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Ceramics International 38 (2012) 6919–6922

CERAMICS INTERNATIONAL

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Short communication

Acoustic emission study of quartz porcelain during heating up to 1150 °C

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Received 12 March 2012; received in revised form 30 April 2012; accepted 8 May 2012
Available online 15 May 2012

Abstract

The acoustic emission (AE) technique was used for the real-time monitoring of microcracking in a green quartz porcelain mixture (50 wt% kaolin, 25 wt% quartz and 25 wt% feldspar) subjected to heating up to 1150 °C with a heating rate of 5 °C/min. Two sources of microcracking were identified. The first one, which begins at a temperature of 50 °C, is connected to the liberation of physically bound water. The second source is caused by differences between the thermal expansion of crystals (kaolinite/metakaolinite, feldspar and α-quartz/β-quartz). The α→β transformation of quartz is not detected with AE. The vanishing of cracking at 600 °C correlates with the increase of the Young's modulus and is ascribed to solid-state sintering, which fortifies crystal interfaces between metakaolinite, feldspar and β-quartz.

Keywords: Acoustic emission; Microcracks; Young's modulus; Quartz porcelain

1. Introduction

The firing of silicate ceramics, which are made of clays with a high content of kaolinite, transforms a green body into a ceramic product [1–3]. The green body exhibits significant changes in its properties, resulting from dehydration at low temperatures, phase changes during dehydroxylation and high-temperature reactions, and densification during sintering [1–3]. All these changes significantly influence the mechanical properties of the fired body as well as its other physical properties. In spite of this fact, mechanical properties are only rarely measured as a function of temperature during firing. Researchers mostly focus their attention on basic thermal analyses, such as DTA, TGA, TDA and XRD, which give information about phase development and the kinetics of reactions during firing. A review of the mechanical behavior of quartz porcelain during firing, for heating and cooling stages, can be found in [4,5].

In-situ mechanical measurements help to obtain a detailed insight into processes taking place in ceramics during firing. They are also important for the design of an optimal firing regime. Mechanical strength and elastic properties are basic quantities, which serve for calculating the maximum heating or cooling rates. Their measurements and the obtained results are described, for example, in [4–8].

Quartz porcelain is a complex multiphase material containing minerals with different coefficients of linear thermal expansion, which is the main reason for cracking during cooling [3,9]. Direct evidence of the cracking during the cooling stage of firing was obtained via acoustic emission (AE) measurements [10]. The study [11], which combined the detection of AE and the modulated-force thermomechanical analysis (mf-TMA), confirmed the results published in [10] and provided additional information regarding cracking at temperatures lower than 600 °C.

The three-point bending test performed during the heating stage of the firing on the green quartz porcelain samples showed that mechanical strength decreased during dehydroxylation [12]. It is evident that the lower values of the mechanical strength between 400 °C and 550 °C correlate

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.05.021

with the start and the maximum rate of dehydroxylation (if measured on laboratory samples). The new structure, metakaolinite, is more porous than kaolinite [13], so this fact explains the strength behavior of the sample during dehydroxylation. A possible creation of new micropores, which can be considered cracks, should be detected by AE. However, we are not aware of any evidence on AE during the heating stage of firing.

The objective of this paper is a study of AE and the Young's modulus of the quartz porcelain mixture during heating up to 1150 °C.

2. Experimental

Samples were made from 50 wt% kaolin, 25 wt% quartz and 25 wt% feldspar mixed with water to produce plastic raw ceramic mixture. The green cylindrical samples were made with the laboratory extruder. The diameter of the green samples was 11 mm and their length was adjusted to the relevant apparatus. After free-drying in the air, the samples contained ~1 wt% of the physically bound water.

The experimental set-up for the AE measurement is shown in Fig. 1. A sample with dimensions ∅11 × 100 mm was mounted to the end of an alumina rod, which served as a waveguide to route AE out of the furnace. A piezoelectric AE transducer MST8S (fabricated by DAKEL ZD Rpety, Czech Republic) was glued to the opposite end of the rod. The computer-controlled DAKEL-XEDO-3 AE system (DAKEL ZD Rpety, Czech Republic) was used to monitor AE. The total gain was 92 dB and the AE signal sampling rate was 4 MHz. The threshold voltage for the total AE count (level 1) was set to 730 mV (slightly above the noise voltage) and the threshold voltage for the burst AE count (level 2) was 1450 mV, which allowed for the detection of large AE bursts. The full scale of the A/D converter was ± 2.4 V. Linear heating with a rate of 5 °C/min was applied during the experiment.

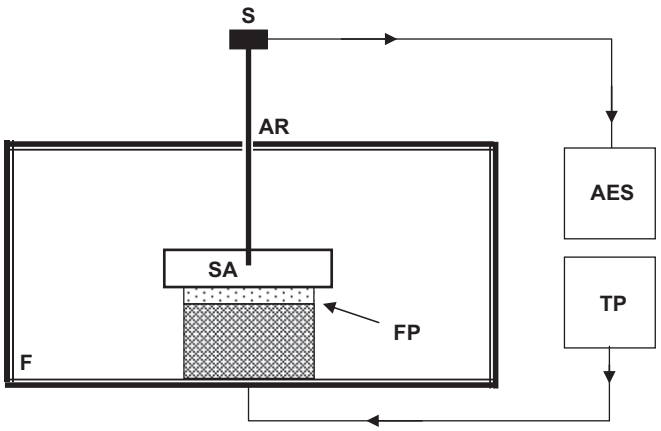

Fig. 1. Scheme of the AE measurement set up: SA=sample, AR=alumina rod (diameter 3 mm), FP=alumina fiber pad, S=AE sensor, F=furnace, TP=temperature programmer and AES=acoustic emission system (DAKEL-XEDO box and a computer).

The method used to measure the resonant frequency was based on the flexural vibration of the sample. The values of the Young's modulus E as a function of temperature were calculated using the formula [14,15]

$$E(t) = 1.26063\left(\frac{l^2 f(t)}{d}\right)^2 \rho\, T \quad (1)$$

where $f(t)$ is the resonant frequency of the fundamental mode at temperature t and l, d are the length and the diameter of the sample, respectively; ρ is the volume mass of the material. The value T=1.02551 is the correction coefficient for the Poisson's ratio μ=0.2 and the ratio l/d=14, which is tabulated in [14] or can be calculated by the formula given in [15]. The resonant frequency was measured on the samples with dimensions ∅11 × 140 mm, using the apparatus described in [16].

It is known that the length, the diameter and the mass of the sample change during heating, e.g. see [1,2], which is also confirmed by our results given in Figs. 2 and 3. Ignoring these changes, i.e. using solely Eq. (1), leads, according to our analysis, to a maximum error of 6%. Since we describe the firing process only qualitatively, this simplified approach is suitable in accomplishing the objective of this study.

Thermal analyses TGA and DTA were performed with a Derivatograph 1000 analyzer (Hungary) on the compact samples, both measured and inert, with dimensions ∅11 × 20 mm. Thermodilatometry (TDA) was performed with a dilatometer described in [17] on the samples with dimensions ∅11 × 40 mm.

3. Results and discussion

First of all, we performed basic thermal analyses DTA, TGA and TDA in order to specify the temperature ranges of the processes that take place in the sample during heating. To decrease temperature shifts between the curves of the different thermal analyses, we used compact cylindrical samples of the same diameter for all measurements. The TGA and DTA curves (Fig. 2) show the escaping of physically bound water at low temperatures, which is

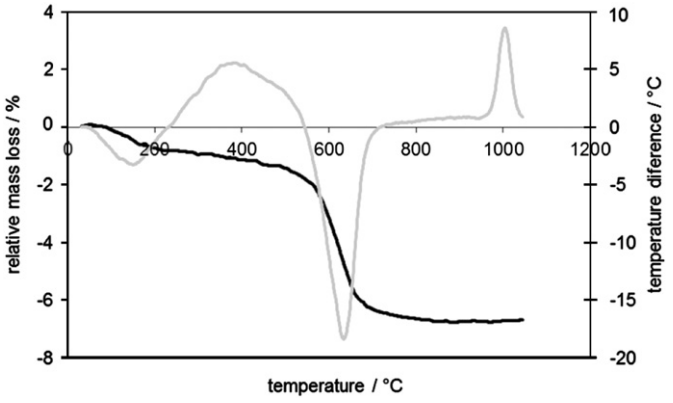

Fig. 2. DTA (gray line) and TGA (black line) results of the green quartz porcelain sample.

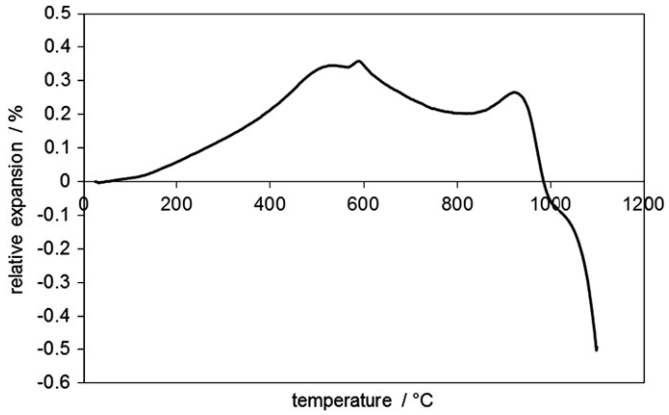

Fig. 3. Thermodilatometric curve of the green quartz porcelain sample during heating stage of firing.

followed by the endothermic transformation of kaolinite into metakaolinite (400–700 °C) and the exothermic transformation of metakaolinite into spinel and mullite above 950 °C. The α→β transformation of quartz, which takes place at ~573 °C, is concealed by dehydroxylation. The α→β transformation of quartz is clearly visible in the TDA curve as the small maximum at ~590 °C, see Fig. 3.

As follows from Fig. 4, weak AE signals appear sporadically between the temperatures 20–200 °C, which can be related to the liberation of water located in the pores, which sets the crystals closely. Friction between the crystals and their little shifts are probably the sources of the AE signals. The TDA curve shows (see Fig. 3) a small expansion of the sample between 20 and 200 °C, which is connected to an intensive increase in the Young's modulus, see Fig. 5. This can be explained by closer setting of the crystals.

During heating from 200 °C to 400 °C, there are no phase changes in the sample. Residual water molecules, which are bound with electrostatic forces on the crystal surfaces, especially on kaolinite, need more energy to leave these surfaces, therefore their liberation takes place at temperatures up to 400 °C. A decrease in the Young's modulus and an increase in the linear expansion of the sample have the same source, which is the weakening of the interatomic forces at elevated temperatures. Both processes, a) the packing of the crystals tighter due to the escape of the last residual water and b) the release of the mechanical stress that arises from the differences between thermal expansion of crystals (kaolinite, feldspar and α-quartz), lead to AE signals between 200 °C and 400 °C as visible in Fig. 4. These AE signals are most probably linked to the creation of microcracks at crystal interfaces. The nucleation of microcracks and their multiplying (see Fig. 4) is another reason for the decrease of the Young's modulus at this temperature interval (see Fig. 5).

Dehydroxylation, which is the source of the new high-defect phase (metakaolinite) [13], begins at ~420 °C. This process is connected to a significant mass loss and contraction of the kaolinite crystals (see Figs. 2 and 3). Relatively strong AE signals appear above this temperature and some weaker signals also appear between 500 °C and

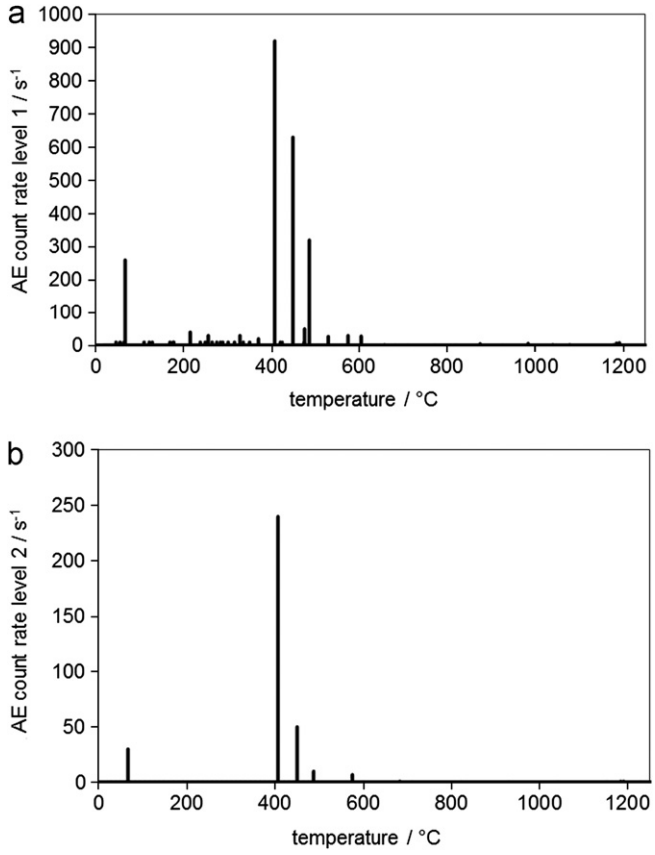

Fig. 4. (a) AE count rate from the green quartz sample during heating. The measurement was performed with the lower AE threshold (level 1). (b) AE count rate from the green quartz sample during heating. The measurement was performed with the higher AE threshold (level 2).

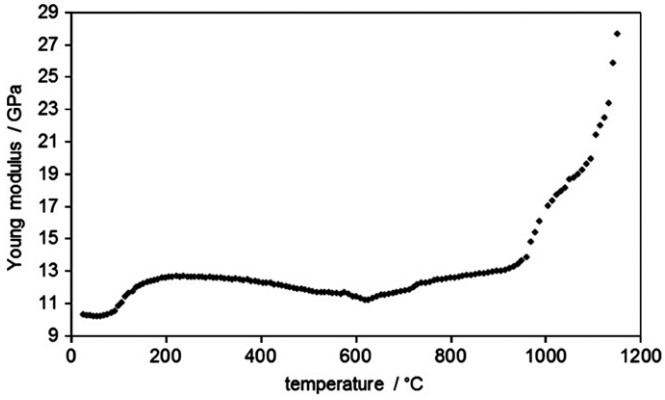

Fig. 5. Relationship between Young's modulus and temperature of green quartz sample during heating stage of firing up to 1150 °C with heating rate 5 °C min^{-1}.

600 °C. The Young's modulus continues to decrease in this temperature interval, which can have the same sources as described above. The transformation of α-quartz→β-quartz is expressed as a small maximum in Figs. 3 and 5. But this is not registered with AE, probably because this transformation is accompanied by a small volume increase. Such volume

increase has a healing effect on the surrounding of the quartz crystals, i.e. radial stress closes the microcracks around them [11].

The cessation in the generation of new microcracks (as indicated by vanishing AE) correlates with the increase in the Young's modulus observed above 620 °C. Furthermore, another mechanism, i.e. solid-state sintering, which fortifies crystal interfaces (between metakaolinite, feldspar and β-quartz), is present above ~600 °C. This mechanism dominantly influences the Young's modulus, and abating dehydroxylation does not play any significant role anymore. Above 950 °C high-temperature reactions begin in metakaolinite. The first is its transformation into spinel (or γ-Al_2O_3, this problem is not unambiguously solved) [5,18,19], which is accompanied by the sample contraction and increase in a volume mass [2,3]. The value of the Young's modulus increases rapidly above the temperature of 950 °C in every sample, which contains kaolin as the initial raw material [4,6,8]. Then mullite is created at temperatures above 1100 °C [2,3,5,19] and Young's modulus continues to rise up to the firing temperature of 1150 °C, when feldspar intensively melts and a glassy phase occurs. This temperature was chosen as the upper limit where liquid-phase sintering does not yet occur. Above this temperature, the creation of microcracks is not expected.

4. Conclusions

The acoustic emission (AE) technique has proven to be an efficient research tool in the real-time monitoring of microcracking in quartz porcelain subjected to temperature changes. Results obtained by the AE technique during heating reveal two sources of microcracking. The first one is connected to the liberation of physically bound water and begins at a temperature of ~50 °C. The second source is connected to differences between the thermal expansion of crystals, which are kaolinite, feldspar and quartz before dehydroxylation and metakaolinite, feldspar and quartz during and after dehydroxylation.

The transformation of α-quartz→β-quartz, which takes place at ~573 °C, is not detected with AE.

The vanishing of the cracking at ~600 °C correlates with an increase in the Young's modulus. Solid-state sintering, which fortifies boundaries between crystals (metakaolinite, feldspar and β-quartz) does not generate AE signals.

Acknowledgment

This work was supported by the grant VEGA 1/0646/12, financed by the Ministry of Education of Slovakia. Author F. Chmelík gratefully acknowledges financial support from research grant P108/11/1267 financed by the Czech Science Foundation and author A. Trník gratefully acknowledges financial support from the Czech Science Foundation, Project no. P105/12/G059.

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