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A. Winnubst, M.A.C.G. van de Graaf, K. Keizer, A. Burggraaf. TETRAGONAL ZrO₂ - Y₂O₃ PART I: PREPARATION METHODS AND CHARACTERIZATION. Journal de Physique Colloques, 1986, 47 (C1), pp.C1-569-C1-573. 10.1051/jphyscol:1986186 . jpa-00225617

HAL Id: jpa-00225617

<https://hal.science/jpa-00225617>

Submitted on 4 Feb 2008

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TETRAGONAL $ZrO_2 - Y_2O_3$ PART I : PREPARATION METHODS AND CHARACTERIZATION

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Résumé - Des échantillons polycristallins de zircone tétragonale (Y-TZP) sont préparés par des méthodes chimiques en voie humide. On obtient ainsi par frittage réactif, des céramiques avec des tailles de grains aussi faibles que 0,1 μm . Le vieillissement dans l'air et dans l'eau à haute température a été étudié par diffraction X. Les principaux facteurs du vieillissement sont la teneur en yttrium, le taux d'impureté et la taille des grains. Les Y-TZP avec 6,1 moles % $YO_{1,5}$ et une taille de grains de 0,1 μm ne présentent pas de dégradation en phase monoclinique même après 5 heures à 450 K dans l'eau.

Abstract - Y_2O_3 -containing tetragonal ZrO_2 polycrystals (Y-TZP) are prepared by wet chemical methods. This results in sinterreactive ceramics with grain sizes down to 0.1 μm . The aging behaviour in air and water at high temperatures has been studied by X-ray diffraction. Important factors on aging are Y-concentration, impurity level and grain size. Y-TZP with 6.1 mol% $YO_{1,5}$ and a grain size of 0.1 μm do not show degradation to monoclinic phase even after 5 hours at 450 K in water.

I - INTRODUCTION

In the system $(100-x)ZrO_2-xYO_{1,5}$ several phases exist at low yttria concentrations ($0 < x < 15$) /1/. At room temperature these phase mixtures consist of a monoclinic and a cubic fluorite (m+f) phase, while at higher temperatures tetragonal (t) and f phases are present (1). According to Scott /1/ a monophasic t-phase region exists at $YO_{1,5}$ concentrations lower than 5 at% ($0 < x < 5$) and temperatures between 800 K and 2500 K. This high temperature t-phase can be "frozen" to room temperature when small ceramic grains ($< 0.3 \mu m$) are present /2/. Lange /3/ reported that this critical grain size (D_c), which arrests the t-m transformation during cooling, increases from 0.2 to 1.0 μm when x increases from 4 to 7 at% $YO_{1,5}$. This tetragonal material (afterwards called Y-TZP) is relatively tough due to the martensitic stress induced transformation from t-m /2,3/.

A phase transformation t-m also takes place after aging at elevated temperatures /4,5,6,7/. This effect is striking at $T=470-570$ K in air /4,5/ or in H_2O at $T=400-500$ K /6,7/. The degradation depends on grain size and yttria content of the ceramic material. Here also a critical grain size is found which increases from 0.2 to 0.5 μm when x increases from 4 to 9.5 at% $YO_{1,5}$ /4/. A material aged for 2000 hours at 480 K shows a decrease in flexural strength from 1000 to 100 MPa if compared with sintered materials /5/. Tsukuma /8/ has found the highest fracture toughness value (K_{IC}) for $x=2$ at% ($K_{IC}=10$ MPa \sqrt{m}). This material with a grain size of 0.4 μm , disintegrates, however, to powder after several thermal cycle tests between room temperature and 1070 K.

It is obvious that degradation of Y_2O_3 -stabilized tetragonal zirconia (Y-TZP) especially takes place at relatively large ceramic grain sizes (0.2-0.5 μm). The

commercially available Y-TZP powders result in dense ceramics after (hot) pressing and sintering at 1670 K or higher temperatures. The grain size of the ceramic obtained in this way is 0.4 μm or more, which in most cases leads to thermal degradation /4,5,6,7,8/.

For the preparation of Y-TZP, with grain sizes smaller than 0.4 μm , lower sintering temperatures have to be used. It is necessary to start with ultrafine, homogeneous and weakly agglomerated powders to obtain a dense ceramic in this case. In this paper two wet-chemical powder preparation methods are used as described elsewhere /9/. The sintering characteristics and thermal stability of this material are studied. In a second paper the mechanical and electrical properties are described /10/.

II - EXPERIMENTAL

The zirconia powders were prepared by two hydrous gel precipitation techniques. These imply hydrolysis of a metal alkoxide-benzene solution in water or of a metal chloride-HCl solution in NH_4OH . After thoroughly washing with water and alcohol the resulting gels were dried at 390 K and calcined at 820 K for two hours. More details of these wet chemical preparation methods are described elsewhere /9/. The powder $(100-x)\text{ZrO}_2 \cdot x\text{YO}_{1.5}$ with $x = 5.5$ (ZY5.5) was prepared by the "alkoxide" method while for the powders with composition $x = 6.1$ or 11 (resp. ZY6.1 and ZY11) the "chloride" method was used. X-ray fluorescence spectroscopy was applied for the analysis of the overall composition. The powders were pressed isostatically at 400 MPa, presintered at 1170 K for 3 hours and finally sintered at temperatures between 1380 and 1660 K. The ceramic samples were sawn to the desired dimensions for mechanical and electrical measurements /11/. X-ray diffraction experiments were performed on as sawn and aged specimens using a Philips X-ray diffractometer PW 1710 with $\text{CuK}\alpha$ -radiation. The samples were aged in air for 1000 hours at 525 K or 1025 K. Also some aging experiments were performed at 450 K in H_2O for 5 hours in an autoclave. The grain sizes of polished and thermally etched samples were investigated using a scanning electron microscope (SEM) type JEOL-JSM 35 CF. The grain size was determined according to Mendelsohn /11/. Ceramic densities were measured using the Archimedes technique (in Hg).

III - RESULTS AND DISCUSSION

Sintering behaviour

The ceramic powders had a composition as given in table I. The BET-surfaces of the powders are about 100 m^2/g and there is not much difference between the alkoxide and chloride syntheses. All specimen had a density of 47% of the theoretical one after isostatically pressing at 400 MPa.

In table I the final sintering temperature and time is given after the twostep sintering procedure resulting in a relative density of 97% or more. No difference was observed in the sintering behaviour between the samples prepared by the "chloride" or by the more time consuming "alkoxide" method /9/. The table shows that a relatively low sintering temperature can be obtained if compared with literature. The resulting ceramic grain sizes can be kept smaller, especially when sintered at 1380 K for 70 hours (0.1 μm). These crystallite sizes are in the order of tetragonal microdomain sizes (60 nm) in single crystalline ZY5.8 /12/.

In Fig.1 typical microstructures are shown of polished and thermally etched specimens sintered at 1660 K. It is clear from Fig.1b that ZY11 consists of two different types of grains after sintering at 1660 K: small grains with a size of 0.5 μm and large grains of 2.3 μm (table I).

The ceramic grain sizes obtained in Y-TZP materials are generally smaller if compared with cubic yttria stabilized zirconia prepared by the "alkoxide" method /13/. The grain sizes of cubic ZY17 amount 0.75 μm and 2.5 μm when sintered at 1525 K or 1680 K respectively /13/. The slow grain growth in the sintered tetragonal materials may be due to the t-phase itself or to the lower yttria content, if compared with cubic material. Preliminary Auger experiments on ZY5.5 showed an enrichment of Y at the surface with a factor 5 after a temperature treatment of 48 hours at 1030 K. The same temperature treatment shows for cubic ZY17 an Y segregation to the surface and grain

boundaries with an Y-enrichment factor of 1.8 /14/. It is suggested that the grain growth can be impeded by the fact that Y segregation to the grain-boundary interface keeps up with the grain boundary ("impurity" drag mechanism) /15/. A higher Y-enrichment factor at the grain boundary of Y-TZP may therefore act as a stronger grain-growth inhibitor.

Table I: Sintering and X-ray diffraction results of the investigated materials.

Sample Code	sintering conditions temp.(time)	grain size (μm)	X-ray diffraction*			
			as sawn	525 K 1000 hours	1025 K 1000 hours	450 K 5h.(H ₂ O)
ZY5.5	1525K (3h)	0.2	t;a=5.101(1)	t;a=5.098(1)	t;a=5.100(1)	t;a=5.102(1) +m (0.1)
ZY5.5	1660K (3h)	0.4	t;a=5.097(1)	t;a=5.096(1)	t;a=5.097(1)	m (0.9)
ZY6.1	1380K(70h)	0.1	t;a=5.098(2)	t;a=5.102(2)	t;a=5.096(2)	t;a=5.099(1)
ZY6.1	1660K (3h)	0.4	t;a=5.096(2)	t;a=5.092(2)	t;a=5.088(4)	t;a=5.100(1) +m (0.7)
ZY11	1525K (3h)	0.3	f;a=5.136(1)	f;a=5.137(2)	f;a=5.138(1)	f;a=5.139(2)
ZY11	1660K (3h)	0.5+ 2.3	f;a=5.136(1)	f;a=5.133(2)	f;a=5.137(1)	f;a=5.135(1)

* t: tetragonal phase; the size of the a axis is given in 10^{-10}m ; the standard deviation in the last decimal figure is given in parentheses; the ratio of the tetragonal c and a axes is 1.015 in all cases.

m: monoclinic phase; the intensity ratio $\{I^m(\bar{1}11)+I^m(111)\}/\{I^m(\bar{1}11)+I^m(111)+I^t(111)\}$ is given in parentheses.

f: cubic fluorite phase with a as the lattice constant (10^{-10}m).

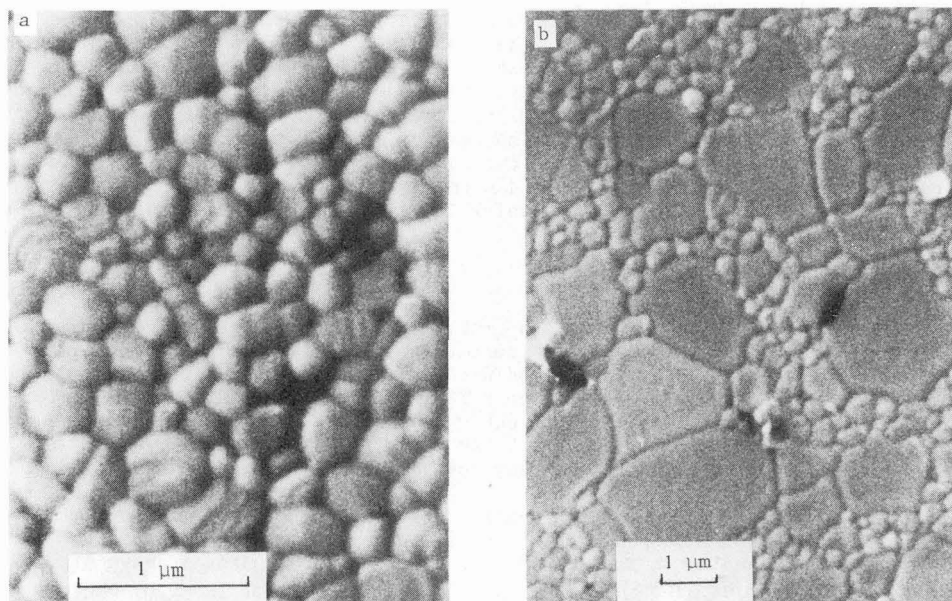


Fig.1 : SEM pictures of polished and thermally etched specimens; sintered at 1660 K (a)ZY 6.1 (b) ZY 11 .

X-ray diffraction

X-Ray diffraction data are given in table I. It is interesting that after sawing of the ceramic no detectable quantities of a monoclinic phase are found. This means that in all cases the ceramic grains are small enough to stabilize the high temperature tetragonal phase to room temperature. This is in agreement with literature /3/. The sample ZY 11 showed some broadening of the 311 and 400 fluorite X-ray diffraction peaks. This may be due to some tetragonal distortion which is very difficult to determine with this composition. In this sample grain growth kinetics proceed in a complicated way. The small grains in Fig.1b "behave" like tetragonal grains while the larger ones resemble cubic grains /13/ (see also previous section). These results may indicate that the tetragonal phase itself exhibit a slower grain growth kinetics. However Nakajima et.al /6/ found two different phases in a ZY 10 material sintered at 1820 K. This specimen consisted of two types of grains. The small grains ($< 1 \mu\text{m}$) had a composition of ZY6.5 as determined by EPMA. These ZY6.5 grains were assigned to the metastable tetragonal phase. The larger grains with sizes of several micrometers had a composition of ZY14 and were cubic. From this literature results one may conclude that the large grains in Fig.1b are cubic grains, which contain more Y_2O_3 than the smaller tetragonal grains.

Table I shows that after aging in air fully tetragonal (or cubic) materials are found. The influence of water on the phase distribution is clearly observed and depends on the ceramic grain size. For the samples aged in air no t \rightarrow m phase transformation was observed. According to Watanabe et al./4/ the critical grain size for ZY5.5 is less than $0.3 \mu\text{m}$ to avoid the t \rightarrow m transformation after aging for 1000 hours at 575K. The critical grain size (D_c) for our ZY5.5 sample is at least $0.4 \mu\text{m}$ in this case. This difference may be due to the impurity level of the samples. Watanabe et al./4/ used commercial ZrO_2 and Y_2O_3 powders which subsequently were mixed and ground by wet ball-milling. These type of powders can contain Al_2O_3 (up to 2 wt%) and SiO_2 /7/. TEM/EDS analysis on these sintered samples indicate an amorphous grain-boundary phase around the t and c grains which is rich in Y_2O_3 , SiO_2 and Al_2O_3 /7/. When the thickness of the amorphous phase layer is smaller the degradation is retarded during aging /7/. The ZY5.5 sample used in this study, which is prepared by the "alkoxide" method, only contains 0.04 wt% Si and 0.03 wt% Al /13/. These small amounts of impurities may enlarge D_c . After aging in water at 450 K (5h) the degradation to a monoclinic Zr is dependent on grain size and Y amount (see Table I). ZY5.5 with a grain size of $0.4 \mu\text{m}$ almost shows complete degradation after water aging. ZY6.1 and ZY11 with about the same grain sizes showed some or no degradation respectively. The dense ceramic sintered at 1380K and a grain size of $0.1 \mu\text{m}$ (ZY6.1) remained fully tetragonal. The t \rightarrow m transformation of all tetragonal grains was reported by Nakajima /6/ for ceramic samples with composition between ZY5 and ZY9.5 after aging under the same conditions (5h at 450K in water). This difference with our results may be due to the fact that in /6/ a relatively high sintering temperature of 1820K is used which leads to larger grains and therefore a faster degradation.

IV-Conclusions

The preparation of Y-TZP by hydrolysis of metal alkoxide or metal chloride compounds result in sinterreactive powders. Dense ceramics with a low impurity level can be obtained after sintering for 70h at 1380K with a resulting grain size of $0.1 \mu\text{m}$. The grain growth rate and grain size of these Y-TZP materials is smaller after sintering at higher temperatures if compared with cubic materials. This may be due to the higher grainboundary enrichment factor of Y in Y-TZP which inhibits grain growth. The investigated materials do not show any degradation after aging in air for 1000 hours at 525K or 1025K. The amount of tetragonal grains which transforms to monoclinic ones during aging in water at 450K for 5 hours decreases with increasing amount of Y and decreasing grain size. No aging is found for a ZrO_2 ceramic with 6.1 mol% $\text{YO}_{1.5}$ and a grain size of $0.1 \mu\text{m}$. So it can be concluded that chemical degradation is suppressed by the use of very fine-grained ceramic.

Acknowledgement.

We would like to thank Mr . H . van Benthem and Mrs . Y . Roman for their assistance with synthesis and X-ray diffraction experiments.

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