Production of polytetrafluoroethylene nanoparticles at cryogenic temperatures

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Polytetrafluoroethylene (Teflon-4) ablation and degradation under different thermal conditions and CO_2-laser irradiation have been studied. It has been shown that as the temperature of the irradiated samples decreased, the size of the produced particles decreased too (down to several tens of nanometers).

Introduction

Methods for production of powders from various materials are now intensely studied, and fine powders find wide application in science and technology. Teflon $[-CF_2-CF_2-]_n$ powder is usually produced by two methods, both involving destruction of a large-size sample of bulk material.

One of the methods is based on mechanical crushing of pieces, and in some cases additional activation of the initial material by UV radiation[1] or prior treatment by an electron beam is used, because Teflon is unstable to hard radiation (if the radiation dose is $5 \cdot 10^4$ J/kg, ultimate tensile strength of Teflon decreases by 50–90%).

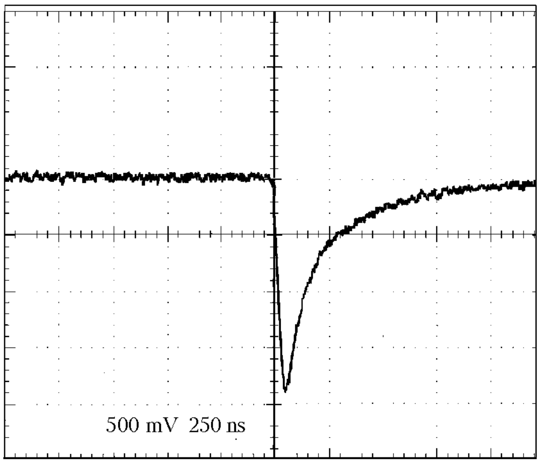
In the other method, the initial material degrades as a result of exposure to ArF laser radiation at the wavelength $\lambda = 193$ nm (Ref. 1).

Tolstopyatov et al.,[2] have shown that, though Teflon weakly absorbs CO_2 laser radiation ($\lambda = 10.6$ μm), abnormally quick, nearly resonant destruction of the material occurs. This is explained by the break of the C–C bond (the energy of the C–C bond in the carbon skeleton of organic molecules ranges within 352–368 kJ/mol [Ref. 3]) and formation of the unstable tetrafluoroethylene monomer $CF_2{=}CF_2$, which exists only in the gas state. While flying apart, some monomers couple with each other and deposit as a powder onto a substrate. As a consequence, if varying the conditions, it is possible to produce fine powders at a relatively low cost.

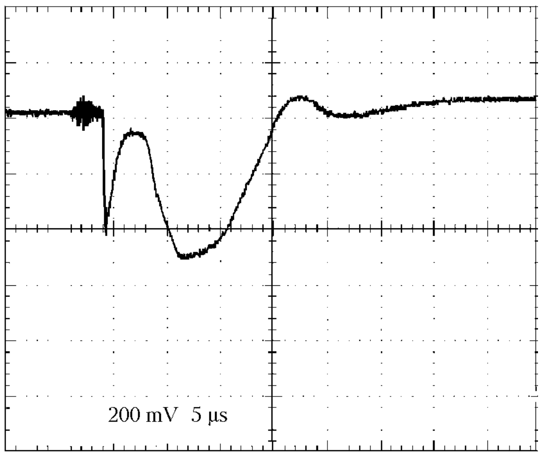
The aim of this paper is to study ablation and degradation of Teflon-4 exposed to the CO_2 laser radiation under different thermal conditions.

Experimental setup and technique

The experimental setup comprised of pulsed lasers, an optical system, and a chamber for housing samples. The samples were exposed to the radiation of two CO_2 lasers ($\lambda = 10.6$ μm): a KASKAD laser[4] with the pulse energy ~3.5 J and full width at the pulse half-maximum (FWHM) of 100 ns (Fig. 1*a*) or pulse energy ~6 J and FWHM of 15 μs (Fig. 1*b*), and a FOTON-2 laser[5] optimized for operation on CO_2 molecules with the pulse energy up to 750 mJ, FWHM from 50 to 100 ns; the pulse shape was almost unchanged (Fig. 2).



a



b

Fig. 1. Oscillograms of pulses of the KASKAD laser operated on CO_2 molecules under different conditions: pulse FWHM $\tau_{1/2}$ = 100 ns (*a*) and $\tau_{1/2}$ = 15 μs (*b*).

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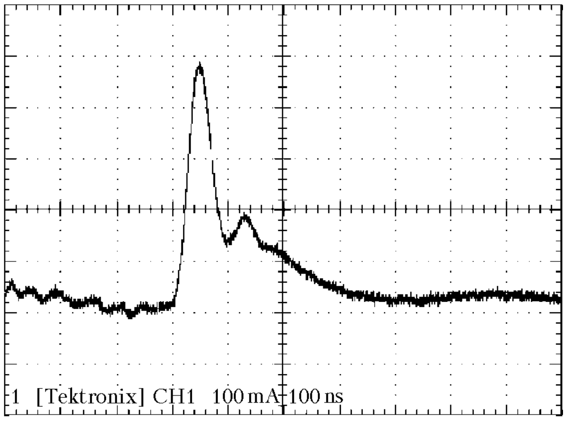


Fig. 2. Oscillogram of a pulse of the FOTON-2 laser operated on CO_2 molecules.

The laser beam at the output from the laser setup was divided by the BaF_2 beam splitter plate. A part of the beam was used for diagnostics. The beam energy was measured with an IKT-1, and the pulse shape and FWHM were measured with a FP-1. Electric signals were recorded with a Tektronix TDS-220 oscilloscope. The major part of the beam transmitted by the plate was focused by a NaCl lens (focal length of 12.4 cm) onto the surface of a Teflon plate. The effect of the laser irradiation of 2.0- and 7.5-mm thick polytetrafluoroethylene plates was studied under different temperatures of the plates. A Teflon plate was either heated from the rear side by a thermal gun or cooled by liquid nitrogen. In the case of heating, the temperature was monitored by a thermocouple. The quantities estimated in the experiment were the amount of the substance M deposited during a pulse, the dependence of M on temperature and pulse duration, and the particle size distribution as functions of the target temperature. The powders were collected onto quartz plates. Irradiation was carried out in air. The size of Teflon particles was analyzed with an MMR-4 microscope at 620X magnification.

Results and discussion

Upon irradiation of the samples, the Teflon degradation product deposited onto the quartz substrate. The results of processing of the experimental data are summarized in Tables 1 and 2, where M_1 is the amount of the substance deposited for a series of pulses; P is the power of pulsed radiation incident on a sample.

For illustration, Fig. 3 depicts the amount of the substance deposited for a pulse.

The data obtained at the target temperature equal to the liquid nitrogen temperature are omitted in Tables 1 and 2, because we failed to estimate the mass of the emitted substance and the size of deposited particles. By now we succeeded only in estimating the thickness of the deposited "film" (Fig. 4).

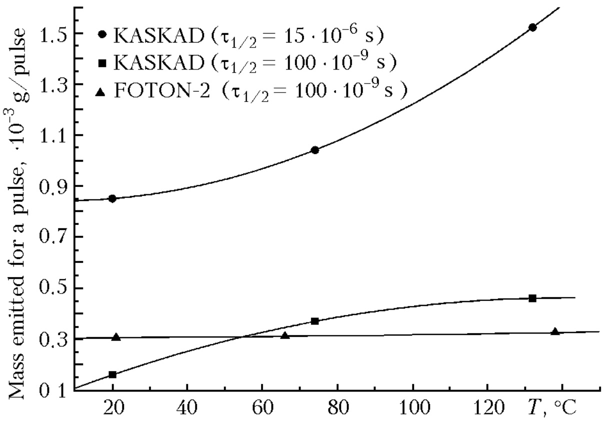


Fig. 3. Mass of the substance emitted for a pulse vs. target temperature at different pulse energy and duration.

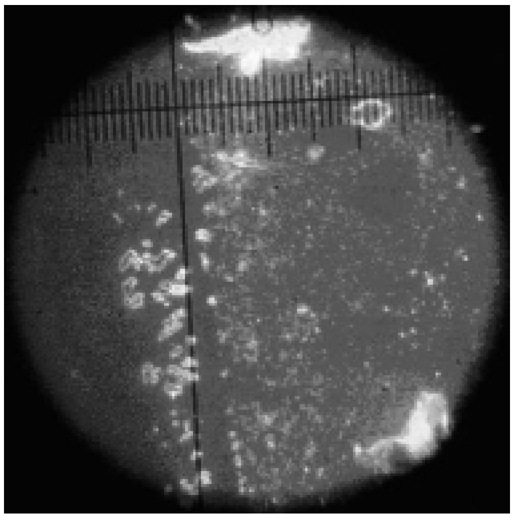


Fig. 4. Photograph of a film deposited on the quartz substrate as a result of irradiating, using a FOTON-2 laser, a Teflon sample cooled to a cryogenic temperature.

Table 1. Results obtained as a tetrafluoroethylene plate was exposed to KASKAD laser radiation

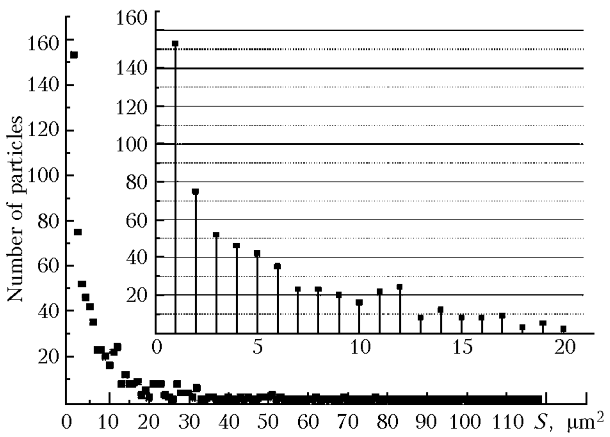
$\tau_{1/2}$, s	~15 · 10^{-6}			~100 · 10^{-9}		
Number of pulses	30			30		
T, °C	21	71–78	131–133	21	71–78	131–133
P, W/cm^2	$2.9 \cdot 10^6$	$2.86 \cdot 10^6$	$2.33 \cdot 10^6$	$3.6 \cdot 10^8$	$3.3 \cdot 10^8$	$3.0 \cdot 10^8$
M_1, g	$25.6 \cdot 10^{-3}$	$31.2 \cdot 10^{-3}$	$45.6 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$11.2 \cdot 10^{-3}$	$13.8 \cdot 10^{-3}$
M, g/pulse	$8.5 \cdot 10^{-4}$	$10.4 \cdot 10^{-4}$	$15.2 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$

Table 2. Results obtained as a tetrafluoroethylene plate was exposed to a FOTON-2 laser radiation

$\tau_{1/2}$, s	~$100 \cdot 10^{-9}$		
Number of pulses	90	80	100
T, °C	20	66	138
P, W/cm^2	$2.94 \cdot 10^6$	$2.11 \cdot 10^6$	$1.436 \cdot 10^6$
M_1, g	$27.44 \cdot 10^{-3}$	$24.85 \cdot 10^{-3}$	$32.59 \cdot 10^{-3}$
M, g/pulse	$3.05 \cdot 10^{-4}$	$3.11 \cdot 10^{-4}$	$3.26 \cdot 10^{-4}$

The thickness of the film obtained at the liquid nitrogen temperature was from ~ 800 nm at the center to ~ 300 nm at the distance of 5 mm from the center of the spot. It should be noted that at a large distance the thickness was even smaller.

The results of digital processing of microphotos of Teflon particles are shown in Fig. 5.



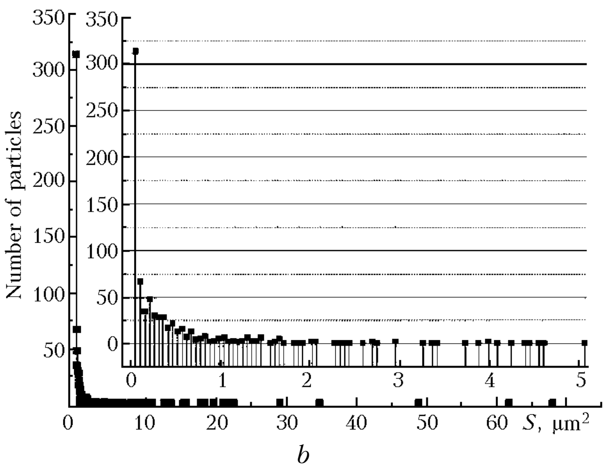


Fig. 5. Size distribution of particles on the surface of a quartz plate as obtained upon exposure to the FOTON-2 laser radiation. The temperature of the Teflon sample was 134 (*a*) and 21°C (*b*).

It can be seen that as the target temperature decreased, the mean size of particles decreased, while the number of particles with such a size increased. Note that if the target temperature is high, the amount of the emitted substance is much greater and the emitted particles are larger than at a low target temperature.[6] At a high temperature, the substance is mostly emitted due to bursting of gas bubbles formed in the volume of the material additionally heated by the radiation.[2] At cryogenic temperatures of the material, only ablation (evaporation from the solid phase directly to the gas phase) is likely taking place.

It should be noted that the shorter the pulse duration or, more precisely, the steeper the leading edge of the pulse, the higher the probability of ablation. Consequently, in this case, at a short pulse duration, the size of the particles produced is smaller. Ablation starts only when the energy E_1 exceeds the weakest bond energy E_2 in molecules of the substance and the time t_1 needed to the radiation pulse to reach the energy E_1 is shorter than the time of the thermal front propagation in the target volume t_2. This means that, on the one hand, the substance is emitted almost without heating of the surface layers. On the other hand, the particles emitted as a result of irradiation have the smallest size at the given level of the radiation energy.

If E_1 is higher than E_3, where E_3 is the bond energy exceeding E_2, then the particle size is smaller than in the first case. Therefore, ablation is now addressed only if the pulse duration is within several nanoseconds.

It follows from our experiments that by cooling the target it is possible to obtain the effect of laser ablation at much longer pulse durations.

As known, the intensity of the radiation transmitted through a substance varies by the following law:

$$I = I_0 \, e^{-kl},$$

where k is the natural absorption coefficient, in cm^{-1}; l is the thickness of the substance layer, in cm. If the radiation intensity is low, the absorption coefficient is independent of the radiation energy being determined only by optical properties of the substance. Thus, the absorption coefficient for a particular material depends on its temperature, density, and molecular composition, as well as on the presence of admixtures and defects in it, and can vary during the irradiation. Therefore, from variation of the absorption coefficient during a pulse we can judge on the variation of Teflon properties in the interaction volume.

The process of ablation during irradiation of a material almost does not affect the absorption coefficient of a sample. In this case, the substance is emitted almost without heating of the surface layers. Consequently, the absorption coefficient of the material as a whole must remain practically unchanged. If the substance in our experiments is emitted due to bursting of gas bubbles, according to the theory proposed by Tolstopyatov with his co-workers, that is, upon preliminary heating of the surface layer of the material, the absorption coefficient must change.

Conclusions

The investigation of the interaction between polytetrafluoroethylene and the CO_2 laser radiation in three thermal modes has enabled us to reveal that the variance and mean size of particles decreases as the target temperature decreases, while the number of particles increased, the yield of the "useful" substance (powder) decreased, and the volume of the sample actively interacting with the radiation reduced.

To keep the process of laser ablation at the increased pulse duration, it is proposed to use cooling of samples before laser irradiation. So we can expect application of lasers with the extended pulse duration at simultaneous cooling of samples in those activities, where the effect of ablation is used, like for example, growing of single- and polycrystal structures and thin films, as well as surface polishing.

References

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