Ceramics International 23 (1996) 247-249
© 1997 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/97 $17.00+0.00
PII: S0272-8842(96)00034-X

Permeability of the Electroceramics to Gas and its Dependence on the Firing Temperature

Igor Štubňa & Tomáš Kozík

College of Education, A. Hlinku 1, 949 01, Nitra, Slovakia

(Received 7 December 1995; accepted 26 February 1996)

Abstract: Permeability and porosity of electroceramic material (50% kaolin, 25% quartz, 25% feldspar) were measured after firing at temperatures of 20–1300 °C. Experimentally it was found that the permeability (measured by means of the penetration of the pressed air through the sample), caused by dehydroxylation, increased by 37%. The porosity (measured by the pycnometric method) increased by 6%, which is in agreement with geometric calculations. The value of the permeability is explained by creating the micropores in metakaolinite. © 1997 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Kaolin, feldspar and quartz (or alumina) are generaly used in ceramic technology. No pressing can expel the pores of these minerals from the ceramic body. The pores between particles are mostly open. This basic porous structure of the unfired ceramic material remains during the firing up to temperatures where high temperature sintering with a presence of melted feldspar takes place.

The main changes of the porosity occur twice during the firing: a dehydroxylation increases porosity by 4–6% and then the porosity obtains the minimum value at the high temperature sintering.[1,2]

This article reports on the development of the permeability and its coherence with increasing the porosity after dehydroxylation.

2 EXPERIMENTAL PROCEDURE

The measurement of the permeability was carried out on an apparatus which worked on the principle of passing the pressed air through the sample over a chosen time. A coefficient of the permeability was calculated from a formula[3]

$$K = l\eta V/Spt \qquad (1)$$

where V is the volume of the pressed air which passed through the sample in the time t. S and l are the area of the cross section and the thickness of the sample, respectively. $\eta = 1.71 \times 10^{-5}$ Pa s^{-1}, is an air viscosity at room temperature, and p is the air pressure.

Values of the porosity were obtained by means of pycnometric method.[3]

Samples were prepared from kaolin (50%), feldspar (25%) and quartz (25%). A cylinder with diameter of 4 cm formed by means of vacuum extruder was cut into discs with a thickness of 0.5 cm. The sets of 6 samples were fired at temperatures between 300 and 1300 °C with 10 min isothermal exposure at the firing temperature. The coefficient of the permeability was measured at room temperature.

3 RESULTS AND DISCUSSION

The results of measuring the porosity and coefficient of permeability are shown in Figs 1 and 2, where experimental points represent the average values. The dehydroxylation causes the increasing of the open porosity at the temperatures of 400–600 °C, which leads to an increase in the permeability. The extinction of the open porosity at temperatures higher than 1150 °C causes the extinction of the permeability.

After dehydroxylation the coefficient of permeability rises by 37%, see Fig. 2. We attempt this increasing by means of the results listed in works of Freund,[4] Norton,[5] Rambousek[6] and Kiselev.[7] Formula (1) is derived from Darcy's law for a stationary flow of viscous medium

$$\mathbf{q} = \frac{K}{\eta} \operatorname{grad} p \qquad (2)$$

where $\mathbf{q}$ is the density of the flow, and the meanings of K, p and η are described above. We have for the one dimensional case of the parallel pores $|\operatorname{grad} p| = \Delta p/l$ and we can also write $q = lV/St$. After substituting these relations into eqn (2) we obtain

$$\frac{V}{t} = \frac{\Delta p}{\eta l} SK \qquad (3)$$

The value S is the total sum of the cross-sections of the parallel pores. The relation (3) is formally identical with (1), where S represents the cross-section of the sample. The value V/t for one pore with length of l and radius of r is given by Poiseuill's formula

$$\frac{V}{t} = \frac{\Delta p}{\eta l} \pi r^2 \frac{\pi r^2}{8\pi} \qquad (4)$$

Comparing eqns (3) and (4) we give a notion of the physical meaning of the coefficient of permeability. It is the value proportional to the sum of the pore cross-sections of an ideal sample with parallel pores.

The direct cause of increasing the coefficient K in the sample is the increasing of the pore cross-sections. The change of the radii of the pores can be expressed by means of porosity which is a ratio of the volume of pores $n\langle r\rangle^2 l$ (where n is the amount of the pores in the volume of l^3, r is the average radius of the pores) to the volume of l^3. Then the porosity is $P \cong n\langle r\rangle^2 l/l^3$. The permeability is proportional to $n\langle r\rangle^2$ or $K \cong Pl^2$, where l is the thickness of the sample. Generally, the change of the permeability can be caused by the change of r as well as n. Then

$$\Delta K/K = \Delta P/P + 2\Delta l/l \qquad (5)$$

where ΔK, ΔP, Δl are the changes of the coefficient of permeability, porosity and thickness of the sample after dehydroxylation. The porosity after dehydroxylation is

$$P + \Delta P = 1 - \frac{V_s(1 + \Delta V_s/V_s)}{V_t(1 + \Delta V_t/V_t)} \qquad (6)$$

where V_s is volume of the solid phase, V_t is volume of the sample before dehydroxylation and ΔV_s, V_t are their changes caused by dehydroxylation. The value $\Delta V_s/V_s$ can be expressed as a sum of volume changes of individual minerals of the electroceramic material. The base surface of the kaolinite crystals 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,[4] which represents a shrinkage of the kaolin crystals of 5%. This transition is irreversible. The feldspar and quartz crystals go through reversible volume changes during the firing in the temperature interval of 20–800 °C. The resultant change of the solid phase volume is $\Delta V_t/V_t = -2.5\%$. The volume changes of the samples were measured before and after firing at the temperatures mentioned above and it was found that the average value $\Delta V_t/V_t = +0.05\%$.

After substituting the numerical values ($P = 0.3$, $V_s/V_t = 0.7$, $\Delta V_s/V_s = -0.025$, $\Delta V_t/V_t = +0.0005$)

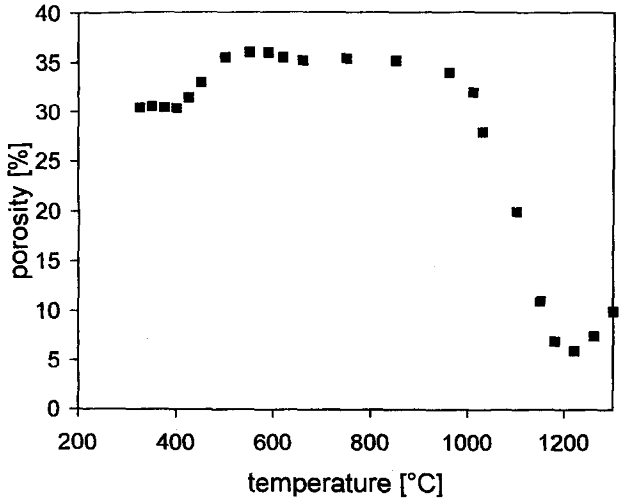

Fig. 1. Dependence of the porosity on the firing temperature.

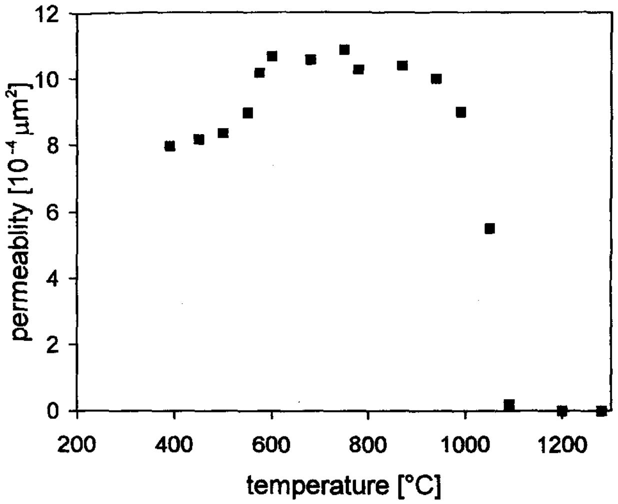

Fig. 2. Dependence of the coefficient of the permeability on the firing temperature.

into eqn (6) we obtain $\Delta P = 0.02$ or $\Delta P/P = 6.66\%$, which represents the increasing of the porosity after dehydroxylation derived from geometrical calculation. This value agrees with the experimental value in Fig. 1.

From eqn (5) the increasing of the porosity is approximately equal to the increasing of the permeability ($\Delta l/l$ can be neglected), which is about 37%, see Fig. 2. As the calculation showed, this high value can not be explained by changes of dimensions of the original pores but creation of new pores must be assumed. This assumption is supported by the result of measuring the surface area of kaolin, which rose from 11 to 15 m^2/g, i.e. in 36%.[5] As the surface of the kaolinite crystals decreases owing to their shrinkage, the increasing of the surface area of kaolin can be explained by means of new surfaces which a rise inside kaolinite crystals. Porosimetric analysis of the electroceramic material fired at 500 °C and 600 °C showed that the portion of small pores increases on the background of the increasing porosity.[6] Also, an investigation of the physical properties of kaolin after firing at different temperatures gave results which were caused by the microporosity.[7]

4 CONCLUSION

Comparing the experimental results of the permeability of the electroceramic material caused by dehydroxylation with the calculated value of the permeability, it is suggested that new micropores are created in metakaolinite particles.

REFERENCES

1. ŠATAVA, V., *Introduction in Physical Chemistry of Silicate Materials*. SNTL Prague, Bratislava, 1965.
2. KOUBEK, V., ŠTUBŇA, I. & KOZÍK, T., The porosity and Young's modulus of ceramic material after thermal treatment. *Sklář a keramik*, **31** (1981) 156–158.
3. ŠAŠEK, L., *et al.*, *Laboratory Methods in Ceramic Technology*. SNTL Prague, Bratislava, 1981.
4. FREUND, F., Kaolinite–metakaolinite, a model of a solid with extremely high lattice defect concentration. *BDKG*, **44** (1967) 5–13.
5. NORTON, F. H., *Fine Ceramics — Technology and Applications*. McGraw-Hill, New York, 1970.
6. RAMBOUSEK, V., Study of sintering the alumina-enriched porcelain. PhD thesis, Czech Technical University, School of Chemical Technology, 1979.
7. KISELEV, I. M., Firing the kaolin and investigation of the fired product. PhD thesis stored in ONIITECHIM, Tcherkassy, 1978, No. 1762178.