Optica Applicata, Vol. XXXIV, No. 1, 2004

Photoacoustic determination of the thermal diffusivity for thin metallic samples

KONRAD ŁUKASZEWSKI, KRZYSZTOF PIESZYŃSKI

Institute of Physics, Technical University of Łódź, Wólczańska 219, 93-005 Łódź, Poland

The ratio of the signals produced in the photoacoustic cell for the front and back illumination of the metallic sample is analyzed. Both the theory and the experiment conducted prove that the slope of the frequency dependence of this ratio gives the measure of the sample's thermal diffusivity.

Keywords: photoacoustic, photothermal, laser.

1. Introduction

Thermal properties of materials used in various branches of engineering must be precisely determined very frequently. This can be the essential condition of the proper choice of material and subsequently of the reliability and durability of final products. One of the basic thermal parameters is the thermal diffusivity α which is expressed by the thermal conductivity k, the density ρ and the specific heat c. The classical method for evaluating α is based on the separate measurements of the specific heat and conductivity. The latter parameter can be found, for instance, through the matching of the temperature measured experimentally at several points of a steadily heated sample with the solutions of the differential equation of heat conduction for a steady state with internal heat generation (Poisson's equation). One of the modern methods of examinating thermal diffusivity, which measures it directly, is the so-called laser flash method (LFM). In LFM method the temperature history of the back side of a sample is recorded after the illumination of the front side with the pulse of neodymium laser of sufficiently short duration and big power [1]. The rate of the temperature growth gives the measure of the thermal diffusivity. Apart from these two quite different possibilities of the static and pulsed heating the third and very interesting method exists when with the periodic heating thermal waves are generated in the medium examined. The thermal wave is just the propagation of the disturbance of the temperature field within the sample.

It is claimed that this method was invented by Ångstrom, who examined the oscillations of temperature at the end of a long rod which was periodically heated at the opposite end. Though different methods of thermal waves generation by the periodic heating can be conceived the most common modern method makes use of light, especially of laser beams. It ensures the simplicity of intensity modulation for a light beam in the frequency range from less than 1 Hz to several kHz and the possibilities of precise localization of the heated region as well as the scanning of the sample. Furthermore, the heating through illumination is fully non-contact method, which in many cases is an important advantage.

Generation of thermal waves through the absorption of the light beam energy belongs to a whole class of photothermal phenomena which also includes: the generation and propagation of acoustic wave inside the sample and in the circumjacent gas; changes of the refractive index of the gas near the illuminated surface with the resulting gradient of this index; modulation of the optical properties of the sample, *e.g.*, its reflection; deformation of the surface connected with thermal expansion; an infrared emission. All these effects have one primary reason – the periodic heating with the modulated light beam, so they all proceed synchronously and are often very closely related. That is why when investigating the thermal wave propagation one can make use of either the photoacoustic effect and detect the sound in the gas in contact with the sample or can apply the beam deflection method when change of direction of the probing beam, connected with the gradient of the gas refractive index, is observed.

Photoacoustic examination of the heat transport phenomena in solid bodies initiated with the work of ROSENCWAIG and GERSHO [2] is nowadays the well-established and important method. It is applied practically as a standard, for instance, in the case of semiconductors but is also introduced into the new regions of research, such as studies of polymers and biological objects [3], [4].

Photothermal signals are detected with the aid of sensitive microphones (photoacoustic technique), photosensitive elements (beam deflection) or piezoelectric transducers. These detectors produce signal with the same frequency as that of modulation of the

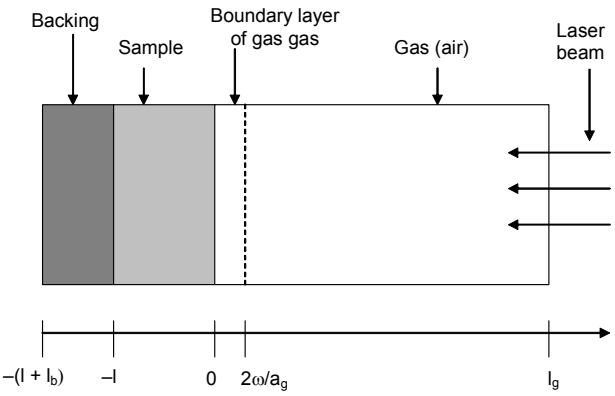

Fig. 1. Schematic diagram of a photoacoustic cell.

light beam which is the source of thermal energy. This circumstance makes it possible to apply the method of selective detection with lock-in amplifiers where the reference signal is provided straight from the modulator. It is a very sensitive detection technique and even slight changes of the parameters which influence the amplitude and phase of the photothermal signal can be registered. On the other hand the method detects the total signal of the given frequency generated in the whole setup with all possible distortions introduced, for instance, by the geometry of the cell. This is the case of the so-called Helmholtz resonances in photoacoustic experiments.

The author describes how to avoid such and other distortions of the frequency characteristics in the experiment aimed at the evaluation of the thermal diffusivity α.

2. Theory

The theory of the photoacoustic generation of sound in the gas in contact with the solid sample exposed to the intensity modulated light beam was presented by ROSENCWAIG and GERSHO [2]. Their approach to the description of this phenomenon was founded on the solution of the heat diffusion equation in the system including the gas, the light absorbing sample and the backing (Fig. 1) with the appropriate boundary conditions.

Thermal properties of the sample and the gas are characterised by the following parameters: k – the thermal conductivity, ρ – the density, c – the specific heat, $\alpha = k/\rho c$ – the thermal diffusivity, $a = (\omega/2\alpha)^{1/2}$ – the coefficient of thermal diffusion, $\mu = 1/a$ – the thermal diffusion length.

The coefficients with the subscripts s, g, b are for the sample, the gas and the backing, respectively, while ω is the modulation frequency of the laser light projected onto the sample.

These boundary conditions are the consequence of the assumption of temperature and thermal flux continuity on both borders of the sample ($z = 0$, $z = -l$) and the fact that the temperature of the cell (for $z = l_g$, $z = -(l + l_b)$) is constant and equal to the ambient temperature. The expression for the periodic changes of temperature (ac component) derived by Rosencwaig and Gersho (RG) for the sample gas boundary has the following form:

$$\theta = AB \tag{1}$$

where

$$A = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)},$$

$$B = \frac{(r-l)(b+l)\exp(\sigma_s l) - (r+l)(b-l)\exp(-\sigma_s l) + 2(b-r)\exp(-l\beta)}{(g+l)(b+l)\exp(\sigma_s l) - (g-l)(b-l)\exp(-\sigma_s l)},$$

while: $b = k_b a_b/k_s a_s$, $g = k_g a_g/k_s a_s$, $r = (1-i)\beta/2a_s$, $\sigma = (1+i)a_s$, and β is the optical absorption.

Considering the oscillations of the gas near the sample induced by its temperature changes proves that the sound wave begins to propagate in the gas. The amplitude of the pressure changes characterizing this wave is proportional to the temperature oscillations at the gas–sample boundary.

The alternative way of describing the temperature changes on the sample's surface and as stated above the pressure oscillations of the acoustic wave was presented by BENNET and PATTY [5]. Bennet adopted the method known from the description of wave interference to the case of propagating disturbances of temperature fields. Thermal waves are generated in the light absorbing layer of the sample and the depth of this layer depends on the value of the light absorption coefficient. The waves propagate both in the direction of the front (illuminated) surface of the sample and towards its back. When the sample is thinner than the thermal diffusion length μ (this parameter is frequency dependent) one has to take into consideration the possibility of multiple passages through the sample. In this situation, the temperature at the surface must be considered as the sum of a series of disturbances generated at different depths and connected with different number of passes in the sample's material. Instead of the boundary conditions for the continuity of temperature and thermal flux one has to take account of the relevant coefficients of reflection and transmission (in fact, these coefficients are strictly connected with the boundary conditions through an equivalent of Fresnel's equations) [6]. Bennet's formula for the amplitude of temperature changes on the illuminated side of the sample is as follows:

$$\theta = CD \tag{2}$$

where

$$C = \frac{I_0 \beta T_g}{4 k_s \sigma_s},$$

$$D = \frac{\frac{1}{\beta + \sigma_s}\{1 - \exp[-(\beta + \sigma_s)L]\} + R_b \exp(-2\sigma_s L)\frac{1}{\beta - \sigma_s}\{1 - \exp[-(\beta - \sigma_s)L]\}}{1 - R_b R_g \exp(-2\sigma_s L)}$$

R and T with the appropriate subscripts are the coefficients of reflection and transmission for the thermal wave at the sample's boundaries .

Much shorter formulae can be derived from Eq. (2) for any of the six main groups into which all solid samples can be divide according to the relations between three parameters: the optical absorption length, the thermal diffusion length and the thickness of the material [6]. In all these cases the results are concurrent with those obtained by simplification of the general RG formula. That proves a full equivalence of RG and Bennet's approaches.

When examining the photoacoustic response of the sample illuminated with the intensity modulated light for the wide range of frequencies (or for the given frequency but for many samples of different thickness) one has to use the general form of RG

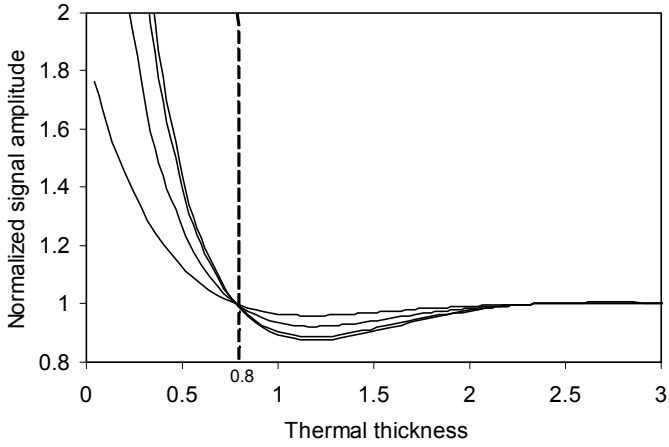

Fig. 2. Photoacoustic signal (or the temperature at the sample's surface) *vs.* the reduced thickness for several samples of different materials (or for different substrates).

and Bennet's formulae. Such general characteristics both for the amplitude and phase exhibit some interesting features and can be used to find out the thermal parameters of the samples' material (or the thickness of the sample of known thermal properties). For instance, from the dependence of the normalized photoacoustic signal on the thermal (or reduced) thickness $x = L/\mu$, the value of α can be obtained. Analysing the whole family of curves of the kind plotted in Fig. 2 one can notice that for the reduced thickness equal to 0.8 the acoustic signal (or the temperature amplitude on the sample's surface) is the same as for the infinite thickness. It must be stressed that this special value of thickness does not depend on the sample's material (all the curves for different materials intersect just at this point). For this reason the x coordinate of the intersection point of the line asymptotic to the experimental curve (in the normalised coordinates) with the initial descending part of this curve can be used to evaluate the thermal diffusion length. Finally, from the obtained value of the thermal diffusion length [7] and the modulation frequency for the analysed data one can find the thermal diffusivity α.

For this procedure of α measurement the reference sample, which can be treated as infinitely thick, is needed, what in practice (for metallic samples and the frequencies bigger than 10 Hz) means that such a sample must be at least 1 mm thick. This can be a problem in some situations, for instance, in the examination of thin metal sheets of a specific composition when thicker sheets are not available or are not produced.

The analysis of the formulae for the photoacoustic signal generated by metallic sheets led us to another method of α determination for which no reference sample is required. The idea is founded on the observation that for a relatively thin sample with the gas on both sides (no substrate) there are two photoacoustic (PA) signals: one in the gas near the illuminated (front) side and the other near the shaded (back) side. One does not have to use two microphones to measure them. Instead one can only change

the direction of illumination by 180° relative to the sample. The signal is in both cases generated in the same volume of gas, within the photoacoustic cell, while the heating of the gas is realized first straight by the illuminated surface and then by the shaded surface of the sample. The temperature of the back side also oscillates because of the propagation of the thermal waves across the sample. We found out that the examination of the ratio of the amplitudes of these two signals is a simple and for some reasons very convenient method of measuring thermal diffusivity. This statement will be justified below and in the experimental part of the paper the results of the practical realization of the proposed method will be presented.

It is assumed that because of metal's high optical absorption the modulated light which is projected onto the sample penetrates into and is absorbed in a very thin film near the surface. This film becomes the surface heater and the source of the thermal wave propagating deeper into the sample. The photoacoustic signal generated in the gas on the illuminated side of the sample described as a complex quantity characterized with the amplitude and phase is proportional to the complex temperature changes on the sample's surface

$$Q_{\text{front}} = C\frac{T_g}{k\sigma}\left[\frac{1 + R_g \exp(-2\sigma L)}{1 - R_g R_g \exp(-2\sigma L)}\right] \tag{3}$$

where k and σ refer to the material of the sample, while T_g, R_g are the coefficients of transmission and reflection of thermal waves on the sample–gas boundary.

It is assumed in this formula that there is no substrate, *i.e.*, on both sides of the sample there is the same gas. The proportionality constant C depends on the geometry of the photoacoustic cell, the kind of gas (for this is the medium in which the photothermally generated acoustic signal propagates) and on the parameters of the applied detector of the sound wave. In general, C is the function of frequency. This frequency dependence manifests itself, for instance, through the occurrence of the so-called Helmholtz resonances, when one observes a great increase of signal for the frequencies of the free vibrations of the gas between the acoustic cell and the microphone (see Fig. 5 in the experimental part).

The photoacoustic signal generated in the same cell after 180° rotation, *i.e.*, after the illumination of the back side of the sample, obtained with the interference method is

$$Q_{\text{back}} = C\frac{T_g}{k\sigma}\exp(-\sigma L)\left[\frac{1 + R_g \exp(-2\sigma L)}{1 - R_g R_g \exp(-2\sigma L)}\right]. \tag{4}$$

The constant C does not depend on the direction of illumination relative to the sample. This is so because in both cases the same surface of the sample plays the role of a heater of the gas in the cell and eventually is the source of the acoustic signal. The

conditions of generation and propagation of this signal are the same in both cases. Upon this assumption the ratio of the photoacoustic signals for front and back illumination is as follows:

$$\frac{\text{amplitude}(Q_{\text{front}})}{\text{amplitude}(Q_{\text{back}})} = \text{amplitude}\left(\frac{Q_{\text{front}}}{Q_{\text{back}}}\right). \tag{5}$$

One can introduce the reduced thickness (thermal thickness) $x = L/\mu$, where L is the actual thickness and μ is the thermal diffusion length. Then the above ratio of amplitudes acquires the form

$$F(x) = \frac{\exp(x)}{(1 + R_g)}\sqrt{1 + R_g\exp(-4x) + 2R_g\exp(-2x)\cos(2x)}. \tag{6}$$

Since the thermal diffusion length is frequency dependent the above function also depends on the frequency even for the sample of a given thickness.

The explicit variable x is proportional to the square root of ω. When the thickness of the sample is several times bigger than μ (one enters this range of x by increasing the frequency) the exponential functions of negative exponents become very small and the whole expression can be reduced to $\exp(x)/(1 + R_g)$. Then the natural logarithm of the function $F(x)$ drawn *vs*. $\omega^{1/2}$ should give (for relatively big frequencies) a straight line and its slope $\tan(\Phi)$ can be simply connected with the thermal diffusivity

$$\alpha = \frac{L^2}{2\tan^2(\Phi)}. \tag{7}$$

3. Experiment and results

The experiment was conducted in the system illustrated in Fig. 3. The light beam from the argon laser propagates along the optical fibre, then goes through the modulator and illuminates the metal sample. The modulator is of the mechanical type. Upon the incidence on the sample the laser beam generates the acoustic signal. The main chamber (acoustic cell) is connected with the microphone and the pressure fluctuations are converted into the electric signals. These signals are analysed with the lock-in amplifier and their magnitude and phase are recorded. In this type of amplifier only signals with frequency coinciding with the reference signal are amplified and analysed, which makes it possible to extrude the signal from the noise of acoustic and electric origin. The reference signal is provided by the chopper.

Digital data acquisition and processing is realised by a PC connected to the amplifier. A suitable program also makes it possible to operate both the lock-in amplifier and the chopper from the computer.

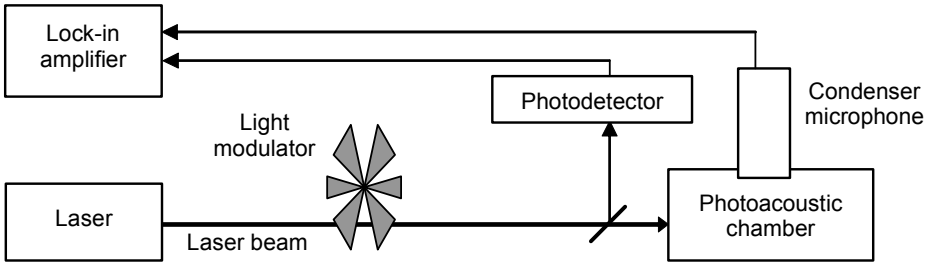

Fig. 3. Schematic of the system for examining the photoacoustic effect.

A cylindrical photoacoustic head is shown in Fig. 4. The diameter of the acoustic cell is 5 mm and the height 2 mm. It is closed with a glass window from one side and the sample from the other. The cell is filled with air at atmospheric pressure. The channel 0.5 mm wide and 2 mm long connects the acoustic cell with the hollow where the microphone is inserted.

The construction of the cell, where the acoustic signal propagates, meets the conditions described in many fundamental papers, *e.g.* [8]. Its length was, even for the lowest modulation frequencies applied, bigger than the thermal diffusion length in the air. The diameter of the pass between the acoustic cell and the microphone was chosen so that the frequency of Helmholtz resonance was near the end of the frequency interval of our measurements. In fact, the fulfilment of this condition, when as we propose the ratio of the front and back acoustic signals is being analyzed, is no longer as critical as usually. We expected that the division of these signals, which can be regarded as some kind of normalization of one signal relative to the other, would remove the dependence of the ratio thus obtained on the geometry of the cell (for the constant C is the same function of frequency for both cases described with formulae (3) and (4)).

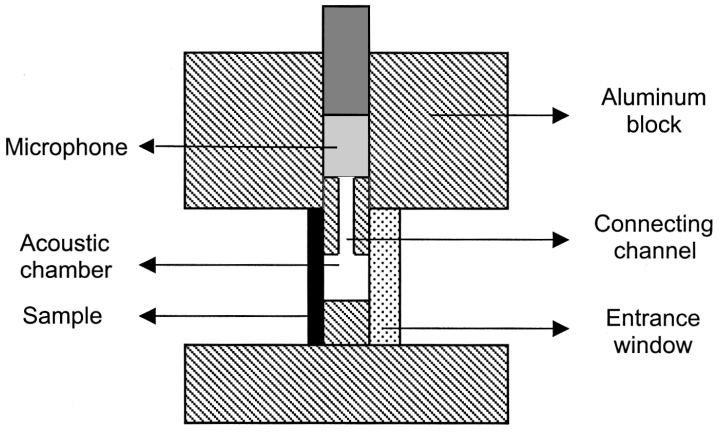

Fig. 4. Cross-section of the acoustic head used in the examination of the photoacoustic effect.

Below the main results of our experiment are presented. Changes of the PA signal generated by the front (illuminated) surface of the sample are presented as a function of the square root of frequency ω in Fig. 5. The effect of the acoustic resonance (Helmholtz resonance) is clearly visible near the abscissa value of about 123 [$Hz^{0.5}$]. The authors were aware of the fact that apart from the PA signal generated by the sample there is additional PA signal connected with the illumination of the inner surfaces of the acoustic chamber with the scattered light. It was possible to measure

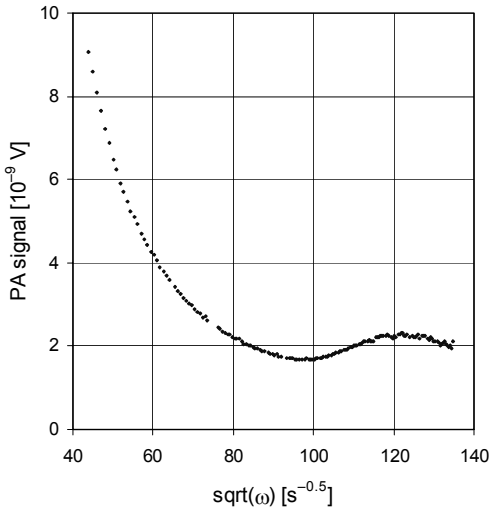

Fig. 5. Experimental PA signal generated by the front (illuminated) surface of the copper sample 0.1 mm thick *vs*. the square root of the frequency ω.

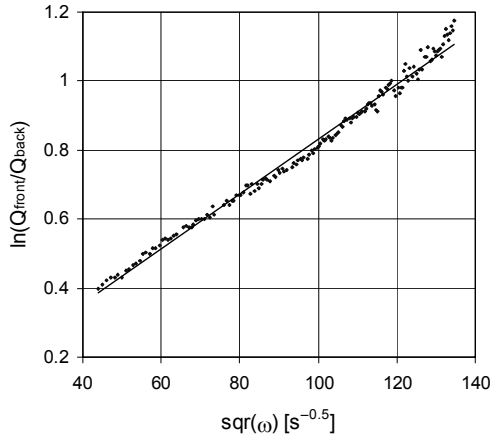

Fig. 6. Logarithm of the ratio of signals for the front and the back illumination *vs*. the square root of frequency ω. The straight line which approximates this dependance is also presented.

this additional signal separately by covering the sample with the optically transparent film of enamel, thick enough to thermally insulate the air in the chamber from the sample. Substraction of this component from the total PA signal generated when the sample is not painted led to the dependence illustrated in Fig. 5.

The frequency dependence of the PA signal produced in the case of back illumination (also cleared with the procedure described above) seems similar to that from Fig. 5 and we do not present it here.

The most interesting is the ratio of the two signals for the front and the back illumination. The logarithm of this ratio as a function of the square root of the frequency ω can be quite well approximated with the straight line, as shown in Fig. 6.

The tangent of the slope and the thickness of the copper sample (0.01 mm) were used to calculate thermal diffusivity α in the way described in the theoretical section of this paper (Eq. (6)).

The obtained value of the thermal diffusivity was 78×10^{-6} m^2/s^{-1}, which proves that the method proposed is correct. It should be underlined here that it also avoids some problems connected with the appearance of Helmholtz resonances and other spurious components in the total PA signal.

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Received October 16, 2003