# LENGTH CHANGES OF SLIP CASTING ALUMINA-ZIRCONIA CERAMICS

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Submitted February 15, 2007; accepted April 17, 2007

**Keywords:** FGC, $Al_2O_3$, $ZrO_2$, Slip casting, Shrinkage

*The main topic of this study is the preparation of functionally graded zirconia-alumina ceramics. The ceramics were prepared by utilizing a slip casting method into a porous mold. From the technological point of view, the preparation of functional layered alumina and zirconia ceramics requires the development of a defect-free interface between the compound layers. The important factor in the preparation of these ceramics is the study of length changes between each individual layers. The first part of this work focuses on the preparation of mono-layer bodies with variable zirconia-alumina composition. The optimal deflocculant content was proposed based on colloidal and rheological properties of the $Al_2O_3$–$ZrO_2$ systems. Dilatometric behavior was studied on green samples during firing. The results indicated a critical temperature interval having the biggest differences of linear expansion coefficient, i.e. 20-400°C. Based on measurements conducted in this temperature range, it was observed that increasing volume of deflocculant causes the coefficient of linear expansion and the temperature of shrinkage to rise. In the next part two characteristics were studied on zirconia samples - whether the difference in dilatation changes is caused by firing of deflocculant or by porosity of bodies. It was observed that dilatation changes are caused by the porosity and distribution of pores within the dried samples at the low temperature range. The content of deflocculant influences the size of linear changes.*

## INTRODUCTION

The functionally graded materials (FGM) are composite material with inhomogeneous microstructures and properties. Graded materials themselves are not new, however, the realization of gradients designed at a microstructure level to tailor specific materials for their functional performance in an attractive notion [1]. FGM have been developed for many applications. Aluminum oxide ceramic has been in use in orthopedic implants since 1970 due to its excellent biocompatibility, corrosion resistance, low coefficient of friction, phase stability and sufficient mechanical strength to resist fatigue. Zirconia ceramic has been used in orthopedic applications since 1985 when the first zirconia femoral heads were implanted. Zirconia ceramic has higher fracture strength than alumina [2]. For that reason the graded alumina-zirconia ceramics have been developed for medical applications.

In this work the preparation of $Al_2O_3$–$ZrO_2$ layers functional graded ceramic (FGC) is described. This type of ceramic was prepared from the concentrated suspensions of $Al_2O_3$–$ZrO_2$ mixtures with variable content of $Al_2O_3$–$ZrO_2$. The FGC ceramic was prepared by utilizing slip casting method. The suitable rheological behavior of suspensions is important for the preparation ceramic by slip casting. The next important factor for the preparation of defect free FGC is the coordination of the temperature expansion of individual layers [3].

## EXPERIMENTAL

$\alpha$-$Al_2O_3$ - AKP 53 (SUMITOMO Chemical Co. Ltd) and zirconia powders TZ-3Y-E (TOSOH Corporation Japan) were used in this study. The average size of particles of $\alpha$-$Al_2O_3$ is 200 nm and the average size of particle of $ZrO_2$ is 26 nm. An organic polyelectrolyte Dolapix (Zschimmer-Schwarz, BRD) was used as a deflocculant. The suspensions were prepared by homogenization in a planetary mill.

The composition of suspensions is shown in Table 1. Rheological properties were determined by viscometer RotoVisco 1. The optimal deflocculant content was determined according to rheological properties of suspensions (Table 1). The cylindrical shape samples were prepared by utilizing a slip casting method into a porous mold.

The porosity and the size of pores were measured by Hg porosimetry (Table 2). The results show that the samples prepared from suspensions with constant solid loading but with increasing $ZrO_2$ ratio present growth

up of porosity. This trend is caused by the changes in ratio between $ZrO_2$ and $Al_2O_3$ particles ($d_{50}ZrO_2$ = 26 nm, $d_{50}Al_2O_3$ = 200 nm). The lower value of porosity of $Al_2O_3$ bodies is caused by the colloidal-chemical state of the suspension. The lower viscosity values allow more efficient packing of particles in the suspension and in the green cast bodies [4]. The deflocculant content was sufficient to enhance electrostatic repulsion between particles that assisted to obtain a more efficient packing of the particles [4, 5]. This result is in accordance with the ESA measurements (ESA 8000, Matec Instruments), see Figure 1.

The length changes were measured in green state using the LINSEIS dilatometer.

The coefficient of linear expansion α was evaluated according the Equation (1).

$$\alpha = \frac{dl}{l_0 dt}\left[K^{-1}\right] \quad (1)$$

with $l_0$ - original length of sample, $dl$ - the change of length of sample, $dt$ - the temperature change.

The Figure 2 shows the dependence of coefficient of linear expansion in relation with temperature. The further work will draw attention to the temperature interval 100-400°C. The difference of sample shrinkage and the expansion changes can be caused by different content of deflocculant, different porosity and different thermal expansivity between $Al_2O_3$ and $ZrO_2$ samples in temperature interval 100-400°C. The highest difference of expansion is observed between $ZrO_2$ samples and the others samples (Figure 2b).

The following part of the work focuses on examination of factors that can influence the expansion changes of samples prepared from $Al_2O_3$–$ZrO_2$ system.

Based on the changes in length depending on temperature, the lowest values on the dilatation curves were determined (Figure 3); they represent the temperature corresponding to the end of the body shrinkage (TCES) in temperature interval 100-400°C. It was found, that by increasing $ZrO_2$ content in the samples TCES of samples is increasing (see Figure 4).

The differential thermal analysis (DTA) was made in order to analyse the behavior of samples during the thermal treatment. There is the exothermic peak at temperature interval 170-440°C (Figure 5), indicating the chemical change of the deflocculant decomposition and burning. The end of burning out of deflocculant in each system was in the temperature approximately 440°C.

In the further work, the hypotheses that decreasing deflocculant content in suspension can lead to the decreasing of dilatation changes, was used. The reduction of deflocculant content has an influence on the rheological properties. Further $ZrO_2$ suspensions with 76 wt.% solid loading and with different content of deflocculant, i.e. 0.8-1.2 wt.% were prepared. As the optimal content for 76 wt.% solid loading $ZrO_2$ suspension 1.0 wt.% of deflocculant was found. The typical difference between suitable rheological behavior and the wrong rheological behavior is demonstrated on Figure 6. Table 3 shows the apparent viscosities values. The comparison of the viscosities values of 77 and 76 wt.% solid loading show that there are no important changes in rheological properties of the suspensions.

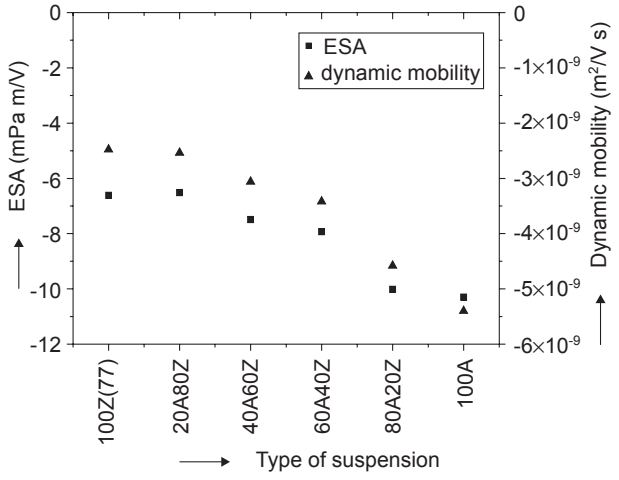



Figure 1. The ESA and dynamic mobility in relation to type of suspension.

Table 2. The characteristic of dried samples.

| Type of sample | Median pore radius (μm) | Porosity (%) |
|---|---|---|
| 100Z | 0.0161 | 41,4 |
| 20A80Z | 0.0155 | 37.9 |
| 40A60Z | 0.0161 | 35.6 |
| 60A40Z | 0.0164 | 34.3 |
| 80A20Z | 0.0165 | 32.2 |
| 100A | 0.0178 | 31.2 |

Table 1. The characteristic of suspensions.

| Marking | $ZrO_2$ (wt.%) | $Al_2O_3$ (wt.%) | Deflocculant content (wt.%) | Solid content (wt.%) | Apparent viscosity $\eta(\gamma = 100\ s^{-1})$ (Pas) |
|---|---|---|---|---|---|
| 100Z | 100 | 0 | 1.4 | 77 | 0.091 |
| 20A80Z | 80 | 20 | 0.9 | 77 | 0.055 |
| 40A60Z | 60 | 40 | 0.8 | 77 | 0.048 |
| 60A40Z | 40 | 60 | 0.7 | 77 | 0.046 |
| 80A20Z | 20 | 80 | 0.6 | 77 | 0.039 |
| 100A | 0 | 100 | 0.5 | 75 | 0.027 |

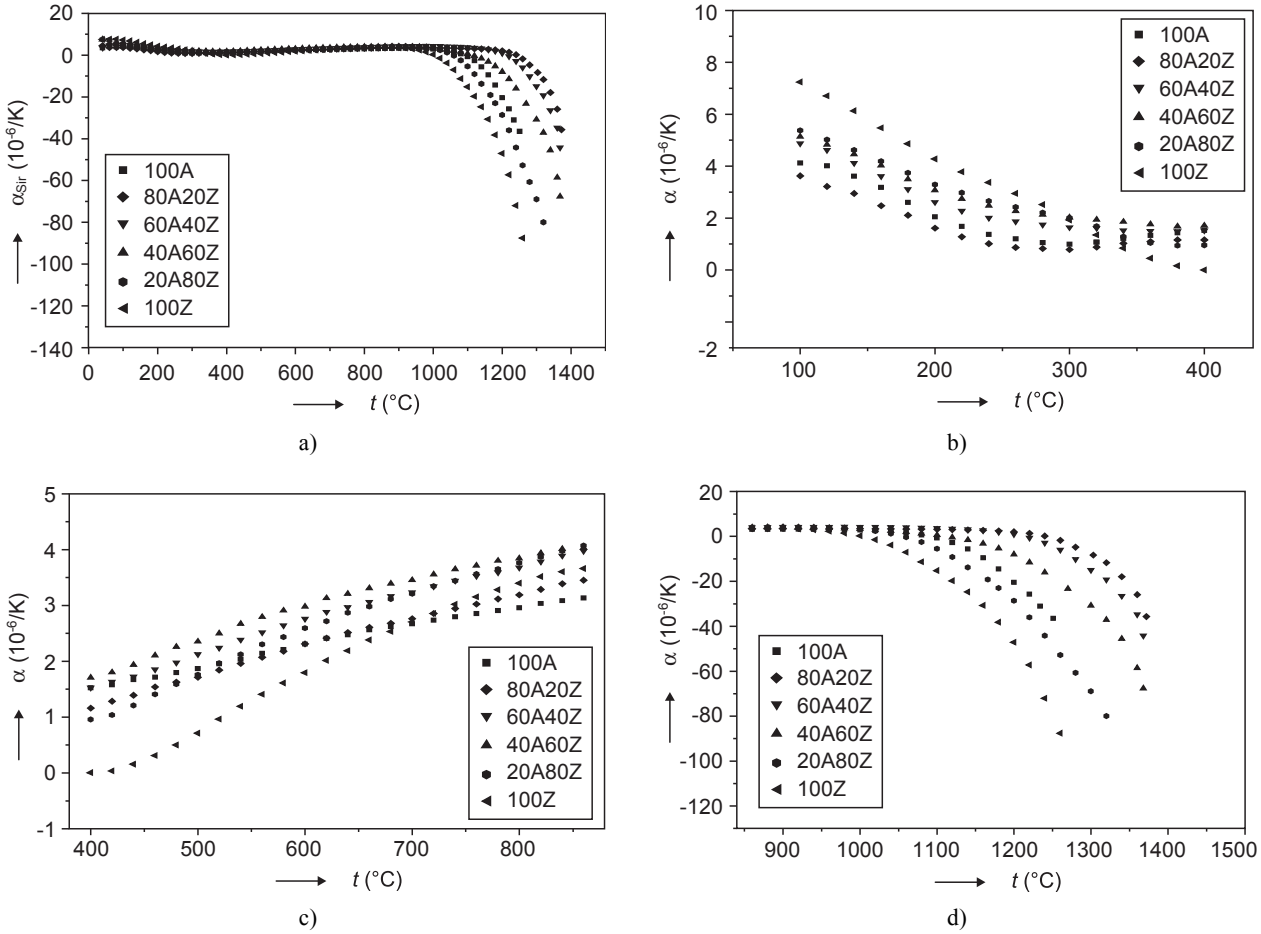



Figure 2. The coefficient of linear expansion α of the $Al_2O_3$–$ZrO_2$ samples in relation with temperature. a) 20-1380°C, b) 100-400°C, c) 400-860°C, d) 860-1380°C.

The porosity and size of pores were measured on dried bodies prepared by slip casting method, see Table 4. From the comparison of porosity and size of pores of bodies of 77 and 76 wt.% $ZrO_2$, it was found that decreasing content of solid did not cause the difference in porosity, respectively the difference in distribution of pores. However, the decreasing content of solid loading allows to reduce deflocculant content i.e. from 1.4 wt.% to 1.0 wt.%.

Table 3. The value of apparent viscosity $ZrO_2$ suspensions in relation with shear rate.

| Solid content (wt.%) | Apparent viscosity η (Pas) | | | |
|---|---|---|---|---|
| | $\gamma = 50\ s^{-1}$ | $\gamma = 100\ s^{-1}$ | $\gamma = 500\ s^{-1}$ | $\gamma = 1000\ s^{-1}$ |
| 77 | 0.119 | 0.091 | 0.033 | 0.028 |
| 76 | 0.105 | 0.085 | 0.041 | 0.034 |

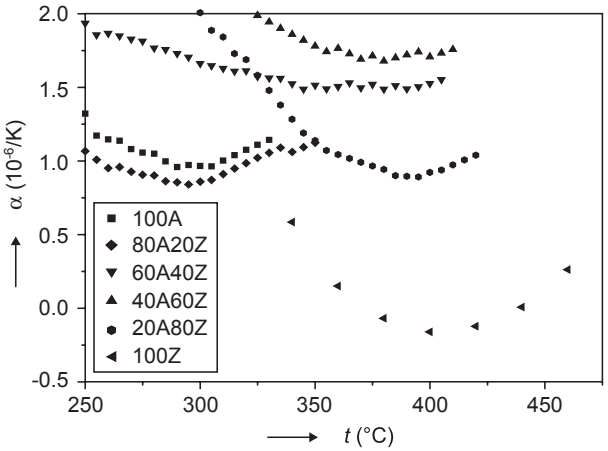



Figure 3. The coefficient of linear expansion in the temperature interval 250-450°C for evaluating the TCES.

Table 4. The porosity of $ZrO_2$ samples.

| Solid content (wt.%) | 76 | 76 | 76 | 76 | 76 | 77 |
|---|---|---|---|---|---|---|
| Deflocculant content (wt.%) | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 | 1.4 |
| Median pore radius (μm) | 0.0172 | 0.0175 | 0.0160 | 0.0165 | 0.0165 | 0.0161 |
| Porosity (%) | 40.1 | 41.2 | 41.0 | 40.7 | 41.2 | 41.4 |

Linear expansivity of dried samples was studied. Based on dilatation curves in temperature interval 100-400°C the dependence of coefficient of linear expansion α in relation to temperature was evaluated (Figure 7). The TCES was determined using the dependencies α = α(t) (Figure 8).

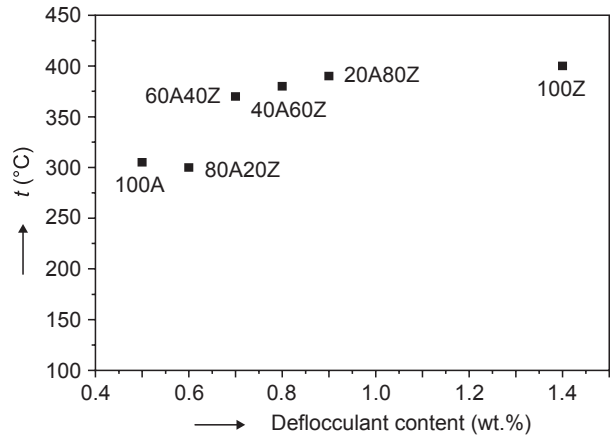



Figure 4. TCES in relation with the content of deflocculant.

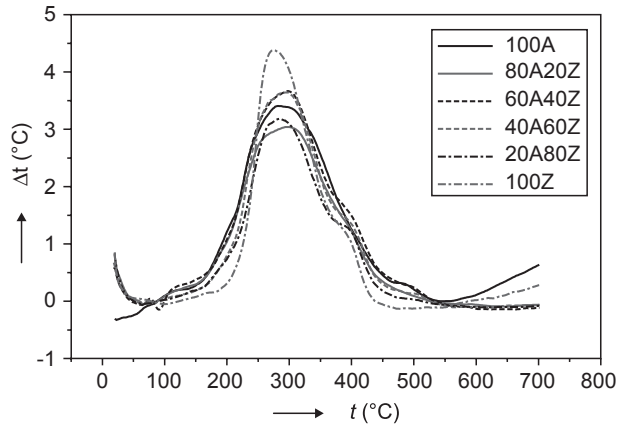



Figure 5. DTA curves of the $Al_2O_3$–$ZrO_2$ system.

The Figure 9 shows the dependence of value of coefficient of linear expansion in the TCES of $ZrO_2$ samples in relation with content of deflocculant.

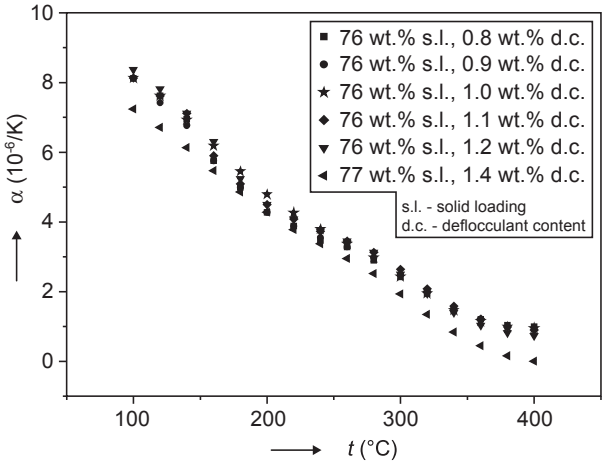



Figure 7. The coefficient of linear expansion α of $ZrO_2$ samples in relation with the temperature in temperature interval 100-400°C.

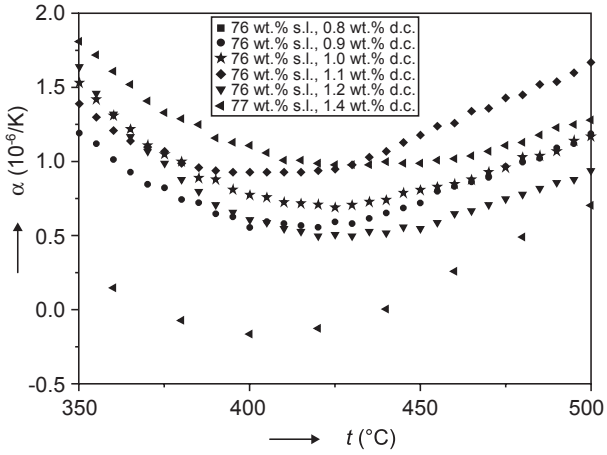
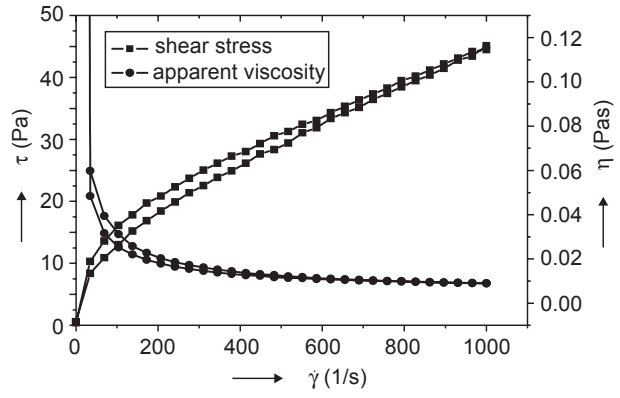
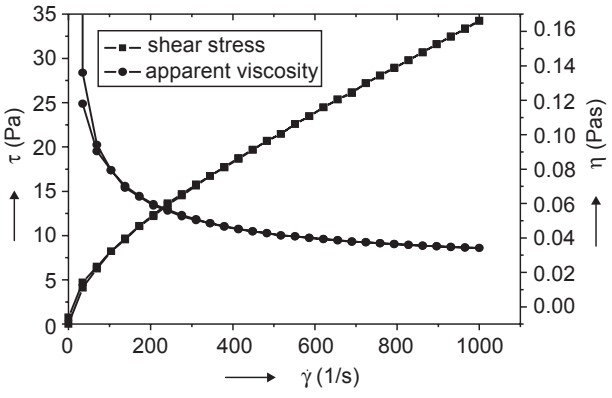



Figure 8. The coefficient of linear expansion of $ZrO_2$ bodies in temperature interval 350-500°C for evaluating the TCES.




a)




b)

Figure 6. Shear stress and apparent viscosity in relation with shear strain for the $ZrO_2$ suspension with 76 wt.% solid loading and content of deflocculant a) 0.8 wt.% - wrong rheological behavior, b) 1.0 wt.% - suitable rheological behavior.

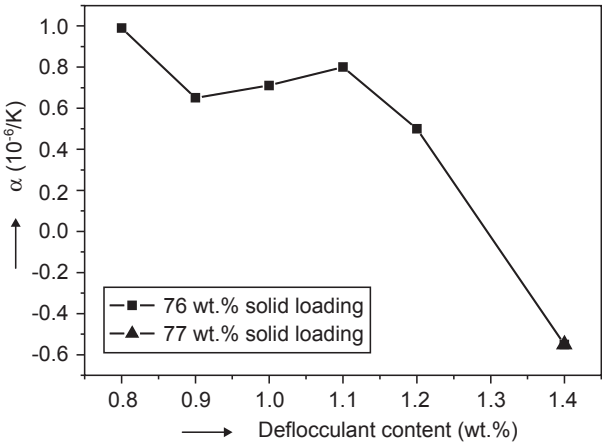



Figure 9. The coefficient of linear expansion α of $ZrO_2$ samples in relation with solid loading and deflocculant content.

The results show that the TCES remains the same, i.e. 415 ± 5°C, independent on content of deflocculant in suspension. The reduction of deflocculant content caused growth the coefficient of linear expansion α. The reduction of content of deflocculant from 1.4 wt.% to 1.0 wt.% causes increase of the coefficient of linear expansion α from $-0.6 \cdot 10^{-6}$ to $0.7 \cdot 10^{-6}$ $K^{-1}$ in the low temperature interval 100-400°C. This increase in $ZrO_2$ system by means of optimalization of deflocculant ratio allows the approach the coefficient of linear expansion in the system of variable solid content of $Al_2O_3$–$ZrO_2$.

## CONCLUSION

The reduction of $ZrO_2$ content in suspension allows the approach of coefficient of linear expansion ZrO2 samples with samples of $Al_2O_3$–$ZrO_2$ in variable compound in the temperature interval 100-400°C without the influence on rheological characters $ZrO_2$ suspension and physical properties of the samples. It could be also seen that the temperature corresponding to the end of the body shrinkage is influenced by the porosity of samples and the distribution of pores. The deflocculant ratio has no important influence on the temperature corresponding to the end of the body shrinkage; it has important influence on the value of coefficient of linear expansion α.

## Acknowledgement

*The authors would like to acknowledge the help of the colleagues from Technische Universität Freiberg, Institut für Keramik, Glas- und Baustofftechnik for the study on thermal behaviour of the samples. We would also like to thank to Mr. R. Herbig and his colleagues from Technische Universität Freiberg, Institut für Keramische Werkstoffe for performing the ESA measurements.*

*This work was part of project No 2A-1TP1/063, "New glass and ceramic materials and advanced concepts of their prparation and manufacturing", realized under financial support of the Ministry of industry and trade of the Czech Republic.*

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## DÉLKOVÉ ZMĚNY KERAMIKY NA BÁZI $Al_2O_3$–$ZrO_2$ PŘIPRAVENÉ LITÍM

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Práce se zabývá přípravou funkčně gradientní keramiky na bázi $Al_2O_3$–$ZrO_2$ litím suspenzí do porézní formy. Významnou roli pro přípravu bezdefektní kompozitní keramiky hrají rozdíly délkové roztažnosti mezi jednotlivými vrstvami při výpalu těles.

První část této práce je zaměřena na přípravu jednovrstvých těles s proměnným složením $Al_2O_3$–$ZrO_2$ (0-100 hmot. %). Z koloidně-reologických vlastností soustavy s proměnným složením byly určeny optimální obsahy ztekutiva. Z těchto suspenzí byla litím do sádrové formy připravena tělesa, u kterých byly studovány délkové změny během výpalu. Z dilatometrických měření těles bylo zjištěno, že velké rozdíly koeficientu délkové roztažnosti mezi tělesy proměnného složení jsou v oblasti teplot 100-400°C. Na základě výsledků bylo stanoveno, že obsah ztekutiva může ovlivnit koeficient délkové roztažnosti. Fakt, zda zjištěný rozdíl délkových změn je způsoben pouze vyhořováním ztekutiva nebo souvisí i s pórovitostí těles, byl studován na tělesech připravených z čistého $ZrO_2$. Na základě naměřených výsledků lze říci, že průběh délkových změn je ovlivněn pórovitostí a rozdělením velikosti pórů vysušených těles v nízkoteplotním intervalu. Obsah ztekutiva v suspenzi má vliv především na velikost délkových změn v nízkoteplotním intervalu.