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Influence of Oxygen Partial Pressure on the Metastability of Undoped Zirconia Dispersed in Alumina Matrix

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Abstract

The influence of oxygen content in the sintering atmosphere on zirconia phases in alumina–zirconia ceramics was studied. As was demonstrated, in the case of samples sintered in an atmosphere with oxygen partial pressure between $2{\cdot}80 \pm 10^{-5}$ *Pa and* $2{\cdot}80 \times 10^{-2}$ *Pa, 100% of zirconia was found to be in the cubic form. The appearance of transformable cubic zirconia is a result of oxygen vacancy concentration in zirconia. The increase of oxygen partial pressure and decrease of oxygen vacancy concentration leads to a breakdown of the cubic phase which transforms to the t- and/or m-phases. Critical values of oxygen vacancy concentration responsible for the metastability of cubic and tetragonal zirconia were estimated.*

1 Introduction

Transformation toughening in ZrO_2-containing ceramics requires the presence of metastable tetragonal (t) zirconia, so that the toughening obtainable from the stress-induced martensitic transformation to monoclinic (m) symmetry can be realized. As has been shown recently,[1-3] when this type of ceramic is sintered in oxygen-deficient conditions, transformable cubic (c) phase appears, as a result of nonstoichiometry of ZrO_2. The metastability of t- and c-ZrO_2 at low temperatures either in powder state or in compact form was proposed by different theories and hypotheses.[4-1] Unfortunately, the controlling mechanisms responsible for metastability of high-temperature phases of zirconia are still unknown.

The present work is aimed to explain the effect of oxygen content in sintering atmosphere and related oxygen vacancy concentration on c–t inversion in undoped zirconia grains dispersed in alumina matrix.

2 Experimental Methods

The starting material was a powder composition containing : 99·55 wt% Al_2O_3, 0·20 wt% MgO and 0·25 wt% Y_2O_3. Alumina powder (made by CEMAT-Skawina, Poland) was 99·99 wt% pure and the average grain size below 0·5 μm. The remaining two components were of the same purity.

The components of the composition were homogenized for 48 h in a ball mill in distilled water. Then 10 wt% zirconia—obtained from zirconyl chloride by chemical methods described earlier[12]—was added and homogenized for further 48 h. The powders were cold isostatically pressed at 140 MPa into rectangular die (41 × 65 mm). The samples were sintered at 1973 K of 90 min either in a gas furnace (air atmosphere) or in an electric furnace under eleven levels of oxygen partial pressure (p_{O_2}) in sintering atmosphere between $2{\cdot}8 \times 10^{-5}$ Pa and $1{\cdot}07 \times 10^{+4}$ Pa. The values of p_{O_2} were realized by controlled introduction (by using electronic valves) of air into the high-vacuum chamber of the furnace or earlier prepared oxygen–argon gas mixtures.

The critical stress-intensity factor, K_{Ic}, was determined after Evans[13] on notch-beam specimens of configuration described earlier[12] and an Instron TIM type testing machine. The bearing spacing was 36 mm and the rate of loading 0·1 mm min^{-1}.

The bending strength was determined by three-point bending on bars 5 × 5 × 50 mm using the same testing machine, the same rate of loading and bearing spacing. These tests were performed on 15 samples for each composition.

Table 1. Mechanical properties of alumina ceramics containing 10 wt% zirconia

Properties	*Sintering atmosphere*	
	Air	*0·133 mPa vacuum*
	Oxygen partial pressure (Pa)	
	$2{\cdot}1 \times 10^{+4}$	$2{\cdot}8 \times 10^{-5}$
Critical stress-intensity factor, K_{Ic}, MPa $m^{1/2}$	6·60 ± 0·57	8·00 ± 0·67
Bending strength, MPa	324·40 ± 58·7	397·80 ± 28·5
Grindability, mm	0·1	0·01

The measurement of grindability was carried out with a Mackensen blower using 500–630 μm SiC powder, 0·15 MPa pressure and a cell of 28 cm^3 volume. To intensify the abrasion by the grinding powder, the test was repeated three times at the same place on the samples. As a measure of grindability, the depth of the hole blown by the grinding powder in 15 samples for each composition was recorded.

The phase composition of zirconia in each of the free and fractured surfaces ceramics was determined by X-ray diffraction (Siemens diffractometer Kristalloflex 4). The measurements were carried out in the 2Θ-angle 20–160° at 293 K using monochromatized $\mathrm{Cu}K_{\alpha_1}$ radiation (quartz, $(10\bar{1}1)$ reflection Johanson type) in steps of 1/16 deg min^{-1}. The precision of goniometer was tested using an ultrapure silicon powder standard.

The phase content was estimated using integral intensities of the strongest lines taking into account the polarization, Lorentz, structure and multiplicity factors.[14] The lattice parameters were calculated using the least-squares Cohen method.[14]

The loss of oxygen in ZrO_2 of samples sintered in atmospheres with increasing p_{O_2} was estimated by measuring the weight increasing during its reoxidation in air at 1273 K (1000 h). This allows the level of the oxygen vacancy concentration to be determined.

3 Results and Discussion

As can be seen from the data shown in Table 1, the critical stress-intensity factor, K_{Ic}, of ceramics sintered in high vacuum (0·133 mPa) is really higher than that for the air-sintered ceramics. The bending strength and Mackensen's grindability of these ceramics also differ in the same way.

Table 2. Zirconia phases in Al_2O_3–10 wt% ZrO_2 measured from free surface as a function of sintering atmosphere

Sintering atmosphere	*Phases of zirconia (%)*		
	Monoclinic	*Tetragonal*	*Cubic*
Air	16·5	83·5	—
0·133 mPa vacuum	—	—	100

Table 3. X-ray data of c-ZrO_2 in Al_2O_3–10 wt% ZrO_2 sintered in vacuum (free surface)

	2θ, degrees	I/I_0	*h*	*k*	*l*
1	30·12	100	1	1	1
2	34·96	17	2	0	0
3	50·22	32	2	2	0
4	59·74	16	3	1	1
5	62·68	2	2	2	2
6	73·94	1	4	0	0
7	81·76	2	3	3	1
8	84·40	3	4	2	0
9	94·74	1	4	2	2
10	102·68	1	3	3	3
11	125·40	1	5	3	1
12	128·64	<1	6	0	0

The observed differences can be correlated with the presence of zirconia phases in the matrix. In the case of air-sintered samples, 83·5% of zirconia is in the tetragonal form (Table 2).

X-ray analysis of samples sintered in high vacuum indicates 100% presence of the cubic form. The X-ray data of c-ZrO_2 obtained from free surface are listed in Table 3.

As can be seen from the phase diagram of the system Zr–O (Fig. 1) determined by Ruh & Garrett,[15] the presence of c-ZrO_2 at 1973 K (the tetragonal–cubic phase transformation temperature is at 2558 ± 15K) is possible under the conditions of high anion deficiency equal to $2 - x = 1{\cdot}688 - 1{\cdot}740$.

It seems that the appearance of metastable c-ZrO_2 in alumina ceramics is a result of sintering in high vacuum (under very low oxygen partial pressure) accompanied by oxygen nonstoichiometry. Furthermore, the constraint of the alumina matrix prevents the c-phase transforming during cooling from the sintering temperature to room temperature.

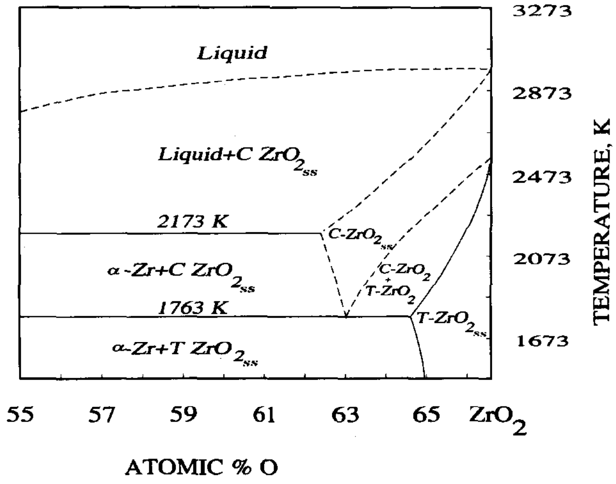

Fig. 1. Phase diagram of the Zr–O system.[15]

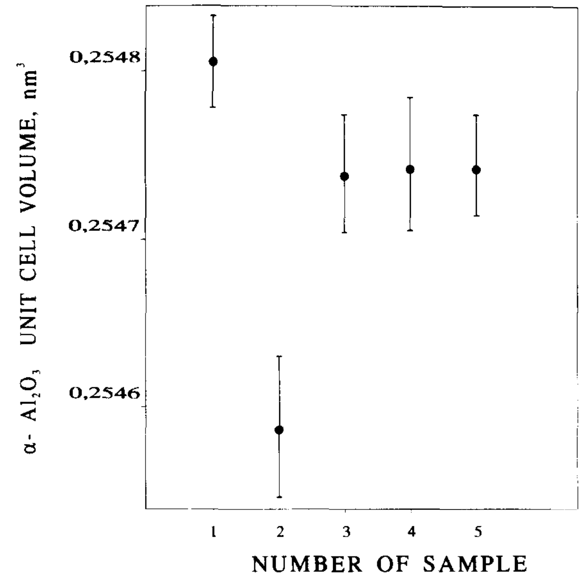

Fig. 2. Volume of α-Al_2O_3 unit cell in Al_2O_3–10 wt% ZrO_2 versus sintering and measuring conditions. The measured samples are: (1) α-Al_2O_3 matrix; (2) free surface of high vacuum-sintered alumina–zirconia ceramics; (3) free surface of air-sintered alumina–zirconia ceramics; (4) fractured surface of high vacuum-sintered alumina–zirconia ceramics; (5) fractured surface of air-sintered alumina–zirconia ceramics.

The presence of the stress field in the ceramics confirms the X-ray results for the α-Al_2O_3 unit cell volume for the alumina matrix with and without zirconia particles sintered in air and in vacuum (Fig. 2). As shown, the largest deformation of the α-Al_2O_3 unit cell is in samples where only the c-phase of ZrO_2 exists. In other samples deformations are relaxed. It should be expected that the particles of c-ZrO_2, when placed in the locally enhanced tensile stress field at the tip of an advancing crack, are freed from the constraint of the matrix and transform to the forms stable at the lower temperature range.

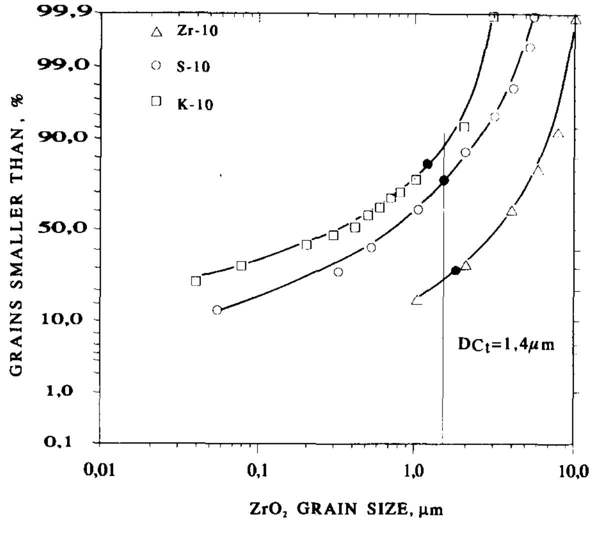

Fig. 3. Zirconia grain-size distribution of air-sintered alumina ceramics containing 10 wt% Zr-type ZrO_2, 10 wt% S-type ZrO_2 and 10 wt% K-type ZrO_2.[2] ●, Content of the finest ZrO_2 grains corresponding to the content of tetragonal form.

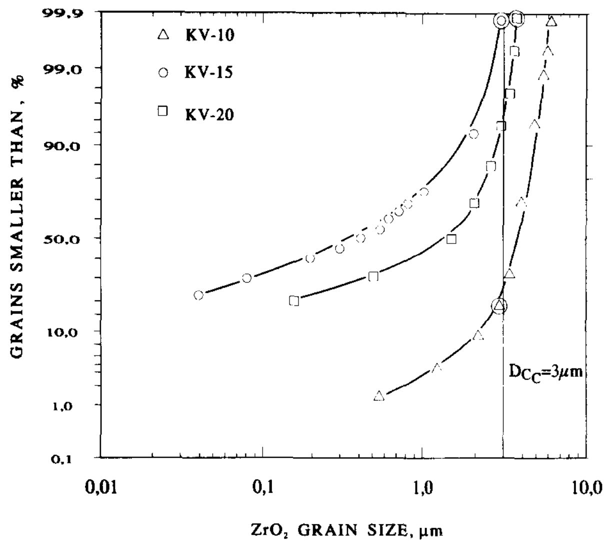

Fig. 4. Zirconia grain-size distribution of high vacuum-sintered alumina ceramics containing 10 wt%, 15 wt% and 20 wt% ZrO_2 of K-type (obtained by chemical method).[2] ○, Content of the finest ZrO_2 grains corresponding to the content of cubic form.

Tetragonal and monoclinic zirconia on fractured surfaces of vacuum-sintered ceramics show that the cubic form is the transformable phase and is responsible for enhancing the toughness of the ceramics.[3] This phase then appears to play the same role as the tetragonal form in the case of ceramics sintered in an oxidizing atmosphere.

The critical grain size of t-ZrO_2 inclusions in the case of air-sintered ceramics is $d_{\mathrm{ct}} = 1{\cdot}4$ μm (Fig. 3).[12] This value was estimated by comparison of ZrO_2 grain size distribution with the content of retained t-ZrO_2. A similar estimation made for samples sintered in high vacuum (Fig. 4) indicates an increase of the critical grain-size inclusion for c-ZrO_2 up to a value of $d_{\mathrm{Cc}} = 3{\cdot}0$ μm.[2] Obviously, the reason for the enhancement of the critical grain-size inclusion could be found in the non-stoichiometry of ZrO_2.

According to the present results, if the oxygen vacancy concentration plays a decisive role in the metastability of c-phase, it would then be possible to transform it to t- or m-phase, due to the reduction of the vacancy concentration in the ZrO_2 lattice as a result of sintering alumina–zirconia ceramics in atmospheres richer in oxygen. After Kountouros *et al.*,[11] a critical minimum and a critical maximum vacancy concentration for each ZrO_2 phase should also exist.

As can be seen from Table 4, in the p_{O_2} range between $2{\cdot}80 \times 10^{-5}$ and $2{\cdot}80 \times 10^{-2}$ Pa, the cubic form is the only phase of zirconia. However, an increase of oxygen content in the sintering atmosphere causes changes in the lattice parameters of the c-phase (see Table 5 and Fig. 5). An increase of the constant a values and the unit cell volume is observed. These results seem to be an effect of oxygen loss decrease from the zirconia structure

Table 4. Zirconia phases in Al_2O_3–10 wt% ZrO_2 measured from free surface as a function of oxygen content in sintering atmosphere

Oxygen partial pressure (Pa)	*Oxygen vacancy concentration (%)*	*Phases of ZrO_2 (%)*		
		m	*t*	*c*
$2{\cdot}80 \times 10^{-5}$	14·85	—	—	100
$2{\cdot}80 \times 10^{-4}$	13·65	—	—	100
$2{\cdot}80 \times 10^{-3}$	12·90	—	—	100
$2{\cdot}80 \times 10^{-2}$	9·13	—	—	100
$1{\cdot}40 \times 10^{-1}$	5·25	—	20·6	79·4
$1{\cdot}80 \times 10^{-1}$	3·12	Traces	100	—
$1{\cdot}07 \times 10^{0}$	0·45	5·6	94·4	—
$1{\cdot}00 \times 10^{1}$	0·145	7·0	93·0	—
$0{\cdot}85 \times 10^{2}$	0·05	8·0	92·0	—
$1{\cdot}39 \times 10^{3}$	0	8·4	91·6	—
$1{\cdot}07 \times 10^{4}$	0	10·6	89·4	—
$2{\cdot}10 \times 10^{4}$	0	16·5	83·5	—

Table 5. Lattice parameters of c-ZrO_2 as a function of oxygen content in sintering atmosphere

Oxygen partial pressure (Pa)	*Lattice constants a (nm)*	*Volume of unit cell (nm^3)*
$2{\cdot}80 \times 10^{-5}$	0·512 49 ± 0·000 16	0·134 604 ± 0·000 129
$2{\cdot}80 \times 10^{-4}$	0·512 98 ± 0·000 11	0·134 989 ± 0·000 089
$2{\cdot}80 \times 10^{-3}$	0·513 19 ± 0·000 08	0·135 155 ± 0·000 063
$2{\cdot}80 \times 10^{-2}$	0·514 63 ± 0·000 02	0·136 302 ± 0·000 017
$1{\cdot}40 \times 10^{-1}$	0·514 14 ± 0·000 32	0·135 908 ± 0·000 253

during sintering in less oxygen-deficient atmospheres. The decrease of the X-ray mean half breadth (Fig. 6) and lattice parameter scattering from a value of 0·000 16 to 0·000 02 (see Table 5) also indicates an improvement in the c-phase structure.

When the oxygen content in the sintering atmosphere decreases below the critical p_{O_2} value for the c-phase. t-ZrO_2 appears and coexists with c-ZrO_2 (see Table 4—$p_{O_2} = 1{\cdot}40 \times 10^{-1}$Pa).

In the case of $1{\cdot}80 \times 10^{-1}$ Pa oxygen pressure t-ZrO_2 is the only form of zirconia present, but from $1{\cdot}07 \times 10^{0}$ Pa oxygen pressure is accompanied by m-ZrO_2. It indicates that the critical minimum vacancy concentration for t-phase has been exceeded. A further increase of the oxygen content (air atmosphere) leads to an increase of m–ZrO_2 up to 16·5%.

In a similar way to the cubic form, an increase of the oxygen content in the sintering atmosphere influences the lattice parameters of the t- and m-phases (Tables 6 and 7). As can be seen from Fig. 7 the tetragonality (*c/a* axial ratio) of t-ZrO_2 considerably improves. An increase of the m-phase unit volume is also observed (Table 7). Figures 8 and 9 illustrate the changes of zirconia phase composition with oxygen content in a sintering atmosphere.

The presence of the stress field in samples with c-ZrO_2 is also confirmed by XRD results of the α-Al_2O_3 unit cell volume of samples sintered in p_{O_2} atmospheres between $2{\cdot}80 \times 10^{-4}$ and $2{\cdot}80 \times 10^{-2}$ Pa (see Fig. 10). Calculated deformation of α-Al_2O_3 unit cell is equal to 0·2% (see Table 8). In other samples with t-ZrO_2 the unit cell volume becomes similar to values typical for alumina ceramics without zirconia. In this way, t-ZrO_2 seems to be a factor responsible for the relaxation of stresses caused by c-ZrO_2 in the matrix.

Table 6. Lattice parameters of t-ZrO_2 as a function of oxygen content in sintering atmosphere

Oxygen partial pressure (Pa)	*Lattice constants (nm)*		*c/a*	*Volume of unit cell (nm^3)*
	a	*c*		
$1{\cdot}40 \times 10^{-1}$	0·360 661 ± 0·000 059	0·518 793 ± 0·000 087	1·438 45 ± 0·000 48	0·067 482 72 ± 0·000 033 63
$1{\cdot}80 \times 10^{-1}$	0·360 265 ± 0·000 021	0·519 391 ± 0·000 039	1·441 69 ± 0·000 19	0·067 412 20 ± 0·000 012 89
$1{\cdot}07 \times 10^{0}$	0·360 275 ± 0·000 017	0·519 365 ± 0·000 039	1·441 58 ± 0·000 18	0·067 412 52 ± 0·000 011 28
$1{\cdot}00 \times 10^{1}$	0·360 271 ± 0·000 016	0·519 382 ± 0·000 041	1·441 64 ± 0·000 18	0·067 410 31 ± 0·000 011 09
$0{\cdot}85 \times 10^{2}$	0·359 981 ± 0·000 156	0·519 848 ± 0·000 038	1·444 10 ± 0·000 17	0·067 365 3 ± 0·000 010 7
$1{\cdot}39 \times 10^{3}$	0·360 409 ± 0·000 188	0·519 299 ± 0·000 049	1·440 86 ± 0·000 21	0·067 454 3 ± 0·000 013 4
$1{\cdot}07 \times 10^{4}$	0·360 409 ± 0·000 042	0·519 006 ± 0·000 070	1·440 05 ± 0·000 36	0·067 416 2 ± 0·000 024 9
$2{\cdot}10 \times 10^{4}$	0·360 159 ± 0·000 092	0·519 340 ± 0·000 016	1·441 97 ± 0·001 73	0·067 366 5 ± 0·000 055 2

Table 7. Lattice parameters of m-ZrO_2 as a function of oxygen content in sintering atmosphere

Oxygen partial pressure (Pa)	*Lattice constants (nm)*			*Volume of unit cell (nm^3)*
	a	*b*	*c*	
$1{\cdot}07 \times 10^{0}$	0·513 253 ± 0·000 408	0·517 343 ± 0·000 339	0·530 255 ± 0·000 425	0·138 998 21 ± 0·000 328 81
$1{\cdot}00 \times 10^{1}$	0·513 438 ± 0·000 795	0·516 957 ± 0·001 005	0·530 112 ± 0·000 498	0·139 011 33 ± 0·000 637 25
$0{\cdot}85 \times 10^{2}$	0·513 476 ± 0·000 277	0·518 789 ± 0·000 433	0·529 819 ± 0·000 303	0·139 437 45 ± 0·000 286 96
$1{\cdot}39 \times 10^{3}$	0·513 435 ± 0·000 565	0·517 513 ± 0·000 893	0·530 798 ± 0·000 443 8	0·139 267 98 ± 0·000 529 16
$2{\cdot}10 \times 10^{4}$	0·515 450 ± 0·000 110	0·530 900 ± 0·000 110	0·518 390 ± 0·000 110	0·140 006 12 ± 0·000 148 50

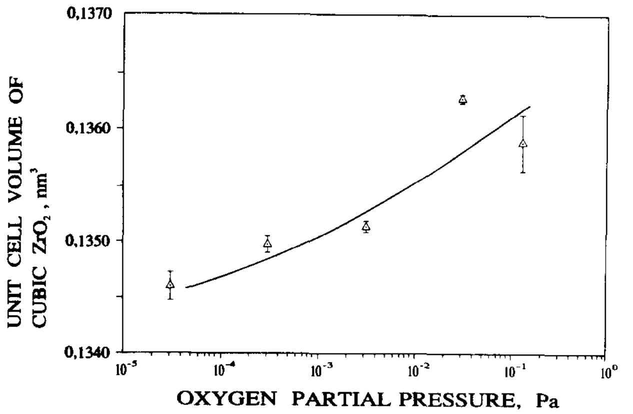

Fig. 5. Cubic zirconia unit cell volume as a function of oxygen content in sintering atmosphere.

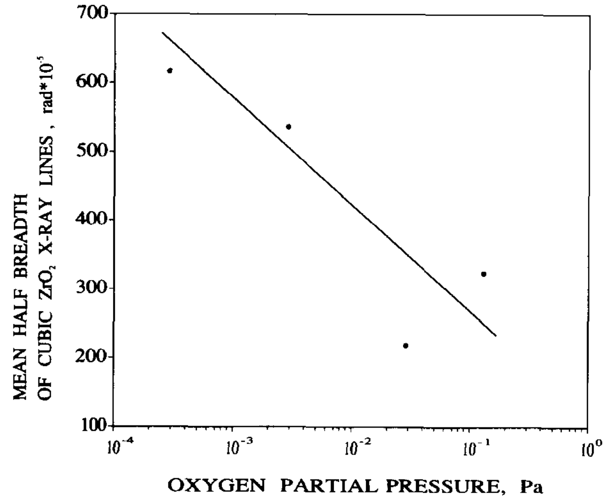

Fig. 6. Mean half breadth of X-ray lines of c-ZrO$_2$ as a function of oxygen content in sintering atmosphere.

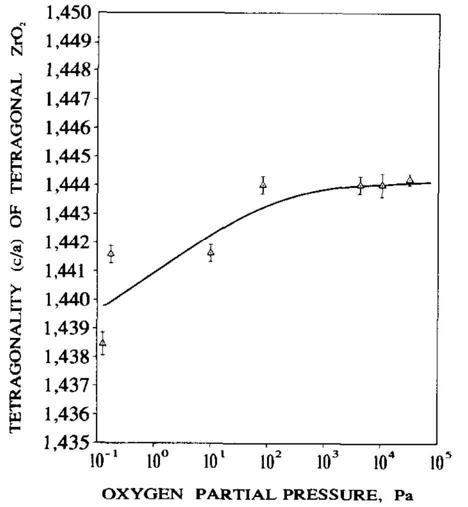

Fig. 7. Tetragonality (*c*/*a*) of t-ZrO$_2$ as a function of oxygen content in sintering atmosphere.

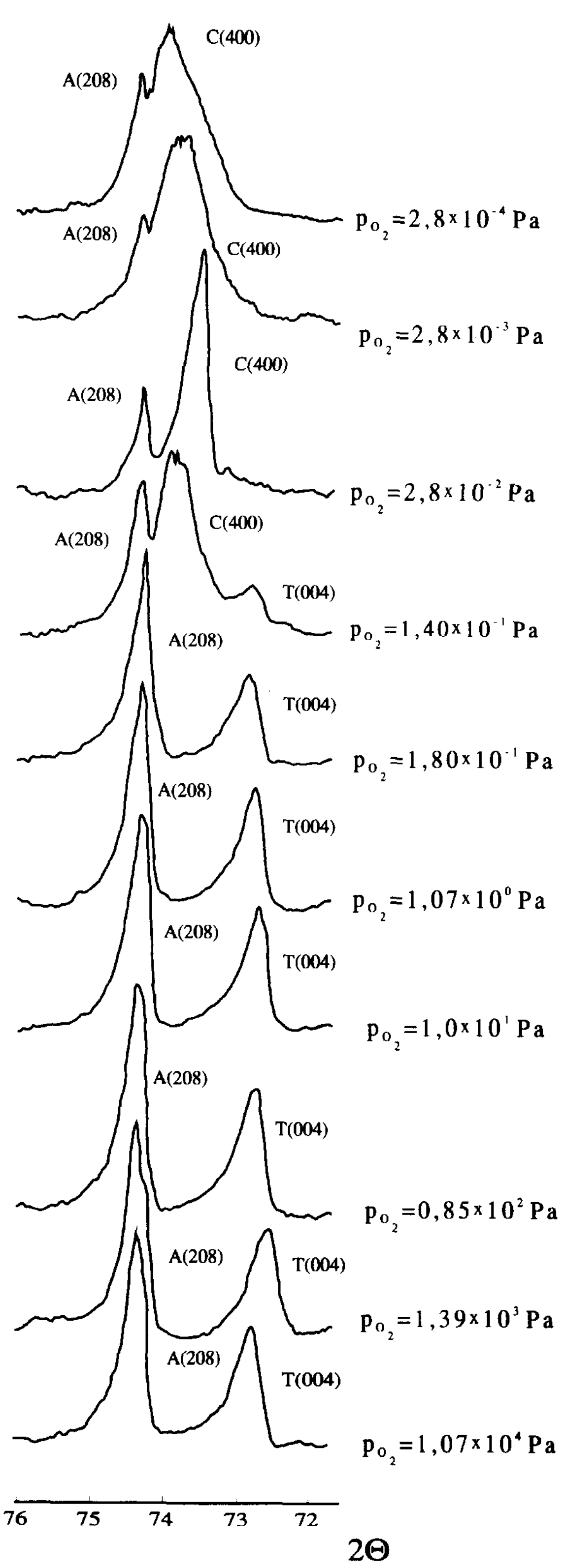

Fig. 8. Changes of XRD profiles of Al_2O_3-10 wt% ZrO_2 ceramics (2Θ = 72–76°) as a function of oxygen content in sintering atmosphere. A = α-Al_2O_3, C = cubic, T = tetragonal zirconia respectively.

Samples sintered in p_{O_2} atmosphere equal to 1·40 × 10^{-1} Pa, where 20·6% of the tetragonal form coexists with 79·4% of the c-phase, are a good confirmation of the previously mentioned thesis.

The main conclusion concerning the influence of oxygen vacancy concentration on the metastability of zirconia phases comes from thermogravimetric determinations. In this case, samples sintered in oxygen-deficient conditions were reoxidized by reheating in air at 1273 K for 1000 h and an increase of their weight was recorded. Results of oxygen vacancy concentration in zirconia are listed in Table 4.

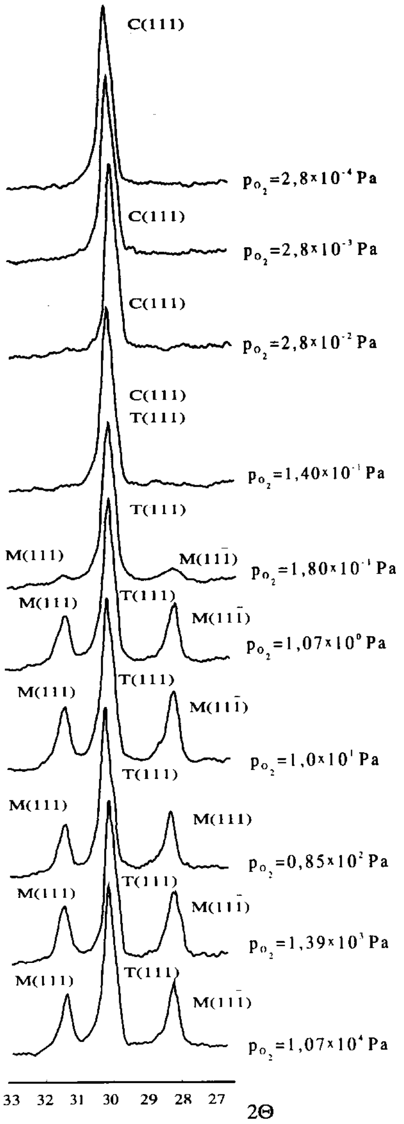

Fig. 9. Changes of XRD profiles of Al_2O_3–10 wt% ZrO_2 ceramics (2Θ = 27–33°) as a function of oxygen content in sintering atmosphere. C = Cubic, T = tetragonal and M = monoclinic zirconia respectively.

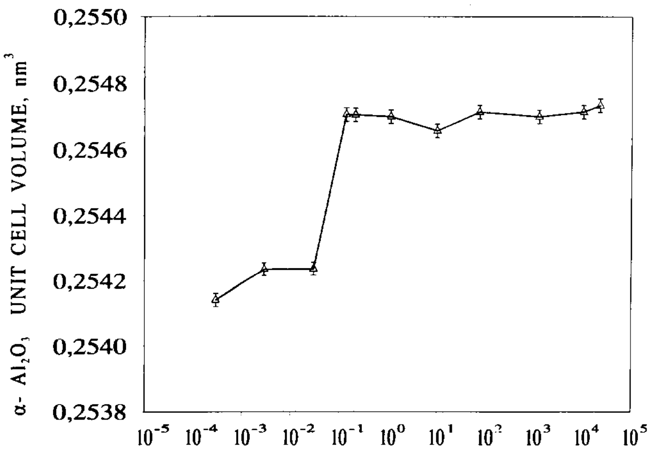

Fig. 10. Changes of α-Al_2O_3 unit cell volume in Al_2O_3–10 wt% ZrO_2 ceramics as a function of oxygen content in sintering atmosphere.

Table 8. Changes of unit cell volume and mean half breadth X-ray lines of αAl_2O_3 in Al_2O_3–10 wt% ZrO_2 as a function of oxygen content in sintering atmosphere

Oxygen partial pressure (Pa)	*Change of unit cell volume ΔV/V (%)*	*Mean half breadth (rad)*
$2{\cdot}80 \times 10^{-4}$	0·225	0·002 69
$2{\cdot}80 \times 10^{-3}$	0·182	0·002 75
$2{\cdot}80 \times 10^{-2}$	0·183	0·002 19
$1{\cdot}40 \times 10^{-1}$	0·002	0·001 35
$1{\cdot}80 \times 10^{-1}$	0·000	0·001 47
$1{\cdot}07 \times 10^{0}$	0·005	0·001 62
$1{\cdot}00 \times 10^{1}$	0·022	0·001 53
$0{\cdot}85 \times 10^{2}$	0·001	0·001 77
$1{\cdot}39 \times 10^{3}$	0·003	0·001 64

As was shown, the cubic form is the only phase of zirconia which exists in the oxygen vacancy concentration between 14·85 and 9·13%, that corresponds to a oxygen partial pressure in the sintering atmosphere in the range $2{\cdot}80 \times 10^{-5}$ Pa to $2{\cdot}80 \times 10^{-2}$ Pa. When the oxygen content increases to $1{\cdot}40 \times 10^{-1}$ Pa and the oxygen vacancy concentration decreases to a value of 5·25%, c-ZrO_2 coexists with the tetragonal form. Complete inversion to t-ZrO_2 is observed for 3·12% of oxygen vacancy content and this value seems to be a critical minimum value of oxygen vacancy concentration for this phase. Increasing the oxygen content in the sintering atmosphere the volume

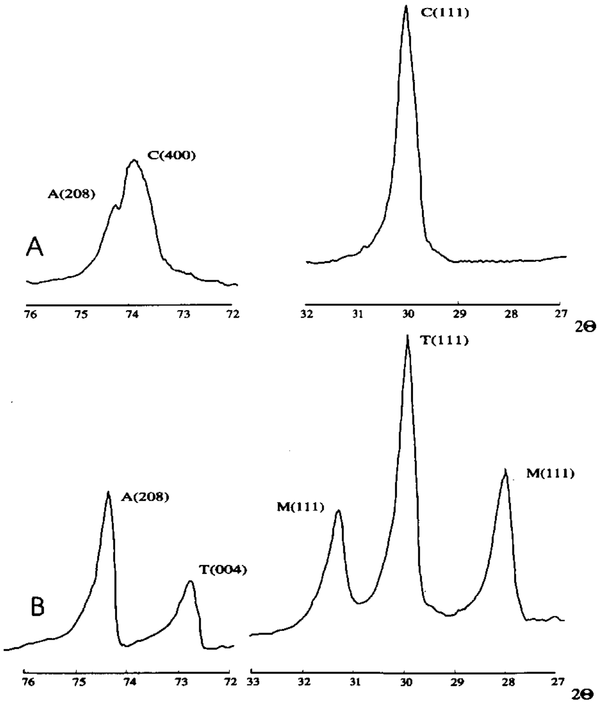

Fig. 11. Changes of zirconia phase composition as result of reoxidation heating of alumina–zirconia ceramics. A, Sample of ceramics sintered in atmosphere with oxygen partial pressure equalled $2{\cdot}80 \times 10^{-3}$ Pa; B, the same sample after reoxidation heating at 1273K for 1000 h in air. Explanation: A = α-Al_2O_3, C = cubic, T = tetragonal and M = monoclinic zirconia respectively.

of m-ZrO_2 increases also up to value of 16·5%, typical for samples sintered in oxidizing (air) atmosphere.

These results confirm the earlier thesis[11] that the oxygen vacancies in zirconia are mainly responsible for the metastability of c- and t-phases. Decreasing the oxygen vacancy concentration with an increase of the oxygen partial pressure in the sintering atmosphere below the critical minimum value leads to a breakdown of the c-phase which transforms to the t- and/or m-phase (see Fig. 11).

4 Conclusions

This study demonstrated that the oxygen content in a sintering atmosphere clearly influences the phase composition of undoped zirconia grains dispersed in alumina matrix.

In the case of ceramics sintered in atmospheres with oxygen partial pressure between $2{\cdot}80 \times 10^{-5}$ Pa and $2{\cdot}80 \times 10^{-2}$ Pa, 100% of zirconia is in the cubic form. The appearance of transformable c-ZrO_2 is a result of oxygen vacancy concentration in zirconia. The concentration of oxygen vacancy equal to 9% seems to be the critical minimum value for this phase. Decreasing the oxygen vacancy concentration, as a result of increasing the oxygen content in the sintering atmosphere, below 9%, causes an increase of the t-ZrO_2 content. The critical value of the oxygen vacancy concentration for the tetragonal form is 3%. A further increase of the oxygen content to $1{\cdot}07 \times 10^{0}$ Pa and a decrease of oxygen vacancy concentration to 0·5% lead to the appearance of m-ZrO_2.

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