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Sound Velocity of Kaolin in the Temperature Range from 20 °C to 1100 °C

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Abstract The sound velocity of Sedlec kaolin during heating from 20 °C to 1100 °C was investigated by modulated force thermomechanical analysis (mf-TMA). In the interval from 20 °C to 250 °C, the sound velocity increases which can be explained by liberation of the water molecules from pores and micropores. Dehydroxylation (450 °C to 650 °C) presents itself with a decrease of the sound velocity. After dehydroxylation, a two-step increase of the sound velocity was observed. The first step of the increase of the sound velocity is due to solid-state sintering at low temperatures. The second step starts at 950 °C as a consequence of the collapse of the metakaolinite structure. After the maximum, a steep increase of the sound velocity follows as a result of solid-state sintering.

Keywords Kaolin · Modulated force thermomechanical analysis (mf-TMA) · Resonant method · Sound velocity

1 Introduction

Modulated force thermomechanical analysis (mf-TMA) is a technique used for measurements of the sound velocity, elasticity modulus, and coefficient of internal friction. The analysis uses a time-dependent periodic force affecting the sample [1]. Mf- TMA is a suitable method for direct experimental study of mechanical properties of refractory materials as well as for exploring the sintering process [2,3].

The main substance of kaolin is kaolinite. Kaolinite is a major clay mineral. It has a quite stable chemical composition and good physical properties for ceramic

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products. Kaolinite is a plastic refractory material with small shrinkage during drying and a melting temperature of 1750 °C. After firing, it has a white color [4,5].

Kaolin and kaolin clays are the main raw materials for traditional ceramics, bricks, and pottery. Washed kaolin with quartz and feldspar are raw materials for production of porcelain. Kaolin is also used by other industries, e.g., medicine, cosmetics, and the oil industry [4,6–8].

An investigation of the structure and different physical properties of kaolin has been in progress for over 10 years. During this time a lot of information about the structure and properties of kaolin was obtained. Nevertheless, only a few studies deal with dynamical mechanical properties of kaolin. In this paper we show the changes of the sound velocity in kaolin during heating from 20 °C to 1100 °C.

2 Measurement Method and Samples

2.1 Resonant mf-TMA

The most commonly used method for determination of the speed of propagation of longitudinal waves (i.e., the sound velocity) is the resonant technique. The resonant technique is relatively simple and produces very small mechanical stress, not initiating inelastic processes in the 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 most reliable arrangement of the experiment is based on flexural vibrations of the sample. The advantage of flexural vibrations is simple excitation and measurement which is favorable at high temperatures. This method, which was employed in [3,5–8] is described in detail in [9]. The sound velocity c_{L} can be calculated from the formula [9],

$$c_{\mathrm{L}} = K\frac{l^2 f}{d}\sqrt{T} \tag{1}$$

where f is the resonant frequency of the fundamental mode, 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, and $K = 0.97284$ for a prismatic sample with a uniform square cross section. If a sample with the ratio $l/d < 20$ is used, it is necessary to use a correction coefficient T as shown in Eq. 1. For circular and rectangular cross sections, the coefficient T can be calculated from [9]

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

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

Table 1 Parameters A, B, C, D, F for the fundamental mode

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

where μ is Poisson's ratio and the constants A, B, C, D, F are listed in Table 1 [9]. Another way of obtaining the correction coefficient is described in [10].

Mf-TMA was carried out with the apparatus designed by the authors [11]. The apparatus is based on the construction described in [3,9].

2.2 Thermodilatometry

As follows from Eq. 1, the sound velocity at temperature t is

$$c_{\mathrm{L}}(t) = K\frac{l^2(t)\,f(t)}{d(t)}\sqrt{T}, \tag{4}$$

where $l(t), d(t)$, and $f(t)$ are the length, thickness of the sample, and resonant frequency at temperature t, respectively. Determination of the sound velocity requires measuring the true dimensions of the sample during heating. This task can be easily solved by thermodilatometry.

Thermodilatometry is a widely used and well-known method for investigation of kaolin- based ceramics and its constituents, e.g., quartz, kaolin, feldspar, and corrundum. We used a push-rod dilatometer as described in [12]. Having the relative expansion $\Delta l(t)/l_0$ measured by the dilatometer and the initial dimensions l_0, d_0, we can determine the length and thickness of the sample as

$$l(t) = l_0 + \Delta l(t) \quad \text{and} \quad d(t) = d_0 + \Delta d(t). \tag{5}$$

These values can be substituted into Eq. 4.

2.3 Samples

The samples were prepared from kaolin Sedlec, see Table 2.

The samples were molded from the water slurry by casting in a gypsum form. After free drying in open air, the samples contained ∼1 mass% of the physically bonded water. The samples had the dimension $9.5 \times 9.5 \times 140\,\mathrm{mm}^3$ for mf-TMA and $9.5 \times 9.5 \times 40\,\mathrm{mm}^3$ for thermodilatometry.

The green samples were heated in the mf-TMA apparatus or dilatometer in air. The temperature was increased linearly at a rate of $5\,^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$ from 20 °C to 1100 °C.

Table 2 Chemical composition of the kaolin Sedlec (mass%)

LOI	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
12.95	45.80	37.31	0.98	0.17	0.58	0.46	1.17	0.58

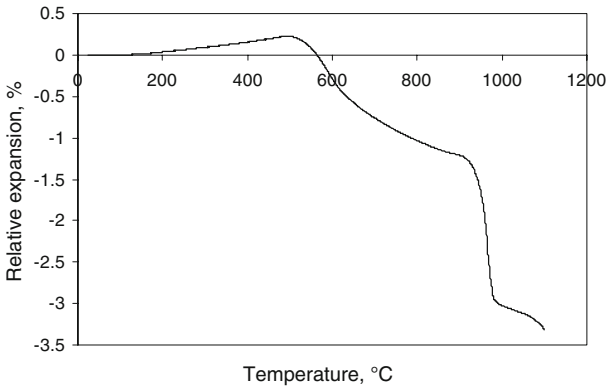

Fig. 1 Relative expansion of the kaolin sample

3 Results and Discussion

During heating, the structure and composition of a kaolin sample are changed. These changes determine the mechanical and dilatometric behavior of the sample. Our results of thermodilatomery for the kaolin sample are shown in Fig. 1. Although the dilatometric results are supplementary from the sound velocity viewpoint, they offer useful information.

The dilatometric curve can be divided into typical parts corresponding to processes in kaolin:

- The liberation of physically bound water at temperatures from 20 °C to 250 °C leads to more tight contacts between kaolinite crystals and, subsequently, to the shrinkage of the sample. On the other side, thermal expansion takes place at the same time which increases the size of the sample. The curve between 20 °C and 250 °C follows from these two mechanisms. After liberation of the physically bound water, only the thermal expansion takes place.
- Dehydroxylation at temperatures from 450 °C to 650 °C is accompanied by the creation of metakaolinite. Its crystals are of the same type as kaolinite crystals, but have a smaller *c*-parameter, so shrinkage of the sample can be observed. The beginning of solid-phase sintering also gives rise to more shrinkage which continues to the end of heating.
- The collapse of metakaolinite and the creation of alumina spinell (metastable phase) and primary mullite take place above 950 °C. This new structure significantly improves the shrinkage.

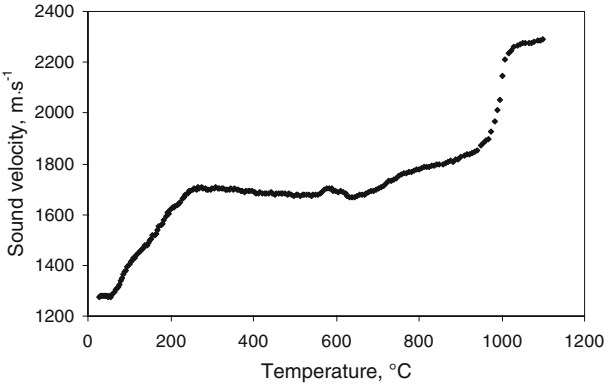

Fig. 2 Mf- TMA curve of the kaolin sample

From the dilatometric results, we can determine $\Delta l(t)$ and $\Delta d(t)$. Substituting them into Eq. 5, the measured resonant frequency $f(t)$ and the actual values of $l(t)$ and $d(t)$ determine the sound velocity using Eq. 4. The results are depicted in Fig. 2.

Similarly, the curve of mf-TMA (see Fig. 2) can be also divided into the same typical parts:

- The liberation of physically bound water from pores and micropores and crystal surfaces at temperatures between 20 °C and 250 °C leads to more tight contacts between kaolinite crystals, and subsequently, to better conditions for mechanical energy transport, which is reflected in a higher sound velocity.
- A moderate decrease of the sound velocity between 250 °C and 500 °C is due to kaolinite in which no processes appear—liberation of physically bound water is completed and dehydroxylation has not yet begun.
- Dehydroxylation occurs at temperatures from 450 °C to 650 °C. The creation of a high-defect metakaolinite lowers the sound velocity. This effect is partially superimposed by the solid-phase sintering.
- Solid-state sintering occurs at temperatures from 500 °C to 1100 °C.
- The collapse of metakaolinite and the creation of alumina spinell (metastable phase) and primary mullite take place above 950 °C. This new structure significantly improves mechanical properties and, subsequently, the sound velocity. This process mixes with solid-state sintering which is impossible to separate by the mf-TMA.

4 Conclusion

Mf-TMA based on the measurement of the resonant frequency follows the processes in the kaolin sample during heating. Both curves, mf-TMA and TDA, can be divided into typical parts corresponding to processes in the kaolin sample during its heating to 1100 °C:

– the liberation of physically bound water at temperatures from 20 °C to 250 °C which increases the sound velocity,

– dehydroxylation at temperatures higher than 450 °C, which decreases the sound velocity, and
– the collapse of a metakaolinite lattice at ∼ 950 °C and the creation of spinel and mullite which increases the sound velocity.

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