

YOUNG'S MODULUS OF PORCELAIN MIXTURE AFTER FIRING IN THE DEHYDROXYLATION REGION

IGOR ŠTUBŇA, ANTON TRNÍK

Department of Physics, Constantine the Philosopher University, A. Hlinku 1, 949 74 Nitra, Slovak Republic

E-mail: istubna@ukf.sk

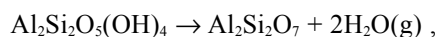
Submitted September 26, 2006; accepted February 23, 2007

Keywords: Dehydroxylation, Young's modulus, Porosity

Samples were prepared from a raw material mixture containing 50 % of kaolin, 25 % of quartz, and 25 % of feldspar and extruded from the plastic paste. Young's modulus was measured by the resonant method using flexural vibrations. The results of Young's modulus measurement at the room temperature, obtained from the samples fired at a temperature in the range 420-740°C, show that it is necessary to consider the increase of the porosity during dehydroxylation as the most important cause of the decrease of the values of Young's modulus. The role of the $\beta \leftrightarrow \alpha$ reversible transformation of quartz grains inside the ceramic material as well as the role of the solid state sintering in the considered temperature interval turns out to be negligible.

INTRODUCTION

During heating of a green sample containing kaolin and kaolinite clay, dehydroxylation is the most important process in the temperature region of 400-900°C. It is generally accepted that dehydroxylation of kaolinite begins at temperatures from the interval 420-450°C. The chemical equation representing this process is



where $\text{Al}_2\text{Si}_2\text{O}_7$ is metakaolinite, a product of dehydroxylation. Water steam carries away 13.96 % of the mass of the stoichiometric kaolinite during dehydroxylation. The result of this is the decrease of the density of the kaolinite crystal from 2.64 g/cm³ to 2.51 g/cm³ and the increase of the kaolin specific surface area by ~5 m²/g [1].

Such extensive changes in a large part of the green porcelain sample (about 50 % of the sample volume) have to be reflected in its mechanical properties. The creation of new phases influences the mechanical properties in the dehydroxylation region: a) metakaolinite as a new phase which appears instead of kaolinite and b) micropores which are created in kaolinite crystals. The mechanisms leading to the creation of metakaolinite and micropores during dehydroxylation are not quite clearly understood. The following two explanations are most probable.

MacKenzie [2] supposes that both homogeneous and inhomogeneous mechanisms of the dehydroxylation are possible. In the homogeneous process water is formed by the reaction between adjacent OH groups and

then migrates through the crystal. A consequence of this is a big disruption of the crystal lattice. In the inhomogeneous process migration of protons and the corresponding counter-migration of cations between nearby microscopic regions is assumed. Water disappears from the former regions, which thus become micropores, while the structural continuity is preserved in the latter regions, which thus become metakaolinite. The mechanism of dehydroxylation was investigated in detail in [3] and it was determined there that this mechanism is inhomogeneous for the temperatures lower than 455°C. Usually, the mechanism of dehydroxylation is considered homogenous.

A different view of the metakaolinite structure can be found in [4]. About 22 % of the crystal volume is affected by the outflow of H₂O, which theoretically decreases the lattice parameter c from the value 0.713 nm to 0.556 nm (the parameters a , b remain constant). However, experimentally the value $c = 0.685$ nm was found. This disagreement was resolved by a new model of metakaolinite structure with a high concentration of the polarized vacancies and micropores. Such a structure is unstable, with an excess of the lattice energy. This energy is released during an exothermic reaction at the temperature 950°C when the structure shrinks by ~20 % and metakaolinite changes into a new phase.

Another process, which occurs simultaneously with and also after dehydroxylation is a low-temperature solid phase sintering [5]. Particles of green ceramic are so small that the contact areas are relatively large and the pores between them are small. In this structure sintering is possible even at temperatures lower than 700°C.

The next process, which appears at 573°C in samples containing quartz grains is the reversible $\beta \rightarrow \alpha$ transformation of quartz at heating and the $\alpha \rightarrow \beta$ transformation at cooling. These transformations are accompanied by the changing of the quartz grains' volume by $\sim 0.68\%$ [1].

The aim of the present paper is to show that it is necessary to consider the increase of porosity during dehydroxylation as the most important cause of the decrease of the values of Young's modulus.

EXPERIMENTAL

The samples were prepared from a raw material mixture containing 50 % of kaolin, 25 % of quartz and 25 % of feldspar. The samples were prepared with the help of a laboratory extruder from the plastic paste and were dried to the equilibrium moisture at which the content of the physically bound H₂O was ~ 1 mass %. The dimensions of dry samples were $\varnothing 11 \times 150$ mm. Then the samples were heated up at the rate of 5°C/min and, upon reaching the de-sired temperature, the heating was interrupted and the samples were let cool freely down together with the furnace. The maximal temperatures were in the region of the dehydroxylation of kaolin: 400, 420, 440, ... 740°C. On the cooled off samples we measured the mass loss, modifications of sizes, porosity, and Young's modulus.

The porosity P was determined after firing at the showed temperatures from the formula [6]

$$P = \left(1 - \frac{\rho_{ms}}{\rho_p} \right) 100\%, \quad (1)$$

where ρ_{ms} is the bulk density calculated from the mass and size of the sample and ρ_p is the density determined by the pycnometric method on the powder samples.

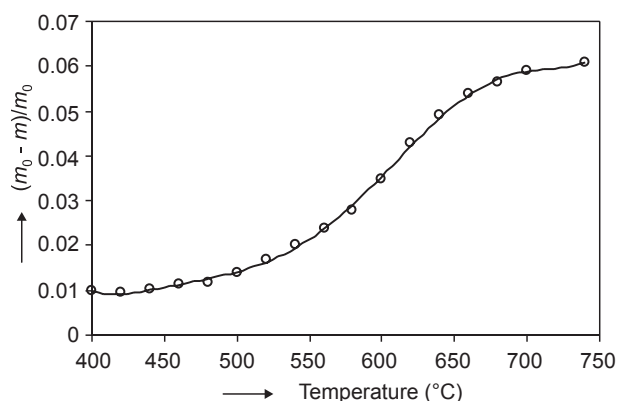


Figure 1. The dependence of the relative mass loss on the firing temperature.

The measurement method of Young's modulus is described in [7]. The Young's modulus is measured by the resonant method based on the flexural vibration of the sample on the apparatus described in [8]. The values of Young's modulus E were calculated from the formula given in [7]

$$E = 1.26063 \left(\frac{l^2 f}{d} \right)^2 \rho T, \quad (2)$$

where f is the resonant frequency of the fundamental mode of vibration, l and d are the length and the diameter of the cylindrical sample, respectively, ρ is the bulk density of the sample material, and $T = 1.02551$ is the correction coefficient for the Poisson ratio $\mu = 0.2$ and the ratio $l/d = 15$, which was calculated according to [7].

RESULTS AND DISCUSSION

During the dehydroxylation the value of the kaolinite crystals' density decreases from 2.64 g/cm³ to 2.51 g/cm³, i.e., by $\sim 5\%$ [1]. Because the irreversible length contractions of the samples after the dehydroxylation measured at the room temperature are less than 0.15 %, the relative volume changes of the samples is less than 0.45 %. It then follows that the porosity is mostly determined by the changes of kaolinite crystals' density, i.e., by the dependence of the relative mass loss $(m_0 - m)/m_0$ on the firing temperature, where m is the mass of the sample after firing and m_0 before firing, see Figure 1. This interpretation also confirms the results obtained in [9], where the air permeability through the samples fired from the same material at different temperatures was measured. The samples' porosity was 32 % before heating. The dependence of the porosity of the sample on the firing temperature is shown in Figure 2. This dependence is basically consistent with the dependence measured on the same material in [10].

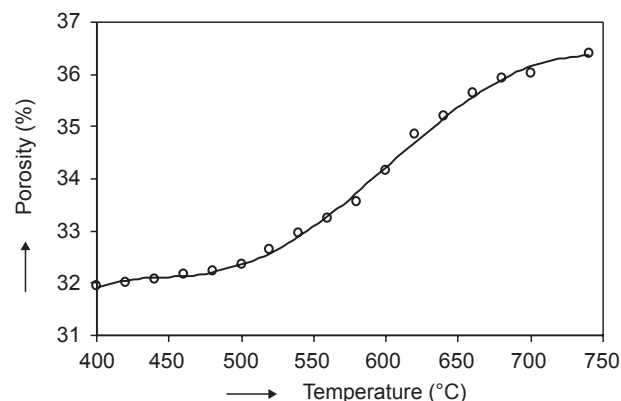


Figure 2. The dependence of the porosity on the firing temperature.

Young's modulus measured at the room temperature on the sample fired at temperatures in the range 420-750°C are shown in Figure 3. From the dependences in Figures 2 and 3 it is possible to obtain the dependence of Young's modulus on the porosity, see Figure 4.

The dependence $E(P)$ can be fitted with the help of some of the functions which describe this experimentally obtained dependence. These functions are given in [11]. However, here we do not have a simple case when Young's modulus is only a function of the porosity, which is implicitly assumed in formulae from [11].

There is no doubt that the increase of Young's modulus is caused by the decrease of the sample's porosity. However, there is also another cause. During the dehydroxylation the composition and the structure of the plastic constituent representing ~50 % of the green material are changed. As shown in Figure 1, metakaolinite with its new structure in the crystals is created at the temperature range of 420-740°C. Consequently, there are two reasons for the decrease of Young's modulus with the firing temperature. It is not possible to separate the influence of the porosity from the influence of the new metakaolinite structure on the values of Young's modulus. As follows from Figure 4, the influence of the porosity prevails.

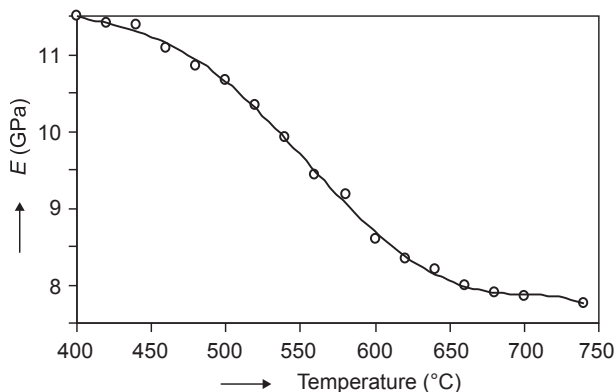


Figure 3. The dependence of Young's modulus on the firing temperature.

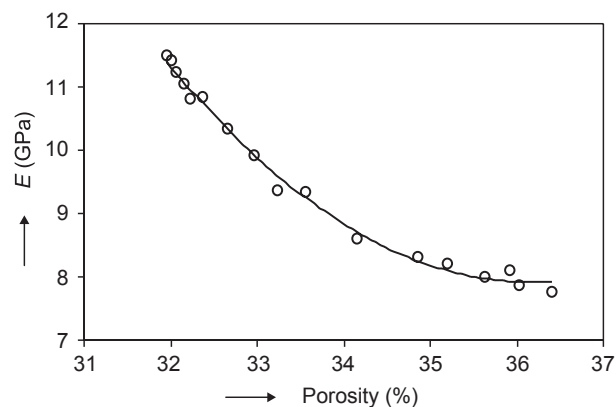


Figure 4. The dependence of Young's modulus on the porosity.

At the temperature of 573°C the volume of the quartz grains occurring in the samples increases by ~0.7 %. It can be supposed that there is a compression of the quartz crystals' surroundings during heating and the disappearance of a certain number of pores in this region. This could cause an increase of the values of E at temperatures $t > 573$ °C. Because the relationship E on the firing temperature measured at room temperature shows no significant disruptions around the temperature 573°C (see Figure 3), the sample should restore its original state of the quartz crystal surroundings during the cooling process. This as well shows that the porosity is more important for the values of Young's modulus than the new metakaolinite structure inside the crystals.

The third possible process taking place during the heating over 600°C is the solid state sintering which can emerge in the fine ground kaolin phase. Such sintering leads to improving mechanical properties of fired ceramics, i.e., Young's modulus would be higher at room temperature for firing temperatures over 600°C. Nevertheless, we do not observe that in Figure 3. We thus conclude that the solid state sintering plays a negligible role in the relationship $E(t)$ if the firing temperatures are less than 740°C.

CONCLUSIONS

The results of Young's modulus measurements at the room temperature on the samples of green electroporcelain fired at temperature in the range 420-740°C show that it is necessary to consider the increase of the porosity during dehydroxylation as the most important cause of the decrease of the values of Young's modulus. The $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ quartz transformations have a negligible impact on Young's modulus and the sound velocity measured at the room temperature after heating up to 740°C. The same can be said about the role of the solid state sintering in the temperature interval of 420-740°C.

Acknowledgement

This work was supported by the grant VEGA 1/3179/06. The authors wish to thank to the ceramic plant PPC Čab for providing samples.

References

1. Norton F.H.: *Fine ceramics - technology and applications*. p. 240-243, McGraw-Hill Book Co., New York 1970.
2. MacKenzie K.J.D.: *Chemistry in New Zealand*, No.3, 8 (1978).
3. Suitch P.R.: *J.Am.Ceram.Soc.* 69, 61 (1986).
4. Freund F.: *Ber. Deutsche Keram. Ges.* 44, 5 (1967).
5. Monteiro S.N., Vieira C.M.F.: *Ceram.Int.* 30, 381 (2004).

6. *Spravočník po proizvodstvu stroitel'noj keramiki. Izd. po stroitel'stvu i stroitel'nym materialam*, Moskva 1961 (in Russian).
7. ASTM C 1198-01: *Standard test method for dynamic Young's modulus for advanced ceramics by sonic resonance*, (published in June 2001, Standard Documents, Philadelphia USA).
8. Trník A., Vozár L., Štubňa I.: in: 27th International Czech and Slovak calorimetric seminar, p.191-194, University of Pardubice, Svatka 2005 (in Slovak).
9. Štubňa I., Kozík T.: *Ceram.Int.* 23, 247 (1997)
10. Koubek V., Štubňa I., Kozík T.: *Sklář a keramik* 31, 156 (1981) (in Slovak).
11. Pabst W. et al.: *Ceramics - Silikáty* 48, 165 (2004).

MODUL PRUŽNOSTI PORCELÁNOVEJ ZMESI
PO VÝPALE V OBLASTI DEHYDROXYLÁCIE

IGOR ŠTUBŇA - ANTON TRNÍK

*Katedra fyziky, Univerzita Konštantína Filozofa,
A. Hlinku 1, 949 74 Nitra, Slovensko*

Vzorky z plastickej surovínovej zmesi 50 % kaolínu, 25 % kremeňa a 25 % živcov boli vytiahnuté na laboratórnom lise. Modul pružnosti bol meraný rezonančnou metódou s použitím ohybového kmitania vzorky. Výsledky merania modulu pružnosti meraného pri izbovej teplote na vzorkách vypálených pri teplotách 420-740°C ukázali, že pórovitosť zvýšená počas dehydroxylácie je hlavnou príčinou znížených hodnôt modulu pružnosti. Vplyvy $\beta \leftrightarrow \alpha$ transformácie kremeňa a nízkoteplotného spekania v tuhej fáze na hodnoty modulu pružnosti sú zanedbateľné.