ALUMINA TOUGHENED ZIRCONIA MADE BY ROOM TEMPERATURE EXTRUSION OF CERAMIC PASTES

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A novel preparation route for ATZ (alumina toughened zirconia) ceramics is presented, using a commercial ATZ powder (a mixture of 20 wt.% alumina and 80 wt.% zirconia containing 3 mol.% yttria) as a solid filler and an ATZ sol or gel (of the same composition) as a liquid binder for paste extrusion at room temperature. The pastes have a total oxide content of approx. 70 wt.% and during heat treatment the binder composition accommodates to the composition of the filler powder. Extruded samples are characterized before and after heat treatment by determining their shrinkage, bulk density, apparent density and apparent porosity. The optimal firing temperature is determined to be about 1550 °C. Quantitative X-ray phase analysis is used to establish the phase composition (ratio of monoclinic to tetragonal zirconia) and to calculate a (spatially averaged) mean value for the true density of the prepared nanocomposite after firing, which is 5.45 g cm⁻³. For optimally sintered specimens the bulk density is approx. 5.06 g cm⁻³, i.e. 92.8 % of the theoretical value. The total porosity after sintering is approx. 6.8 % (open 4.7 %, closed 2.1 %).

INTRODUCTION

Alumina toughened zirconia (ATZ) is a composite ceramic material consisting of small (order of magnitude 1 μ m after firing) alumina particles in a very fine matrix of (nanosized) zirconia particles. Although the fracture toughness values reported in literature do not achieve those reported for other zirconia-containing ceramics (5 - 6 MPa m^{1/2} for ATZ, compared to 7-10 MPa $m^{1/2}$ - exceptionally even up to 15 MPa $m^{1/2}$ - for other zirconia-containing ceramics), ATZ ceramics exhibit the highest bending strengths known for ceramics at room temperature (up to 1800 - 2400 MPa for hot isostatically pressed ceramics) and unusually high bending strengths also at elevated temperatures (higher than 800 MPa at 1000 °C) [1, 2, 3, 4, 5]. Apart from that, due to the relatively high thermal conductivity and the similar thermal expansion coefficient of alumina (orientational values reported in the literature for α -alumina with purity > 99.9 % are $\lambda =$ = 30 - 39 W m⁻¹ K⁻¹ and α = 6.5 - 8.9 10⁻⁶ K⁻¹) compared to zirconia (depending on the type and content of stabilizer $\lambda = 1 - 3$ W m⁻¹ K⁻¹ and $\alpha = 6.8 - 10.6 \ 10^{-6}$ K⁻¹), the thermal shock resistance of ATZ ceramics is very high ($\Delta T = 470$ °C) [2, 4, 6]. Furthermore it is known, that a serious drawback of TZP ceramics (tetragonal zirconia polycrystals), namely its strength degradation due to the tetragonal-monoclinic phase transformation at the surface, which is kinetically favored at relatively low temperatures (150 - 250 °C), especially in the presence of water or water vapor, can be significantly reduced by the addition of alumina [3, 6]; even alumina contents as low as 0.25 wt.% significantly improve this resistance to surface degradation at these slightly elevated temperatures [4, 5].

Although research has been done on many different types of ATZ compositions, only a few compositions have been developed into commercially competitive large-scale products, the most successful of which is an ATZ composition with 20 wt.% alumina and 80 wt.% zirconia (containing 3 mol.% yttria as a stabilizing agent) [4, 5].

While a certain economic advantage results from the fact that part of the (expensive) zirconia is replaced by (cheaper) alumina, a rather unagreeable feature of this ATZ type (and most other ceramics in the zirconiaalumina system) is the fact, that most high-performance properties have so far only been achieved by expensive, and highly energy-consuming processing of the raw material powders, e.g. by hot isostatic pressing (HIP). This fact might in the long run restrict the competitive capability of ATZ ceramics and their potential intrusion into new market niches. And this is one of the reasons why research on economically less demanding processing technologies is currently being intensified. E.g. for biomedical applications ATZ ceramics might become promising competitors of alumina, because, while many mechanical parameters are comparable or better than those of alumina, its stiffness (rigidity) is significantly lower than that of alumina (Young's modulus approx. 260 GPa, compared to approx. 380 -410 GPa for alumina and approx. 200 - 210 GPa for zirconia) [7], and can therefore be more easily adapted to that of bone, when the porosity is appropriately designed.

Instead of powder processing by hot isostatic pressing (HIP), possible alternative routes for the preparation of ATZ ceramics are powder forming methods using slurries or pastes (e.g. slip-casting, pressure slip casting, extrusion or injection molding) or colloidal processing (e.g. by the sol-gel route), both possibly in combination with conventional pressureless sintering. Sol-gel methods as such, naturally, have a serious disadvantage: the extremely high shrinkage. Paste-forming technologies, on the other hand, are dependent on the availability of appropriate binder compositions (obeying certain ecological and hygienic standards) and frequently require more sophisticated and expensive equipment for extrusion or injection molding at elevated temperatures. In this work, first results are presented on a novel processing technology, in which a commercial ATZ powder (type TZ-3Y20A, TOSOH, Japan) is used as a solid filler and an ATZ sol or gel of the same composition as a binder of a ceramic paste. The paste is formed by extrusion at room temperature. During heat treatment the binder composition accommodates exactly to the phase composition of the filler powder.

EXPERIMENTAL PART

Preparation of the binder and the ceramic paste

The ATZ sol or gel, which serves as a binder for the paste, is prepared by mixing a zirconia precursor sol (containing the appropriate yttria content) with a commercial alumina powder (type AA03, SUMITOMO CHEMICAL, Japan) of submicron size (median approx. 0.3-0.4 mm). The zirconia precursor is prepared by dissolving zirconyl nitrate hydrate $ZrO(NO_3)_2 \times xH_2O$ $(x \approx 6.5)$ (SIGMA-ALDRICH, Germany) in ethanol, adding an appropriate amount of nitric acid solution of yttria (LACHEMA-CHEMAPOL, Czech Republic) to yield 3 mol.% of Y_2O_3 in the final oxide mixture after calcination. After slow evaporation of the solvent component (several days) the appropriate amount of alumina powder is added to the highly viscous sol (before gelling sets in) and carefully mixed. After this preparation of the binder the ATZ powder (type TZ 3Y20A, TOSOH Corporation, Japan) is gradually added under incessant mechanical stirring. Total oxide concentrations of about 70 wt.% (transformed into "nominal" volume concentrations in water-based ATZ suspensions this would correspond to about 30 vol.% of solid phase) have been achieved in this way.

Extrusion of the ceramic paste and heat treatment

Pastes with an oxide content of about 70 wt.% were found to be suitable for extrusion. The extrusion of this ceramic paste was performed at room temperature with a self-made laboratory extruder (a batch- or piston-extruder) in vertical position, so that asymmetric deformation of the samples due to gravity is minimized. A stainless steel tube (capillary) with internal thread and an internal diameter of 4 mm and a length of 80 mm was used as an orifice. The bodies were slowly dried in air at room temperature for several days and subsequently fired at different temperatures (700, 1050, 1570, 1610, 1620 °C) according to a fixed firing

schedule (heating rate 2 °C / min, dwell 120 min). For reasons of comparison, two reference samples, an unshaped ATZ gel (made from zirconia sol and alumina powder) and an extruded ATZ ceramic body (made from ATZ gel and ATZ powder), have been fired to 900 °C (heating rate 2 °C / min) with a dwell time of only 15 min.

X-ray phase analysis

XRD measurements were performed with the diffractometer DRON (with a digital data recording system) in Bragg-Brentano arrangement using CuK_a radiation and a Ni-filter (acceleration voltage 30 kV, current 20 mA, collimator slit aperture 1 °, receiving slit aperture 0.025 °, step width 0.02 °, scan velocity 1 ° 20 / min). Evaluation of the diffractograms was done with the help of a commercial software package (DIFPATAN).

Four types of samples have been examined by XRD:

- Sample A: Calcinated ATZ gel (unshaped body, crushed and milled) made from zirconia sol and commercial alumina powder (type AA03, Sumitomo, Japan) fired at 900 °C (2 °C / min, dwell 15 min).
- Sample B: Calcinated mixture (extruded body after bisque-firing, crushed and milled) of ATZ gel (see sample A) and commercial ATZ powder (type TZ 3Y20A, Tosoh, Japan) fired at 900 °C (2 °C / min, dwell 15 min).
- Sample C: Calcinated mixture (extruded body after sintering, crushed) of ATZ gel (see sample A) and commercial ATZ powder (type TZ 3Y20A, Tosoh, Japan) fired at 1570 °C (2 °C / min, dwell 120 min).
- Sample D: Commercial ATZ powder (type TZ 3Y20A, Tosoh, Japan), unfired.

Samples A and B were crushed and milled in an alumina crucible to powders with a grain size of 10-100 μ m, sample C was only crushed to a grain size of about 500 μ m and sample D is the as-received powder (submicron grain size). Texture effects could in all cases be excluded because of the high degree of isometry of the particles.

Qualitative phase analysis was performed by identification of each peak in the JCPDS data base after previous determination of the peak positions and relative peak heights, and calculation of the corresponding *d*-values according to the Bragg equation:

$$\lambda = 2d\sin\theta \tag{1}$$

where λ is the X-ray wavelength (0.15418 nm for CuK_a), *d* the normal distance of planes with the Miller indices (hkl) and θ the Bragg angle.

Quantitative phase analysis (determination of the ratio of monoclinic to tetragonal zirconia) was performed by the polymorph method [8] using the integral intensities of the zirconia peaks monoclinic-(111), monoclinic-(111) and tetragonal-(111) determined with the software DIFPATAN (after a background correction has been made). To a first approximation the mass fraction of monoclinic zirconia (with respect to the total zirconia content) is given by the Garvie-Nicholson equation [9, 10]:

$$x_{\rm m} = \frac{I_{\rm m}(111) + I_{\rm m}(11\overline{1})}{I_{\rm m}(111) + I_{\rm m}(11\overline{1}) + I_{\rm t}(111)}$$
(2)

where $I_{\rm m}(...)$ and $I_{\rm t}(...)$ are integral intensities.¹⁾

For a more precise quantification it has be remembered, that the mass fraction need not depend linearly on the intensity ratio. The correction which allows for this nonlinearity can be performed by a formula derived by Toraya et al. [11] (cf. also [10]):

$$X_{\rm m} = \frac{C x_{\rm m}}{1 + (C - 1) x_{\rm m}}$$
(3)

where $X_{\rm m}$ is the Toraya-corrected mass fraction and is a composition-dependent correction factor calculated from theoretical considerations. For zirconia with 3 mol.% Y₂O₃ we use = 1.32 - 1.34, see Toraya et al. [11].

Determination of body characteristics

The heat-treated ceramic bodies (bisque-fired or sintered) were weighed in the dry state, then boiled for 2 h in distilled water (followed by a soaking period of 24 h in water), subsequently weighed in water, and finally the water-saturated bodies were weighed in air immediately after the surface has been wiped off with a moist sponge. For weighing a digital analytical balance (SARTORIUS, Germany) has been used. These input data were used to determine the bulk density ρ_{bulk} , the apparent density $\rho_{apparent}$ and the apparent (i.e. open) porosity P_{open} :

$$\rho_{\text{bulk}} \equiv \frac{m_{\text{solid}}}{V_{\text{solid}} + V_{\text{open}} + V_{\text{closed}}} = \frac{m_{\text{dry}}}{m_{\text{sat.(air)}} - m_{\text{sat.(water)}}} \rho_{\text{water}} (4)$$

$$\rho_{\text{apparent}} \equiv \frac{m_{\text{solid}}}{V_{\text{solid}} + V_{\text{open}}} = \frac{m_{\text{dry}}}{m_{\text{dry}} - m_{\text{sat.(water)}}} \quad \rho_{\text{water}} \quad (5)$$

$$P_{\text{bulk}} \equiv \frac{V_{\text{open}}}{V_{\text{solid}} + V_{\text{open}} + V_{\text{closed}}} = \frac{m_{\text{sat.(air)}} - m_{\text{dry}}}{m_{\text{sat.(air)}} - m_{\text{sat.(water)}}}$$
(6)

In the above equations (4) - (6) m_{solid} (or m_{dry}) is the mass of the solid skeleton (or the dry ceramic body), $m_{sat.(air)}$ and $m_{sat.(water)}$ are the masses of the water-saturated bodies weighed in air and in water, respectively, and V_{solid} , V_{open} and V_{closed} are the partial volumes of the solid skeleton, the open pore space and the closed pore space, respectively. Dimensional changes (linear and volume shrinkage) have been measured by a digital slide caliper. With the knowledge of the true solid phase density of the mixture after heat treatment (theoretical density) calculated using the phase composition (20 wt.% alumina, 80 wt.% zirconia) and the ratio of monoclinic and tetragonal zirconia (obtained by the quantitative phase analysis from XRD) it is straightforward to calculate also the total and the closed porosity.

RESULTS AND DISCUSSION

Figures 1 through 4 show the XRD plots of samples A, B, C, and D. In sample A containing ATZ gel (made from zirconia sol and alumina powder), but no commercial ATZ powder, all peaks are uniquely identifiable either as α -Al₂O₃ or as tetragonal ZrO₂ (t-ZrO₂) and none of the important peaks of these phases is missing in the measured range (see figure 1). Thus it must be concluded that in this sample the content of monoclinic ZrO_2 (m- ZrO_2) is below the detection limit of XRD. In sample B, on the other hand, which contains additionally commercial ATZ powder, m-ZrO₂ is distinctly visible (note the small m-ZrO₂-peaks $(11\overline{1})$ at $2\theta = 28.2^{\circ}$ and (111) at $2\theta = 31.3^{\circ}$ on figure 2). After firing at 1570 °C (sample C, distinguished from sample B only by the firing temperature), the monoclinic phase is still detectable (in this case the (111)-peak is hidden in the background, whereas the (111)-peak is even more expressed than that of sample B, cf. figure 3). This clearly indicates a certain difference of the two types of samples (samples B and C as compared to sample A) in the phase composition after heat treament (although the chemical composition of all samples is of course identical), the reason of which has to be sought in the commercial powder, which contains monoclinic phase from the very beginning. Figure 4 confirms this hypothesis already by a mere qualitative inspection of the X-ray diffractogram (rather high m-ZrO₂ peaks). Note that after a heat treatment at 900 °C the prevailing zirconia phase originating from the ATZ gel precursor is tetragonal. This finding is well known for zirconia orginating from amorphous gels, even at lower temperatures [12, 13].

¹⁾ Note that, depending on whether the primitive tetragonal cell or the face-centered tetragonal cell (derived from the cubic polymorph, which has fluorite structure) is taken as the unit cell, the tetragonal (111) peak is sometimes denoted (101).



Figure 1. X-ray diffractogram of sample A (ATZ gel without ATZ powder, calcined at 900 °C); $A = \alpha$ -alumina, t = tetragonal zirconia.



Figure 2. X-ray diffractogram of sample B (extruded body, crushed and milled, ATZ gel with ATZ powder, fired at 900 °C); A = α -alumina, t = tetragonal zirconia, m = monoclinic zirconia.

It has to be remembered that no attempt was made here to distinguish a cubic phase from the tetragonal phase. For the calculation of the theoretical density such a distinction is unessential.

The phase analysis was quantified by magnifying the corresponding 2θ range with the software DIFPATAN, subtracting an averaged background line and determining the integral intensities (areas) under the zirconia peaks monoclinic-(111), monoclinic-(111) and tetragonal-(111). The discrimination of overlapping peaks was done manually. Table 1 shows the relative concentration (in wt.%) of monoclinic zirconia with respect to the total zirconia content (which is not to be confused with the absolute concentration of m-ZrO₂ in the ATZ samples, of course), calculated directly by equation (2) from the determined integral intensities



Figure 3. X-ray diffractogram of sample C (extruded body, crushed, ATZ gel with ATZ powder, calcined at 1570 °C).



Figure 4. X-ray diffractogram of sample D (ATZ powder, as-received).

Table 1. Relative concentration (wt.%) of monoclinic zirconia with respect to the total zirconia content, calculated directly by equation (2) from the ratio of the integral intensities and corrected according to equation (3), respectively.

sample	$x_{\rm m}$ calculated by equation (2) directly from the ratio of integral intensities	$X_{\rm m}$ corrected according to equation (3) with $C = 1.32 - 1.34$	
A	-	-	
В	9.7	12.3-12.7	
С	9.6	12.2-12.4	
D	18.3	22.8-23.0	



Figure 5. Bulk density of fired ATZ ceramics in dependence of the firing temperature (the horizontal line indicates the maximally attainable theoretical density).

and corrected according to equation (3), respectively. Interestingly, the relative content of monoclinic phase (with repsect to the total zirconia content) is between 12.2 and 12.7 wt.% (with Toraya-correction) for both samples B and C, i.e. remains essentially unchanged by differences in the heat treatment. In the commercial ATZ powder the relative m-ZrO₂ content is approximately twice as high (22.8-23.0 wt.%).

Assuming 5.6 g cm⁻³ as the true density of m- ZrO_2 and 6.1 g cm⁻³ for t-ZrO₂ the theoretical density of the ATZ nanocomposite ceramics after heat treatment can be easily calculated. Taking into account the uncertainty in the m-ZrO₂ content (12.2-12.7 wt.% versus 87.8-87.3 wt.% t-ZrO₂) it is 5.45 ± 0.02 g cm⁻³. Figures 5 and 6 show the bulk density (volume mass of the body including open pores) and the apparent density (volume mass of the body without open pores), respectively, of ATZ nanocomposite bodies after heat treatment at the respective temperatures (indicated on the abscissa of both figures). The calculated theoretical density is drawn on these figures as a dotted horizontal line at 5.45 g cm⁻³. The maximum bulk density which could be attained in practice was 5.06 ± 0.02 g cm⁻³ at temperatures higher than 1500 °C, i.e. approx. 92.8 % of the theoretical density. At firing temperatures higher than 1570 °C the bulk density values seem to decrease (see figure 5 and table 2). Figure 6 shows the apparent density, which is very close to the theoretical density and practically constant for all firing temperatures higher than 1000 °C (5.35 ± 0.05 g cm⁻³, i.e. 98.2 % of the theoretical density), cf. table 2. That means that most of the porosity is open porosity (interconnected and connected with the external macroscopic surface of the body) and remains so even after sintering. Figure 7, which compares the (directly measured) open porosity and the (calculated) total porosity, respectively, shows that the two curves are practically identical and thus confirms this finding. The minimum total porosity after sintering at optimum temperature (about 1550 °C) is



Figure 6. Apparent density of fired ATZ ceramics in dependence of the firing temperature (the horizontal line indicates the maximally attainable theoretical density).

Table 2. Bulk density, apparent density, apparent porosity, total porosity and closed porosity of extruded ATZ samples after heat treatment.

<i>Т</i> (°С)	$ \substack{\rho_{bulk} \\ (g \ cm^{-3}) }$	$\rho_{apparent}$ (g cm ⁻³)	P _{open} (%)	P _{total} (%)	P _{closed} (%)
700	2.56	5.18	50.6	53.0	2.4
1050	2.89	5.40	46.5	47.0	0.4
1500	5.04	5.34	5.6	7.6	2.0
1570	5.08	5.33	4.7	6.8	2.1
1610	5.00	5.35	6.6	8.3	1.7
1620	4.97	5.35	7.0	8.8	1.8



Figure 7. Open porosity (directly measured) and total porosity (calculated) of fired ATZ ceramics in dependence of the firing temperature.

 \times - open, \blacksquare - total, \square - closed

approx. 6.8 % and consists of 4.7 % open porosity and 2.1 % closed porosity. At higher temperatures (1610 - 1620 °C) the total porosity shows again a slight increase (to 8.3 - 8.8 %), while the closed porosity remains essentially unchanged for temperatures in the range 1500 - 1620 °C, namely at approx. 2 %, cf. table 2. The prevailing open porosity after sintering is clearly a remnant of the very open gel structure (network) which forms the grain boundary phase between the ceramic submicron grains.

Due to the gel contained in the starting mixture the shrinkage of the extruded bodies is relatively large. The linear drying shrinkage is approx. 5.1-7.5 % (average values from measurements normal and parallel to the direction of extrusion), the volume drying shrinkage approx. 10-15 %. When the dimensions after drying are taken as starting dimensions for the determination of the firing shrinkage, the linear shrinkage increases monotonically from 1.7 % for bodies fired at 700 °C to 22.2 % for bodies fired at 1620 °C. The corresponding volume shrinkage increases from 5.1 % to 53.0 %. For our material the approximation that the volume shrinkage is three times the linear shrinkage, is only valid for firing temperatures below 1000 °C.

CONCLUSION AND OUTLOOK

In this paper a novel preparation route for ATZ (alumina toughened zirconia) ceramics has been presented, using a commercial ATZ powder (20 wt.% alumina, 80 wt.% zirconia containing 3 mol.% yttria) as a solid filler and a prototype ATZ sol or gel (of the same composition) as a binder phase for paste extrusion. One main advantage of this route is that with the proposed mixture extrusion is possible at room temperature. Furthermore, the binder is bifunctional in the sense that after fulfilling its primary function (of serving as transport medium during the forming step), its main components (the oxides) make up the grain boundary phase after calcination (firing). Because of the identical composition of binder phase and ATZ powder, there is no danger of introducing foreign ions or chemical composition inhomogeneities via the binder. Naturally, microstructural inhomogeneities can occur as everywhere in extrusion. Nothing is known so far about the burnout behavior (kinetics) of possible relics of volatile binder components (ethanolates, hydrates and nitrates, which decompose finally to H₂O, CO₂ and NO_x), but since none of the bodies fractured during firing it seems that binder burnout is not a critical step for our materials, at least for bodies of the composition and dimensions studied (cylindrical bodies with diameters of 4 mm).

It was found that the binder phase (the ATZ gel) results in relatively pure tetragonal zirconia. At first sight this seems to be clearly positive. But if the tetragonal phase results from the extremely fine particle size (as can be assumed for the gel-derived zirconia), it cannot be excluded that such nanoparticles will show also an abnormal stability of the tetragonal phase and thus reduced transformation capability for toughness enhancement. An estimate of the average particle size can be gained from an quantitative analysis of the XRD peak broadening (Scherrer equation). This will be done in a subsequent paper.

A major problem results from the fact that the oxide content in a well extrudable paste is not too high (approx. 70 wt.%) and the shrinkage is relatively large due to the gel content. Therefore the dimensional accuracy of extruded ATZ bodies is comparatively poor. Another as yet unsolved problem is the surface roughness of the extruded samples, which is a major obstacle for obtaining defect-free samples which would give reliable strength values. Better homogenization of the paste by shear mixing, organic additives (lubricants) or repeated extrusion are possible ways to improve the surface quality (smoothness). Future research will be focussed on the mechanical properties of extruded ATZ ceramics.

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ATZ KERAMIKA PŘIPRAVENÁ EXTRUZÍ KERAMICKÝCH PAST PŘI POKOJOVÉ TEPLOTĚ

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Je představována nová metoda přípravy ATZ ("aluminatoughened zirconia") keramiky extruzí. Pro přípravu keramické pasty je jako plnivo použit komerční prášek ATZ (20 hmotn.% Al_2O_3 , 80 hmotn.% ZrO_2 s obsahem 3 mol % Y_2O_3), jako pojivo (plastifikátor) laboratorně připravený ATZ sol nebo gel stejného složení. Celkový obsah oxidů je cca 70 hmotn.%. Extrudované vzorky jsou charakterizovány před a po tepelném zpracování (teplota výpalu od 700 do 1620 °C) na základě stanovení smrštění, objemové hmotnosti, zdánlivé hustoty a zdánlivé (tj. otevřené) pórovitosti. Je stanovena optimální teplota výpalu cca 1550 °C. Pomocí kvantitativní rentgenografické fázové analýzy je určeno fázového složení (poměr monoklinické a tetragonální fáze oxidu zirkoničitého, které vychází po výpalu cca 12.2-12.7 hmotn.% m-ZrO2 k 87.3-87.8 hmotn.% t-ZrO2) a vypočtena průměrná hodnota skutečné hustoty připravovaného nanokompozitu (cca 5.45 g cm-3). Pro optimálně slinuté vzorky je objemová hmotnost rovna cca 5.06 g cm-3, tj. 92.8 % teoretické hodnoty. Celková pórovitost po slinování je cca 6.8 % (otevřená 4.7 %, uzavřená 2.1 %). Vzhledem ke gelové složce, obsažené v extrudovaných tělesech, a nepříliš vysokému obsahu oxidů v připravené keramické pastě je smrštění poměrně velké, což znemožňuje dodržení přísných rozměrových tolerancí. Lineární smrštění sušením je cca 5.1-7.5 %, objemové 10-15 %. Dodatečné lineární smrštění po výpalu narůstá s teplotou výpalu od 1.7 % pro tělesa vypálená při 700 °C až na 22.2 % pro tělesa vypálená při 1620 °C, resp. objemové smrštění od 5.1 % až na 53.0 %. Největším stávajícím problémem je jakost povrchu, která zatím neumožňuje seriózní stanovení mechanických vlastností takto připravované keramiky.