Measurements of Thermal Conductivity of Aluminum Nanopowders by Photoacoustic Spectroscopy

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MEASUREMENTS OF THERMAL CONDUCTIVITY OF ALUMINUM NANOPOWDERS BY PHOTOACOUSTIC SPECTROSCOPY

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ABSTRACT

This paper concerns the use of photoacoustic spectroscopy (PAS) as a powerful technique to estimate thermal properties of aluminum nanosized powders. Aluminum nanopowders are considered as effective constituents of energetic materials. Thermal conductivity is an important factor in ignition behavior of aluminum nanopowders. For this work, graphite was used as reference material. The experiments showed that nanosized aluminum revealed the same behavior as that of graphite at photoacoustic measurements (similar values of the signal amplitude at various frequencies). It allowed us to assume that both materials have the same thermal diffusivity length.

1. INTRODUCTION

The rapid increase in nanoscience and nanotechnology requires new approaches in the use of traditional diagnostic methods. Photoacoustic spectroscopy (PAS) has become an effective technique for materials characterization [1, 2]. In photoacoustic spectroscopy, the studied sample is irradiated with a source of monochromatic light. The sample absorbs the photon energy and this energy is then transformed into heat energy through non-radiative deexcitation processes. In case of solids and liquids, it appears as vibrational energy of ions and atoms which can be detected by an external sound detector.

Aluminum nanopowders are promising materials as constituents of energetic materials, e.g. propellants and explosives [3,4]. Aluminum nanopowders absorb well light that is important for their ignition. One of the most important thermal characteristics of aluminum nanopowders is their thermal conductivity, because is supposedly lower than that of regular aluminum. This property seems to be useful for the auto-heating of the particles during ignition.

The present paper concerns the results of thermal conductivity measurements realized in a photoacoustic setup which includes a 20 W CO_2 continuous laser as an excitation source, sensitive microphone, sample holder and lock-in-amplifier. The measurements were made for non compacted and compacted samples of the aluminum nanopowder in order to determine the role of the bulk density of the studied samples.

2. EXPERIMENTAL APPROACH

In this study, aluminum nanosized powders prepared by wire electrical explosion (WEE) in the High Voltage Research Institute (Russia) were used. WEE is well known as an effective technique for fabricating very fine and reactive powders [4].

The experimental photoacoustic setup used for determination of thermal conductivity of the nanopowders obtained is schematically presented in Fig. 1. A 20 W CO_2 laser (Synrad, Mukilteo,WA, USA) was used as a irradiation source of wavelength of 10,6 µm.

The photoacoustic signal was detected using a highly sensitive microphone (Bruel & Kjaer, type 4144 having 1 inch diameter and a sensitivity of 44 mV/Pa) located at an angle of 45 degrees and at a distance of 5 cm to the sample holder. The amplitude of the photoacoustic signal was detected and measured by the lock-in amplifier (SR850, Stanford Research Systems, USA). The power of the laser was measured using the

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laser power meter Power Wizzard™ 250 (Synrad, Mukilteo,WA, USA).

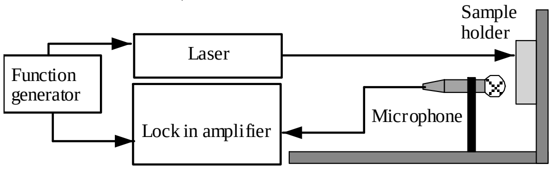

Fig. 1. Photoacoustic set-up.

They were irradiated by the laser for 1-2 seconds for each measurement. The experiments were conducted under normal conditions: room temperature and atmospheric pressure in air.

3. RESULTS AND DISCUSSION

The electroexplosive aluminum nanopowder studied in this work was passivated by a long exposure to air. Morphologically, the powder represents 2-5 μm agglomerates of spherical particles the average particle size of which is approximately 100-120 nm (Fig. 3). The specific surface area of the aluminum nanopowder measured using the BET method is about 7-13 m^2/g.

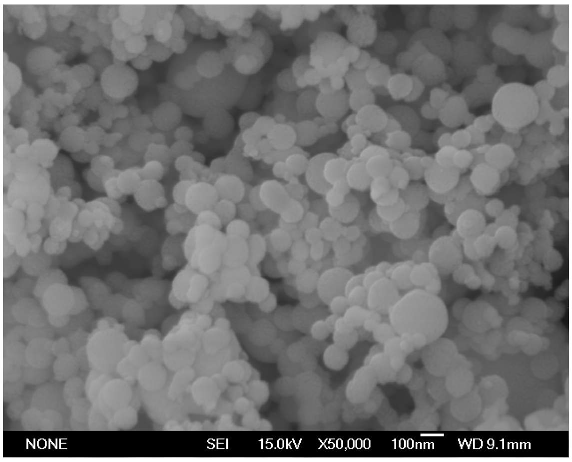

Fig.3. SEM microphotograph of the aluminum nanopowder prepared by electrical explosion

In contrast to regular micron and submicron aluminum, nano-sized powders are black-colored materials in the non compacted state. For this reason, they are capable of absorbing light as a black body. This fact was proved by our photoacoustic experiments, when we used graphite as a black body reference material. The experiments showed that the photoacoustic signal amplitude of the black body reference corresponded to that of the aluminum nanopowder in the whole range of studied frequency (7-150 mV).

According to the Rosencwaig-Gerscho theory [1], the log-log plot of the experimental photoacoustic signal with frequency shows (Fig.5) the f^{-1} behavior for graphite and the aluminum nanopowder. This means that the optical absorption length (l_β) of an opaque material is shorter than the thickness of a studied sample (l_s). At the same time, the thermal diffusion length μ_s is defined by the following expression:

$$\mu_s = (2\alpha_s / \omega)^{1/2} \qquad (1)$$

where α_s is the thermal diffusion coefficient, m^{-1}; ω is the chopping frequency, Hz.

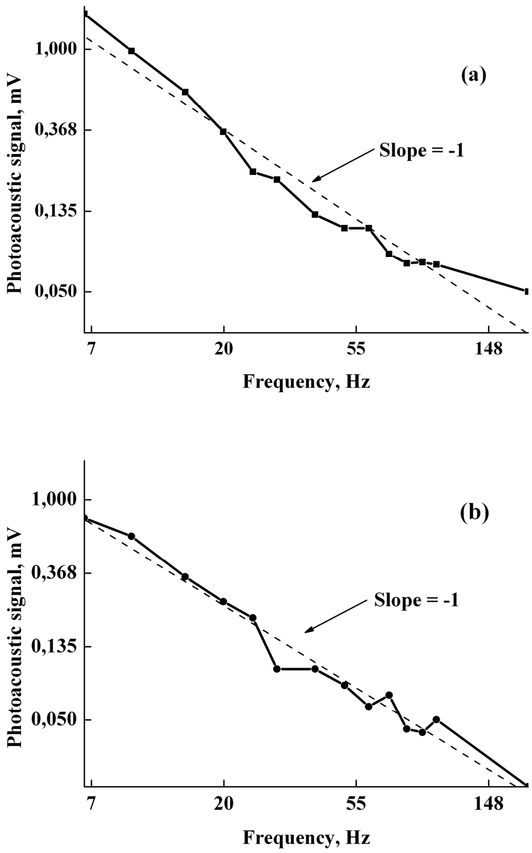

Fig. 4. Log-log plots of the photoacoustic signal for graphite (a) and compacted aluminum nanopowder (b) versus frequency.

Let us assume that if graphite and the aluminum nanopowder behave identically as thermally thick solids (l_β<l_s), they can then possess the same value of the thermal diffusion coefficient (α_s) which is determined by this equation:

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$$\alpha_s = \frac{k_s}{\rho_s \cdot C_s} \qquad (2)$$

where k_s is the thermal conductivity coefficient of a sample, W.m^{-1}.K^{-1}; ρ_s is the specific mass of a sample, kg.m^{-3}; C_s is the specific heat capacity of a sample, J.kg^{-1}.K^{-1}.

In this case, the thermal conductivity coefficient of the aluminum nanopowder k_{Al} can be expressed through the thermal conductivity coefficient of graphite k_{gr} as follows:

$$k_{Al} = k_{gr} \cdot \frac{\rho_{Al} \cdot C_{Al}}{\rho_{gr} \cdot C_{gr}} \quad (3)$$

where ρ_{gr}, ρ_{Al}, C_{gr}, C_{Al} is the specific mass and the specific heat capacity of graphite and the aluminum nanopowder, respectively.

The aluminum nanopowder was compacted with a press using a 10-mm mold under a pressure varying from 5 to 35 MPa. The 6 aluminum nanopowder samples with specific mass ranging from 1070 to 1390 kg.m^{-3} were studied.

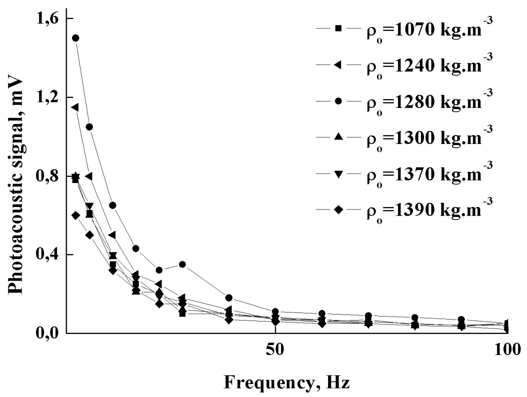

Fig. 5. Photoacoustic signal for the compacted aluminum nanopowder of different specific mass.

The PA signal amplitude (Fig. 5) depends generally on the density of the compacted aluminum nanopowder. It decreases slightly with the increase in the density and stabilizes at frequencies higher than 50 Hz. Apparently, such behavior is related to the change in the absorption coefficient of compacted aluminum which is proportional to the PAS amplitude for the black body.

The Wiedemann-Franz-Lorenz law [5] which states that the ratio of thermal (k_s) to electrical conductivity (σ_s) is linearly related to absolute temperature (T) was applied in order to determine thermal conductivity of the graphite reference. The value of thermal conductivity was then calculated according to the following expression:

$$\frac{k_s}{\sigma_s} = C_L \cdot T \qquad (4)$$

where C_L is the Lorenz number, 2,45·10^{-8} W·Ω·m.

In spite of good electrical conductivity of aluminum, the Wiedemann-Franz-Lorenz approach is not suitable for the aluminum nanopowder because of its high oxidation degree. According to chemical analysis, the aluminum nanopowder contains more than 5 wt% of oxides (thickness of the oxide layer is 10-15 nm), whereas the oxide content in the micron-sized aluminum powder is less than 1 wt% (thickness of the oxide layer is less than 4 nm). The oxide/metal ratio is negligible for regular micron- and submicron-sized Al powders, while it is important for nanoparticles. Therefore, photoacoustic spectroscopy seems to be a convenient method to determine thermal conductivity of aluminum nanopowders. For the thermal conductivity measurements a cylindrical bar (10 mm in diameter, 50 cm in height) was made from Carbone Lorraine (Paris, France) electrode graphite. Resistance of the graphite bar was measured using a digital multimeter METRAHit 29S (Gossen-Metrawatt, Germany). The value of resistivity calculated for the bar was 7,56·10^{-8} Ω·m. Under normal conditions, the value of the k_{gr} for graphite is 95,78 W.m^{-1}.K^{-1}.

It is known that in case of the poor conductivity, the oxidation processes in the nanopowder occur under conditions of thermal explosion [6]. So, this condition was presumed to determine it either thermal conductivity of the aluminum nanopowder was low or not. As stated above, we assumed that the values of the thermal diffusivity length are analogous, their thermal conductivities are then linearly proportional. In this case, the thermal conductivity coefficient k_{Al} of the aluminum nanopowder for several compaction levels can be estimated using equation (3) (Table 1).

Table 1. Measured thermal conductivity for the compacted aluminum nanopowder.

Specific mass of the nanopowder ρ_{nano}, kg.m^{-3}	800	1070	1240	1280	1300	1370	1390
Thermal conductivity coefficient of the nanopowder k_{nano}, W.m^{-1}·K^{-1}	47,17	63,49	73,22	75,69	76,68	80,91	81,84

Normal pure aluminum is a good thermal conductor: its thermal conductivity coefficient is 237 $W \cdot m^{-1} \cdot K^{-1}$. Meanwhile, the aluminum nanopowder exhibits a lower thermal conductivity corresponding only to 20-35 % of the normal value. Such low values can be explained both by the presence of aluminum oxide layer the thermal conductivity of which is low (30 $W.m^{-1} \cdot K^{-1}$) and porous structure of nanosized aluminum even in the compacted state. This fact allows us to anticipate that namely the low conductivity of the compacted aluminum nanopowder will lead to explosive character of its oxidation during laser ignition.

4. CONCLUSIONS

The thermal conductivity of aluminum nanopowders was measured using the photoacoustic spectroscopy technique. It was found that the PA amplitude for the compacted aluminum was practically equal to that for graphite taken as a reference material. The log-log plot of the PA signal versus frequency indicated that both graphite and nanosized aluminum revealed f^{-1} behavior. According to the Rosencwaig-Gerscho theory, this corresponds to the case of thermally thick solid for which the sample thickness is more than the optical absorption length. It was assumed that graphite and aluminum nanopowder have the same thermal diffusion length. The photoacoustic measurements showed that the thermal conductivity coefficient of aluminum nanopowder increased with the increase in density, from 47,17 to 81,84 $W.m^{-1}K^{-1}$ when specific mass evolves from 800 to 1390 $kg.m^{-3}$.

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