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SURFACE DIFFUSION AT SUBCRITICAL TEMPERATURES: SELECTED RIGOROUS RESULTS

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Abstract. A statistical mechanical approach to study surface diffusion by lattice-gas models is presented. General formulas for the coverage dependences of chemical and jump diffusion coefficients are discussed at low temperatures and in the local equilibrium limit. An application to a specific two-dimensional model is considered.
Keywords: Coverage dependence, low temperatures, phase transition, surface diffusion coefficient

УДК: 534-16:549.6

СКОРОСТЬ ЗВУКА И МОДУЛЬ УПРУГОСТИ ЮНГА СМЕСЕЙ ИЛЛИТА И ЛЕТУЧЕЙ ЗОЛЫ

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Аннотация. Образцы из иллита с различным содержанием летучей золы были исследованы при комнатной температуре после обжигов при температурах в интервале 20°C - 1100°C. Измерение скорости звука (СЗ) и модуля упругости (МУ) осуществлялись методом импульсного возбуждения свободных поперечных колебаний. Для определения СЗ и МУ необходимо знать плотность и размеры образца и резонансную частоту. Потеря массы возрастает с ростом температуры обжига и достигает 8% в зависимости от содержания летучей золы. Изменения объёма образцов до 500°C были незначительными и увеличились до 5 % при температурах обжига свыше 900°C. Значительный рост СЗ и МУ наблюдались свыше 900°C, что связано со спеканием.
Ключевые слова: скорость звука, модуль упругости, керамика, иллит, летучая зола

SOUND VELOCITY AND YOUNG MODULUS OF ILLITE – FLY-ASH MIXTURES

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Abstract: Illite samples with different content of fly-ash were investigated at room temperature after firing at temperatures from an interval of 25 – 1100 °C. The measurement of sound velocity (SV) and Young modulus (YM) were performed by the impulse excitation method based on the free flexural vibration. To determine SV and YM is necessarily to know the bulk density and dimensions of the sample as well as resonance frequency. It was found out that mass loss increases with the firing temperature and reaches up to 8 % depending on the fly-ash content. The volume changes of the samples were negligible up to 500 °C. The significant changes of the volume up to 5 % were observed for temperatures higher than 900 °C. Significant changes of SV and YM were observed for temperatures over 900 °C, which is connected with sintering of the sample.
Keywords: sound velocity, Young modulus, ceramics, illite, fly-ash

1. Indroduction

Illite is one of clays used for the production of traditional ceramics. Illite structure is considered by the repetition of tetrahedron – octahedron – tetrahedron (TOT) layers [1].Two outer layers are constituent of tetrahedron SiO_4 and the inner layer is constituent of hydroxyl groups. The interlayer space is mainly occupied by poorly hydrated potassium cations responsible for van der Waals binding. Structurally, illite is quite similar to muscovite with slightly more silicon, magnesium, and iron.

Power plant fly-ash is a by-product of lignite or the subbituminous coal combustion process. Its release into the atmosphere would have an adverse impact on the environment, so it must be separated from the flue gas by electrostatic or mechanical separating. It has been classified as a hazardous waste so the long-term storage is a significant environmental burden due to the increase of heavy metals (Hg, Pb, Cd, Zn) [2]. A million tons of fly-ash is produced annually all around the world. Fly-ash, featuring a high content of SiO_2, Al_2O_3 and CaO[3], can replace part clay as one kind of the raw material of ceramics. There are some works which studied adding the fly-ash into bricks and tiles [4 – 9].

Adding fly-ash to building ceramics indicates some changes of the material properties. In this work we study the influence of fly-ash on the sound velocity (SV) and Young modulus (YM) of ceramic mixtures. For technical practice is necessary to know the material parameters as YM and SV. The elastic constant can tell, how a material will respond to pressure, strain, torsion or bend. In fact the YM and SV are temperature dependent; therefore they are not true constants. The changes in elastic constants also reflect the phase changes [10, 11] induced by heat. Furthermore, elastic constants are very closely dependent on microstructure of the material, so through their measure we can find useful information about material structure [12 – 16].

One of many methods is the impulse excitation method based on free flexural vibrations of the sample after a mechanical pulse [17, 18]. The free vibrations are registered by the sensor, stored and then analyzed using the fast Fourier transformation (FFT). The result of FFT is a frequency spectrum where the frequency of the fundamental mode of the free vibrations can be identified. The mechanical pulse can be realized by the steel or ceramic projectiles which fall down on the sample, or by an electromagnetic pulse tool. This method exploits the formula derived from frequency equations that are derived from a partial differential equation that describes the vibrating motion of the sample. The measurement quantities, which are necessary for calculation of YM, are dimensions and mass of the sample and the resonant frequency [17, 19 – 22].

Most measurements of Young's modulus at elevated temperatures exploit the flexural vibration because of its simple excitation, large amplitude of deflection, and reliability. A goal of the paper is to study the influence of power plant fly-ash on sound velocity and Young modulus in illite – fly-ash mixtures samples.

2 Experimental

2.1 Samples

In this work we used illite clay from the Tokaj region of Hungary. The first step to prepare the samples was to grind and mill the illite agglomerates in a laboratory mill. The milling process guarantees the homogenization of the illite powder. For sample preparation illite powder with particles lower than 100 μm were used.

Table1. Chemical composition of the fly-ash Nováky, Slovakia

Compound	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	other
Mass (%)	35.50	12.20	29.20	6.10	2.90	0.69	1.20	12.21

The other compound of the samples was fly-ash from a power plant in Nováky, Slovakia. The fly-ash is by-product of lignite combustion. Usually it is formed as fine powder with spherical particles. The major compounds are SiO_2 and Al_2O_3see Table 1.

The samples were prepared from illite, grog and fly-ash. Before adding fly-ash into the mixture it needed to be hydrated to change free CaO to $CaCO_3$. After the hydration process the fly-ash was dried. For sample production powder with particles lower than 200 μm were used.

The last compound of the final mixture was illite fired at 1100 °C. After this modification we obtained an opening material that is not affected by water and increased the rate of drying and reduced shrinkage of the samples. For sample production was used sieved opening material to separate particles lower than 100 μm. The mineral composition of all compounds illite, fired illite and fly-ash is presented in Table 2.

Table2. Mineral composition of materials for sample preparation (%)

Minerál	Material		
	Illite	Fired illite	Fly-ash
Illite	52.9	-	-
Quartz	17.5	42.5	37.4
Muscovite	23.5	-	5.7
Potasium-Feldspar	5.8	-	5.7
Calcite	-	-	4.2
Anhydrite	-	-	17.5
Plagioclase	-	-	11.1
Portlandite	-	-	9.5
Hematite	-	4.2	7.9
Periclase	-	1.1	1.1
Spinel	-	18.9	-
Mullite	-	18.0	-
Sanidine	-	10.5	-
Diopside	-	2.6	-

We prepared 4 kinds of illite – fly-ash mixtures with different content of fly-ash. The initial compound of samples and the samples names are presented in Table 3. The cylindrical samples were made by a laboratory extruder and their dimensions were ∅12×150 mm. After the samples were dried, they were subjected to testing. Young modulus were measured at room temperature. The tested samples were preheated at temperatures from 100 – 1100 °C with 100 °C intervals.

Table3 Sample composition (wt. %)

	Sample name			
	Illite	H1	HU10	HU20
Illite	100	60	60	60
Fly-ash	0	0	10	20
Firedillite (grog)	0	40	30	20

2.2. Methods

The resonant frequency was measured by the impulse excitation technique (IET) [17, 18]. This method is based on natural flexural vibrations of a sample with free ends after a mechanical pulse. Free vibrations are registered by sensor. The results were analyzed using the fast Fourier transformation (FFT).

Young's modulus was calculated for a cylindrical sample by formula [20]

$$E = 1.6067 \frac{L^3 f^2 m}{d^4} T \quad , \tag{1}$$

where L is sample length, f is a resonant frequency of the fundamental mode of the flexural vibration, m is sample mass, d is the diameter of the sample and T is a correction coefficient for $L/d > 20$ (2) calculated by a formula

$$T = 1 + 4.939(1 + 0.0752\mu + 0.8109\mu^2)\left(\frac{d}{L}\right)^2 - 0.4883\left(\frac{d}{L}\right)^4 - \\ - \left[\frac{4.691(1 + 0.2023\mu + 2.173\mu^2)\left(\frac{d}{L}\right)^4}{1 + 4.754(1 + 0.1408\mu + 1.536\mu^2)\left(\frac{d}{L}\right)^2}\right] \tag{2}$$

Poisson's ratio $\mu = 0.2$ is typical for ceramics materials [19].
The sound velocity v can be calculated by equation

$$v = \sqrt{\frac{E}{\rho}} \quad , \tag{3}$$

Where E is Young's modulus and ρ is sample volume mass.

2.3 Apparatus for IET measurement

The apparatus for IET measurements basically consist of three parts: a sample support system, a piezoelectric sensor that converts mechanical vibration into electric signal, a signal amplifier and the computer for recording this signal. The frequency decomposition using of FFT was provided in program environment Matlab® R2009a. The diagram of the apparatus is shown on Fig. 1.

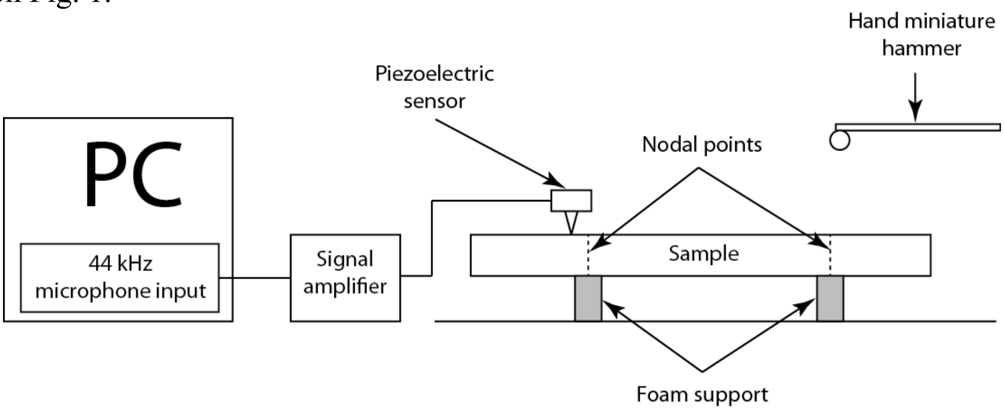

Fig. 1 Block diagram of the used test apparatus.

The sample was supported at its nodal points of the first mode of flexural vibration in distance 0,224·L from both sides of the sample. The piezoelectric sensor was placed near nodal points in order to minimize its effect on natural vibration. Vibration was excited by mechanical impulse and free vibration was recorded.

3 Results and discussion

During firing the samples manifest structural changes that appear as bulk density change (Fig. 2), mass change (Fig. 3) or volume change (Fig. 4). We can observe that grog (fired illite) and fly-ash addition increase the sample porosity which can be registered as a decrease of bulk density (Fig. 2).The lowest values of bulk densities can be observed for samples HU10 and HU20 with 10 wt. % and 20wt. % of fly-ash addition. A small decrease of bulk density (Fig. 2) at interval 25 – 200 °C for all samples is connected with liberation of physically bonded water in samples pores. This process is also connected with mass loss (Fig. 3). On the other hand, volume changes observed in Fig. 4 were neglected. The other significant reaction in illite ceramics that occurs at interval 500 – 700 °C is well known as dehydroxylation. During this reaction illite structure decomposes contributing to an increase in the porosity [23]. The dehydroxylation can be observed as a bulk density decrease (Fig. 2) connecting with mass loss (Fig. 3). In Fig. 4 this reaction is recorded as 1 % increase of volume. At temperatures over 900 °C a high temperature processes like sintering occurs [24]. The rapid increase of bulk density (Fig. 2) and significant changes of volume, up to 5 wt. % (Fig. 4) were observed.

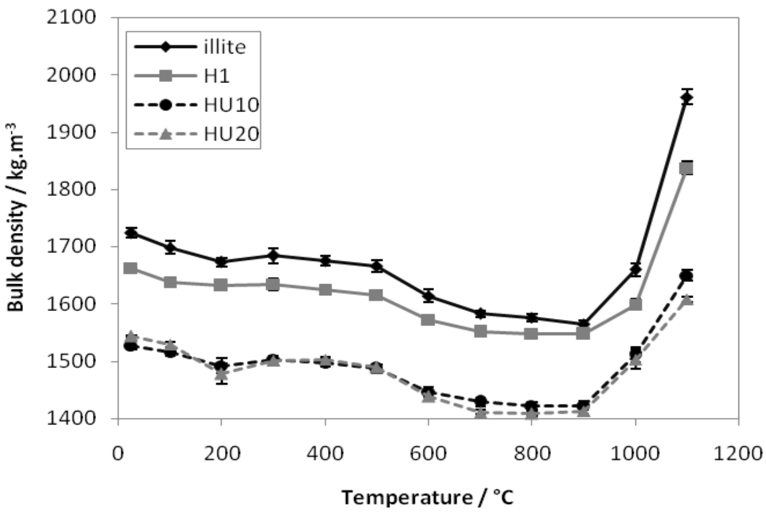

Fig. 2. Bulk densities of samples in dependence on temperature

The influence of fly-ash addition in the illite samples on sound velocity and Young modulus are depicted in Fig. 5 and Fig. 6. In both cases, a small decrease of SV and YM of H1, HU10 and HU20 curves can be observed compared to the illite curve. This is due to higher porosity of samples with grog and fly-ash addition. The liberation of physically bond water is connected with an increase of SV and YM in the temperature interval 25 – 200 °C. The small increase continues up to 400 °C. Dehydroxylation of illite has an influence on decrease of SV and YM. The significant changes of SV and YM can be observed over the temperature 900 °C due to a sample sintering.

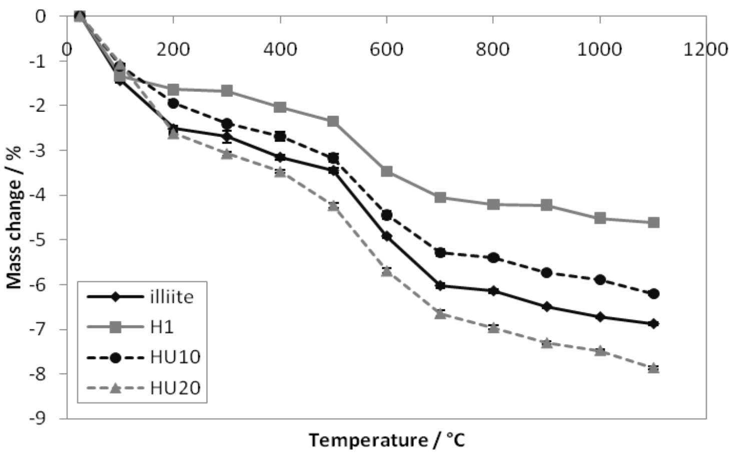

Fig. 3. Mass change of samples in dependence on temperature.

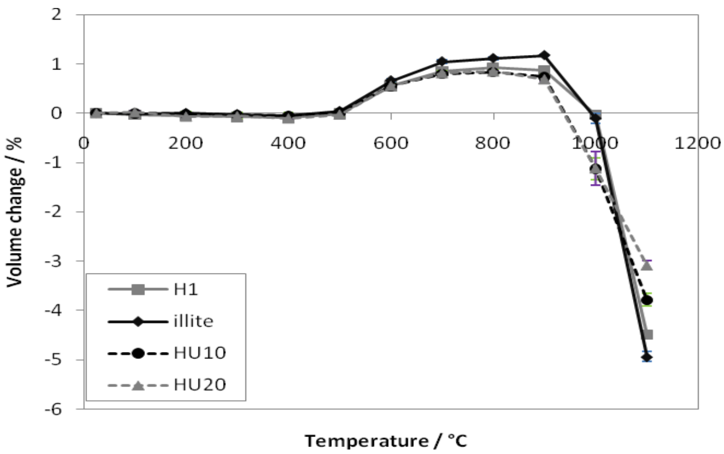

Fig. 4. Volume change of samples in dependence on temperature.

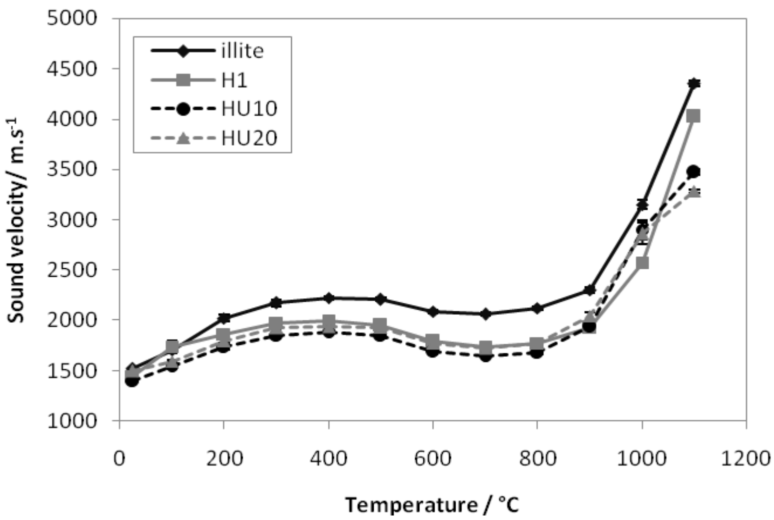

Fig. 5. Sound velocity of samples in dependence on temperature.

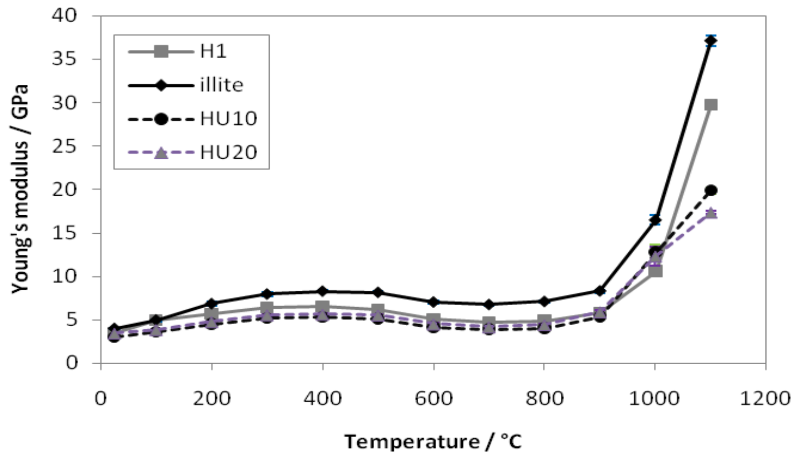

Fig. 6 Young's modulus of samples in dependence on temperature.

4 Conclusions

The impulse excitation technique (IET) was used to measure the sound velocity and Young's modulus at room temperature. Results obtained by the IET reveal two sources of increasing SV and YM. The first one is connected to the liberation of physically bounded water and occurs at the temperature interval 25 – 200 °C. The second source is connected to densification of the sample over the temperature 900 °C. The replacement of grog by fly-ash doesn't have a significant influence on SV and YM up to the temperature 800°C. Over this temperature the SV and YM significantly increase due to sintering. Addition of fly-ash decreases SV and YM of the ceramic samples fired at the temperature above 800 °C.

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SOUND VELOCITY AND YOUNG MODULUS OF ILLITE – FLY-ASH MIXTURES

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Abstract: Illite samples with different content of fly-ash were investigated at room temperature after firing at temperatures from an interval of 25 – 1100 °C. The measurement of sound velocity (SV) and Young modulus (YM) were performed by the impulse excitation method based on the free flexural vibration. To determine SV and YM is necessarily to know the bulk density and dimensions of the sample as well as resonance frequency. It was found out that mass loss increases with the firing temperature and reaches up to 8 % depending on the fly-ash content. The volume changes of the samples were negligible up to 500 °C. The significant changes of the volume up to 5 % were observed for temperatures higher than 900 °C. Significant changes of SV and YM were observed for temperatures over 900 °C, which is connected with sintering of the sample.
Keywords: sound velocity, Young modulus, ceramics, illite, fly-ash