Journal of Applied Mechanics and Technical Physics, Vol. 50, No. 4, pp. 646–650, 2009

EFFECT OF THE POROSITY AND PARTICLE SIZE OF MATERIALS ON SOUND-WAVE VELOCITY

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UDC 536.46

Methods were developed to measure longitudinal and transverse sound velocities in porous materials — various Zn–S mixtures and KBr samples. It is shown that, on exposure to ultrasound with a wavelength far exceeding the pore size in pressed samples, a porous body behaves as a continuous medium. Sound velocity in a porous material was found to depend on the quantitative ratio of vacuum, air, and toluene in the pores. Bulk sound velocities estimated using an additive method agree with experimental data within an error not more than 10%. *It was found that removal of moisture traces from porous samples led to significant absorption of sound waves.*

Key words: *longitudinal, shear and bulk sound velocities, porous body, elastic modulus.*

Introduction. Measurements of sound velocity C in solids provide important information on the physical and mechanical properties of materials, in particular, their elastic moduli (rigidity), characteristic Debye temperatures, shock-wave formation as a result of superfast chemical reactions. At the same time, measurements of C in porous materials is greatly complicated by the need to prepare press pellets (ideally, without pores) or to carry out measurements for samples with different porosity and extrapolation of the obtained data to the density of a monolithic sample. In the case of very hard materials, for example, diamond powders, it is generally impossible to produce press pellets without using binders. In addition, wave perturbations propagate in porous solids by a very complex mechanism; therefore, the measured quantities may be only conditionally called sound velocities.

The lack of sufficient information on the elastic properties of porous solids prevents their use for the solution of new technological problems, for example, for nanocrystalline materials. At the same time, measurements of elastic moduli B_0 of monolithic solids with various crystal grain sizes have shown that the grinding of solids (by physical or chemical methods) influences the elastic properties of porous materials. According to available experimental data, depending on the values of B_0 in conversion from macroparticles (m) to nanoparticles (n), the materials can be divided into three groups: 1) Mo, Ni, W, Fe_2O_3, CeO_2, TiO_2, AlN, and Si_3N_4, where $B_m < B_n$; 2) CuO, MgO, and ε-Fe, where $B_m \approx B_n$; 3) ZnS, PbS, CdSe, W_2N, Al_2O_3, ReO_3, and MgO, where $B_m > B_n$ [1, 2]. At present, there is no satisfactory explanation of this distribution of substances; therefore, it is reasonable to continue the accumulation of experimental data. In doing this, it is convenient to use measured sound velocities since $B_0 = \rho_0 C_0^2$ (ρ_0 is the density of the material and C_0 is the bulk sound velocity). It has been found that the range of the sound velocity change due to conversion from macrocrystalline to nanocrystalline samples varies with the structure and composition of substances. Thus, for tungsten, the conversion $m \to n$ is accompanied by an increase in the value of B_0 from 297 to 318 GPa and an increase in the sound velocity from 3.92 to 4.06 km/sec due to an increase in the density during grinding of the crystal [3]. In AlN, in conversion from macroparticles to nanoparticles of the wurtzite modification, the sound velocity increases from 8.0 to 9.7 km/sec, and in the V1 structural modification, it increases from 8.62 to 8.90 km/sec [4]. For MgO, the sound velocity in the macromaterial is equal to 6.62,

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 0021-8944/09/5004-0646

TABLE 1

Longitudinal Sound Velocity in Porous Zn–S Samples

ρ_{00}/ρ_0	C_L, km/sec	C_{ad}, km/sec	C_L/C_{ad}
0.708	0.975	0.856	1.139
0.755	1.300	0.957	1.358
0.795	1.560	1.064	1.466
0.847	1.790	1.243	1.440
0.860	1.890	1.298	1.456
0.892	2.040	1.456	1.401
0.900	2.185	1.501	1.456
0.911	2.270	1.569	1.447
0.926	2.430	1.672	1.453

and in the nanophase, it is 6.22 km/sec [4]. The factors responsible for these significant changes in transition from macromaterials to nanocrystalline materials are not yet understood. In the present work, we measured wave perturbation velocities in porous solids to study their dependence on the crystal grain size.

Procedure for Measuring Sound Velocity in Porous Samples. Longitudinal sound wave velocities C_L were measured on press pellets with various diameters and porosities using two ultrasonic methods. A Zn–S mixture was first studied. Solid-state detonation in this mixture has been studied previously in shock-wave experiments [5].

In the first classical method, the sound velocity in the samples was determined using two buffer rods 38 mm in diameter and 250 and 60 mm long made of tempered 60S2N2A steel with carefully polished and ground planes of the edges. These rods were used to produce a stationary acoustic wave, which then entered the sample being measured. An ultrasonic pulse source with a pulse-modulating frequency of about 5 MHz (a piezoelectric transducer 28 mm in diameter and 0.5 mm thick) was placed at the lower end of the long rod fixed upright. An identical piezoelectric transducer was placed at the upper end of the second (short) rod and received the ultrasonic pulse transmitted through both buffer rods. The examined sample in the form of a disk 50 mm in diameter and 5 mm thick with ground surfaces was placed between the ends of the rods, resulting in an increase in the transit time of the ultrasonic pulse due to its passage through the examined sample. The pulse was measured using an I1-8 high-precision phase-shift generator (a resolution of 10^{-7} sec).

Using the second method, the propagation velocity of a longitudinal deformation jump ΔC_L was measured directly on press pellets of the examined substance by two piezoelectric sensors pressed through a thin layer of an acoustic liquid to the planes of the sample, which were alternatively sources and receivers of ultrasonic pulses. A short pulse (125 nsec) with an amplitude of 80 V was sent to the source. The measuring procedure allowed repeated passage of an elastic deformation jump through the sample, providing a significant (severalfold) increase in the accuracy of the results. The measured ΔC_L on the metal plates (Cu, Al, and Fe) and single crystals (NaCl and KBr) cut along various crystalllographic directions coincide with literature values of C_L [6]. The values of ΔC_L measured in Zn–S pellets 17 mm in diameter and 4 mm thick of various porosity differ, on the average, by 20 m/sec from the values of C_L obtained by the classical method for samples of three times greater diameter. The longitudinal sound velocities in stoichiometric Zn–S samples pressed to various relative densities ρ_{00}/ρ_0 (ρ_{00} is the density of the porous solid) are given in Table 1.

It is of interest to compare the measured sound velocities with calculation results. The experiments were performed using carefully mixed powders of Zn and S microparticles pressed to various values of porosity. Since, at a frequency of 5 MHz, the acoustic wavelength is several hundreds of micrometers (for velocities of about one kilometer per second), i.e., is more than three orders of magnitude greater than the pore size (which is a few tenth of a micrometer), such a medium with uniformly distributed inclusions, as a first approximation, can be considered homogeneous relative to sound propagation.

Batsanov [7] describes an additive method for calculating sound velocities in porous solids in the form of two plates – a monolithic body and air, whose thicknesses are determined by the volume fractions x and $1 - x$, respectively; the fractions related to unit area are numerically equal to the volumes V of the monolithic body and air in the given sample. From known sound velocities in the monolithic body (C_{m}) and in air ($C_{\text{a}} = 0.3315$ km/sec), it is possible to determine the sound travel time through these plates:

$$\tau = x\,\frac{V_{\text{m}}}{C_{\text{m}}} + (1 - x)\,\frac{V_{\text{a}}}{C_{\text{a}}}.$$

TABLE 2

Relative Diameters of Nodal Circles for Some Harmonics

Number of harmonics	d_i/D
1	0.746
2	0.455, 0.833
3	0.330, 0.604, 0.876
4	0.259, 0.474, 0.688, 0.900
5	0.213, 0.391, 0.566, 0.742, 0.917

In this case, the ratio of $V_\mathrm{m} + V_\mathrm{a}$ to the sound travel time through both plates is equal to the sound velocity in the porous body:

$$C = (V_\mathrm{m} + V_\mathrm{a})/\tau.$$

The bulk sound velocity C_0 in the monolithic mixture can be calculated as follows. The mole volumes of Zn and S are equal to 9.16 and 15.52 cm^3/mole, and the bulk sound velocities are 2.80 and 2.13 km/sec, respectively [7]. Hence, the sound travel times through the Zn and S layers, whose volumes are related to unit area, are equal to $9.16/2.8 = 3.271 \cdot 10^{-5}$ sec and $15.52/2.13 = 7.286 \cdot 10^{-5}$ sec, respectively, and the ratio of the total path length 24.68 cm to the total sound travel time $10.557 \cdot 10^{-5}$ sec is equal to 2.34 km/sec (this value is the additive sound velocity C_ad in the monolithic Zn–S mixture). The sound velocity in the monolithic mixture can also be calculated by a different additive scheme:

$$(C_0^2)_{\mathrm{Zn-S}} = 0.671(C_0^2)_{\mathrm{Zn}} + 0.329(C_0^2)_{\mathrm{S}}.$$

Here the values of 0.671 and 0.329 are the mass fractions of Zn and S, respectively. Then, $C_0 = 2.6$ km/sec. The spread in the values obtained by two methods described above characterizes the degree of closeness of the described approaches. Below, for the monolithic mixture we shall use the average value $(C_0)_{\mathrm{Zn-S}} = 2.47$ km/sec.

To calculate the bulk sound velocity in porous Zn–S mixtures, we divide the ratio ρ_{00}/ρ_0, where $\rho_0 = 3.95$ g/cm^3 (density of the monolithic mixture) by the value of 2.47 km/sec and the quantity $1 - \rho_{00}/\rho_0$ by the sound velocity in air equal to 0.3315 km/sec. The obtained sound travel times through the monolithic Zn–S layer and the air layer should be summed up; the reciprocal of this sum is the additive sound velocity in the porous mixture considered. These values of C_ad are given in Table 1. The table also gives the ratios C_L/C_ad, whose average value is $1.43 \pm 2.40\%$ at a relative density of the mixture higher than 0.755. The average value of C_L/C_ad is close to the value obtained in the well-known engineering method of calculating bulk sound velocity by dividing C_L by a coefficient equal to 1.4. The density value $\rho_{00}/\rho_0 = 0.755$ is close to the sphere packing density ($\rho_{00}/\rho_0 = 0.74$), indicating the establishment of a rigid skeleton of solid particles, which provides shear resistance in the body considered.

In the present work, the transverse velocity C_T in a Zn–S sample at $\rho_{00}/\rho_0 = 0.9$ was measured by a method based on exciting tangential resonant vibrations at a frequency f_i in disk-shaped samples:

$$C_T = \pi D f_i/a_i. \tag{1}$$

Here i is the harmonic number (number of nodal circles), D is the diameter of the disk, a_i are the roots of the equation $J_2(a) = 0$, and J_2 is a second-order Bessel function of the first kind. For the first five harmonics, we have $a_1 = 5.13562$, $a_2 = 8.41724$, $a_3 = 11.61984$, $a_4 = 14.79595$, and $a_5 = 17.95982$.

In the experiment, two probes in the form of pointed metal rods 200 mm long were used. Piezoelectric transducers made of TsTS-19 material (diameter 25 mm and thickness 16 mm) were placed at the flat ends of the probes to induce and receive tangential resonant vibration of a disk made of a Zn–S pressed powder mixture and fixed at the nodal points. The pointed ends of the probes were at a small angle to the plane of the disk. The probes edge were placed on the nodal circles to eliminate the influence of the probes on the resonant frequency of the disk. The ratios of the diameters d nodal circles to the diameter of the sample D for the first five harmonics are given in Table 2.

The transverse sound velocity is calculated by formula (1) using measured resonant frequency. The measured resonant frequencies for five harmonics are given in Table 3, from which it follows that the value of C_T averaged over five measurements is equal to 1.233 km/sec $\pm$ 0.2%. Substituting this value into the well-known formula

$$C_0 = \sqrt{C_L^2 - 4C_T^2/3},$$

TABLE 3

Shear Wave Velocities in Zn–S Samples at $\rho_{00}/\rho_0 = 0.9$

i	f, kHz	a_i	f_i/a_i, kHz	C_T, m/sec
1	39,641	5.13562	7718.33	1230.7
2	65,400	8.41724	7769.77	1238.8
3	89,841	11.61984	7731.69	1232.7
4	114,312	14.79595	7725.90	1231.8
5	138,956	17.95982	7737.05	1233.6

TABLE 4

Mechanical Properties of Various KBr Samples

KBr Sample	τ, h	ρ, g/cm^3	C_L, km/sec
Chemical reagent	0	2.73	2.67
	1	2.68	2.93
	2	2.70	2.96
	4	2.70	2.98
Single crystal	0	2.72	2.88
	1/2	2.65	2.97
	1	2.71	2.95
	2	2.67	2.92
	4	2.68	2.95
	Impact compression	2.72	3.03
Precipitate	0	2.71	2.97
	1	2.72	2.98
	2	2.71	3.03

where $C_L = 2.185$ km/sec (see Table 1), we obtain $C_0 = 1.657$ km/sec, which is 156 m/sec larger than the values of the additive velocity $C_{\text{ad}} = 1.501$ km/sec; in this case, $C_L/C_0 = 1.32$. Thus, the bulk sound velocities calculated by the additive method agree with the experimental data with an accuracy of 10%, which allows this method to be used to perform estimates.

Sound Velocity in KBr Samples with Various Densities and Particle Sizes. The propagation velocity of a longitudinal deformation jump was measured in KBr samples pressed from various powders: a chemical reagent of the pure for analysis grade, a ground single crystal, and a precipitate produced by addition of alcohol to a concentrated water solution. All these powders were milled in a ball mill, in which the containers with the samples fixed on a disk was rotated at a speed of 240 rpm in one direction and the disk was rotated at the same velocity in the opposite direction. In the container (depth 40 mm and internal diameter 55 mm) there were a KBr sample weighing 5 g and six balls of VK-6 alloy (diameter 11.2 mm and weight 10.75 g). The grinding time was varied from 0 to 4 h. In the first series of experiments, C_L was measured on pellets 17 mm in diameter and 4 mm thick produced at the same press force (20 tons). After removal of the samples from the press mould, we measured their dimensions in order to determine their density after weighing. Sound velocity was measured using the second method described above. The average values obtained in three experiments for each sample and the density and time of mechanical treatment are listed in Table 4. In addition, Table 4 gives the measured longitudinal sound velocity in the ground KBr single crystal sample subjected to impact compression by a plane scheme at a pressure of 9 kbar.

From Table 4, it follows that grinding of the grains leads to an increase in the sound velocity (rigidity) of the material, which is the larger the smaller the value of C_L for the initial sample. After grinding, the density of the pressed sample (at a constant press force) is usually slightly decreased due to the increased rigidity of the material.

The experiments revealed the following feature of the acoustic behavior of the samples made of the KBr chemical reagent: after drying at a temperature of 130°C for 3 h or storage in an evacuated desiccator for 12 h, a pellet with a 2% porosity did not transmit sound in the device used in the experiments. After the sample was removed from the desiccator and kept in air for several hours, it again began to transmit sound waves. This effect can be explained by the occurrence of acoustic contacts due to the inclusion of water molecules between the KBr particles and the pores of the surface layers. The removal of the acoustic liquid from the pore boundaries enhances sound-wave scattering and interferes with signal transmission.

TABLE 5

Mechanical Characteristics of Porous KBr Samples

ρ_{00}/ρ_0	C_L, km/sec	C_{ad}, km/sec	C_L/C_{ad}
0.81	2.00	1.10	1.82
083	2.03	1.16	1.75
0.88	2.43	1.37	1.77
0.96	2.97	1.92	1.55
1.00	3.55	2.40	1.48

To solve the key question of whether elastic perturbations propagate through the skeleton of solid particles or through the entire material as a continuous solid (relative to the sound wave), we measured sound velocity in porous samples with various pore contents. Thus, for the sample produced by pressing the KBr chemical reagent in air at $\rho = 2.67$ g/cm^3, $C_L = 2.67$ km/sec, and for the sample pressed to the same density under vacuum, $C_L = 1.98$ km/sec; after one week of storage of the sample in a closed polyethylene package, the sound velocity in it increased to 2.35 km/sec. This effect was checked on samples of different densities. In each experiment with pellets pressed under vacuum, the sound velocity was lower than that in samples of the same density pressed without removal of air. It is obvious that if a sound perturbation propagates only in the system of adjoining solid particles, the value of C_L should not vary. In another experiment for a powder sample prepared from a ground single crystal and pressed to a density of 2.23 g/cm^3, $C_L = 1.999$ km/sec, with sequential impregnation of the pellet surface with toluene drops which were absorbed by the sample, the value of C_L varied as follows: 1.999 km/sec $\rightarrow$ 2.072 km/sec $\rightarrow$ 2.110 km/sec $\rightarrow$ 2.132 km/sec, which was caused by replacement of the air from the pore by toluene, in which the sound velocity is 1.328 km/sec.

Table 5 gives the mechanical characteristics of porous KBr samples and bulk sound velocities calculated by the additive method for a value of 3.55 km/sec for C_L in the single crystal [6] and for a value $C_0 = 2.40$ km/sec obtained for $\rho_0 = 2.75$ g/cm^3 and $B_0 = 15.8$ GPa [1]. From Table 5 it follows that the ratio C_L/C_{ad} varies over a wider range ($1.67 \pm 8\%$), than that for the Zn–S mixture. This is due to the ability of porous pellets to absorb the acoustic liquid used in measurements by the second method in low-density samples, resulting in an increase in the value of C_L. Nevertheless, the regular variation in the measured and calculated sound velocities is observed in the case, too.

Conclusions. The experiments show that a porous solid consisting of particles with sizes much smaller than the sound wavelength behaves as a continuous solid (gray) body with some intermediate sound velocity and the corresponding elastic modulus.

REFERENCES

1. S. S. Batsanov, *Experimental Foundations of Structural Chemistry*, Moscow Univ. Press, Moscow (2008).
2. O. Yeheskel, R. Chaim, Z. Shen, and M. Nygren, "Elastic moduli of grain boundaries in nanocrystalline MgO ceramics," *J. Mater. Res.*, **20**, No. 3, 719–725 (2005).
3. Y. Ma, Q. Cui, L. Cui, and Zh. He, "X-ray diffraction study of nanocrystalline tungsten nitride and tungsten to 31 GPa," *J. Appl. Phys.*, **102**, No. 1, 013525 (2007).
4. L. H. Shen, X. F. Li, Y. M. Li, et al., "Pressure-induced structural transition in AlN nanowires," *Appl. Phys. Lett.*, **89**, No. 14, 141903 (2006).
5. D. L. Guriev, Yu. A. Gordopolov, S. S. Batsanov, et al., "Solid-state detonation in the zinc–sulfur system," *Appl. Phys. Lett.*, **88**, No. 2, 024102 (2006).
6. M. P. Shaskol'skaya, *Acoustic Crystals* [in Russian], Nauka, Moscow (1982).
7. S. S. Batsanov, "Additive method for calculating sound velocity in porous materials," *Neorg. Mater.*, **43**, No. 10, 1195–1197 (2007).