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Functional gradient alumina ceramic materials—Heat treatment of bodies prepared by slip casting method

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Abstract

The work deals with the study of heat treatment of functional gradient alumina ceramics with controlled microstructure. The bodies with different porosity layers were prepared by slip casting into a porous block. The sol–gel transition of AlO(OH) was used to stabilize the pore-generating agents with a particle size of 150–190 μm and the preparation of a reproducible aqueous suspensions of α-Al_2O_3 for the slip casting of bodies with defined porosity. From the technological point of view, the preparation of functional gradient alumina ceramics requires the development of a defect-free interface between compounded layers conditioned by an appropriate combination of the compounded layers with different porosity and different irreversible dilatation changes. The linear model of dilatation changes did not result in the preparation of a defect-free composite ceramics. The non-linear model developed has aided to describe the admissible difference of dilatational changes $\Delta\alpha_{irr}$, between individual compounded layers of green bodies during the firing process. The deformation as a result of non-uniform body formation was related to the total body thickness and did not occur for the composite bodies with thickness larger than 5×10^{-3} m. The value of admission difference of irreversible dilatation changes was used to predict the optimal preparation conditions of defect-free composite alumina ceramics with compounded layers possessing controlled porosity.

Keywords: Firing; Slip casting; Composites; Optical microscopy; Porosity; Al_2O_3; Biomedical applications; Structural applications

1. Introduction

Ceramics based on Al_2O_3 or tetragonal ZrO_2 has been applied for many years for bio-inert replacement of human skeleton preparation, ceramic implants. These ceramic materials are fully sintered and their density is close to these systems' theoretical densities. Despite very good mechanical and physical properties, as for example mechanical strength and resistance against abrasion (ISO 6474), their disadvantage is fragility and a considerable difference in values of the Young's modulus of elasticity and fracture toughness between the implant and bone tissue. This discrepancy of mechanical properties is linked with the transport of non-physiological stress problems between implant and bone tissue that can cause pain or inflammation and thus deteriorate the implant fixation. This phenomenon could lead to the bone weakening or its withering caused by the implant stress screening in the bone carrying almost total mechanical load.

The bio-inert implants surface is smooth and polished. Current trends in bio-inert ceramic materials are focused on the utilization of functional gradient and porous ceramics to harmonize mechanical properties of the ceramic implants with those of the bone tissue. There is an considerable effort to harmonize the ceramic texture with the bone tissue and also to improve the implant fixation to the bone tissue via the tissue growing through the implant surface (open pores of size of 10^2 μm enable that growing through).

Solving these problems is associated with the improvement of functional gradient ceramic materials with controlled porosity enabling rapprochement of oxide ceramics for surgical applications and bone tissue properties. The porosity gradient brings a positive effect in terms of the ability of Young's ceramics modulus to more closely resemble Young's modulus of bone. Furthermore, it dependents on the possibility of pore formation allowing implant fixation by bone tissue ingrowths into opened pores on the implant surface layer.[1–8]

The aim of this work was to prepare functional gradient alumina ceramics with controlled porosity change by the slip casting into the porous mould from suspension and to determine the optimum conditions for appropriate combination of the

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compounded layers with different porosity and different irreversible dilatational changes. The work was divided into two steps. The first step was to prepare and determine the coefficient of irreversible dilatational changes of the alumina ceramic green bodies with variable constant porosity. In the second step the functional gradient alumina ceramics with layers of variable porosity were prepared and the admission difference of irreversible dilatation changes $\Delta\alpha_{irr}$ between compounded layers was determined to achieve the defect-free bodies.[9]

2. Materials and methods

The work was carried-out with the powder α-Al_2O_3 (AKP 15-Sumitomo Chemical Co. Ltd., Japan), $d = 0.6–0.8.10^{-6}$ m. Thin-walled balls of average particle size of 150–190 μm were used as the pore-generating agents, consisting of α phase of Al_2O_3. To prevent sedimentation of the thin-walled balls and to stabilize the suspension, we utilized the boehmit gel AlO(OH) (Dispersal sol P2, CONDEA Chemie GmbH, BRD). For suspension stabilization the Sokrat 32A (CHZ Sokolov, CZ) as a deflocculant was used. Bulk density ρ_v was determined by the double weighing method (Archimedes' method). From bulk density ρ_v and ultimate density ρ the porosity PS as the volume of open and closed pores and cavities in the sample/total volume of sample (including all pores and cavities) ratio was calculated in accordance with Eq. (1):

$$\mathrm{PS}\,(\%) = \frac{V_o + V_n}{V_a} \times 100 = \left(1 - \frac{\rho_v}{\rho}\right) \times 100 \qquad (1)$$

where V_o is the volume of open pores, V_n the volume of closed pores and V_a is the total volume of the sample. Dilatational changes of green bodies on the dilatometer ADAMEL LHOMARGY DI 24 were detected. Coefficient of irreversible dilatation changes of green bodies or layers of green bodies during firing process is expressed in Eq. (2):

$$\alpha_{irr} = \frac{\Delta L}{L_0\,\Delta T} \qquad (2)$$

where L_0 is initial body length, ΔL is length change within the temperature interval ΔT. The optical micrographs of bodies were created using optical analysis LUCIA.

3. Experimental procedure

3.1. Preparation of casting suspension and testing bodies

The suspension for the bodies' preparation by slip casting was prepared by mixing of the basic components, i.e. Al_2O_3, deflocculant Sokrat, pore-generating agents and boehmit AlO(OH). The original utilization of the sol–gel transition of AlO(OH) for kinetic stabilization of resulting suspension is based on appropriate wetting of the Al_2O_3 particles surface by the formulated gel. On the basis of rheological measurements, the optimum composition of the reproducible kinetic and aggregate stable aqueous suspension was determined. The results concerning the rheological measurements have already been reported.[10,11]

From the experimentally verified model of the body creation kinetics from suspensions containing different content of the pore-generating agents the time for the body of requisite thickness creation was determined. On basis of the specified parameters of the casting process the bodies of constant variable porosity and functional gradient bodies with compounded layers of variable porosity were prepared. The bodies were dried and investigated for the temperature dependencies of the irreversible dilatational changes. The irreversible length changes measuring within the temperature intervals 20–1570 °C were carried-out on the dried bodies in prism form of size of $3 \times 3 \times 25 \times 10^{-3}$ m with content of pore-generating agents within the interval of 0–6.8 wt.%. For the bodies fired to temperature of 1570 °C by the chosen regime (2 °C/min, 1570 °C within 2 h) the porosity (PS) was determined.[9]

4. Results and discussion

4.1. Linear model of the length changes within the temperature interval of 20–1000 °C

From the curves of irreversible dilatation changes determined during thermal exposure of the bodies within the temperature range from 20 to 1000 °C the coefficient of irreversible dilatation changes α_{irr} was evaluated for the temperature intervals of 20–400, 20–800 and 20–1000 °C. The evaluated dependencies of coefficient of the irreversible dilatation changes α_{irr} on the porosity PS of the bodies are presented in Fig. 1. From Fig. 1 is evident, that the evaluated dependencies of the irreversible dilatational changes coefficient α_{irr} on the porosity have approximately the identical course within the different temperature intervals, but with increasing temperature interval the α_{irr} values increase. Assuming the differences of the coefficients of irreversible dilatational changes between layers of different porosity are constant within the whole temperature interval, the dependence α_{irr} on the porosity is fitted by the linear model $\alpha_{irr} = f(\mathrm{PS})$ in the chosen temperature intervals.

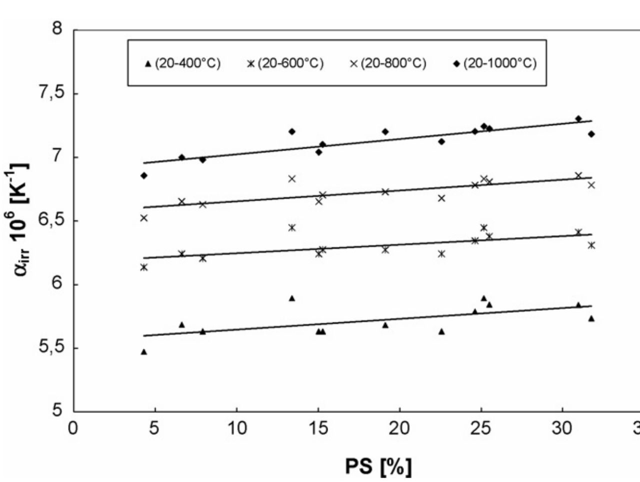

Fig. 1. Dependence of coefficient irreversible dilatational length changes α_{irr} on the bodies' porosity in mentioned temperature intervals—linear model.

In order to estimate the admissible difference of irreversible dilatational changes between the individual compounded layers the difference of admissible irreversible dilatation changes $\Delta\alpha_{irr}$ was chosen between the individual layers $\Delta\alpha_{irr} = 0.2 \times 10^{-6}\,K^{-1}$ as an initial estimation for the temperature interval of 20–1000 °C. Granted the linear model validity and the admissible value $\Delta\alpha_{irr}$ are kept, the bodies are mutually joined as follows: (content of pore-generating agent in individual compounded layers): 0–0; 0–0.5; 0.5–1; 1–1.5; 15–2; 2–26; 26–32; 32–38; 3.8–4.4; 4.4–5.0; 5.0–5.6; 5.6–6.2; 6.2–6.8 wt.%. The linear model shows that the differences $\Delta\alpha_{irr}$ between the individual compounded layers do not exceed the presented value $\Delta\alpha_{irr} = 0.2 \times 10^{-6}\,K^{-1}$ within the whole temperature range and some of them are significantly lower.

By means of elaborated casting procedure the two-layer bodies there were prepared in the board form of total thickness of 2×10^{-3} m and the casting time of individual layers was determined in such way to reach the total thickness of 1×10^{-3} m of each layer. On basis of the linear model the two-layer bodies with above-mentioned content (0–0; 0–0.5; 0.5–1; 1–1.5; 1.5–2; 2–2.6; 2.6–3.2; 3.2–3.8; 3.8–4.4; 4.4–5.0; 5.0–5.6; 5.6–6.2; 6.2–6.8 wt.%) were prepared. The prepared two-layer bodies were fired at 1570 °C. Interface character between individual layers of bodies is documented on micrograph in Fig. 2. Consequently the deformation of the sintered bodies was evaluated.

4.2. Deformation of the two-layer bodies of variable porosity

The suitability of the linear model $\alpha_{irr} = f(PS)$ was verified by the two-layer bodies deformation measuring in the dried state and after firing. The deformation value was determined from the micrographs obtained from the optical microscope analysis. The deformation of the fired samples was specified by measuring the maximum deflection Δx in the body central point of the vertical axis assuming the symmetric deformation demonstrated in Fig. 3.

The evaluated deformations of the fired two-layer bodies were made in accordance to the pore-generating agent content in individual sample layers as shown in Table 1.

The results suggest that all the prepared two-layer bodies were deformed during the firing. Regarding the deformation of body consisting merely of alumina without the pore-generating agents (i.e. two-layer body with the layers composition 0–0 wt.% of pore-generating agents), the deformation is not caused only by the irreversible dilatation change differences. The stress probably originates even during the formation process as a result of the irregular suction of the porous plaster form. The body deformation consisting of the alumina without the pore-generating agents is lower compared with those of the two-layer bodies with the pore-generating agents. Moreover, from the bodies evaluation resulted, in layer composition of

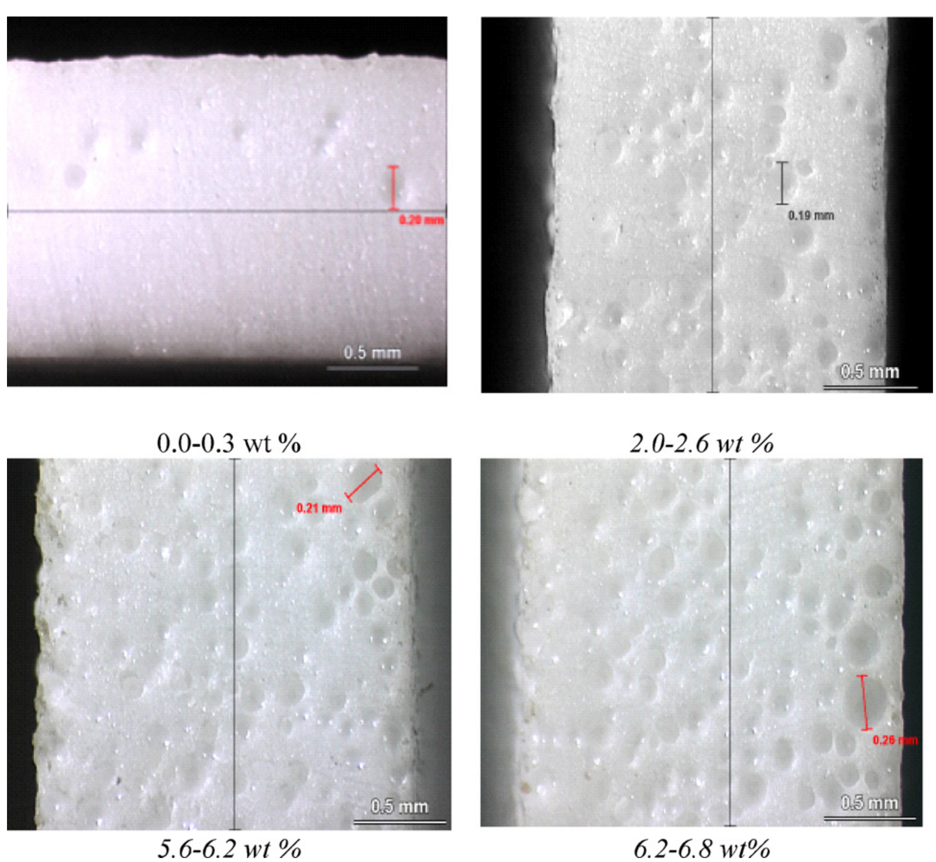

Fig. 2. Character of two-layer bodies with different pore-generating agent content (bottom: pore-generating agent content in the green body layer, black line-layers-interface).

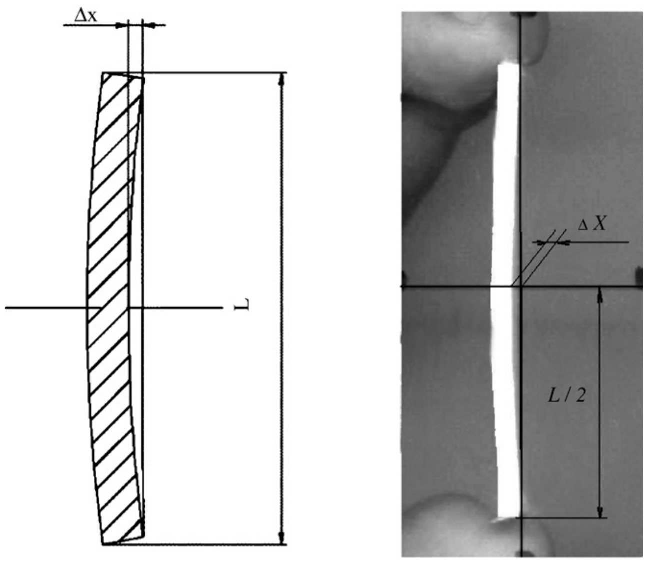

Fig. 3. Determination of bodies' deformation–illustration and reality.

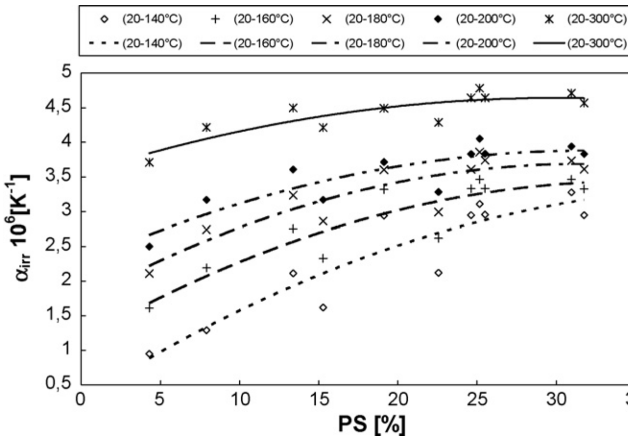

Fig. 4. Dependencies of coefficient of irreversible dilatational changes α_{irr} on the bodies' porosity in chosen temperature intervals—non-linear model.

0 and 0.5 wt.% of the pore-generating agents the deflection is higher compared with those containing the pore-generating agents approximately to 3.8 wt.%. The layer harmonization, corresponding layer joining without and with the pore-generating agents is therefore significant for the stress-free composite state solution.

Nevertheless, the deformation of the all prepared bodies suggests that the simplified linear model $\alpha_{irr} = f(PS)$ can only be a rough estimation for evaluation of suitable composition of layers with different porosity. The irreversible dilatation changes difference between compounded layers evaluated using this model did not exceed the value $\Delta\alpha_{irr} = 0.2 \times 10^{-6}\,K^{-1}$. However, the estimated bodies' deformation exhibited an exceeding of this critical difference. For this reason it was necessary to specify the model and thus the body deformation extent without the pore-generating agents can be considered as the deformation standard value which occurs on all the samples in consequence of irregular suction of plaster form.

Table 1
Deformation of the two-layer bodies with different pore-generating agents content in compounded layers

Pore-generating agent content in layers (wt.%)	Deformation (mm)
0.0–0.0	1.283
0.0–0.5	1.675
0.5–1.0	1.544
1.0–1.5	1.436
2.0–2.6	1.388
2.6–3.2	1.421
3.2–3.8	1.817
3.8–4.4	1.954
4.4–5.0	2.158
5.0–5.6	2.338
5.6–6.2	2.595
6.2–6.8	2.182

4.3. Non-linear model of temperature and porosity dependence α_{irr}

For more detailed evaluation of the irreversible dilatation changes of green bodies within the temperature interval of 20–1000 °C the dependences α_{irr} on the porosity within the temperature intervals 20–140, 20–160, 20–180, 20–200 and 20–300 °C were evaluated from the measured curves of the irreversible dilatation changes of bodies.

The specified dependencies are presented in Fig. 4. The obtained α_{irr} dependencies on the porosity PS were plotted by the non-linear function in the chosen temperature intervals as presented in Table 2. From the α_{irr} values were expressed the irreversible dilatation changes differences $\Delta\alpha_{irr}$ dependences on the porosity for the chosen temperature intervals seen in Fig. 5. Utilization of the non-linear model $\alpha_{irr} = f(PS)$ for the temperature zone of 20–300 °C has allowed the precise expression of the $\alpha_{irr} = f(PS)$ dependence. It was shown that within the temperature range of 20–300 °C the $\Delta\alpha_{irr}$ exceeded the $\Delta\alpha_{irr}$ value of $0.2 \times 10^{-6}\,K^{-1}$, particularly for the layers combination of 0.0–0.5 wt.%. From the 20–300 °C temperature range analysis it obvious that this temperature interval is the most critical in terms of the green bodies irreversible dilatation changes difference and thus also due to the possible stress between the composite body layers which can be one of the causes of its deformation during firing. The stress generated within this temperature zone is linked to the deffloculant thermal degradation and boehmit dehydroxidation. The curves shape shown in Figs. 4 and 5 suggests that it is very important to compound the

Table 2
The dependence of α_{irr} on porosity PS—non-linear model

Temperature range (°C)	Fitted function	Regression coefficient
20–140	$\alpha_{irr} = 4.150(1.060 - \exp(-0.0389PS))$	0.9189
20–160	$\alpha_{irr} = 2.852(1.349 - \exp(-0.0613PS))$	0.9107
20–180	$\alpha_{irr} = 2.443(1.594 - \exp(-0.0817PS))$	0.8974
20–200	$\alpha_{irr} = 2.077(1.916 - \exp(-0.0943PS))$	0.8804
20–300	$\alpha_{irr} = 1.479(3.159 - \exp(-0.1170PS))$	0.8810

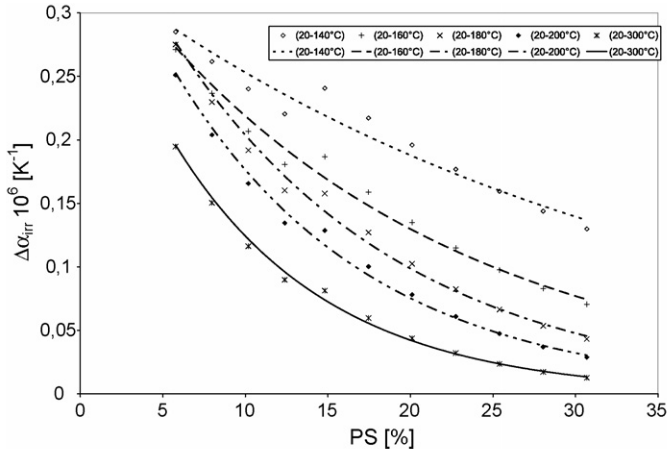

Fig. 5. Dependence of difference of irreversible dilatational changes $\Delta\alpha_{\mathrm{irr}}$ on porosity PS in chosen temperature intervals—non-linear model.

layer with and without the pore-generating agents where are the highest value of difference of irreversible dilatational changes $\Delta\alpha_{\mathrm{irr}}$.

4.4. *Determination of the irreversible dilatational changes within the high-temperature zone*

For the measured data processing within the temperature up to 1570 °C the procedure using the non-linear model of the irreversible dilatational length changes in partial temperature intervals was used. Within the high temperature zone between 1000 and 1570 °C the dilatational length changes are influenced by volume changes during ceramic sintering. For this reason the evaluation based on the bodies' shrinkage measuring in dependence on the sintering temperature was carried out. This have shown that with the increasing pore-generating agents the total shrinkage decreases and the highest differences in the shrinkage are concentrated between the non-porous and porous layer and in the layers areas with little amount of the pore-generating agents respectively. With increasing porosity of both joined layers these differences considerably decrease. From the view of the functional gradient ceramics the most important will be the layers shrinkage on the interface between the layer without the porous agents and the porous layer. The results are in full accordance with the knowledge presented in Section 4.3. The results were experimentally verified by testing the two-layer bodies composed of a layer without the pore-generating agents and of a second layer with gradually increasing pore-generating agents.

4.5. *Deformation of the two-layer bodies where the one layer is of variable porosity*

Two-layer bodies were prepared for the experiment. The bodies consisted of one layer always without the pore-generating agents, and in the second layer the pore-generating agents content was gradually increased in such way that the difference of irreversible dilatation changes between layers $\Delta\alpha_{\mathrm{irr}}$ value gradually increased in the prepared green bodies in range from 0.2 to $2.1 \times 10^{-6}\,\mathrm{K}^{-1}$ (for the temperature interval of 20–140 °C). The total thickness of all two-layer bodies was constant, i.e. 2×10^{-3} m. Both layers are of the same thickness of 1×10^{-3} m. It was shown, that even if the value α_{irr} of $0.2 \times 10^{-6}\,\mathrm{K}^{-1}$ was kept the bodies deformation occurred as seen in Fig. 6. That deformation is approximately identical with that of the body prepared by the two-layers joining without the pore-generating agent, where the irreversible dilatation changes difference is zero Table 3. If the limit value is exceeded the two-layer bodies defection increases significantly.

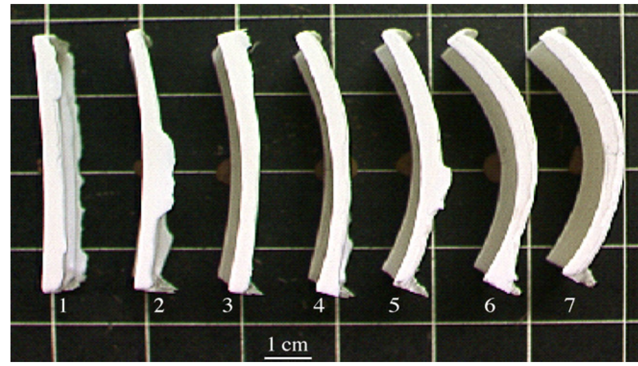

Fig. 6. Two-layered bodies (as fired) with increasing content of pore-generating agent in second layer: (1) (0.0–0.3)*; (2) (0.0–1.2)*; (3) (0.0–1.7)*; (4) (0.0–2.7)*; (5) (0.0–3.8)*; (6) (0.0–5.7)*; (7) (0.0–6.8)*; *numbers in brackets give the pore-generating agent content in the layer in wt.%.

4.6. *The body thickness effect on its deformation*

By observing this fixed value $\Delta\alpha_{\mathrm{irr}} = 0.2 \times 10^{-6}\,\mathrm{K}^{-1}$ it could be eliminated the deformation contribution caused by the admissible difference of irreversible dilatational changes and are able to study the composite thickness effects on composite deformation. For this purpose the two-layer bodies with a constant difference of irreversible length changes $\Delta\alpha_{\mathrm{irr}} = 0.2 \times 10^{-6}\,\mathrm{K}^{-1}$ were prepared by the layer connection without the pore-generating agents and the layer with the 0.3 wt.% of the pore-generating agents. In the bodies only the thickness T of both layers and total thickness T_{c} of the two-layer body were changed. The deformation or the bodies' deflection was evaluated in accordance with the procedure described in Section 4.2. It was determined that

Table 3
Deformation of two-layer bodies with growing difference of irreversible dilatational changes between compounded layers $\Delta\alpha_{\mathrm{irr}}$

Pore-generating agent content in layers (wt.%)	$\Delta\alpha_{\mathrm{irr}}$ ($\times 10^{-6}\,\mathrm{K}^{-1}$)	Deformation (mm)
0.0–0.0	0.0	1.283
0.0–0.3	0.2	1.265
0.0–0.5	0.4	1.675
0.0–1.2	0.8	2.639
0.0–1.7	1.0	3.827
0.0–2.7	1.4	5.012
0.0–3.8	1.7	7.290
0.0–5.7	2.0	8.617
0.0–6.8	2.1	9.089

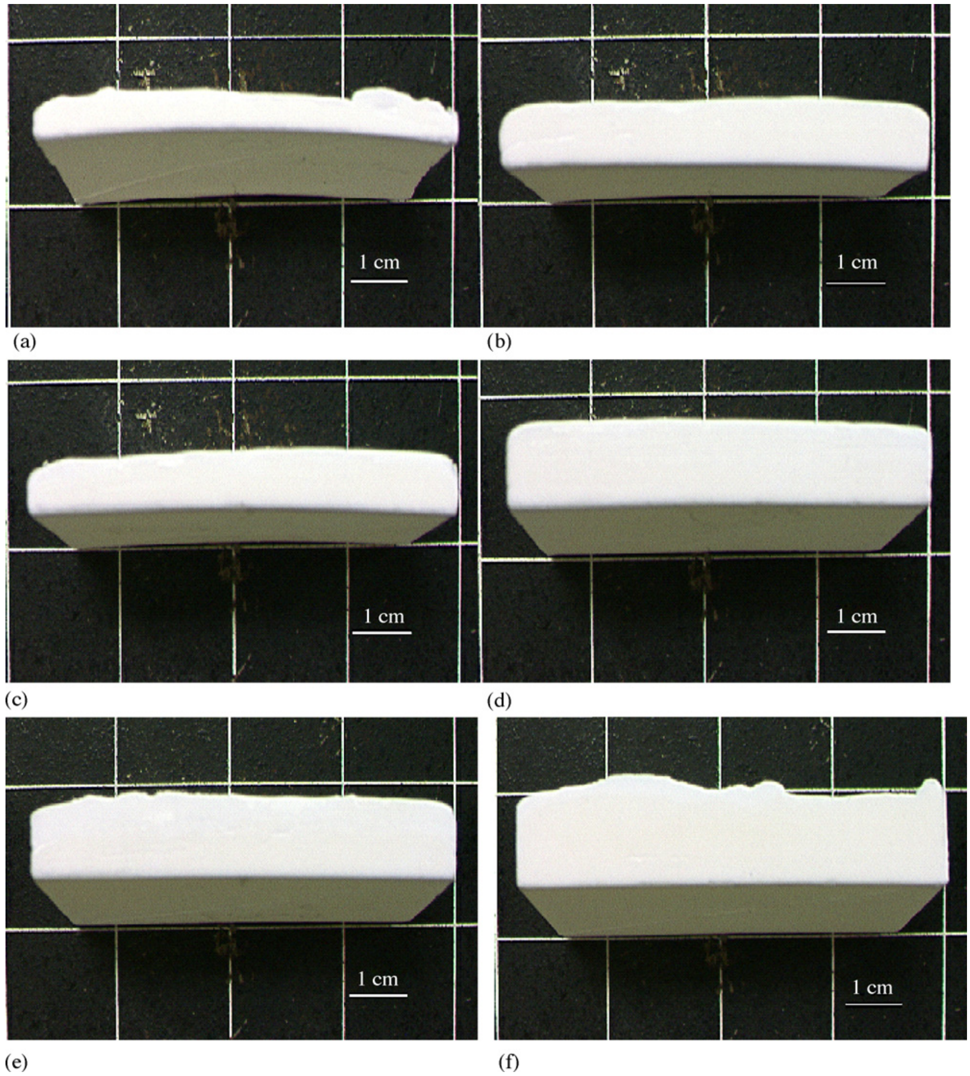

Fig. 7. Character of bodies' deformation with growing layer thickness–two-layered bodies with the following individual layers thickness: (a) 1–1 × 10^{-3} m; (b) 2–1 × 10^{-3} m; (c) 2–2 × 10^{-3} m; (d) 2–3 × 10^{-3} m; (e) 3–3 × 10^{-3} m; (f) 2–5 × 10^{-3} m.

at the total thickness $T_c = 5 \times 10^{-3}$ m (or more) there was no deformation. The results of the deformation evaluation along with the data on the layer thickness in the bodies are presented in Table 4. The character of bodies' deformation is seen in Fig. 7.

Table 4
Deformation of bodies with variable layer thickness with constant difference of the irreversible dilatational change between compounded layers $\Delta\alpha_{irr} = 0.2 \times 10^{-6}\,K^{-1}$

Thickness of pore-generating agents free layer (mm)	Thickness of layer with pore-generating agent 0.3 wt.% (mm)	Deformation (mm)
1	1	1.265
2	1	0.933
2	2	0.450
2	3	0.000
3	3	0.000
2	5	0.000
4	4	0.000

5. Conclusion

It could be concluded from this study that if the bodies consist of the compounded layers with content of 0 and 0.3 wt.% of the pore-generating agents the value admissible difference of irreversible dilatation changes $\Delta\alpha_{irr} = 0.2 \times 10^{-6}\,K^{-1}$ remains constant in the temperature range of 20–1570 °C. The possible deformation caused by the difference of irreversible dilatational changes was virtually eliminated. The deformation was elicited by either the imperfect technology of the bodies' preparation or by the bodies' deformation which occurred at the temperature over 1000 °C. A linear model of the irreversible dilatational changes of the green bodies did not result in the preparation of a defect-free composite ceramics with layers of controlled porosity, whilst the non-linear model developed allowed for determination of the admissible difference of dilatational changes between the individual compounded layers. A decrease of the body deformation was observed as its total thickness increased. The deformation resulting from non-uniform body formation was shown to be related to the body thickness and did not occur for composite bodies with thicknesses of more than 5×10^{-3} m. The validity of the findings presented was set into relation to the properties of the alumina and the pore-generating agent used and to the measured porosity ranges of the bodies.

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