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Research paper

Investigation of dynamic mechanical properties of Estonian clay Arumetsa during firing

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ABSTRACT

Elastic and inelastic properties of ceramic clay from Estonian locality Arumetsa (59% of clay minerals, mostly illite; 25% of quartz, 12% of K-feldspars and 3% of carbonates) were investigated by a dynamical thermomechanical analysis during the heating and cooling stages of firing performed up to 900, 1000, and 1100 °C. Complementary analyses DTA, TG, thermodilatometry, and XRD were also performed. During heating, the release of the physically bound water set the clay crystals closer to each other, which increases Young's modulus (YM) and decreases internal damping (ID). On the other hand, dehydroxylation did not influence YM and ID significantly. This means that the properties of the phase boundaries are more important for YM than the intrinsic mechanical properties of the crystals themselves. Heating above 700 °C caused solid-phase sintering, later creation of the melt and an intensive liquid-phase sintering. The values of YM significantly depend on the maximal firing temperature. After heating to 900 °C and 1000 °C, YM reached low values (~8 GPa) because sintering was not sufficient for substantially eliminating the porosity. The heating up to 1100 °C brought the value of YM to 47 GPa due to a high part of the glassy phase. As a result of the microcracks creation, the values of YM dropped down significantly from their highest values at 800 °C. Their relative decrease represented 38% after firing at 1000 °C and 1100 °C and 36% after firing at 900 °C.

1. Introduction

Clays are essential components of building ceramic mixtures because of their plasticity, workability, green strength and final properties obtained by their thermal treatment, which can be performed in relatively large temperature intervals with the highest temperature commonly not exceeding 1000 °C (Das Kshama et al., 1992). The most important minerals in ceramic clays are kaolinite and illite. Other minerals, which are often present in clays, include quartz, muscovite, montmorillonite, carbonates, feldspar, iron oxides, and sulfides. In addition, clay can contain some organic material.

Since clays are crucial components of building ceramics they must fulfill specific mechanical and thermophysical parameter requirements. Therefore, an important task is to investigate these parameters in clays during firing as well as after their firing. Required mechanical properties of building ceramics are associated mainly with mechanical strength and Young's modulus (E). These two parameters are largely dependent on structural characteristics such as porosity, defects and newly formed phases (Hlaváč, 1981; Vieira et al., 2005). The final structural features of the ceramics are developed during processing and consolidated during firing, in which physical and chemical reactions occur among the different clay phases (Čičel et al., 1981; Hlaváč, 1981; Kruglitsky et al., 1984; Pytlík and Sokolář, 2002). Transformation of the phases during the heating stage of firing is often studied using thermal analyses (mainly DTA, TG, TDA) and XRD (Kruglitsky et al., 1984; Das Kshama et al., 1992; Aras, 2004; Ferrari and Gualtieri, 2006; Haq et al., 2009; Manoharan et al., 2011; Escalera et al., 2012; Csáki et al., 2017). After reaching the highest firing temperature and keeping the ceramic body at this temperature, the cooling stage of the firing follows. Although only the $\beta \rightarrow \alpha$ transition of quartz takes place during cooling, the final mechanical properties are formed at this stage of firing. The highest value of the mechanical strength and E are observed at around the glass transition temperature 750–800 °C. The mechanical properties decrease during cooling from this temperature down to the room temperature, which can be indirectly registered via acoustic emission and directly via dynamical thermomechanical analysis (D-TMA) (Chmelík et al., 2011; Knapek et al., 2016; Nigay et al., 2017). Observed variations in the final properties are explained as a function of mineralogy, crystallinity and the amount and nature of the impurities present in the clays.

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The object of this study is the clay from Estonian locality Arumetsa that is a part of Riga gulf region where 10 deposits with total resources of 4.3×10^6 m^3 of ceramic clay are located (Rattas et al., 2010). Some of these deposits were successfully exploited for brick manufacturing and pottery in the past but only the Arumetsa deposit is still in use. The use of this clay can be also attractive as a main part of the ceramic body together with a fly-ash from the oil-shale-burning thermal power station in Narva, Estonia (Kaljuvee et al., 2014). The goal of this paper is to study the development of the phases and its influence on the elastic and inelastic mechanical properties of this clay during the heating and cooling stages of the firing.

2. Experimental

2.1. Samples

The raw material was crushed, milled in planetary ball mill, sieved (100 μm mesh) and mixed with distilled water (25 mass%) to obtain a plastic mass. The plastic mass was afterwards molded into prismatic gypsum forms. The samples were air-dried freely, and their cross-section after drying and abrading was 12×10 mm^2. The lengths of the samples were adapted to the requirements of used measuring units (see below). The chemical composition of the Arumetsa clay is given in Table 1.

2.2. Methods

The phase analysis of the green clay Arumetsa was performed using the powder X-ray diffraction (XRD) on the BRUKER D8 Advance diffractometer with a Cu anticathode ($\lambda_{\alpha 1}$ = 1.54060 Å), an accelerating voltage of 40 kV and a beam current of 40 mA. The amount of 4.5 mass % of zincite was added to the powder as an internal standard for the quantitative phase analysis.

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed on a modernized apparatus Derivatograph 1100° (Podoba et al., 2012) using green compact samples with dimensions of $12 \times 10 \times 16$ mm. TDA was performed on a horizontal alumina dilatometer (described in Jankula et al. (2013)) on the green samples with dimensions of $12 \times 10 \times 30$ mm.

The elastic properties of Arumetsa clay during its heating up to 1100 °C were assessed using D-TMA, in which the resonant frequency of the flexurally vibrating prismatic sample was measured. Then Young's modulus was calculated using formula (ASTM Standard 1259-01, 2001)

$$E = 0.94645\left(\frac{mf^2l^3}{a^3b}\right)C, \quad (1)$$

where l, a, and b are respectively the sample length, thickness, and width, f is the resonant frequency of the fundamental mode of flexural vibration and m is the sample mass. C is a correction factor which is a function of the sample dimensions and Poisson's ratio (refer to (ASTM Standard 1259-01, 2001) for more details). The resonant frequency during heating and cooling was measured with the help of the impulse excitation technique on the apparatus described in (Húlan et al., 2014). The samples for this analysis had dimensions $108 \times 12 \times 10$ mm. The logarithmic decrement δ was determined simultaneously with the measurement of resonant frequency as (Inman, 2008)

$$\delta = \frac{\pi \Delta f}{\sqrt{3} f}, \quad (2)$$

Table 1
The chemical composition of Arumetsa clay in mass% (Kaljuvee et al., 2014).

SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	C_{org}	LOI
56.5	18.4	4.5	0.6	1.5	2.7	6.8	0.3	6.9

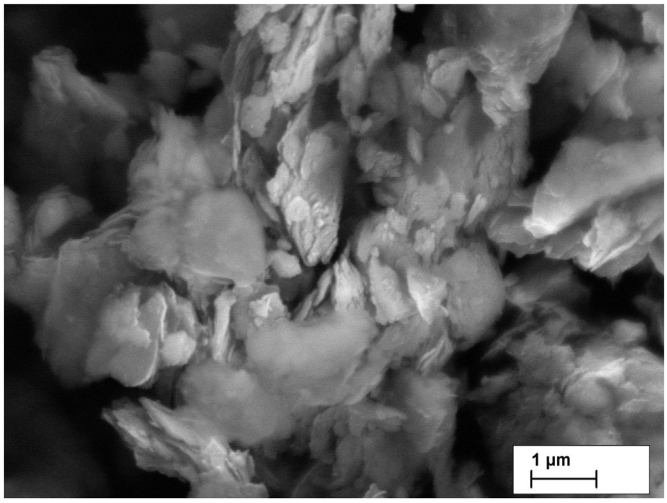

Fig. 1. SEM image of the Arumetsa clay.

where Δf is the width of the resonant peak in its half height. The logarithmic decrement characterizes an internal damping (friction) and, indirectly, defectiveness of the microstructure. Since the dimensions and mass of the samples were changing during heating, their actual values at the temperature T must be substituted into Eq. (1). For this purpose, the results of TDA and TG were exploited.

All the thermal analyses (TG/DTA, TDA, and D-TMA) were conducted at the heating rate of 5 °C/min. TDA and D-TMA were also conducted during cooling from the temperatures 900, 1000, and 1100 °C at the same cooling rate of 5 °C/min. No soaking time was applied at the highest temperature.

3. Results and discussion

As visible in Fig. 1, the fraction of Arumetsa clay consisted of the agglomerates of small (~1 μm) plate-like crystals.

Based on the XRD analysis (Table 2), the raw material contained mainly illite, kaolinite and quartz. K-feldspar, carbonates (calcite and dolomite) and hematite were also present. Reflections of zincite (ZnO) are also visible in the XRD records (Fig. 2) since this mineral was added into the material as an internal standard. The mineral composition of the clay changed during heating, see Fig. 2 and Table 2.

Quartz and K-feldspar are stable phases in the whole temperature interval of interest in this study (25–1100 °C). Amorphous phase (glass) dominated after firing at $T > 1000$ °C (54%). Hematite and spinel phases were formed in small amounts at the temperatures above 1000 °C.

There are four processes responsible for mass loss visible on TG and DTG curves in Fig. 3: 1) an endothermic drying with a mass loss ~1.9% and the maximum at 130 °C; 2) an exothermic thermooxidation of

Table 2
Mineral composition of the raw Arumetsa clay and ceramic bodies fired at 900, 1000, and 1100 °C (mass%).

	Firing temperature			
	Raw	900 °C	1000 °C	1100 °C
Illite/muscovite	41.6	18.8	3.2	–
Kaolinite	17.6	–	–	–
Quartz	25.0	26.9	26.7	25.7
K-feldspar	11.7	9.0	11.3	10.0
Calcite/dolomite	2.6	–	–	–
Hematite	0.5	0.9	2.7	6.4
Spinel	–	–	–	2.9
Amorphous/undefined	1.0	44.4	56.1	55.0