mf-TMA of the Green and Fired Heatproof Ceramics Letovice

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Nyers és égetett hőálló letovicei kerámiák mf-TMA vizsgálata

A 20–1100°C hőmérséklet tartományban végzett, a roncsolásmentes hangrezonanciás mód-szeren alapuló mf-TMA vizsgálat megerősítette, hogy a módszerrel érzékenyen lehet követni a nyers kerámia anyagában a hőkezelés során végbemenő folyamatokat (a fizikailag kötött víz fel-szabadulását, a dehidroxilációt, a szilárd fázisú zsugorodást, a magas-hőmérsékletű reakciókat), valamint az égetett kerámia termék szerkezetében a mikrorepedések jelenlétét.

Kulcsszavak: hőálló kerámia, tűzálló anyag, termomechanikai elemzés, rezonanciás módszer
Key words: heatproof ceramics, refractory, thermomechanical analysis, resonant method

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1. Introduction

An understanding of behavior of ceramics can provide insights on firing processes, the influence of additives and raw materials, densification and sintering properties, reaction kinetics, phase transitions, glaze development, and thermal shock. Thermodila-tometric analysis (TDA) is very suitable and traditional method for investigation of sintering [1]. Sintering is accompanied with vanishing of the porosity, which is connected with shrinkage of the sample measurable by dilatometer. TDA is effective if the shrinkage during liquid phase sintering. But during the solid phase sintering, which takes place at lower temperatures, the shrinkage is small and TDA is less effective. In this case, a mea-surement of the mechanical strength gives more information about processes on the boundaries between crystals [2]. Unfor-tunately, to determine the mechanical strength, many samples (usually more than 10) should be measured. For detailed study of the mechanical strength behavior of the ceramic material in the temperature range of $20 − 1100\,°C$ (e.g., this is the tempera-ture range used in the work described in this paper) by step of $10\,°C$, 1100 samples should be tested. Every measurement takes a certain time, so the continual measurement during increasing temperature is impossible. This dilemma can be circumvented by measurement of Young's modulus which is linearly propor-tional to the mechanical strength [3].

Mechanical thermal analysis (TMA) which uses a time-depen-dent periodic force affecting the sample, so-called modulated force thermomechanical analysis (mf-TMA), is relatively new method comparing with TDA. Many technical solutions of the method are based on the continual measuring the resonant frequency of the sample during defined temperature regime. The resonant fre-quency serves for calculation of the sound velocity or elasticity moduli (Young's modulus or shear modulus). A next eventuality of the mf-TMA is measuring the temperature dependence of the internal friction. The mf-TMA method is exploited relatively rare. For example, this method was used for investigation of sintering in [4-7] and for investigation of the role of quartz in porcelain in [8, 9]. The mf-TMA is unreplaceable for investigation of the mate-rials which are mechanically exerted at high temperatures [10, 11]. The mf-TMA as a non-destructive method is suitable for continu-ous testing of the sample in the large temperature interval.

As it follows from theory, the relationship between coefficient of the linear thermal expansion and Young's modulus is (see e.g. in [12, 13]). However, the rule "the higher thermal expan-sion the lesser Young's modulus" can be used only qualitatively in general [14]. Formulae connecting the coefficient of the line-ar thermal expansion with elastic constant were derived for the simple cubic monocrystals and do not take into account poro-sity, grains boundary and other defects and structure features of real materials which influence in great measure the elastic pro-perties. 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. In spite of the some com-mon origin these values bring different information.

In this work we show mf-TMA and its abilities for ex-perimental study of the mechanical behavior of the kaolin-contained heatproof stove tile ceramics.

2. Measurement method and samples

2.1 Resonant mf-TMA

The most commonly methods used for determination of the elastic parameters (Young's modulus, shear modulus, sound veloci-ty) of ceramics are resonant techniques, which are relatively simple and produce very small mechanical stress, which does not initiate inelastic processes in tested material. Under such a low stress, the assumptions of the elastic theory of the vibration are well fulfilled and, apart from it, negligible structural changes take place in the sample. The simplest and the most reliable arrangement of experi-ment is based on the flexural vibrations of the sample. An advan-tage of the flexural vibrations is also their simple excitation and measurement which is favorable at high temperatures. This meth-od which was used in [4, 6, 7, 8, 11] is described in details in [15].

The sound velocity c and Young's modulus E can be calculated by formulae [16]

$$c = K\frac{l^2(fQ)}{d} \quad , \qquad E = c^2\rho = \left[K\frac{l^2(fQ)}{d}\right]^2\rho \qquad (1)$$

where constant K for fundamental mode of the flexural vibration is

K = 1,12338   for cylindrical sample,
K = 0,97336   for prismatic sample with square cross-section.

The further values in Eq. (1) are: f – resonant frequency of the fundamental mode [Hz], ρ – volume mass of the sample material [kg/m³], d – diameter of the circular cross-section or side of the square cross-section of the sample [m]. A value Q is a correction coefficient, which have to be used if l/d < 20, where l is length of the sample. The coefficient Q is determined as

$$Q = 1 + \frac{1}{l/d}\left\{\frac{A}{\propto} + \frac{1}{l/d}\left[B + \frac{1}{l/d}\left(C + \frac{D}{l/d}\right)\right]\right\} \qquad (2)$$

where μ is Poisson's ratio and constants A, B, C, D are in Tab. 1, [16]. Another way of the obtaining the correction coefficient is described in [15].

Al2O3	SiO2	Fe2O3	K2O	Na2O	TiO2	CaO	MgO	L.O.I.
23,08	62,4	1,47	2,45	0,72	0,68	14,5	0,4	7,3

Table 1.   Chemical composition of the green ceramic mixture [wt. %]
1. táblázat   A kerámia nyerskeverék kémiai összetétele (tömeg %)

The mf-TMA was carried out with the apparatus designed by the authors. It is based on the construction described in [11, 15].

The green samples were heated in the mf-TMA apparatus in the air up to 1100 °C. After this analysis, the fired samples were subjected to the repeated test up to the temperature of 1100 °C. The temperature was increased linearly with the rate of 5 °C/min.

2.2 Samples

Green ceramic samples were made from a mixture of some commercial raw materials, most of which contain mainly kaolin and illite. The mixture contains significant amount of quartz. Crushed fired ceramics (pieces of the size less than 1 mm) and organic deflocculant were also added to the raw minerals. The mixture is used for production of the heatproof stove tiles at the ceramic plant Letovice, Czech Republic. A chemical composition (after manufacturer) of the dried samples is showed in Tab. 2.

parameter	cross-section	
	circular	**square**
A	-0,01284	-0,03564
B	3,11101	7,88347
C	-3,92254	-10,04634
D	3,92352	12,00459

Table 2.   Parameters A, B, C, D for the fundamental mode
2. táblázat   Az alapmódozat A, B, C és D paraméterei

The samples were prepared from the slurry by casting to the gypsum form. After free drying in the open air, the samples contained ~1 wt. % of the physically bonded water and had the dimensions 10×10×150 mm.

3. Results and discussion

During the heating, the green sample changed its structure and composition. Thus these changes determined mechanical behavior. A directly measured value in mf-TMA is a resonant frequency. Although the resonant frequency is not a material value, it depends on the structure, composition and temperature of the sample. To determine correct values of the sound velocity, thermodilatometry must be done and actual dimensions must be substituted into Eq. (1a). Determining of the Young's modulus requires thermodilatometry and thermogravimetry to calculate actual dimensions and volume mass for Eq. (1b). The graphs, and (where t = temperature [°C]) are similar to each other and it is sufficient for our purpose to show only the graph.
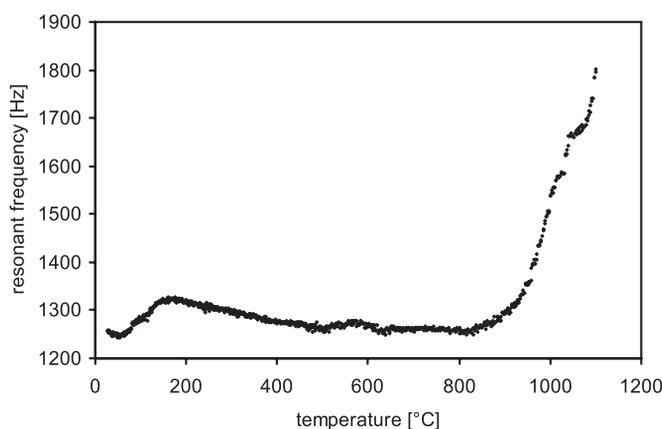

Fig. 1.   mf-TMA curve of the green sample Letovice
1. ábra   A Letovice-i nyersanyag minta mf-TMA görbéje

Results of the mf-TMA of the green sample are shown in Fig. 1. A curve can be divided in typical parts corresponding to processes in kaolin-contained mixture during its firing up to 1100 °C:

- Liberation of physically bound water at temperatures from 20 to 150 °C. This process leads to the more tight contacts between crystals, and subsequently, to the higher resonant frequency.
- Dehydroxylation at temperatures ~400–650 °C. Creation of the high-defect metakaolinite decreases the resonant frequency. This effect is partially superimposed by the solid-phase sintering.
- α → β transformation of quartz at the temperature ~573 °C.
- Solid-state sintering at temperatures ~500–1100 °C.
- Collapse of metakaolinite and creation of alumina spinell (metastable phase) and mullite above 1010 °C. This new structure significantly improves mechanical properties, and subsequently, the resonant frequency.
- Melting the traces of feldspar and creation of the glassy phase above 1080 °C. This is not clearly visible in Fig. 1, because of the small amount of the glassy phase. Its presence more affects a thermodilatometric curve [17].
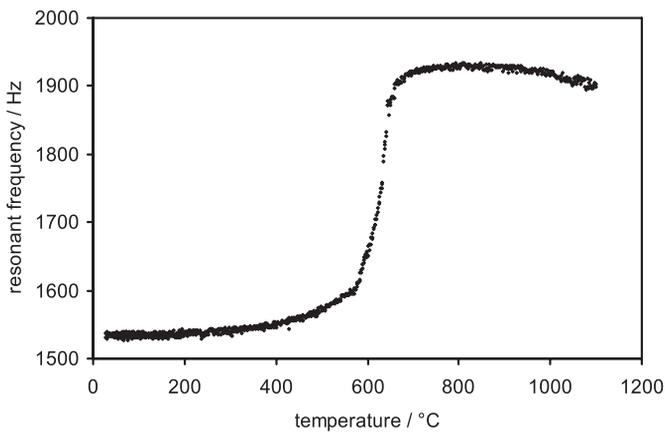
Fig. 2. mf-TMA curve of the fired sample Letovice
2. ábra   A Letovice-i égetett kerámia minta mf-TMA görbéje

Results of the mf-TMA of the fired sample are shown in Fig. 2. Only a few processes run in the sample during its heating:

- Linear thermal expansion and attenuation of the interatomic forces induced by heat which should be accompanied with slow increasing of the resonant frequency. This is not recorded in Fig. 2. A cause of that can be hidden in a competing mechanism which follows from the multiphase structure of the samples. Different thermal expansions of the phases can partially remove microcracks between crystals and, subsequently, improve mechanical properties of the sample.

- $\alpha \rightarrow \beta$ transformation of the unsolved quartz grains at the temperature ~573 °C. If the quartz grains are free and can change their dimensions without obstructions, their relative volume change is +0,68% [18]. But, the quartz grains are not free since they are in a neighbourhood of the glass phase and crystals of the minerals. The quartz grains increase their volume less than 0,68% and generate a compressive stress in their close surroundings. Since many quartz grains have circumferential microcracks around them, the stress has a healing effect, which leads to the rapid increase of the resonant frequency. A similar effect was observed in [9].

4. Conclusion

The results of the mf-TMA analysis based on the non-destructive sonic resonant method confirmed the sensitivity of the method to:

- the processes which take place in the green ceramic material during heating (liberation of the physically bounded water, dehydroxylation, solid phase sintering, high-temperature reactions),

- the presence of the microcracks in the ceramic structure.

The next information was obtained for the green sample:

- liberation of physically bound water significantly improves the mechanical properties of the green sample,

- dehydroxylation, $\alpha \rightarrow \beta$ transformation of quartz and melting the feldspars are reflected in the resonant frequency in lesser measure. That is probably due to the superimposing these processes by the solid-phase sintering.

- collapse of metakaolinite and creation of primary mullite rapidly improves mechanical properties.

For the fired sample were obtained:

- different thermal expansions of the phases can partially remove microcracks between crystals and, subsequently, slightly improve mechanical properties of the sample during heating from 20 to 550 °C.

- $\alpha \rightarrow \beta$ transformation of the unsolved quartz grains induces a radial stress with a healing effect on microcracks which leads to the rapid increase of the resonant frequency.

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