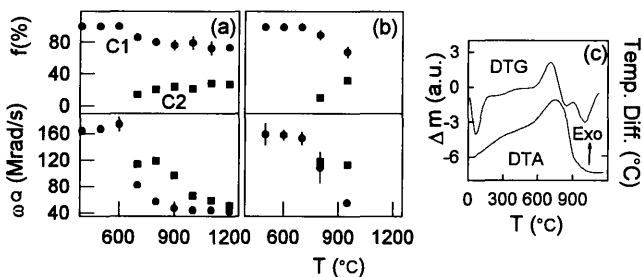


Figure 2: Thermal evolution of phase content and quadrupole frequencies in Y1 (a): powder and (b): coating. (c): Powder DTA - DTG curves.

configurations at room temperature. This experimental evidence was also checked by XRD

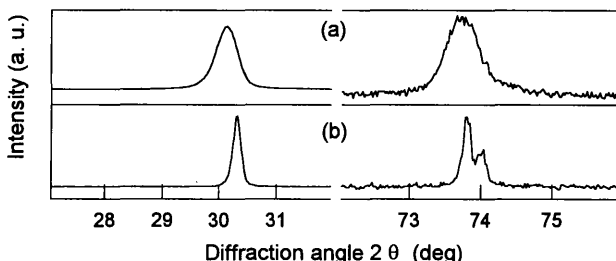


Figure 3: XRD patterns of Y1 samples after anneals at 1000°C: coating (a) and powder (b).

results, as is shown in fig. 3a and 3b for the coating and the powder respectively.

### C-Synthesis Parameters Effects on the Phases

The use of isopropyl alcohol (iPrOH) instead of ethylic alcohol (EtOH) as a solvent in the precursor solution does not produce any appreciable differences in the obtained zirconia powders under acid catalysis conditions. The DTA-TG of the Z2 powder is very similar to the one of Z1 powder. Moreover, the XRD diffractograms of the annealed Z1 and Z2 powders, shown in fig.4 at increasing temperatures up to 1000°C, show the same results.

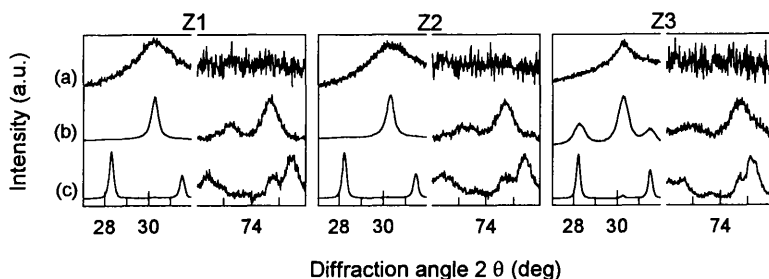


Figure 4: XRD patterns of Z1, Z2 and Z3 powders after 5 hours anneals at (a) 300°C, (b) 500°C and (c) 1000°C.

On the other hand, the thermal analysis and XRD results of the Z3 powder show that there are marked differences between this sample and Z1 and Z2. The DTA of Z1 powder displayed in fig.5 exhibits an endothermic peak near 160°C and two broad exothermic peaks around 290 and 320°C that correspond to the loss of water absorbed physically, loss of chemically bound water and elimination of organic groups, respectively<sup>4</sup>.

At 320°C the (x) phase disappears in the PAC pattern of Z1 powder (fig.1a). This fact, added to its absence in the as-obtained film, showed evidence that the (x)-interaction represents some disordered zirconium neighborhoods still containing organic radicals<sup>3</sup>. Between 450 and 550°C

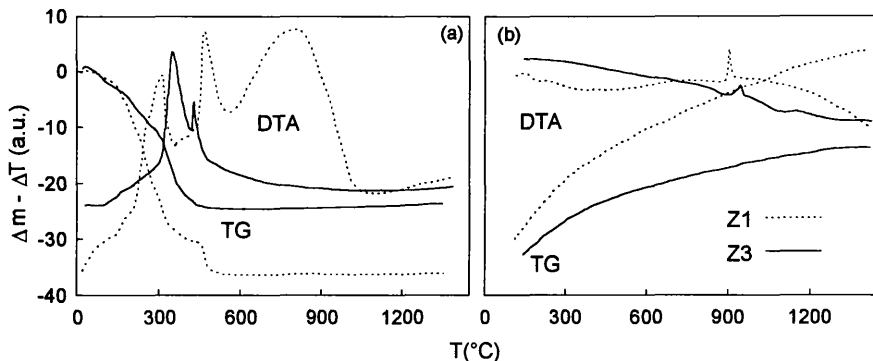


Figure 5: DTA - TG curves of Z1 and Z3 powders. (a) on heating, (b) on cooling.

an exothermic peak is observed, which would correspond to the onset (according to PAC results) of the transformation of the metastable forms ( $t'$ ) and ( $t$ ) towards the monoclinic phase. A very broad exothermic peak appears between 700-900°C corresponding to the disappearance of the tetragonal forms. In the TG curve, on its turn, a subtle mass change at 820°C probably due to a final water elimination, agrees in temperature with the disappearance of the  $t'$ -hyperfine interaction. Finally, the reversible transition  $m \rightarrow t$  can be visualized through an endothermic peak between 1000-1100°C on the heating and a sharp exothermic peak at 910°C on the cooling. In the DTA heating curve of Z3 powder, on the contrary, just two sharp exothermic peaks can be observed (Fig. 5). One near at 350°C, due to the burning of organic groups and the other at 450°C that could be due to the formation of crystalline  $t$ -ZrO<sub>2</sub> or  $c'$ -ZrO<sub>2</sub> from the starting amorphous form. At greater temperatures, the absence of any other peak together with no mass changes would indicate that the  $t$ -ZrO<sub>2</sub> or  $c'$ -ZrO<sub>2</sub> phases remain as metastable phases without transforming to  $m$ -ZrO<sub>2</sub> during the whole heating process. However, two exothermic peaks observed at 1120 and 910°C during the cooling would probably correspond to the transitions ( $c'$ )  $\rightarrow$   $t$  and  $t \rightarrow m$ , respectively. PAC measurements to confirm these hypothesis are in progress.

All XRD of the as-prepared powders show a large disorder. Cooling from 300°C (Fig.4), a wide peak appears at  $2\theta = 30^\circ$  corresponding to the tetragonal/cubic phase. In powders treated at 500°C it can be observed the presence of two additional peaks at  $2\theta = 28,25^\circ$  and  $31,55^\circ$  that correspond to the monoclinic phase. These two peaks, almost irrelevant in the Z1 and Z2 powders, have enough intensity in the Z3 powder. At higher angles, two peaks observed at  $2\theta = 73,1^\circ$  and  $74,4^\circ$ , correspond undoubtedly to the tetragonal structure. After heating at 1000°C, the Z3 powder retains a greater fraction of tetragonal phase than the Z1 and Z2 powders. Considering that in the DTA heating curve of the Z3 powder the metastable tetragonal  $\rightarrow$  monoclinic change is not observed, the room temperature results of XRD for this powder would indicate that the appearance of the monoclinic phase occurs upon cooling.

## CONCLUSIONS

The 11,38 % Y<sub>2</sub>O<sub>3</sub> doped-ZrO<sub>2</sub> coatings and powders prepared by sol-gel from acid hydrolysis of ZNP and yttrium acetate display a cubic structure. This cubic structure is maintained during the whole thermal treatment up to 1400°C and at room temperature. An additional interaction, appearing in the PAC spectra as temperature increases, is assumed to correspond to a change in the defective structure of the cubic phase.

The ZrO<sub>2</sub> powders produced in neutral hydrolysis of ZNP stabilizes the metastable tetragonal phase better than the powders prepared in acid catalysis.

In ZrO<sub>2</sub> samples, the coating retains the metastable tetragonal form better than the powder.

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