THE EFFECT OF TEXTURE ON THE THERMAL DIFFUSIVITY OF A CERAMIC MATERIAL

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The paper presents the results of examination of anisotropic properties of thermal diffusivity for both vacuum- and isostatically pressed raw technical porcelain over the low-temperature range, the anisotropy being due to the technological texture. In the case of isostatically pressed material, the thermal diffusivity does not exhibit any directional dependence owing to the absence of technological texture. With vacuum-pressed material, the thermal diffusivity is strongly anisotropic as a result of the presence of a circular fibriform texture at the circumference of cylindrical pressings. Evidence for this finding was provided by X-ray diffraction analysis.

INTRODUCTION

With ceramic materials containing anisometric crystalline components (kaolin), forming of the plastic mass may lead to orientation of the crystals in certain parts of the volume in preferential directions. The resulting form of macrostructure is called technological texture. The textures arising in the course of forming on a vacuum press belong to the group of fibriform textures [1]. They occur whenever the body being formed has a significant direction, in the given case that of press forming axis. The technological texture in material is responsible for anisotropy of its physical properties, as has been proved by measuring some mechanical and electrical characteristics [2 – 5], and may affect its performance properties. The study had the purpose to establish to what extent the technological texture of a raw ceramic material affects the thermal diffusivity, its variations in the low-temperature firing range, and to attempt an explanation of the dependence established by measurements.

EXPERIMENTAL

Measuring method

The thermal diffusivity was measured by the flash method [6] which is based on the determination of time evolution of temperature after a heat pulse in the specimen. The heat pulse is generated by applying an intensive burst of radiant energy acting instantaneously and uniformly over the area of the front face of a disc-shaped specimen. A record of the time dependence of the relative temperature rise in the opposite specimen face allows the thermal diffusivity to be determined simply by using the equation

$$a = 0.139 l^2 / \tau_{0.5}, \qquad (1)$$

where l is the specimen length and $\tau_{0.5}$ is the time it takes the specimen to heat to one-half maximum temperature rise on the rear face after the heat pulse.

The measurements were carried out on the apparatus described in [7], in air at atmospheric pressure. The specimen was heated linearly at a rate of 5°C/min. The entire measurement and data processing was computer-controlled. As follows from the detailed description of the measuring method in [8], equation (1) is independent of the pulse duration over the interval of 0.05 s to 0.2 s and the specimen length over the range from 2mm to 4mm. This was respected in the selection of measuring parameters.

Experimental material

The specimens were prepared from commercial materials M50 and M6 used in the manufacture of the high-voltage technical porcelain. The materials employed have different chemical compositions and moreover are made by two different technologies and forming methods. They can therefore be assumed to exhibit different degrees of orientation of anisometric crystals. The M50 material obtained by isostatic pressing of granulate under the pressure of 125 MPa contained 30% kaolins, 25% corundum, 30% feldspars and 15% grog. The M6 material was obtained from raw materials used in the manufacture of porcelain of classical composition, namely 49% kaolins, 23% feldspars, 28% quartz. The technological process included grinding in a ball mill, sifting through a sieve with 100 openings/mm^2, pressure filtering and vacuum pressing. The specimens were turned into cylindrical form 9mm in diameter and a length over the interval of 2 to 4mm; grinding in a special gadget ensured that the two bases were perfectly planparallel. The specimens prepared from the original cylindrical pressings 200 and 300 mm in diameter of the M50 and M6 materials were cut from the circumferential layer where the texture is assumed to be most extensive.

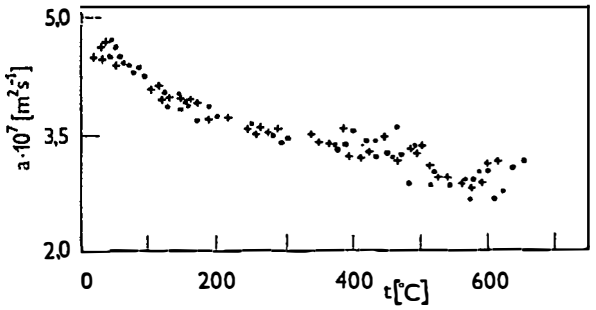

Fig. 1. Temperature dependence of the thermal diffusivity of raw specimens of isostatically press-formed material M50 in terms of texture. The thermal wave propagates in the direction parallel with the radius (R texture), ···, and parallel with the axis (L texture) +++ of a cylindrical pressing.

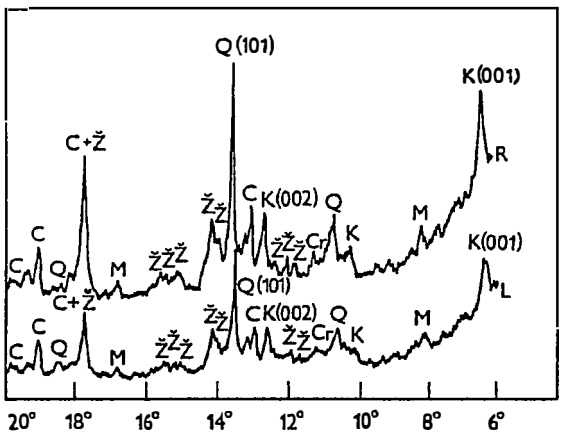

Fig. 2. Diffraction patterns of isostatically pressed raw specimens of M50 material with the vector of the irradiated plane parallel with the radius (record R), and with the axis (record L) of a cylindrical pressing. (C – corundum, K – kaolin, Q – quartz, Z – feldspar, Cr – crystobalite, M – mullite).

The cutting out of the specimens was carried out in two ways: the first group of specimens, designated as having texture of type L, were prepared so as to have the specimen axis, in the direction of heat flow during measurement, parallel with the axis of the original pressing. The other group of specimens, with texture of type R, had the symmetry axis identical with the radius of the original cylindrical pressing. The specimens were dried to an equilibrium moisture content of about 1% free water. A uniform layer of colloidal graphite DAG (ACHESON, Holland) was applied to the front face of the specimens to increase the absorptivity of the surface.

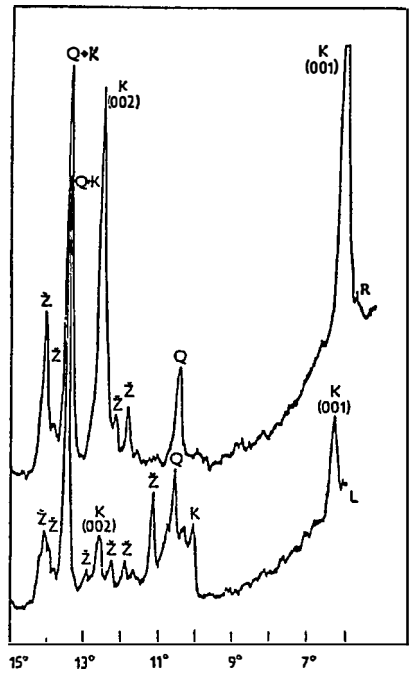

Fig. 3. Diffraction patterns of raw specimens of M6 material, prepared in a vaccum press, with the vector of the irradiated plane parallel with the radius (record R) and with the axis (record L) of a cylindrical pressing. (K – kaolin, Z – feldspars, Q – quartz).

RESULTS AND DISCUSSION

The dependencies of the thermal diffusivity of the specimens of isostatically pressed material on temperature are listed in Fig. 1. The courses of the relationship for specimens cut in the radial and the axial directions do not show any significant differences, values of $a(t)$ are almost identical all over the temperature interval in question. The qualitative course of the $a(t)$ curve for material M50 is comparable to that for the M50 material given in [8] and in agreement with the theoretical prediction. The differences in the $a(t)$ curves of the two groups of isostatically pressed sample groups are not significant enough to assume any directional dependence of the thermal diffusivity due to the texture. The finding is supported by the results of X-ray structural analysis (Fig. 2) made on samples of the same material, taken in the same way from the pressing circumference as in the case of measuring $a(t)$. A comparison of diffraction patterns obtained with ray incidence to the sample plane with its area vector parallel with the pressing radius (R) and to the sample with its area vector parallel with pressing axis (L) did not indicate explicitly the presence of any texture. The differences in the absolute values of intensities are not related with differences in relative intensities.

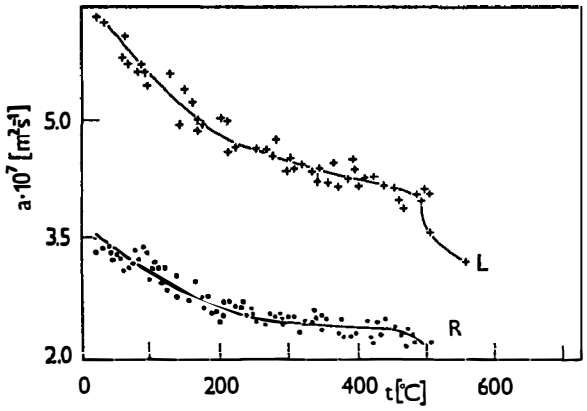

Fig. 4. Temperature dependence of thermal diffusivity a of raw specimens of material M6 formed in a vacuum press, vs. the texture, measured in atmosphere. R and L curves – the thermal wave propagates parallel with the radius and the axis of the cylindrical pressing, respectively.

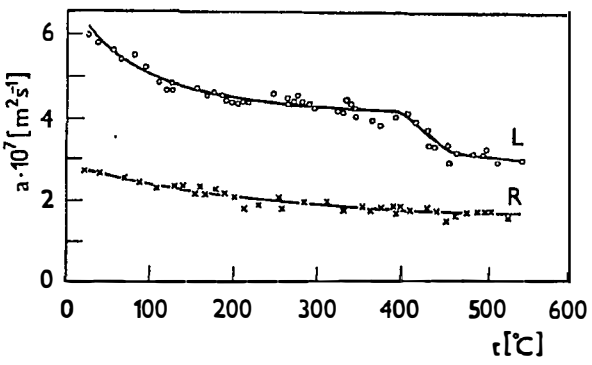

Fig. 5. Temperature dependence of thermal diffusivity a of raw specimens of material M6 formed in a vaccum press, vs. the texture, measured in vacuum with an electron ray as heat source. R and L curve – cf. Fig. 4.

The diffraction patterns of samples of vacuum-pressed raw material M6 indicate explicitly the presence of texture around the circumference of the cylindrical pressing (Fig. 3). The comparison of diffraction patterns was based on the relative intensities of reflections relative to the intensity of quartz line Q(1,0,1), for which the random orientation of crystals is assumed. The intensity of basal kaolinitic reflections (0 0 1) and (0 0 2) of the specimens with texture R was significantly higher than with specimens with texture L, while the other kaolinitic reflections were distinctly suppressed. This indicates orientation of hexagonal kaolinite crystals by their basal plane parallel with the R specimen surface, i.e. perpendicularly to the pressing radius and parallel with its axis. As the specimens were cut from the circumferential part of a cylindrical pressing, this provides evidence for the presence of a circular fibriform texture at the surface, in agreement with [1].

The courses of the temperature dependence of thermal diffusivity of vacuum-pressed material M6 are plotted in Fig. 4. In contrast to isostatically pressed specimens, the given $a(t)$ values of samples with different textures differ significantly primarily with respect to the absolute value. Over the temperature interval of 20 – 500°C, the a values for the sample with texture L attain 1.6 up to double the value of a of samples with texture R. The course of the curves has a character similar to that of the former material. Over the 20 – 200°C temperature range where capillary water is evaporated, as indicated by other measurements [3, 4, 9], the decrease of the values has a somewhat steeper course than above this temperature interval. The measuring abilities of the apparatus for the M6 material with type R texture ended at 500°C; however, with texture L it was still possible to detect the abrupt decrease of thermal diffusivity values due to the dehydroxylation process.

For the sake of comparison, the results of the thermal diffusivity measurements are presented for the same series of specimens but measured in the vacuum by the flash pulse method, where an electron ray was used as the heat source (Fig. 5). This variant of the method is closely described in [8]. Fig. 5 proves a strong directional dependence of thermal diffusivity. The absolute values of $a(t)$ of samples cut in the axial direction and the radial one differ by a factor of more than two. The course of curve L is comparable with that of the corresponding curve in Fig. 4 with respect to both the absolute value and character; only the temperatures at which changes occur in the courses of the curves are somewhat lower. The absolute values of the thermal diffusivity of samples with texture R in Fig. 5 are somewhat lower than those in Fig. 4, which may be due to statistical variations in the texture of the samples. Up to 200°C, the change of $a(t)$ of samples with type R texture is small. Over the temperature interval of 200 to 500°C, the values of $a(t)$ can be regarded as almost constant, which indicates more ready disengagement of physically bound water from the R texture. The samples with type L texture show a somewhat different character of the course of the relationship. The decrease of $a(t)$ values with increasing temperature is greater than with texture R, and greatest with the onset of dehydroxylation. The disengagement of both physically and chemically bound water in the course of heating up to the dehydroxylation temperature is thus responsible for greater changes of the thermal diffusivity in the axial direction than in the radial one.

Qualitative interpretation of the experimental relationships follows from a simple model based on the

assumption that the specific heat capacity changes in the same way with temperature in samples with both longitudinal and transverse textures. The changes in the differences of thermal diffusivity for textures L and R can then be regarded as being directly proportional to the changes in the thermal conductivity, and it is possible to examine them by means of analogy of thermal flux with electric currrent conduction through a system of resistances connected parallel (L texture) and in series (R texture). As the raw vacuum pressed ceramic material can be considered as having a circular fibriform texture around its circumference, it can be regarded as a composition of parallel with the axis elongated pores with a solid phase with a prevailing orientation likewise in the direction of parallel with the axis, where co-axial layers are formed. The thermal resistance of samples with texture of type L is then determined by a low thermal resistance of pores filled with water, so that the thermal diffusivity of a moist sample with an axial texture is high. With evaporation of water and increasing temperature, the thermal resistance of the pores increases and this results in a decreased diffusivity. In the case of samples with type R texture, using the concept of series arrangement of the phases, the final resistance is a sum of the partial ones, that is greater compared with the thermal resistance of the L texture. This explains the lower values of thermal conductivity, and on the assumption of the concept mentioned above, also the thermal diffusivity of samples cut in the radial direction. As the increase in the total thermal resistance due to evaporation of water is lower in the case of texture R, it results in a milder decrease of the thermal diffusivity. A similar explanation can be formulated for the behaviour of samples in the temperature range of dehydroxylation where the material already contains only chemically bound water. Kaolinite, which is to a considerable degree responsible for anisotropy of the samples, can be regarded as a system of platelets with a sandwich structure with alternating layers of SiO_4 tetrahedra and $[Al_2(O,OH)_6]$ octahedra. The thermal resistance of the layer of tetrahedra is independent of the dehydroxylation process, but the thermal resistance of the layer of octahedra increases as a result of the escape of water in OH^- group form. The lower values of $a(t)$ and their smaller changes during the dehydroxylation process for samples cut in the radial direction (with R type texture) can be explained by the thermal resistance of the layer of tetrahedra which is several times higher than that of octahedra. During heat flux through a sample cut in the radial direction, the total thermal resistance in agreement with the concept mentioned above is higher than that of the sample cut in the longitudinal direction, so that the thermal diffusivity of samples with texture R is lower than that of samples with texture L. In the case of samples with the longitudinal texture L, the absolute value of the thermal diffusivity is approximately twice as high as that of samples with the transverse R texture, and the increase in the thermal resistance of the octahedra resulting from dehydroxylation will bring about a marked decrease of the thermal diffusivity.

CONCLUSION

The results of the measurements show that the technology of isostatic pressing does not create any technological texture in the M50 raw ceramic material, which would affect isotropy of the thermal diffusivity. This finding is in disagreement with the conclusion formulated in [4], namely that texture occurs in isostatically pressed specimens. In the case of ceramic material M6, produced by the technology of the vacuum pressing, the considerable mass flux is coming so that samples cut out of the peripheral layer of the pressing exhibit preferential orientation of kaolins by their basal plane perpendicularly to the pressing radius. In agreement with [1], the circular fibriform texture arising at the circumference is responsible for substantial differences in the values of $a(t)$ in the direction parallel with the pressing axis and in the radial direction. The M6 ceramic material, obtained by the vacuum pressing technology, cannot therefore be regarded as isotropic from the standpoint of heat transfer. The values of the thermal diffusivity in the direction of the pressing radius are lower than those in the longitudinal direction. With increasing temperature, the anisotropy of the thermal diffusivity remains virtually unchanged up to the dehydroxylation temperature, so that it may play a significant role in the course of firing the ware. It is in fact an important parameter affecting the optimum rate of heating: its anisotropy may be one of the causes of non-uniform heating and occurrence of internal stresses in ceramic material. The results obtained should also be taken into account in theoretical examination of the thermal field.

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VPLYV TEXTÚRY NA SÚČINITEL TEPLOTNEJ VODIVOSTI KERAMICKÉHO MATERIÁLU

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V práci bol sledovaný vplyv technologickej textúry vznikajúcej pri tvárnení plastickej surovej keramickej masy na anizotropiu súčinitel'a teplotnej vodivosti. V izostaticky lisovanej technickej keramike so zvýšeným obsahom korundu sa difrakčným záznamom nepotvrdila technologická textúra v surovej vzorke. Neprejavila sa ani smerovou závislosťou súčinitel'a teplotnej vodivosti.

Difrakčné záznamy vzoriek zo surovej technickej keramiky klasického zloženia, lisovaných vo vákuovom lise, jednoznačne potvrdzujú usporiadanost' kaolínových kryštálov na obvode valcového výlisku s vektorom bazálnej plochy v smere jeho polomeru. Vytvorený typ textúry je kruhovo vláknový. Uvedený materiál sa z hl'adiska transportu tepla javí ako anizotropný. Súčinitel' teplotnej vodivosti v závislosti na teplote $a(t)$ nadobúda takmer 2 razy nižšie hodnoty pri šírení sa tepla v smere polomeru valcového výlisku ako v smere rovnobežnom s osou. Textúra v materiáli mení aj charakter priebehu $a(t)$. Uvol'ňovanie fyzikálne (do 200°C) aj chemicky viazanej vody (oblast' dehydroxylácie kaolínov od 400-450°C) sa pri svojom nástupe prejaví poklesom súčinitel'a teplotnej vodivosti v smere rovnobežnom s osou výlisku. Anizotropiu súčinitel'a teplotnej vodivosti keramického materiálu je treba zohl'adniť pri vedení optimálnej krivky výpalu a pri teoretickom riešení problémov termoelasticity spojených s výpalom keramík.

Obr. 1. Závislost súčinitel'a teplotnej vodivosti a surových vzoriek z izostaticky lisovaného materiálu M50 na teplote t a textúre. Tepelná vlna sa šíri v smere rovnobežnom s polomerom (R textúra) ···, resp. rovnobežnom s osou (L textúra) +++ valcového výlisku.

Obr. 2. Difrakčné záznamy izostaticky lisovaných surových vzoriek z materiálu M50 s vektorom ožiarenej plochy rovnobežným s polomerom (záznam R), resp. s osou (záznam L) valcového výlisku. (C – korund, K – kaolin, Q – kremeň, Ž – živce, Cr – cristobalit, M – mullit).

Obr. 3. Difrakčné záznamy surových vzoriek z materiálu M6, získaného vo vákuovom lise s vektorom ožiarenej plochy rovnobežným s polomerom (záznam R), resp. s osou (záznam L) valcového výlisku. (K – kaolín, Ž – živce, Q – kremeň).

Obr. 4. Závislost' súčinitel'a teplotnej vodivosti a surových vzoriek z materiálu M6 lisovaného vo vákuovom lise na teplote t a textúre v atmosfére. R, resp. L krivka – tepelná vlna sa šíri v smere rovnobežnom s polomerom, resp. s osou valcového výlisku.

Obr. 5. Závislost' súčinitel'a teplotnej vodivosti a surových vzoriek z materiálu M6 lisovaného vo vákuovom lise na teplote t a textúre vo vákuu, s elektrónovým lúčom ako zdrojom tepla. R, resp. L krivka – obr. 4.