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Thermomechanical and thermodilatometric analysis of green alumina porcelain

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Abstract

A modulated force thermomechanical analysis (mf-TMA) and thermodilatometric analysis (TDA) of the green ceramic mixture of kaolin (27 wt.%), Al_2O_3 (50 wt.%) and feldspar (23 wt.%) up to 1000 °C is presented. The mf-TMA reflects changes during heating the green ceramics with higher sensitivity than TDA. Discrepancies between mf-TMA and TDA revealed that the elastic behavior of the green porcelain samples is determined most importantly by processes on the crystal boundaries (escaping of the water molecules at the low temperatures up to 150 °C and solid state sintering at the temperatures above 450 °C). Processes in the crystal interiors (e.g. dehydroxylation) have a lesser function. Thermodilatometric results depend more on the processes which take place inside the crystals than on the processes on the crystal surfaces.

Keywords: D. Porcelain; Thermomechanical analysis; Resonant method; Thermodilatometry

1. Introduction

An understanding of behavior of ceramics can provide insights into firing processes, the influence of additives and raw materials, the densification and sintering properties, the reaction kinetics, phase transitions, glaze development, as well as thermal shock. Thermodilatometric analysis (TDA) is a very suitable method for investigation of such processes in ceramics, e.g. sintering [1].

Sintering is accompanied with the vanishing of the porosity, which is connected with shrinkage of the sample measurable by dilatometer. Because thermodilatometric patterns of most raw ceramic components are known, the thermodilatometric curve can be useful in estimating the composition of the green sample [2,3]. TDA is recommended as a control test for determining the properties of the firing [4] as well as for determining the properties of the raw materials and a test of their quality [5]. Results of TDA may be used for design of the firing regime [6]. TDA is often combined with other thermal analyses, primarily with DTA and TGA, which provides a more complex view on processes which run in ceramics during firing [7].

Thermomechanical analysis (TMA) which uses a time-dependent periodic force affecting the sample (the so-called modulated force thermomechanical analysis (mf-TMA)) is a relatively new method compared with TDA. Most of the technical solutions of the method are based on continual measuring the resonant frequency of the sample during defined temperature regime. The resonant frequency serves for the calculation of the sound velocity or elasticity moduli (Young's modulus or shear modulus). A next eventuality of mf-TMA is measuring the temperature dependence of the internal friction. The mf-TMA method is rarely employed. For example, this method was used for investigation of sintering in [8–11], for the investigation of the glassy phase in the intergranular space [12], as well as for study of the crack propagation [13] and for studying the role of quartz in porcelain [14,15]. The mf-TMA is appropriate for investigation of the materials used for mechanically loading at high temperatures [16,17]. The mf-TMA as a non-destructive method is suitable for continuous testing of the sample in a large temperature interval.

Both thermal expansion and resistance against mechanical load, have some common features. It can be found from the simple model of two atoms with the potential energy

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concerning an anharmonicity of thermal vibration of the atoms. From theory, the relationship between coefficient of the linear thermal expansion and Young's modulus is $\alpha \cong 1/E$ (see e.g. in [18,19]). However, the rule "the higher thermal expansion the lesser Young's modulus" can be used only qualitatively in general. Formulae connecting the coefficient of the linear thermal expansion with elastic constant were derived for the simple cubic monocrystal and do not take into account porosity, grains boundary and other defects and structure features of real materials which may influence the elastic properties in great measure. However, the coefficient of the linear thermal expansion and Young's modulus cannot be obtain one from the other by calculation but have to be measured. Despite the common origin these values result in different information.

In this work, we show a connection between TDA and mf-TMA and compare their abilities for experimental study of firing the kaolin-contained ceramics.

2. Measurement method and samples

2.1. Resonant mf-TMA

The most commonly used methods for determination of the elastic parameters (Young's modulus, shear modulus, speed of the propagation of longitudinal wave (i.e. sound velocity), speed of the propagation of torsional wave) of ceramics are resonant techniques. The resonant techniques are relatively simple and produce very small mechanical stress, and do not initiate inelastic processes in tested material. Under low stress, the assumptions of the elastic theory of the vibration are fulfilled and negligible structural changes take place in the sample. The simplest and the most reliable arrangement of an experiment is based on the flexural vibrations of the sample. An advantage of the flexural vibrations is the simple excitation and measurement which is favorable at high temperatures. This method which was employed in [8,10,11,14,17] is described in details in [20].

The sound velocity c_L and Young's modulus E can be calculated by formulae [20]

$$c_L = K\frac{l^2 f}{d}\sqrt{T} \quad \text{and} \quad E = c_L^2\rho = \left(K\frac{l^2 f}{d}\right)^2 T\rho, \tag{1}$$

where f is a resonant frequency of the fundamental mode, ρ is a volume mass, l is the length and d is the diameter or thickness of the sample.

Values of the constant K are

K = 1.12334 for a cylindrical sample with a uniform circular cross-section,

K = 0.97286 for a prismatic sample with a uniform square cross-section.

If a sample with the ratio $l/d < 20$ is applied, it is necessary to use a correction coefficient T as shown in Eq. (1). The coefficient T can be calculated from formula [20] for circular and rectangular cross-section as

$$T = 1 + A(1 + 0.0752\mu + 0.8109\mu^2)\left(\frac{d}{l}\right)^2 - B\left(\frac{d}{l}\right)^4 - \frac{C(1 + 0.2023\mu + 2.173\mu^2)(d/l)^4}{1 + D(1 + 0.1408\mu + 1.536\mu^2)(d/l)^2}, \quad l/d < 20 \tag{2}$$

$$T = 1 + F\left(\frac{d}{l}\right)^2, \quad \frac{l}{d} \geq 20 \tag{3}$$

The values of parameters A, B, C, D, F in Eq. (1) and Eq. (2) are in Table 1. The value μ is Poisson's ratio.

The mf-TMA was carried out with the apparatus designed by the authors [21]. The apparatus is based on the construction described in [17,20].

2.2. Thermodilatometry

As noted above, thermodilatometry (TDA) is a widely exploited, well known, and very suitable method for investigation of different processes in ceramics. In this research, a push-rod dilatometer was used [22] for investigation of the low temperature stage of the firing.

2.3. Samples

Green electroceramic samples were made from a mixture of kaolin (27 wt.%), Al_2O_3 (50 wt.%) and feldspar (23 wt.%) with traces of quartz. The mixture was ground and sieved on a 100 mesh/mm^2 sieve and then a plastic material was prepared from this mixture. The cylindrical samples (Ø11 mm × 150 mm) were made for mf-TMA with the laboratory extruder. The samples for TDA were made in the same manner. Their size was Ø11 mm × 40 mm. After air drying, the sample contained ~1 wt.% of the physically bound water and their volume mass was 1922 kg/m^3.

The green samples were heated in the mf-TMA apparatus or in the dilatometer in the air up to 1000 °C. The temperature was increased linearly with the rate of 2.5 °C/min.

3. Results and discussion

A measured value in mf-TMA is a resonant frequency f. We can find from analysis of Eq. (1) how this value is influenced by the changes of the dimensions of the sample.

Table 1
Parameters A, B, C, D, F

Parameter	Cross-section	
	Circular	Square
A	4.939	6.585
B	0.4883	0.868
C	4.691	8.340
D	4.754	6.338
F	4.939	6.585

(a) The influence of the sample dimensions on the correction coefficient T.

Let us take our real case where the sample has the length l = 150 mm and diameter d = 10 mm. Let a sintering leads to contraction of the sample 1%. This produce resulting changing the ratio of l/d = 15 to $l/d \approx 148.5/9.9 \approx 15$. From analysis of Eq. (2) for $\mu = 0.20–0.30$, the correction coefficient is not influenced by the so small changes in the ratio l/d.

(b) The influence of the sample dimensions on the resonant frequency.

If subscript 0 symbolizes initial values in the beginning of the temperature interval, then the resonant frequency following from Eq. (1) is

$$f_0 = \frac{1}{K\sqrt{T}} \frac{c_0 d_0}{l_0^2} \tag{4}$$

Assuming the same relative contraction in both the length and diameter $\Delta l/l_0 = \Delta d/d_0 = s$, then in the end of the temperature interval, the length and diameter have values $l = l_0(1-s)$ and $d = d_0(1-s)$. For the resonant frequency, the following was obtained

$$f = \frac{1}{K\sqrt{T}} \frac{\mathrm{c} d_0}{l_0^2(1-s)} \tag{5}$$

and the relative change of the resonant frequency is

$$\frac{\Delta f}{f_0} = \frac{f - f_0}{f_0} = \frac{c}{c_0(1-s)} - 1. \tag{6}$$

Excluding, formally, the influence of the changing of the sound velocity during heating on the resonance frequency, i.e. $c = c_0$, then for $s = 0.01 = 1\%$, the relative change of the resonant frequency caused by the contraction (or expansion) of the sample is 1%. The mf-TMA is approximately equally sensitive to the intrinsic changes of the sample induced by the heat as TDA if these changes appear only by the change of the sample dimensions.

The result of the mf-TMA of the green porcelain sample is shown in Fig. 1, that is, as a dependence of the relative changing of the resonant frequency, i.e. $(f - f_0)/f_0$ on the temperature, where f_0 = 1120 Hz is a resonant frequency at the room temperature and f is the resonant frequency measured at the actual temperature. A curve may be divided into several parts corresponding to processes in porcelain mixture during its firing up to 1000 °C:

liberation of physically bound water at temperatures from 20 to 150 °C,
dehydroxylation at temperatures higher than 400 °C,
collapse of a metakaolinite lattice at ~950 °C and creation of spinel and mullite.

The $\alpha \rightarrow \beta$ transformation of quartz at a temperature ~573 °C is not recorded simply attributable to the very small amount of quartz in the sample.

Fig. 2 shows the results of TDA of the green porcelain sample reflecting the same processes as Fig. 1. Comparing Fig. 1 with Fig. 2, the rule ‘‘the higher thermal expansion, the lesser resonant frequency’’ is not completely fulfilled. In the range 20–200 °C, there is an increase of the resonant frequency. In this temperature range two concurrent mechanisms appear. The first is the escaping of the physically bound water from the finest pores and the surface of crystals. This leads to (a) the more tight contact between crystals and, then, to the increasing of the resonant frequency and (b) also leads to a small contraction. Simultaneously, the thermal expansion makes the resonant frequency lower and dimensions of the sample larger. A net effect of these phenomena illustrates itself a steep growth of the resonant frequency and as a very moderate decelerating of the increase of the thermal expansion up to 120 °C.

Following after the escape of the physically bound water, there is no changing of the structure and composition, so above 200 °C both curves satisfy approximately the rule ‘‘the higher thermal expansion, the lesser resonant frequency’’ as long as dehydroxylation emerges at ~450 °C. This process is illustrated with different ways for mf-TMA and TDA. The TDA catches (a) a shrinkage of the kaolinite crystals which is an outcome of the escaping the crystalline water from their

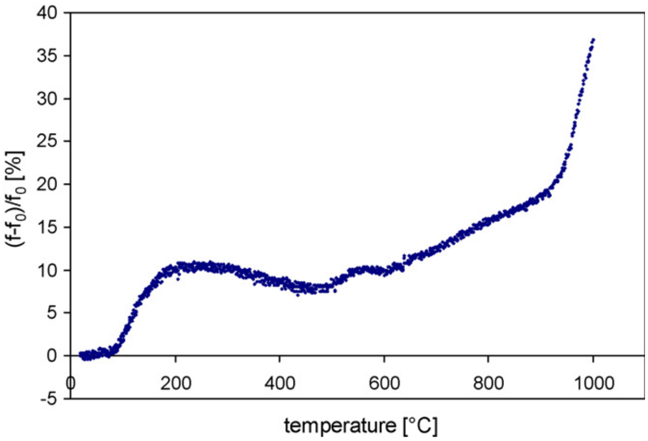

Fig. 1. mf-TMA curve of the green alumina porcelain sample, heating rate 2.5 °C/min, f_0 = 1120 Hz.

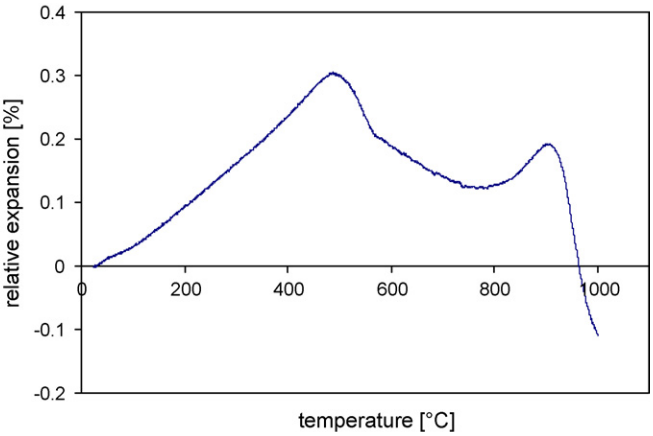

Fig. 2. Relative expansion of the green alumina porcelain sample, heating rate 2.5 °C/min.

octahedral sheets and (b) the thermal expansion of the feldspar and α-corundum.

The mf-TMA is a sum of the results of three phenomena: (a) a creation of defects in the kaolinite crystals interiors (which makes the resonant frequency lower), (b) a solid phase sintering (which makes the resonant frequency higher) and (c) a shrinkage of the sample dimensions (which makes the resonant frequency according to Eq. (5) higher).

As illustrated in Figs. 1 and 2, a thermodilatometric behavior of the sample during dehydroxylation is determined primarily by dehydroxylation process in the kaolinite crystals. The elastic behavior is determined mainly by improving the contacts between crystals as a consequence of the solid phase sintering. Dehydroxylation plays a minor role (except at a short temperature interval 550–620 °C).

The thermal expansion after completing of dehydroxylation terminates at the temperature ~900 °C, when the collapse of the metakaolinite lattice accompanied by rapid shrinkage appears. Identically, there is a steep increasing of the resonant frequency as the response to the faster solid state sintering and on the new structure rather than the defect and microporous metakaolinite.

The resonant frequency follows the processes in the sample during heating with significantly higher sensitivity than thermodilatometry. This is evident from the numerical values of the relative expansion and relative change of the resonant frequency. However, the resonant frequency is not a material quantity (although it does depend on material properties). For practical use it must be transformed into sound velocity or Young's modulus according to Eq. (1). To accomplish it, alterations of the dimensions or even alterations of the mass of the sample must be taken into account. The formula (1) for the sound velocity, rewritten for such a case, takes a form

$$c_L = K\frac{l^2(t)\,f(t)}{d(t)}\sqrt{T}, \tag{7}$$

where $l(t)$, $d(t)$ are the length and diameter of the sample at the actual temperature which are based on the TDA results given in Fig. 2. The value $f(t)$ is the resonant frequency at the actual temperature taken from Fig. 1. A relationship $c_L(t)$ plotted from the results given in Figs. 1 and 2 is shown in Fig. 3. Shapes of the curves c_L and $(f-f_0)/f_0$ in Figs. 1 and 3 are almost identical, attributable to the small values of the relative expansion influence the sound velocity in a very small measure.

The sound velocity characterizes a capability of material to transport the mechanical energy. The transport is realized through crystals of kaolinite (or metakaolinite after dehydroxylation or alumina spinel and mullite after collapse of metakaolinite), feldspar and α-corundum. Feldspar and α-corundum do not change their structure during heating from 20 to 1000 °C. Kaolinite transforms into metakaolinite which is a material identified with a highly defect structure. Despite this, the sound velocity has the tendency to rise intensively in the temperature region 50–150 °C and above 450 °C. This can be explained by improving the contacts between crystals and is a consequence of the solid state sintering of the very fine crystalline particles which occur at temperatures above 500 °C [23].

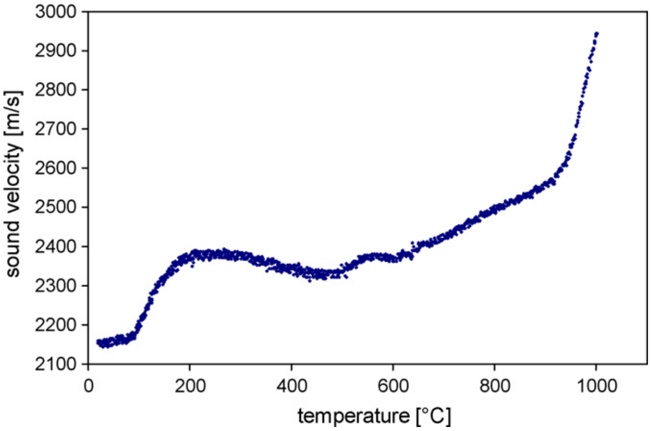

Fig. 3. Sound velocity of the green alumina porcelain sample during firing, heating rate 2.5 °C/min.

4. Conclusions

The mf-TMA based on the measurement of the resonant frequency follows the processes in the sample during heating with significantly higher sensitivity than thermodilatometry. Both curves mf-TMA and TDA can be divided in typical parts corresponding to processes in porcelain mixture during its firing up to 1000 °C:

liberation of physically bound water at temperatures from 20 to 150 °C,
dehydroxylation at temperatures higher than 400 °C,
collapse of a metakaolinite lattice at ~950 °C and creation of spinel and mullite.

A theoretical assumption that "the higher thermal expansion, the lesser sound velocity" is fulfilled only partially in the temperature region 20–1000 °C. Discrepancies between mf-TMA and TDA revealed that the elastic behavior of the green porcelain samples is determined most importantly by processes on the crystal boundaries. In the event of the escaping of the water molecules at the low temperatures up to 150 °C and the solid state sintering at the temperatures above 500 °C. Processes in the crystal interiors (e.g. dehydroxylation) have a lesser function. Thermodilatometric results are dependent more on the processes which take place inside the crystals than on the processes on the crystal surfaces.

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References

[1] M. Paganelli, Using the optical dilatometer to determine sintering behavior, Am. Ceram. Soc. Bull. 81 (2002) 25–30.

[2] W.F. Curtis, Firing studies of Al_2O_3 porcelains by irreversible thermal dilatometry. MS Thesis, School of Ceramic Engineering of Alfred University, Alfred, NY, 1978.
[3] L. Šašek, et al., Laboratory Methods for Silicate Materials, SNTL Praha – Alfa Bratislava, 1981.
[4] D.W. Forbes, The interpretation of thermal expansion data in research and control practices, Ceramic Age 81 (1965) 38–41.
[5] C.F. Hanks, Irreversible thermal expansion, Ceramic Age 83 (1967) 12–18.
[6] T. Kozík, J. Roháč, I. Štubňa, A contribution to optimization of the firing of electroporcelain. II. Influence of the size and rate of firing on mechanical stress, Sklář a keramik 40 (1990) 232–235 (in Slovakian).
[7] R.W. West, Dilatometry of structural clay products, J. Can. Ceram. Soc. 34 (1965) 21–27.
[8] G.J. Churchman, P.K. Forster, Factors affecting thermal shock resistance during fast firing of ceramics, NZ J. Sci. 17 (1974) 59–70.
[9] V. Vlach, J. Bureš, Determination of the physico-mechanical parameters of ceramics during firing, in: Proceedings of the Conference Sintering of Ceramics, Karlovy Vary, 1976, pp. 94–99 (in Czech).
[10] M.O. Marlowe, D.R. Wilder, Sensitive resonant frequency technique for the study of sintering kinetics, J. Am. Ceram. Soc. 50 (1967) 145–149.
[11] M.O. Marlowe, D.R. Wilder, Sintering kinetics study using reduced variables, J. Am. Ceram. Soc. 50 (1967) 509–512.
[12] G. Roebben, et al., Quantitative determination of the volume fraction of intergranular amorphous phase in sintered silicon nitride, Mater. Sci. Eng. A 370 (2004) 453–458.
[13] D. Shi, et al., Kinetics study of ab-plane crack propagation by a modulus measurement in single domain $YBa_2Cu_3O_x$, Physica C 384 (2003) 149–158.
[14] I. Štubňa, T. Kozík, F. Hanic, Young's modulus and mechanical strength of porcelain at the firing cooling stage, Ceram. Int. 18 (1992) 353–354.
[15] I. Štubňa, A. Trník, L. Vozár, Thermomechanical analysis of quartz porcelain in temperature cycles, Ceram. Int. 32 (2007) 1287–1291.
[16] H.L. Brown, Young's modulus measurement above 2000 °C, Rev. Sci. Instr. 34 (1963) 636–639.
[17] J.A. Kaštaljan, Elastic Parameters of Materials at High Temperatures, Naukova dumka, Kiev, 1970 (in Russian).
[18] V.S. Postnikov, Physics and Chemistry of Solid State, Metallurgia, Moskva, 1978 (in Russian).
[19] S.C. Lakhad, Temperature dependence of the elastic constants, J. Appl. Phys. 42 (1971) 4277–4281.
[20] ASTM C 1198-01, Standard test method for dynamic Young's modulus of advanced ceramics by sonic method (published in June 2001, Standard Documents, Philadelphia USA).
[21] A. Trník, L. Vozár, I. Štubňa, The apparatus for thermomechanical analysis of ceramics. Zb. 27. Mezinárodní český a slovenský kalorimetrický seminář. Univerzita Pardubice, Svratka. 2005, s.191-194, ISBN 80-7194-764-4 (in Slovakian).
[22] I. Štubňa, A. Vážanová, G. Varga, D. Hrubý, Simple push-rod dilatometer for dilatometry of ceramics, in: Research and Teaching of Physics in the Context of University Education, SPU Nitra, Nitra, 2007, pp. 69–74.
[23] S.N. Monteiro, C.M.F. Vieira, Solid state sintering of red ceramics at lower temperatures, Ceram. Int. 30 (2004) 381–387.