THE EFFECT OF TEXTURE
ON THERMAL EXPANSION OF EXTRUDED CERAMICS

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Thermodilatometry of ceramic samples prepared from the mixture of 50 wt.% kaolin, 25 wt.% feldspar and 25 wt.% quartz was studied in the temperature range of 20 - 1000 °C. The samples were cut from the surface layer of the extruded ceramic cylindrical body. The X-ray structural analysis showed that the basal planes of the kaolinite crystals in the samples are predominantly parallel with the direction of extrusion. The shrinkage of the samples which was observed is caused by: 1. evaporating the capillary water (20 - 200 °C), 2. escaping of the OH groups from the octahedrical sheets of the kaolinite crystals (430 - 750 °C), 3. high-temperature changes of metakaolinite (above 850 °C). The shrinkage should be bigger in the perpendicular direction to the basal planes. This assumption is confirmed in these temperature ranges except the region of dehydroxylation. To explain this result, the extension of the kaolinite crystals and blocks of these crystals by steam passing along the octahedral sheets and crystal boundaries was supposed.

INTRODUCTION

Anisometric platelike kaolinite crystals represent the main part (up to 50 %) of unfired ceramic mass designed for high voltage insulator production. Forming of wet ceramic mass by means of the vacuum extruder sets the anisometric crystals in order into a new macroscopic structure with a different local degree of the order [1]. This structure is called a technological texture. Measurements show the anisotropy of mechanical strength [2, 3], sound propagation velocity and Young's modulus [4, 5], thermal diffusivity [6], and electrical properties [7, 8]. The texture affects the dimensions of a wet sample during its drying [9] and the sample dilatation during heating up to 900 °C [10]. Also an influence of the texture and the degree of the order on dehydroxylation kinetics was found [10, 11].

The influence of the texture on performance properties is usually unfavourable. Neighbour volume blocks with different texture could cause the defects on block boundaries from elevated mechanical stress to creation of cracks during firing. The most important physical parameters connected with these appearances are the coefficient of linear thermal expansion, module of elasticity and thermal conductivity. The aim of this paper is an experimental study of the linear thermal expansion of samples with different textures in relation to temperature.

EXPERIMENTAL PROCEDURE

Thermodilatometric measurements were performed with a quartz differential dilatometer with low loading on the sample [12] from room temperature to 1000 °C. The measurements were done by raising/lowering temperature at rate of 10 °C min^{-1}.

Samples were prepared as follows: a mixture of powder kaolin (50 wt.%), quartz (25 wt.%), and feldspar (25 wt.%), used for high voltage insulator production, was wet ground and partially deprived of the water by pressure filtering. From the obtained plastic mass a cylindrical body (a blank) with diameter of 200 mm was pressed by a vacuum extruder and after drying the samples (with about 1 wt.% of physically bound water) were cut from this body.

The explanation of the influence of texture on physical properties of vacuum pressed ceramic mass must take into account that the results are very dependent on the blank and the place where the samples were cut from. Every vacuum extruder gets different structure of the blank and the blank is not structurally homogeneous. If the samples are taken from different places of the blank, their shrinkage caused by drying or firing can differ from each other 5 - 15 % [13].

The best texture is created on the surface of the blank as a result of friction and contact of the wet ceramic mass with the exit part of the vacuum

extruder. Although the surface layer of the blank is not representative for the all blank, this layer is most suitable for experimental studying the influence of the texture on physical properties. The samples were cut from the blank by three ways:

- The length of the sample A was parallel with the direction of extruding (axial direction).
- The length of the sample T was parallel with the tangent line to the surface of the blank tangential direction), i.e. the sample T was cut along a chord in the surface layer.
- The length of the sample R was parallel with the radius of the blank (radial direction). The sample R consisted of three parts cut from the surface layer.

The size of the samples were 24 × 4 × 4 mm.

The texture of the samples was found out by X-ray diffraction analysis.

RESULTS AND DISCUSSION

The existence of the A, T and R sample textures was confirmed by results of X-ray diffraction analysis, which are presented in figure 1. The record R is for an X-ray parallel with the radial direction, similarly, the record A, T is for an X-ray parallel with the axial or tangential direction. Diffraction peaks K(0001) and K(0002) belonged to basal planes of kaolinite crystals. The comparison of diffraction peak intensities K(0001) and K(0002) in records R and A, T showed that basal planes of kaolinite crystals were mostly perpendicular to the length of the sample R and mostly parallel with the length of the sample A or T.

Dilatometry of the samples R, A, T as well as ultrasonic measurements of Young's modulus [5] and thermal diffusivity [6] showed that the samples A and T gave very similar results. It is caused by the resemblance of the texture of these samples - the basal planes of kaolinite crystals are parallel with the longest side of the sample. For this reason we present only the results obtained on R and T samples.

The thermodilatometric curves of unfired samples are shown in figure 2. The curves reflect the processes stimulated by heat during the firing:

- liberation of physically bound water at the temperatures from 20 to 200 °C,
- dehydroxylation at the temperatures higher than 400 °C,
- $\alpha \rightarrow \beta$ transformation of quartz at the temperature $\approx$574 °C,
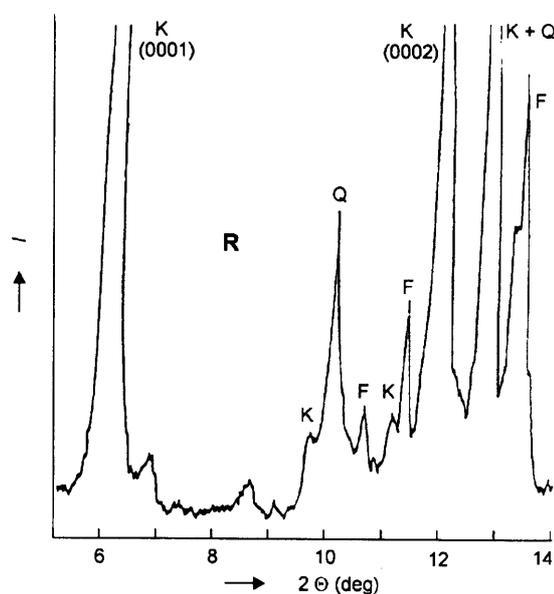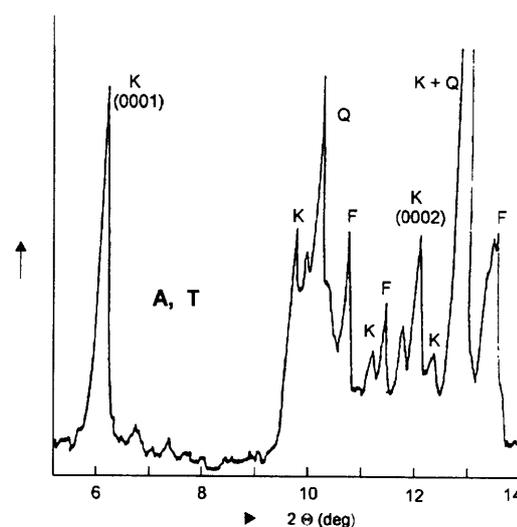- transformation of metakaolinite to a spinel phase at the temperature over 850 °C.

Figure 1. Diffraction patterns of the unfired samples for the axial, tangential, and radial directions.
K - kaolinite, Q - quartz, F - feldspar.

The biggest differences between the thermo-dilatometric curves are in the region of low temperatures. After achievement of equilibrium moisture of the sample ($\approx$1 wt.% of physically bound water) the water molecules remain bound at the surface defects on the sides of kaolinite crystals [14] and in micropores. The shrinkage of the sample R can be explained by removal of the water from micropores parallel with the basal planes of kaolinite crystals. Owing to removing the physically bound water the R samples shrank more than the samples A and T.
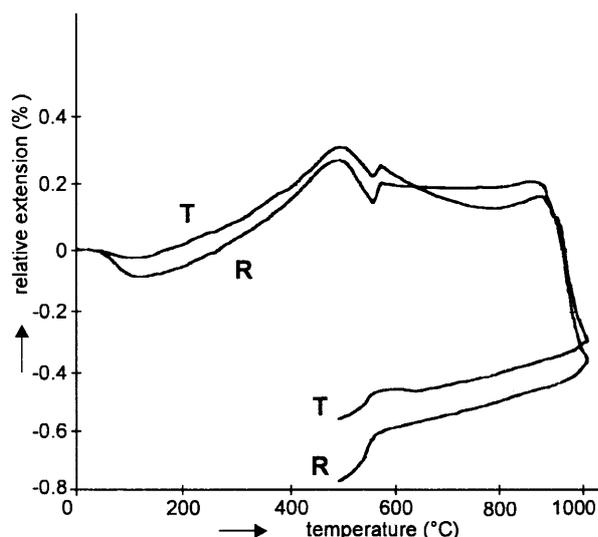
Figure 2. Dilatometric curves of the unfired samples measured in the tangential and radial direction.

Figure 3. Dilatometric curve of the kaolin sample.

After removing the physically bound water the course of the dilatometric curves represents simple thermal expansion. The values of the thermal expansion increase up to the temperature of 430 °C when a dehydroxylation begins to take place and the samples start to contract. The shrinkage of the R sample is bigger, i.e. in the direction which is perpedicular on the basal planes of kaolinite crystals. The area of the basal planes does not change during dehydroxylation but a lattice parameter in the c direction shortens from 7.15×10^{-10} m to 6.8×10^{-10} m [15]. The contraction of thickness of the kaolinite crystals explains the shrinkage of the T and R samples after dehydroxylation. An intensive shrinkage would be expected during the creation of metakaolinite, similarly, as it is seen in the case of Podbořany kaolin (which is a part of the samples), figure 3. The shrinkage would be bigger for R sample than for T sample. The less value of the shrinkage is caused by the expansion of feldspar (at these temperatures the grains of quartz have a small negative coefficient of thermal expansion and their influence can be neglected). But another source of compensation of the shrinkage has to exist, especially for the R samples. It can be increasing the distance between octahedral sheets and crystals of kaolinite by water molecules which remove from the kaolinite crystals and also by the steam. As steam passes along the sheets and predominantly along the basal planes, the effect of this is more demonstrated in R samples. If the texture of T and R samples is not too different, the similar courses of dilatometric curves are measured above temperature of 500 °C.
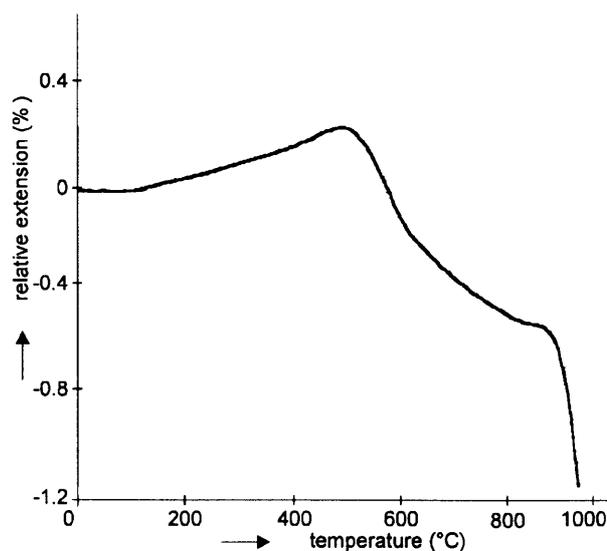
Peaks at 570÷600 °C belong to $\alpha \rightarrow \beta$ quartz transformation which takes place on dehydroxylation background.

After completing dehydroxylation, which is accompanied with shrinkage of the samples, the dilatation of the mixture of metakalinite, quartz and feldspar is observed up to the temperature of transformation of metakaolinite into a spinel phase and amorphous SiO_2 [16]. This transformation changes the defect and vacancy structure of metakaolinite into a structure with closer order. The consequence of this is an intensive contraction of the samples.

CONCLUSION

The main influence on the results of thermo-dilatometry of unfired samples containing kaolin, quartz and feldspar have the kaolinite crystals. The dilatation or contraction in two directions (perpendicular to base planes or parallel with base planes of the kaolinite crystals) is connected with removing of physically bound water and with changes of kaolinite structure, which are different in these two directions.

The shrinkage should be bigger in the perpendicular direction to the basal planes. This assumption is confirmed in these temperature ranges except the region of dehydroxylation. To explain this result, the expansion of the kaolinite crystals and blocks of these crystals by steam passing along the octahedral sheets and crystal boundaries was supposed.

Acknowledgment

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VPLYV TEXTÚRY NA TEPLOTNÚ ROZŤAŽNOSŤ VÁKUOVO LISOVANEJ KERAMIKY

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Sú uvedené výsledky termodilatometrie keramických vzoriek pripravené zo zmesi 50 hmot.% kaolínu, 25 hmot.% živcov a 25 hmot.% kremeňa v teplotnom rozsahu 20 - 1000 °C. Vzorky boli vyrezané z povrchovej vrstvy vákuovo lisovaného výlisku. Roentgenová difrakčná analýza ukázala, že bazálne roviny kaolinitových kryštálov vo vzorkách sú prevažne orientované rovnobežne so smerom lisovania. Zmraštenie vzoriek je vysvetlené: 1. odparením kapilárnej vody (20 - 200 °C), 2. únikom OH skupín z oktaedrických vrstiev kaolinitových kryštálov (430 - 750 °C), 3. vysokoteplotnými zmenami metakaolinitu (nad 850 °C). Zmraštenie by malo byť väčšie v smere kolmom na bazálne roviny. Tento predpoklad sa v uvedenom teplotnom rozsahu potvrdzuje okrem intervalu dehydroxylácie. Na vysvetlenie tohoto výsledku sa prijal predpoklad o rozšírení kaolinitových kryštálov a blokov z týchto kryštálov vodnou parou prechádzajúcou pozdĺž oktaedrických vrstiev a hraníc kryštálov.