ZIRCONIA BASED ORGANIC PRECURSOR INFILTRATION AS A METHOD FOR PREPARATION OF ZTA CERAMICS

PART I - INFILTRATION

DUŠAN GALUSEK, JÁN MAJLING

Department of Ceramics, Slovak Technical University,
Radlinského 9, SK-812 37 Bratislava, Slovak Republic

Received 2. 10. 1995

ZTA ceramics was prepared by liquid infiltration of alumina matrix with two different organic precursors of zirconia. The infiltration procedure, precursor pyrolysis and the phase development during the crystallisation of precipitated zirconia is described. Optimisation of the heating schedule during the precursor pyrolysis as well as optimisation of the maximal heating temperature with respect to the maximal content of tetragonal zirconia is also performed. Dense Al_2O_3 *with high volume fraction of tetragonal zirconia (up to 50 vol. % of* ZrO_2 *in the matrix) homogeneously distributed in the bulk of the alumina body was prepared.*

INTRODUCTION

Zirconia toughened alumina (ZTA) is a promising material for the preparation of ceramic parts requiring high hardness, toughness and abrasive resistance. To obtain optimum mechanical properties of such a ceramic composite, especially its fracture toughness, it is necessary to prepare an alumina matrix with high volume fraction of fine and homogeneously distributed tetragonal zirconia particles with slightly sub-critical dimensions [1]. The sub-critical size of zirconia grains allows their transformation to stable monoclinic modification under the stress field of the propagating crack tip, [2]. The present paper deals with a novel route - zirconia based organic precursor infiltration of Al_2O_3 matrix.

Liquid infiltration is a method frequently used for preparation of multiphase ceramic materials, as alumina-mullite [3, 4], TZP (tetragonal zirconia polycrystals) [5], ZrO_2-Al_2O_3 [6], RBSN (reaction bounded silicon nitride) [7] and AlN-Al [8] composites. The method is based on the infiltration of a liquid phase - a source of secondary phase - into the pre-sintered monophase porous ceramic matrix. Then follows the decomposition of the infiltrant and precipitation of zirconia particles in the matrix. By subsequent densification of the two-phase body it is possible to obtain the ZTA composite with homogeneously distributed zirconia particles at the grain boundaries and at triple points of the alumina matrix.

The above described method brings some benefits compared to the commonly used powder route of ceramic composites preparation:

1. Preparation of only monophase porous ceramic matrix is necessary, i.e. problems with homogeneous mixing of several components in multicomponent systems can be avoided.
2. Distribution of the secondary phase(s) depends on the pore distribution of the pre-sintered monophase ceramic matrix. A carefully prepared matrix with well defined pore distribution is a prerequisite for homogeneous distribution of secondary phase.
3. The density of ceramic green body increases after infiltration due to filling of the open pores with products of thermal decomposition of the infiltrant. Higher green density results in lower shrinkage after sintering so that better volume and shape control of final product can be achieved.

Present paper deals with complete description of infiltration procedure, for two different solutions of organic precursors, as well as with optimisation of processing parameters during sample preparation. Organic precursor pyrolysis and crystallisation of zirconia precipitated within the pores of alumina matrix during precursor decomposition is also studied. The present work was aimed at the preparation of crack-free, three-phase bulk material with a high volume fraction of fine and homogeneously distributed tetragonal zirconia particles.

EXPERIMENTAL PART

Three different alumina powders Martoxid ZS203*), Baikalox SM8**) and Baikalox CR6AS2**) were used for porous alumina matrix preparation. Designation and characterisation of used powders are listed in Table I. Schematic description of the processing is shown in Figure 1.

Table I. The designation and characterisation of starting powders used for sample preparation

Sample	Symbol	Mean grain size (μm)	Impurities
Martoxid ZS-203	M203	2	Σ(Si, Fe, Ti, Ca, P) < 0.2 %
Baikalox CR6AS2	BCR6	0.6	Σ(Si, Fe, K, Na, Ca) < 0.1 %
Baikalox SM8	BSM8	0.2	Σ(Si, Fe, K, Na, Ca) < 0.1 %

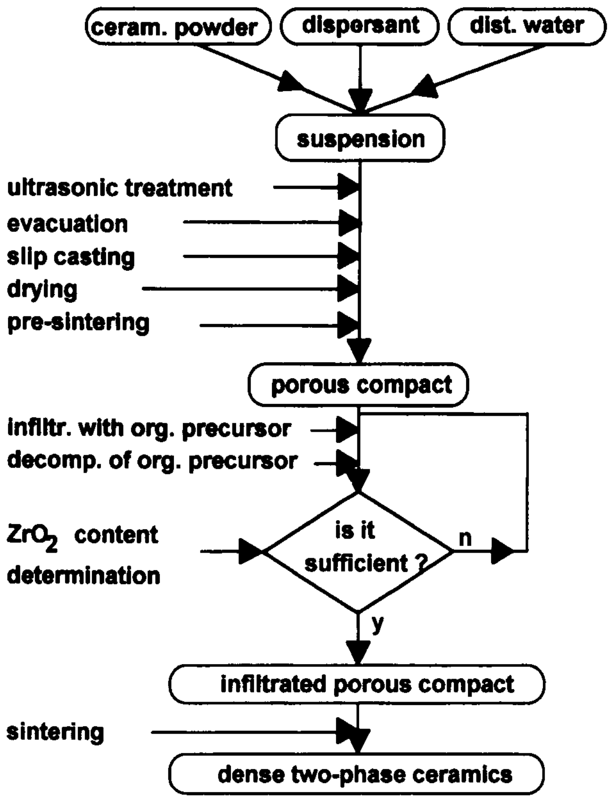


Figure 1. Processing route used for sample preparation

Alumina powder was mixed with distilled water and an appropriate amount of dispersant***) to prepare a suspension containing 50 wt. % of alumina and 1 wt. % of dispersant. The suspension was then ultrasonically treated for 20 minutes to remove soft agglomerates, evacuated to remove bubbles of entrapped air and slip casted to the form put on a plaster of Paris plate. Rectangular bars with dimensions of 5 × 5 × 40 mm were formed. After removing the superfluous water the bars were dried for 24 hours at room temperature and subsequently for 2 hours at 120 °C. Porous alumina green compacts were then pre-sintered at different temperatures (Table II) for 60 minutes (heating rate 10 °C min^{-1}) in order to obtain the desired open porosity network and mechanical strength. Certain level of pre-sintered specimen strength is necessary for comfortable manipulation with the sample and because the destruction of the porous compact by capillary forces during infiltration must be avoided. Sufficient volume fraction and distribution of open pores within the whole body allowed a good penetration of the infiltrant. Temperatures used for pre-sintering and the porosity of different samples are listed in Table II. Pore size distribution and porosity of pre-sintered matrix was measured using mercury porosimetry (Carlo Erba 1500).

Table II. The pre-sintering temperature used and the porosity of pre-sintered alumina matrix obtained

Sample	*T* (°C)	Porosity (%)
M203	1200	40.0
BCR6	750	50.0
BSM8	800	44.0

Porous pre-sintered matrices were infiltered with two different organic precursors of zirconia - water solution of zirconium acetate ($Zr(OOC\text{-}CH_3)_4$, equivalent content of ZrO_2 18 %, abbreviation ZrAc) and the solution of zirconium *n*-propoxide in *n*-propanol ($Zr(O\text{-}(CH_2)_2\text{-}CH_3)_4$, equivalent zirconia content 28 %, ZrPr).

In order to avoid air closure within the matrix, the penetration of the infiltrant into the matrix was secured by capillary forces from the bottom of the sample. (See Figure 2) After filling of open matrix pores with the precursor, the infiltrant was thermally decomposed at

---

*) Martinswerk GmbH, Germany

**) Baikowski, France

***) SOKRAT 32A, Chemické závody Sokolov, Czech Republic temperature 700 °C for 60 minutes. DTA and DTG measurements (Derivatograph type 3427) of infiltered specimens were performed in the temperature range from 20 to 1000 °C with the heating rate of 5 °C min^{-1}, in order to assess the heating regime for pyrolysis. The secondary phases precipitated from the precursor during its thermal decomposition and crystallisation were determined by X-ray diffraction. The real content of zirconia in the matrix was calculated from the weight gain of matrices containing the precipitated zirconia. Concentration profile of zirconia was measured on the polished cross sections of the samples sintered 60 minutes at 1500 °C, heating rate 10 °C min^{-1}, using an X-ray microanalyser JEOL, model JXA 840 A. The analysed cross sections were perpendicular to the longest axis of the specimen. Multiple infiltration was used to obtain higher zirconia contents.

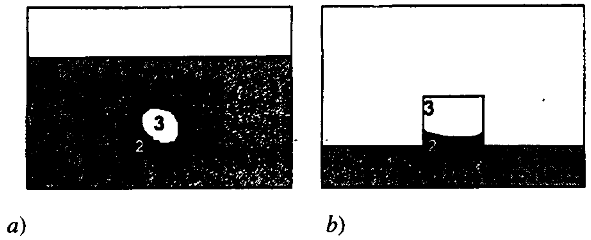


Figure 2. Arrangement of an infiltration experiment
a) - Arrangement which can cause the closure of air bubbles within the matrix; *b)* - Arrangement which allows to avoid the air closure; 1. - Liquid precursor, 2. - Porous compact saturated with the precursor, 3. - Porous compact

RESULTS AND DISCUSSION

Infiltration

Penetration depth of a liquid into the system of continuous pore channels in a porous compact can be described by the Washburn's equation [7,9,11]:

$$x^2 = \frac{\gamma D t \cos\Theta}{4\eta} \qquad (1)$$

where x - depth of penetration, γ - surface tension of the infiltrant, D - equivalent diameter of pore channels, t - time, Θ - wetting angle, η - viscosity of the infiltrant.

For a defined system the viscosity, surface tension, wetting angle and equivalent diameter of pores are constant. Then it can be concluded, that the penetration depth of a liquid is directly proportional to the square root of the infiltration time. In the present work it was experimentally determined that for infiltration of the alumina matrix with zirconium propoxide and zirconium acetate, the velocity of penetration could be described by the Washburn's equation only until approx. 80 % of the pores were filled with the precursor. To fill the alumina matrix completely, longer times are necessary, than it is predicted from the equation (1) (Figure 3). The Washburn equation has been derived for an ideal liquid and semi-infinite porous compact, thus it usually underestimates infiltration times in real systems [10]. However, for zirconium propoxide also other mechanisms, especially the partial hydrolysis of the precursor during infiltration contribute to changes in system parameters. Hydrolysis causes changes in the viscosity of the infiltrant, its wetting angle as well as the geometry of the pore channels by precipitation of products of hydrolysis within the pores. This fact, together with higher viscosity of zirconium propoxide resulted in one order of magnitude longer infiltration time comparing to zirconium acetate (12 hours and 10 minutes respectively, see Figures 3*a*, 3*c*).

For multiple infiltration, a decrease in the rate of infiltration for increasing number of infiltrations was observed. (Figures 3*a*, 3*b*) Prolongation of the infiltration time after the first infiltration is linked with the changes in the wetting behaviour of the system due to the presence of precipitated zirconia on the surface of alumina grains. Further decrease of infiltration rate for the fourth infiltration cycle can be explained by changes in geometry of the pore channels, especially by closure of the pore channels with precipitated particles of zirconia.

The evidence about pore closure in alumina matrix was obtained from the pore size distribution measurements (mercury porosimetry) after each infiltration cycle. The closure of the open pores occurred most readily in samples with the finest microstructure (BSM8). For example, the volume of open pores in BSM8 sample decreased from 0.139 $cm^3\ g^{-1}$ after the first infiltration to 0.133 $cm^3\ g^{-1}$ after second infiltration. After the third infiltration the volume of open pores decreased to 0.118 $cm^3\ g^{-1}$ and remained nearly constant after both the fourth and fifth infiltration (0.114 and 0.112 $cm^3\ g^{-1}$ respectively). In addition, the pores with the size below 16 nm disappeared. It is obvious, that after the third infiltration these pores were closed with the precipitated zirconia and the total pore area diminished.

An influence of pores closure on the amount of zirconia precipitated after single infiltration cycle as well as on the cumulative zirconia content in the matrix was determined (Figures 4, 5). From the Figure 4 it is obvious that the weight fraction of zirconia precipitated in the matrix decreased after each infiltration cycle. It can also be seen, that after the initial slow decrease, the amount of precipitated zirconia fell strongly after the fourth infiltration cycle. This is true especially for the BSM8 and BCR6 matrices and ZrPr infiltrant. For BSM8

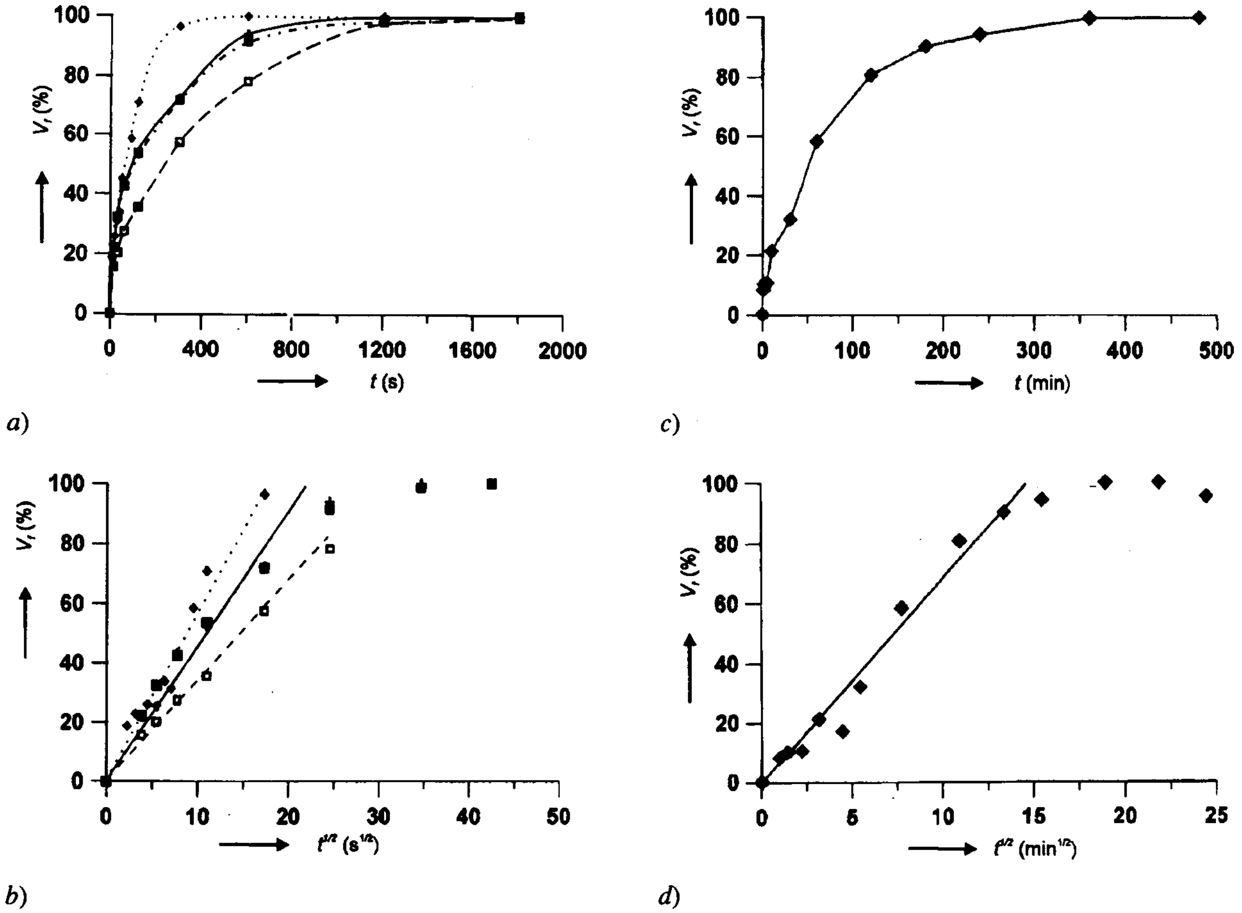


Figure 3. Penetration depth of the liquid precursor as a function of infiltration time and a square root of the infiltration time for BSM8 matrix and ZrAc precursor *a*), *b*) and for BSM8 matrix and ZrPr precursor *c*), *d*)
t - infiltration time; V_f - portion of the porosity filled with infiltrant; ◆ - 1. inf.; ■ - 2. inf.; + - 3. inf.; □ - 4. inf.

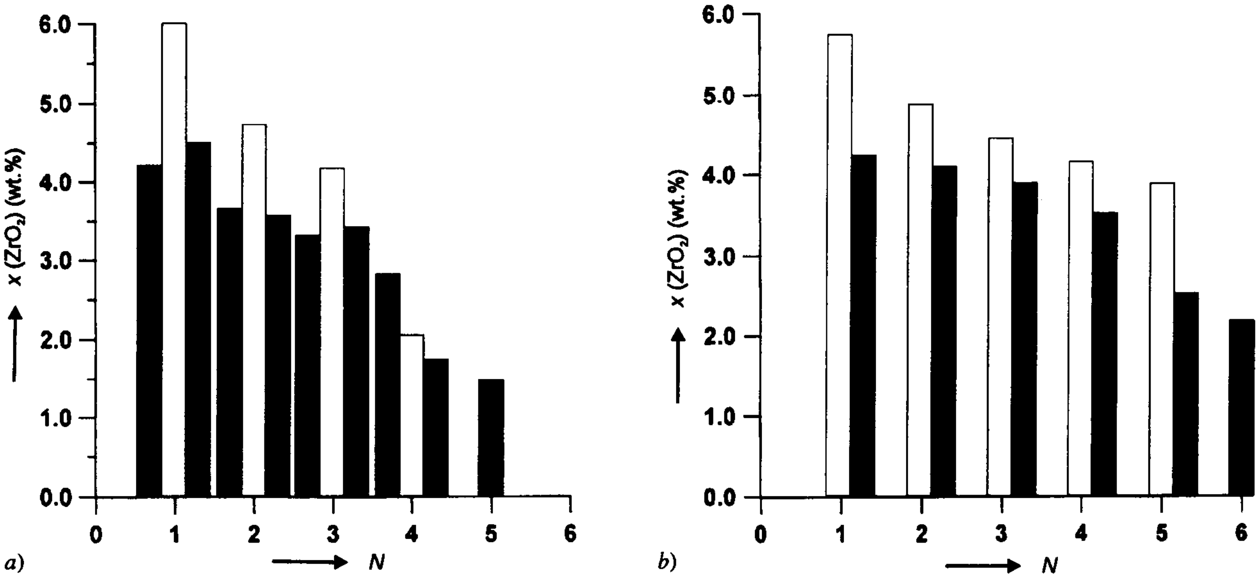


Figure 4. The amount of zirconia introduced into the matrix in single infiltration cycle as a function of the number of infiltrations - ZrPr; *b*) - ZrAc; *N* - number of infiltrations; *x* - amount of zirconia introduced by the *N*-th infiltration; ▨ - M2O3, □ - BCR6, - BSM8

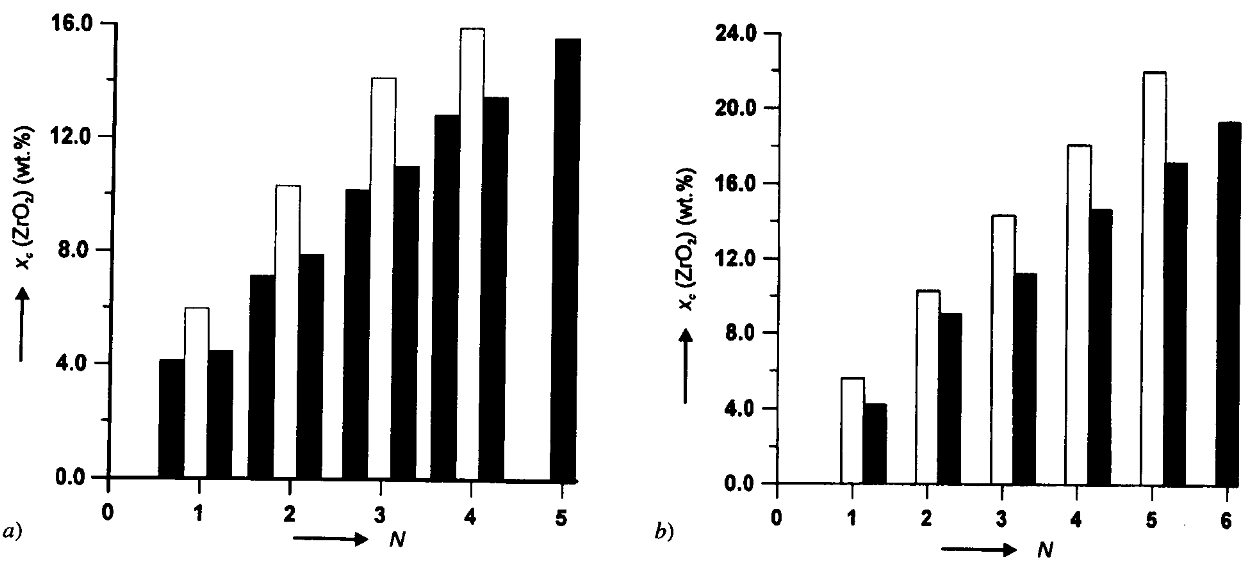


Figure 5. Cumulative ZrO_2 content versus number of infiltrations

a) - ZrPr; *b)* - ZrAc; *N* - number of infiltrations; $x_c(ZrO_2)$ - cumulative zirconia content; ▨ - M203, ☐ - BCR6, ■ - BSM8

matrix and ZrAc infiltrant this effect is observed only after the fifth infiltration. These results are in accord with the results of pore size distribution measurements, showing closing of the pores with the size below 16 nm after the third infiltration for the BSM8-ZrPr system. On the other hand, for M203 matrix the introduced amount of zirconia decreased only slightly with further infiltration cycles. The M203 powder with mean grain size 2 μm creates a coarse microstructure with wide pore channels. As it can be seen from Figure 6., the size of the zirconia precipitates is almost negligible with respect to the size of the pores, i.e. the pore channels remain without barriers for further liquid penetration and closure of the open pores does not occur.

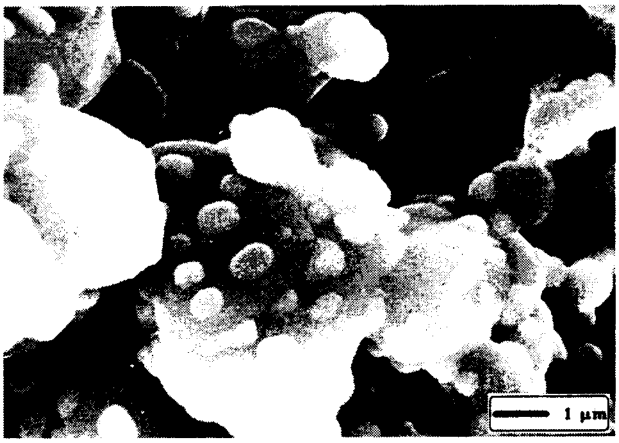


Figure 6. Fracture surface of pre-sintered matrix M203 with precipitated ZrO_2 particles

Different volume fraction of open pores in pre-sintered matrices (see Table II) resulted also in different amount of ZrO_2 precipitated in the matrix after each infiltration, as well as in different cumulative zirconia contents. The amount of ZrO_2 after the first infiltration varied from 4 wt.% (M203, initial porosity 40 vol.%) to 6 wt.% (BCR6, 50 vol.% of initial porosity.) Maximal cumulative zirconia content achieved for BCR6 matrix after seventh infiltration of ZrAc was 21 wt.%.

Decomposition of precursors

During the thermal decomposition of the precursors we attempted:

1. To avoid cracking of ceramic matrix due to gas evolution during pyrolysis.
2. To reach maximal content of tetragonal zirconia.

To avoid cracking, heating schedule during the pyrolysis must be optimised. DTA and DTG measurements of precursor in-situ pyrolysis were performed to determine temperature intervals critical from this point of view. The results of DTA and DTG measurements are shown in Figure 7. Two extremes observed on the DTG curves for both used precursors correspond to the gas evolution accompanied with the weight loss, (Figure 7*a*), the first one with the minimum at 100 (140) °C for ZrPr (ZrAc) precursor. This minimum corresponds to the endothermic effect observed on DTA curves caused by solvent evaporation. The second extreme with the minimum at 330 (400) °C for

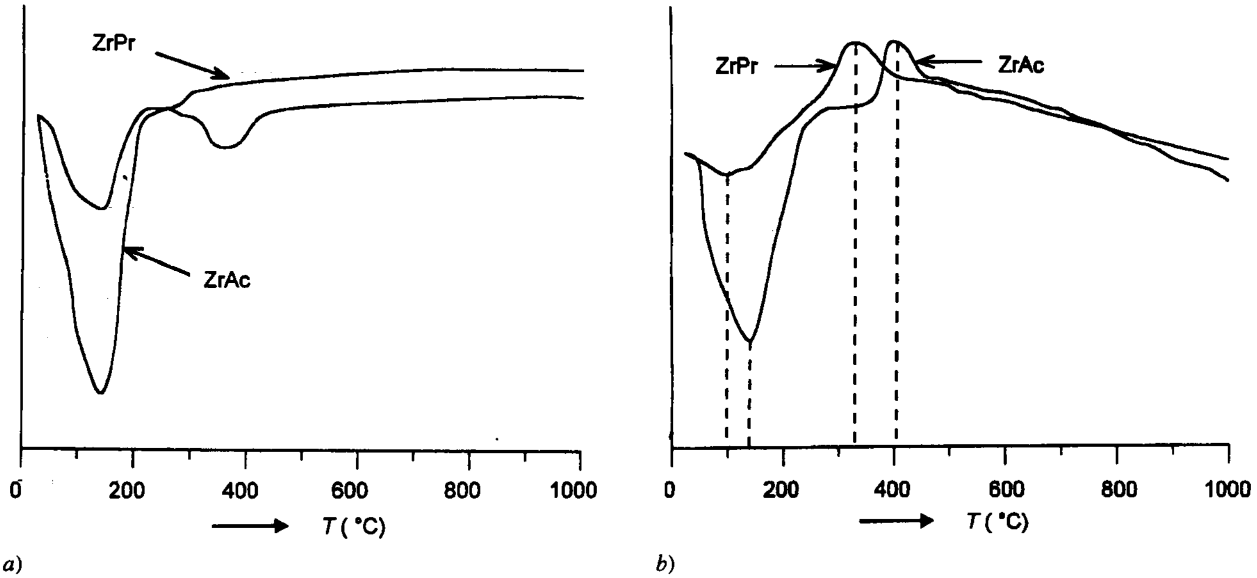


Figure 7. *a*) - DTG; *b*) - DTA curves of thermal decomposition of the precursors; *T* - temperature

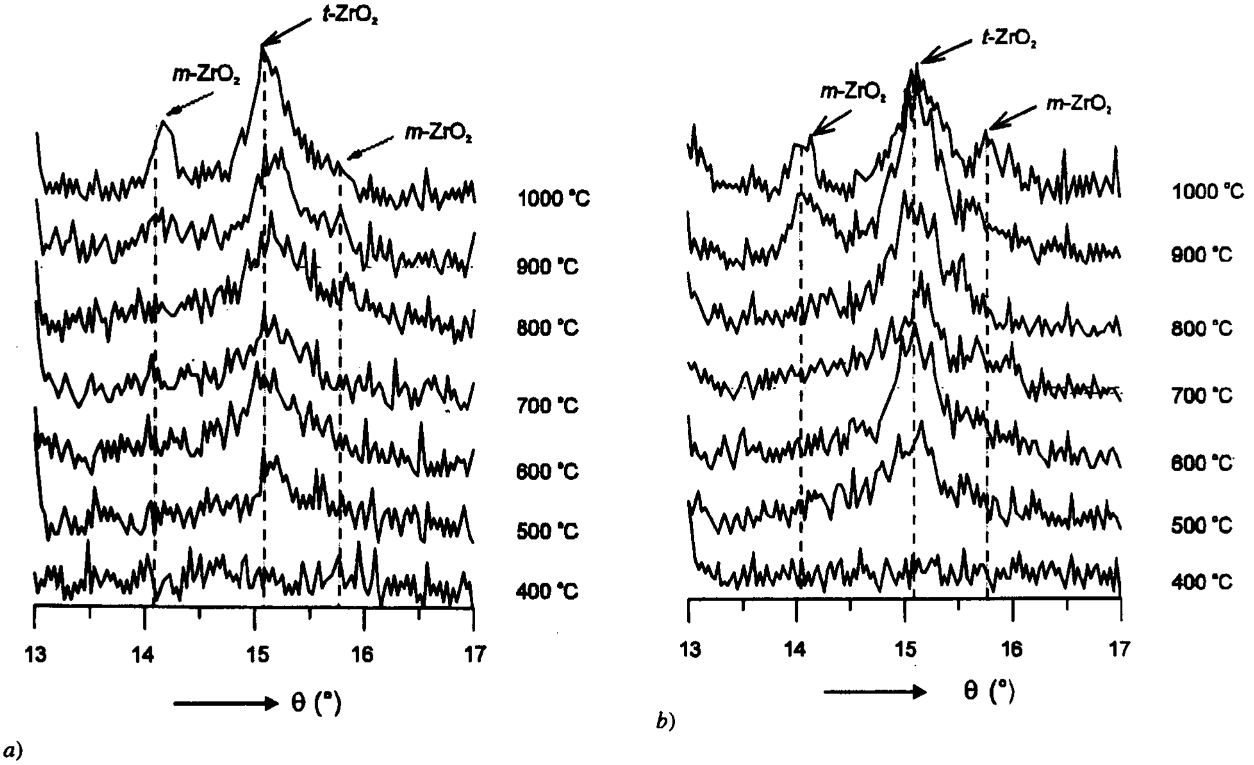


Figure 8. Temperature dependence of the phase development during the crystallisation of precipitated zirconia
θ - diffraction angle

ZrPr (ZrAc) precursor corresponds to the exothermic peak on DTA curve related to the weight decrease observed on the DTG curve. The reason for this weight decrease can be thermal decomposition - pyrolysis - of the organic part of the precursor molecules. An exothermic effect observed in the temperature range 500 - 1000 °C (Figure 7*b*) is not accompanied with the weight change on the DTG curve. This is probably caused by radiation of crystallisation and re-crystallisation heat of ZrO_2.

To confirm this statement, XRD measurement (Dron 2.0) of samples heated at different temperatures from 400 to 1000 °C for 60 minutes was performed (Figure 8) As can be seen from the figure, no crystalline zirconia can be observed at temperature bellow 500 °C. At 500 °C the crystallisation of tetragonal phase starts and at 800 °C fully developed peaks of tetragonal phase were found. At higher temperature a recrystalisation of t-ZrO_2 to monoclinic phase starts and at 1000 °C a mixture of tetragonal and monoclinic zirconia is present in the sample. This phase development is in agreement with the previously published data [11], the only difference is the crystallisation starting temperature (≈500 °C), which in the present work was about 200 °C higher than that published by Cypres et. al. [12].

According to the results discussed above and with respect to the requirement of maximal tetragonal zirconia content in the matrix after sintering, the precursor pyrolysis temperature should not exceed 800 °C. To verify this statement a set of experiments as follows was performed. Samples pyrolysed at different temperatures (see above) were sintered at 1500 °C for 60 minutes with the heating rate of 10 °C min^{-1}. and a nearly theoretical density was achieved. The phase composition of the sintered samples was determined by XRD and the volume fraction of tetragonal zirconia with respect to the total zirconia content was calculated according to the procedure described in [13]. As can be seen from the Figure 9 the maximum content of tetragonal zirconia was found at decomposition temperature of 700 °C for the precursor ZrPr, while for the precursor ZrAc no such a maximum was observed. In further experiments, the decomposition temperature of 700 °C was used for both investigated precursors.

Distribution of secondary phase(s)

Concentration profile of zirconia within the alumina matrix was measured on the polished cross sections of samples (perpendicular to the longest axis) sintered at 1500 °C for 60 minutes using X-ray microanalyser JEOL JXA 840A. The zirconia profiles of the matrix BCR6 infiltered with ZrAc and ZrPr are shown in Figure 10. As can be seen an average zirconia content is constant over the whole cross section. Fluctuations in concentration are due to discrete character of zirconia precipitates, which are located in the parent pores of the alumina matrix. The only exception is the BCR6-ZrPr sample. Its average zirconia content decreases from the surface to the middle of the infiltered

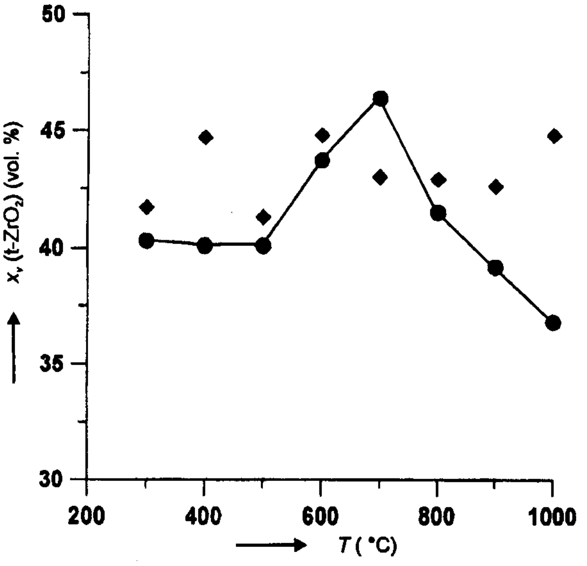
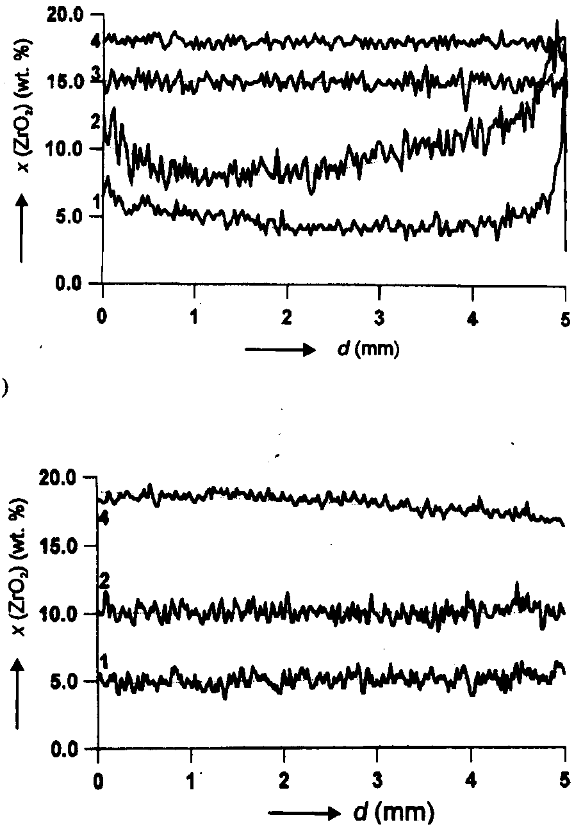


Figure 9. Dependence of the volume ratio of tetragonal zirconia in the samples sintered 60 minutes at 1500 °C on the maximal crystallisation temperature during the precursor decomposition T - temperature of pyrolysis; x_v(t-ZrO_2) - volume fraction of tetragonal zirconiaů; ◆ - ZrAc, ● - ZrPr



a)

b)

Figure 10. Concentration profile of zirconia measured on the polished cross sections of BCR6 samples
a) - infiltered with ZrPr; *b)* - infiltered with ZrAc; *d* - infiltration depth; $x(ZrO_2)$ - zirconia concentration

sample after the first and second infiltration. In this case, high vapour pressure of *n*-propanol favoured the evaporation of solvent during pyrolysis from the pores located nearby the sample surface. Capillary forces then drive the flow of liquid precursor from the central parts of the sample to empty pore space near the sample surface. The result of this precursor redistribution is a decrease of zirconia concentration in the central part of the sample. After multiple infiltration the diameter of pores located close to sample surface is getting smaller because of the presence of precipitated zirconia and therefore the evaporation as well as the reverse capillary flow to surface areas is restricted. As a result, average zirconia content becomes constant over the whole measured cross section.

CONCLUSIONS

The results obtained in this work can be summarised as follows:

1. The rate of infiltration in present system can be described by Washburn's equation. However, negative declination from this equation was observed for the infiltration times longer than 8 minutes and 10 hours i.e. after 80 % of the matrix was filled with the ZrAc and ZrPr precursor, respectively.
2. A decreasing rate of infiltration with increasing number of infiltrations was observed due to the changes in wetting behaviour of the matrix as well as the changes in geometry of the pore channels.
3. Closing of open pores with precipitated zirconia was observed in matrices with finer microstructure (BSM8, BCR6). The amount of zirconia which was possible to introduce into the matrix during particular infiltration was strongly diminished after the third infiltration. For M203 matrix with coarser microstructure and wider pore channels the pores closure was not observed.
4. Multiple infiltration of BSM8 matrix with ZrAc precursor allowed us to prepare the alumina-zirconia ceramic composite with the zirconia content as high as 21 wt.%.
5. Two critical temperature intervals were found during the ZrPr and ZrAc precursor decomposition, where the solvent evaporation (maximum at 100 and 140 °C) and thermal degradation (with maximum at 330 and 400 °C respectively) of the organic part of the precursors take place. These facts together with the results of XRD measurements of phase development during the precursor decomposition allowed us to optimise the pyrolysis temperature as well as the heating schedule during the precursor pyrolysis.
6. Liquid infiltration of porous pre-sintered alumina bodies with ZrPr and ZrAc precursors allowed us to prepare Al_2O_3-ZrO_2 ceramics with different weight fractions of zirconia homogeneously distributed within the bulk of alumina matrix. According to the number of infiltrations the zirconia content could be continuously changed from 0 to 20 wt.%. According to these results, liquid infiltration appears to be a suitable method for preparation of Al_2O_3-ZrO_2 ceramic composites.

Acknowledgement

The authors wish to express their thanks to Dr. Pavol Šajgalík from the Institute of Inorganic Chemistry, Slovak Academy of Sciences, for helpful remarks and revision of this manuscript.

References

1. Becher P.F., Alexander K.B., Bleier A., Waters S.B., Warwick W.H.: J.Am.Ceram.Soc. *76*, 657 (1993).
2. McMeeking R.M., Evans A.G.: J.Am.Ceram.Soc. *65*, 242 (1982).
3. Marple B.R., Green D.J.: J.Am.Ceram.Soc. *72*, 2043 (1989).
4. Marple B.R., Green D.J.: J.Am.Ceram.Soc. *73*, 3611 (1990).
5. Duh J.G., Wan J.U.: J.Mat.Sci.Lett. *12*, 473 (1993).
6. Glass S.J., Green D.J.: pp. 311-318 in *Advances in Ceramics*, Vol. 24, *Science and Technology of Zirconia III*, Proc.Int.Conf., Tokyo, Japan, Ed. Sőmiya et.al., American Ceramic Society, Westerville, OH, 1988.
7. Kleber S., Weiss H.J.: J.Eur.Ceram.Soc. *10*, 205 (1992).
8. Toy C., Scott W.D.: J.Am.Ceram.Soc. *73*, 97 (1990).
9. Glass S.J., Green D.J., pp. 784-791 in *Ceram. Transactions* Vol. 1B, *Ceram. Powder Science II.*, Ed. Messing et. al. American Ceramic Society, Westerville, OH, 1988.
10. Hillig W.B.: J.Am.Ceram.Soc. *71*, C96 (1988).
11. Osendi M.I., Moya J.S., Serna C.J., Soria J.: J.Am.Ceram.Soc. *68*, 135 (1985).
12. Cyprés R., Wollast R., Rauch J.: Ber.Dtsch.Keram.Ges. *40*, 527 (1963).
13. Toraya H., Yoshimura M., Sőmiya S.: J.Am.Ceram.Soc. *67*, C119 (1984).

Submitted in English by the authors

INFILTRÁCIA KORUNDOVEJ MATRICE ORGANICKÝMI PREKURZORMI ZrO_2 AKO METÓDA NA PRÍPRAVU ZTA KERAMIKY
ČASŤ I - INFILTRÁCIA

DUŠAN GALUSEK, JÁN MAJLING

Katedra keramiky, skla a cementu CHTF STU,
Radlinského 9, SK-812 37 Bratislava,
Slovenská republika

ZTA (zirconia toughened alumina) je vhodným materiálom na prípravu keramických súčiastok s vysokou tvrdosťou a lomovou húževnatosťou. Na dosiahnutie transformačného zhúževnatenia je treba pripraviť korundovú matricu s homogénne distribuovanou frakciou častíc tetragonálneho ZrO_2, ktoré sú schopné transformovať na stabilnú monoklinickú modifikáciu.

V uvádzanej práci bola na prípravu ZTA použitá kvapalinová infiltrácia korundovej matrice organickými prekurzormi ZrO_2. Táto metóda poskytuje oproti klasickým metódam prípravy kompozitnej keramiky najmä tieto výhody:

1. Sekundárna fáza sa zavádza do predpripravenej monofázovej matrice. Distribúcia sekundárnej fázy potom závisí len od rozdelenia pórov v matrici. Odpadajú problémy so zabezpečením homogénneho premiešania fáz ako je tomu u klasických práškových metód prípravy viacfázovej keramiky.
2. Čiastočné vyplnenie pórovitosti v matrici precipitovanou sekundárnou fázou znižuje zmršťovanie keramického výrobku pri spekaní, čo umožňuje lepšiu objemovú a tvarovú kontrolu finálneho výrobku.

Pri infiltrácii boli použité dva organické prekurzory ZrO_2 - *n*-propanolát zirkónia (ZrPr) a acetát zirkónia (ZrAc). Charakterizácia použitých korundových práškov je uvedená v Tabuľke I. Postup prípravy vzoriek pozostávajúci z prípravy pórovitej korundovej matrice (odlievanie na sadrovú dosku a predspekanie - teploty použité pri predspekaní a dosiahnuté pórovitosti, pozri Tab. II.), termického rozkladu organického prekurzora a dospekania vzoriek na vysokú hustotu, je schematicky znázornený na Obr.1. V práci je sledovaný a optimalizovaný termický rozklad organických prekurzorov (DTA, DTG). Pomocou RTG fázovej analýzy je identifikované fázové zloženie produktov pyrolýzy v matrici (obsah tetragonálneho a monoklinického ZrO_2). Distribúcia ZrO_2 v matrici (koncentračný profil ZrO_2 v infiltrovanom objeme) je vyhodnotená pomocou RTG mikroanalyzátora JEOL JXA 840A.

Prenikanie roztoku organického prekurzora do systému pórových kanálov bolo zabezpečené kapilárnymi silami. Infiltráciu preto možno popísať Washburnovým vzťahom, podľa ktorého je hĺbka prenikania kvapaliny do nekonečného pórovitého telesa priamo úmerná druhej odmocnine infiltračného času. Z konečnosti reálnych vzoriek vyplýva negatívna odchýlka od Washburnovho vzťahu, pozorovaná v záverečných fázach infiltrácie (Obr. 3). Z rozdielnych vlastností použitých infiltrantov (viskozita, zmáčavosť povrchu matrice) vyplýva rozdielny čas potrebný na infiltráciu celého objemu keramickej matrice, o jeden poriadok väčší pre ZrPr ako pre ZrAc (12 hodín a 10 minút na infiltráciu do hĺbky 5 mm). U ZrPr dochádza naviac v dôsledku čiastočnej hydrolýzy prekurzora (vzdušná vlhkosť) počas infiltrácie k upchávaniu pórových kanálov a k ďalšiemu predĺženiu infiltračného času. Upchávanie pórových kanálov ako aj čiastočné vypĺňovanie pórov precipitovaným ZrO_2 spôsobuje tiež pokles množstva ZrO_2, ktoré je možné zaviesť do matrice opakovanou infiltráciou. (Obr.4.) Nárast celkového obsahu ZrO_2 pri viacnásobnej infiltrácii je potom nelineárny. (Obr.5.) Výnimku tvorí len matrica M203, kde korundové častice so strednou veľkosťou $\approx$ 2 μm tvoria sieť pórov s veľkým priemerom, pričom veľkosť precipitovaných častíc ZrO_2 je zanedbateľná v porovnaní s priemerom pórov (Obr.6.) a k upchávaniu pórových kanálov precipitujúcim ZrO_2 nedochádza. Niekoľkonásobne opakovanou infiltráciou boli pripravené vzorky s obsahom ZrO_2 cca 20 hmot.% (pri jednej infiltrácii max. 6 hmot.%).

Pri termickom rozklade prekurzora bola pozornosť zameraná na optimalizáciu priebehu pyrolýzy s cieľom lokalizovať teplotné intervaly v ktorých dochádza k vývinu plynných produktov pyrolýzy, ako aj optimalizovať fázové zloženie precipitovaného ZrO_2. DTA a DTG meraním (Obr.7.) boli pre oba prekurzory nájdené dva teplotné intervaly v ktorých dochádza k vývinu plynov. Prvý s maximom pri 100 (140) °C pre ZrPr (ZrAc) zodpovedá odparovaniu rozpúšťadla, kým v druhom s maximom pri 330 (400) °C dochádza k termickej degradácii organickej časti molekúl prekurzora. Slabý exotermický efekt pozorovaný na DTA krivke v rozmedzí teplôt 500 - 1000 °C je spôsobený kryštalizačným teplom ZrO_2. RTG fázová analýza potvrdila, že kryštalizácia tetragonálneho ZrO_2 prebieha v rozmedzí teplôt 500 - 700 °C, pri vyšších teplotách dochádza potom k rekryštalizácii na monoklinickú fázu.
(Obr.8.) Experimenty zamerané na stanovenie optimálnej rozkladnej teploty prekurzora z hľadiska maximálneho obsahu tetragonálnej fázy po dospekaní vzoriek na vysokú hustotu ukázali optimálnu rozkladnú teplotu pre prekurzor ZrPr 700 °C. (Obr.9.) Pri tejto rozkladnej teplote $\approx$50 obj.% z celkového obsahu ZrO_2 zostáva po ochladení na laboratórnu teplotu v tetragonálnej forme. Meranie koncentračného profilu ZrO_2 v infiltrovaných vzorkách ukázalo konštantnú koncentráciu ZrO_2 v celom infiltrovanom objeme korundovej matrice. (Obr.10.)

Použitie uvedených prekurzorov na infiltráciu pórovitej korundovej matrice umožňuje pripraviť keramiku s obsahom ZrO_2 do 20 hm.%, pričom koncentrácia ZrO_2 v matrici je konštantná v celom infiltrovanom objeme a 50 obj.% ZrO_2 zostáva pri laboratórnej teplote v tetragonálnej forme.