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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