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O.V. Balaban, B.A. Lukiyanets

Mechanical Effect of Ultrasound in Microscopic Object with Nanoscale Pores

Lviv Polytechnic National University, Kotlyarevsky Str. 1, Lviv, 79013, Ukraine, e-mail: lukbog@ua.fm

Theoretical study of ultrasonic treatment of a microscopic object with nanoscale pores is presented. It is shown that additional pressure created by ultrasonic waves inside the pore is much higher than such pressure on the object. Hence area of the pore is the least mechanically resistant under ultrasonic treatment of the object.

Keywords: ultrasound, nanopore.

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Introduction

It is known that ultrasound is widely used in various fields of human activity, such as medicine, metallurgy, in various technological processes, everyday life [1, 2]. Among such a variety of the materials ultrasonic treatment the achievement of the desired physical characteristics is especially important. In particular, the effects of the conduction electrons interaction with ultrasonic waves became the basis of a new field of functional microelectronics - acoustoelectronics [3]. The physical nature of ultrasound is the subject of intensive experimental and theoretical research. As an example, let us consider some typical solution of the problem. In one of the early works devoted to the interaction of ultrasound waves with the crystal [4], an explanation of the attenuation of ultrasonic waves in a metal was based on the assumption of direct interaction of the waves with conduction electrons. In paper [5] there was studied the kinetics of photoconductivity in silicon before and after ultrasonic treatment. In opinion of authors, the treatment stimulates migration of atoms of alkaline metals to the near-surface region of crystal which causes change of photoconductivity. However, this assumption does not answer how important are non-diffusion changes of defective material due to the formation of complexes of Si in which the lighter atoms (like C, B, O) are present or, and vice versa, them destruction, caused by ultrasound. The obtained electronic states in single crystals ZnS, ZnSe under the influence of both compression and ultrasound authors [6] consider as a result of generation new dislocations and point defects. It should be noted that the dislocation model is widespread. Recently, ultrasound has become widely used as a creation method of nanostructures - objects with geometric size at least in a single spatial direction $\sim 10 \div 100$ nm [7]. In this case the ultrasonic deformation factor is questionable since the nanoobjects are resistant to deformation. It is demonstrated in experiments with nanowires. The surface of nanowires has very small radius of curvature (~ 10 nm), and so the nanowire is strongly compressed. It prevents the movement of dislocations outside and thus prevents formation of microcracks. Extraordinary mechanical resistance (practically absence of plasticity) was observed during studies of correlation between mechanical stress and relative deformation of the different diameters micro samples of Ni and it`s alloys Ni3Al-Ta [8].

Today ultrasound is applied to the purposeful synthesis of nanoscale materials. This method is the essence of the new field of chemistry – sonochemistry [9]. Under the influence of sound waves in liquids there are possible nonlinear effects and especially cavitation. While in sonochemical reactions the cavitation is crucial, it is unlikely that it is so important in solids [9].

This work is devoted to the ultrasonic influence on another type objects specifically on a microscopic object with nanoscale pores. There is some analogy between the nanowire and nanopore namely their geometry. However, the fundamental difference between them is that the nanowire as an object practically does not feel the environment, whereas nanopore is created by it. Therefore using of the above approaches and conclusions in given case requires some caution.

Extraordinary interest in the objects with nanopores is associated with the fact that they are suitable as materials for the creation of the environmentally friendly high-capacity energy storage of new generation. Porous materials have high specific surface area and it is important characteristic for such energy storage.

Electrical capacity investigation of the porous materials before and after their ultrasonic treatment [10] shows different quantitative results. It is logical to assume that this is the result of some irreversible processes that occurred in the objects under the ultrasonic treatment. Below one of the possible treatment mechanisms of nanopore materials is analysed.

I. Model

Consider the ensemble of microscopic particles with nanoscale pores. The real microscopic particle is not supposed to have the correct form and has a great number of chaotically located pores. The parts of them come out on the surface (semi-closed pores), the others pierce the microobject, yet others are closed in the microobject (Fig. 1,a).

For theoretical studies of ultrasound we choose a model in the form of absolutely rigid sphere of radius R with a semi-closed pore which ends with a hemisphere of radius r_0 in the center of the body ($r_0 << R$) which is perpendicular to the front of a plane ultrasonic wave (Fig. 1,b). Other pores are less effective under the influence of ultrasound. The approximation of ”absolute rigidity” is often used in analogical problems with short impulses. It takes place in the case of ultrasound [11].

Before analyze the ultrasonic influence on a model porous material (Fig. 1,b), let`s consider similar influence on an absolutely rigid sphere [12], placed in a homogeneous acoustic medium. Let’s assume that the plane acoustic wave falls on the sphere in liquid medium and the initial pressure of the wave is p_0. It creates an additional pressure p_i, which in spherical coordinate system takes form:

$$p_i = p_{0i} e^{i(kr\cos\theta + wt)}, \quad (1)$$

here r, θ are coordinates of a point, p_{0i} is a pressure amplitude of the wave (here and later it is equal 1), t is time, ω is a cyclic frequency.

In a homogeneous medium the falling impulse may be considered as a perturbation at absence of the reflector [12]. Overal perturbation is the sum of pressure p_i and the additional pressure p_s, caused by the reflection from an obstacle, namely:

$$p_1 = p_i + p_s \quad (2)$$

This perturbation is described by Helmholtz equation [12], which in spherical system of coordinates has the form:

$$\frac{\partial^2 p_1}{\partial r^2} + \frac{2\partial p_1}{r\partial r} + \frac{1}{r^2 \sin^2\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial p_1}{\partial\theta}) + k_1 p_1 = 0 \quad (3)$$

The function p_S should also satisfy the condition of Sommerfeeld's radiation, which in space coordinates is written as:

$$\lim_{r\to\infty} r\,(\frac{\partial p_s}{\partial r} + ik_1 p_s) = 0, \quad \lim_{r\to\infty}(p_s) = 0 \quad (4)$$

Let us introduce such dimensional variables $r^* = \frac{r}{b}$,

$p^* = \frac{p}{r_1^2 c_1^2}$, $c^* = \frac{c}{c_1}$, $k_1^* = k_1 b = \frac{w}{c_1} b$, where b is a radius of the sphere, r_1 and c_1 are density and speed of acoustic wave in the external homogeneous medium. (Below the index * will be omitted).

The following condition must be realized on the sphere surface:

$$\left.\frac{\partial p_1}{\partial r}\right|_{r=1} = \left.\frac{\partial p_i}{\partial r}\right|_{r=1} + \left.\frac{\partial p_s}{\partial r}\right|_{r=1} = 0 \quad (5)$$

Representation of the pressure as the product $p_1 = R(r)\Upsilon(\theta)$ leads to a system of two equations:

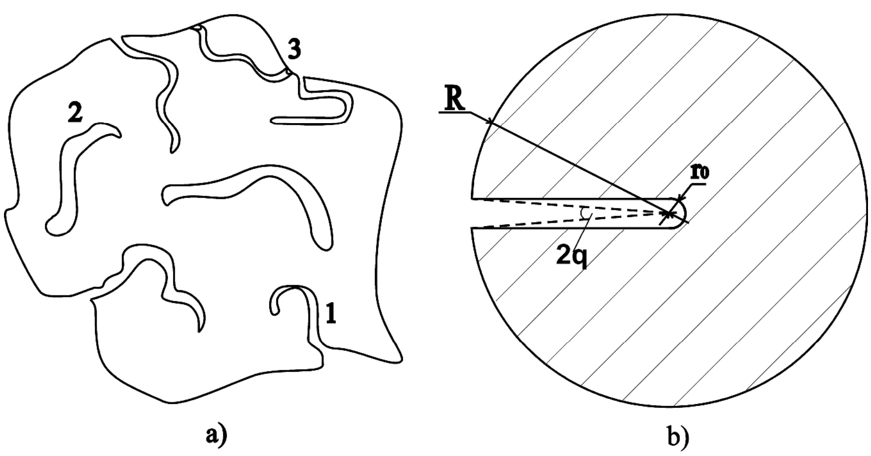

Fig. 1. The porous body (*a*) with semiclosed (*1*), internal (*2*) and open nanopores (*3*); model of the porous body (*b*) ($q = q_0$).

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + (k_1^2 - \frac{m(m+1)}{r^2})R = 0 \quad (6)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d\Upsilon}{d\theta}) + m(m+1)\Upsilon = 0 \quad (7)$$

Solution of the last equation $\Upsilon_m(\theta)$ is expressed trough the Legendre polynomial of the 1-st kind $P_m(\cos\theta)$ [13].

Let`s consider the equation (6). Introduced function $F(r)$, that connected with $R(r)$ by ratio $R(r) = \frac{F(r)}{\sqrt{r}}$. Function $F(r)$ satisfies the Bessel differential equation of the order (m+1/2) [13]. The final solution gives:

$$R_m(r) = \mu_m h_m^{(2)}(k_1 r) \quad (8)$$

Here $h_m^{(2)}(k_1 r) = \sqrt{\frac{p}{2k_1 r}} H^{(2)}_{m+\frac{1}{2}}(k_1 r)$, $H^{(2)}_{m+\frac{1}{2}}(z)$ is a spherical Hankel function [13].

Multiplier μm is determined from the boundary condition (5) for functions p_i and p_s, which are presented as a series of spherical functions, namely:

$$p_i = \sum_{m=0}^{\infty} (2m+1) i^m J_m(k_1 r) P_m(\cos q) \quad (9)$$

$$p_s = \sum_{m=0}^{\infty} \mu_m h_m^{(2)}(k_1 r) P_m(\cos q) \quad (10)$$

Then pressure for fixed values m and angle θ [13] is:

$$p_1(m,\theta) = \frac{(2m+1)i^m}{k_1^2 h_m^{(2)\prime}(k_1)} P_m(\cos\theta) \quad (11)$$

and overall pressure on the sphere will be described by the equation:

$$p_1 = \int_0^p d\theta \sum_{m=0}^{\infty} \frac{(2m+1)i^m}{k_1^2 h_m^{(2)}(k_1 r)} P_m(\cos\theta) \quad (12)$$

Let`s apply this expression to calculate the pressure p1 in the case of model microparticle with nanopore (Fig. 1,b). Its structure can be regarded as an external sphere of radius b = R with a pore which ends with a hemisphere of radius b = r_0. The pore is normal to the plane ultrasound wave front. Since the curvatures of these areas are opposite in a sign, one can predict opposite signs $p_1(R)$ and $p_1(r_0)$.

When calculating the pressure on the outer surface $p_1(R)$ we should omit the part of the surface that is the entrance into the pore. It is achieved by integrating $q \in \left[q_0, \frac{p}{2}\right]$, where $q_0 \approx \arcsin\frac{r_0}{R}$ (R >> r_0). When calculating $p_1(r_0)$ the limits of integration are $q \in \left[\frac{p}{2}, p\right]$. We used the following parameters: frequency of ultrasonic wave was 22 kHz, its velocity in external medium was $c_1 = 1500$ m / s .

Numerical calculations of pressure p_1 using the program Maple for different values of radius show:

a) When choosing region of summation m = [0 .. 10] and m = [0 .. 100] with accuracy up to 10-6 the results of summation are coincide. In other words, the main contribution to the value p_1 is determine a few terms starting with m = 0;

b) Obtained values p_1 are complex numbers. Appearance of Im p_1 should be seen as a result of machine calculation. Below one analyze Re p_1, or more exactly the ration of real parts $p_1(R)$ and $p_1(r_0)$, $\left|\frac{p_1(R)}{p_1(r_0)}\right|$, for different values R and r_0;

c) $p_1(r_0) > 0$ at any parameters.

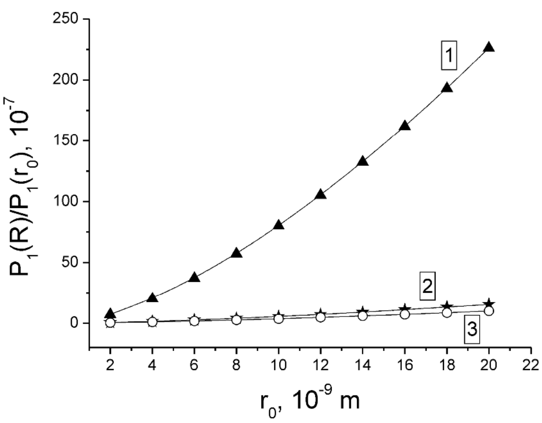

Fig. 2. Dependence of $\left|\frac{p_1(R)}{p_1(r_0)}\right|$ on r_0 at fixed *R* *(mm)*: *R = 100 (1); R = 150 (2); R = 200 (3).*

II. Discussion

Ratio $\left|\frac{p_1(R)}{p_1(r_0)}\right| = f(r_0)$ presented in Fig. 2 shows that for the larger microparticles the ratio practically is independent of the nanopore radius (curves 2, 3), but it increases in several times for the twice reduced radius of the microparticle (curve 1). However, for any radius of the microparticle there is $\left|p_1(R)\right| << \left|p_1(r_0)\right|$. Thus, the perturbing pressure of the ultrasonic wave is mainly determined by tension in the pore.

Pore is a micro nonhomogeneity with internal tension balanced in the volume much smaller than the body volume [14]. Ultrasound can violate this balance. Depending on the real location of the pores, their interaction it can lead to the formation macrotention commensurate with the strength of the material [11]. The possible irreversible phenomena in this case may cause change of the electrical capacitance after ultrasound treatment of porous structures observed in the cited above paper [10].

Balaban O.V. **-** Postgraduate student; Department of Applied Physics and Nanomaterial Science;
Lukiyanets B.A. **-** Doctor of Physical and Mathematical Science, Professor, Department of Applied Physics and Nanomaterial Science. .

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О.В. Балабан, Б.А. Лукіянець

Механічний вплив ультразвуку на мікроскопічний об’єкт з нанорозмірними порами

Національний університет "Львівська політехніка", вул. Котляревського, 1, м. Львів, 79013,e-mail: *lukbog@ua.fm*

Представлено результати теоретичних розрахунків механічного впливу ультразвукової обробки на мікрооб'єкт з нанорозмірними порами. Показано, що додатковий тиск, створений ультразвуковими хвилями всередині пори, значно вищий, ніж такий же тиск на весь об'єкт. Досліджено, що область пори в об'єкті є найменш механічно стійкою до дії ультразвукової обробки.

Ключові слова: ультразвук, нанопора.