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Optical and electron-beam initiation of porous silicon films with different contents of oxidizer and graphene

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Laser and electron-beam initiation of the combustion process of energy-saturated composite films were studied. Composites were produced from porous silicon, a fluorine-containing polymer, and graphene. It is shown that the impact of a high-current electron beam of nanosecond duration does not lead to the excitation of the combustion process. Moreover, the process of film combustion during laser initiation is accompanied in some cases by the appearance of a zone of secondary flame and white smoke.

Keywords: porous silicon, energy-saturated composite, laser initiation, electron-beam initiation, combustion.

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Introduction

The sustained interest in energy-saturated composites (ESCs) based on porous silicon (por-Si) with pore sizes in the nanometer range causes the need to find a reliable and safe method of initiation of charges made of ESCs of this type. In this regard, the optical (laser) method of ESC initiation deserves attention, which is characterized by increased safety, for example, to electromagnetic induction, charges of static electricity and to accidental energy sources. In addition, it is possible to use small-sized semiconductor diodes to implement this method, which is important, for example, in the development of pyroautomatics systems of rocket-space systems [1] or aircraft engines [2].

The initiation of both conventional energy-saturated materials and porous silicon-based ESCs using a high-current electron beam [3] has the same advantages as the optical method, except that a powerful electric energy source is required, which dramatically increases the size of such an initiation system. These disadvantages can be eliminated by the development of pulsed high-voltage technology.

Analysis of the freely available information shows that two main applications of the considered ESCs are consid: replacement of initiating explosives (IE) in detonation means [4] and creation of pyrotechnic compositions for ignition means [5]. It can be noted that, in addition to ESCs based on porous silicon, ESCs based on boron, boron compounds, titanium borides, aluminum, etc. are also considered for the same purposes. [6].

At the same time, research in creating high-efficiency ESC based on porous silicon has been conducted for quite a long time, mainly using various perchlorates as oxidants [6,7]. The use of other compounds as oxidants is sporadic and, accordingly, is not fully described in the scientific literature. And some fairly effective oxidizing agents are almost not considered as such for use in energy composites based on porous silicon. Such oxidizers include, for example, fluorine-containing polymers, which are potentially highly effective oxidizing compounds due to the strong oxidative nature of the fluorine atoms [8]. An exception is the work [9], which considers ESCs based on both nano-silicon and porous silicon with fluoropolymer oxidizer (PTFE). It can also be noted that fluoropolymers (fluorocarbons) are quite widely used in the formulation of pyrotechnic compositions [10,11], where they play the role of both oxidizing agent, which provides activation of combustion, and binder. In addition, fluoropolymers are quite widely used as oxidizing agents for silicon [6,12] based pyrotechnics.

If we talk about optical or electron-beam excitation of explosive transformations in energy-saturated composites (and not only based on porous silicon), then in works [13,14], it was found that the sensitizer role for both initiation methods is played by graphene.

The present work is devoted to the optical and electron-beam initiation of porous silicon with different contents of the fluoropolymer oxidizer and graphene.

1. Methodology for preparing energy composites

On electronic analytical scales DEMCOM DA-65C, test portions were weighed with mass 100 mg of porous silicon KDB-100 with porosity $\sim 80\%$, as well as est portions multilayer (2−5 layers) graphene (Gr) (Fig. 1) in the amount from 2 to 30% of the mass of nano-silicon, masses 30, 20, 10, 5 and 2.5 mg. Gr contained hydroxyl groups, as a result, the oxygen amount in the sample used reached $\sim 9\%$. Graphene was injected into a test portion of porous silicon in a dry form, mixing until a homogeneous powder was obtained, thus obtaining a por-Si+Gr composition.

Synthetic fluorocarbon rubber SKF-32 (GOST 18376-79) ($(\text{-CF}_2\text{-CH}_2\text{-CF}_2\text{-CFCl-})_n$) (fluorine content 54−56%), which is a copolymer of vinylidene fluoride with trifluorochloroethylene was used as oxidizer. SCF-32 was dissolved in acetone under stirring. The mixing process was continued until the polymer was completely dissolved.

The por-Si+Gr test portion was mixed with an acetone solution of SCF-32 synthetic rubber by irradiating them in a „Sapphire" ultrasonic bath with a power of 50 W for 30 min at room temperature. As a result, we obtained the energy-saturated por-Si+Gr+SCF-32 composite test portions in the following ratios (in mg): $100+30+70$, $100+20+80$, $100+10+90$, $100+5+95$, $100+2.5+97.5$, $100+100$. The corresponding mass ratios (in %) are: $50+15+35$, $50+10+40$, $50+5+47.5$, $50+2.5+47.5$, $50+1.25+48.75$.

After the SCF-32 solution was mixed with por-Si+Gr, the resulting composition was a plastic sticky mass, which was

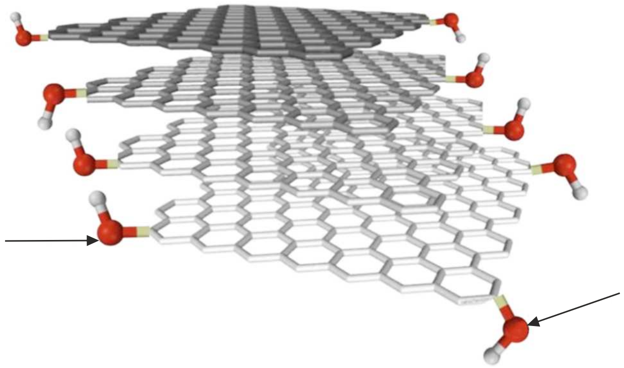

Figure 1. Multilayer graphene containing hydroxyl groups (indicated by arrows).

Figure 2. ESC film (por-Si + Gr + SCF-32).

left to air dry for a day. The cured compound was then thermostatically dried for 3 h at 70−85°C and for 3 h at 120−135°C.

The dried composition appeared as thin films of brown color (Fig. 2). Film formation is due to the fact that the adhesion forces between the filler and the polymer in the organic solvent used are higher than the cohesion forces between the polymer macromolecules. In addition, graphene, due to additional polymer adsorption, reduced the number of free macromolecules not bound to the fillers, which led to greater polymer structurization (SCF-32), and the energy composite became significantly less sticky compared to the por-Si+ SCF-32 composite.

Since it was necessary to put the resulting ESC in a cap for electron-beam initiation, some of the films were reduced to a powdery form. The films were crushed by gently rubbing them with a glass rod at the bottom of a glass Petri dish to obtain a powdery appearance. Pressing of the obtained powdered composition was carried out in metal caps with an outer diameter of 7 mm, inner diameter of 5 mm and height of 2 mm under pressure of 35 MPa. One drop of acetone was placed at the bottom of the cap, a portion of the crushed films was poured in and pressed with fluoroplastic paddles powdered with lead stearate. A circle of fluoroplastic film was placed on top of the composition and pressed. After that, the circle was taken out of the assembly and the operation was repeated until the cap was completely filled. The loaded caps were dried in the thermostat for 1 h at 70−85°C. After cooling, they were weighed on analytical scales DEMCOM DA-65C. The mass of the pressed composition ranged from 40 to 45 mg.

2. Methods, experimental results and discussion

A 1 W semiconductor laser diode with a wavelength of 450 nm (blue) was used for the optical initiation of ESC films. The diameter of the laser beam $d = 2$ mm.

The electron beam was excited by a GKVI-300 high-current pulsed electron gas pedal with an average electron energy in the spectrum of 250 keV and a voltage pulse duration at its half-height of $\sim 20-30$ ns. Electron beam diameter — 8.5 mm. The experiments were performed with a cutoff (by placing a 20 μm thick aluminum foil on the cap in which the pressed compound was placed) of the so-called

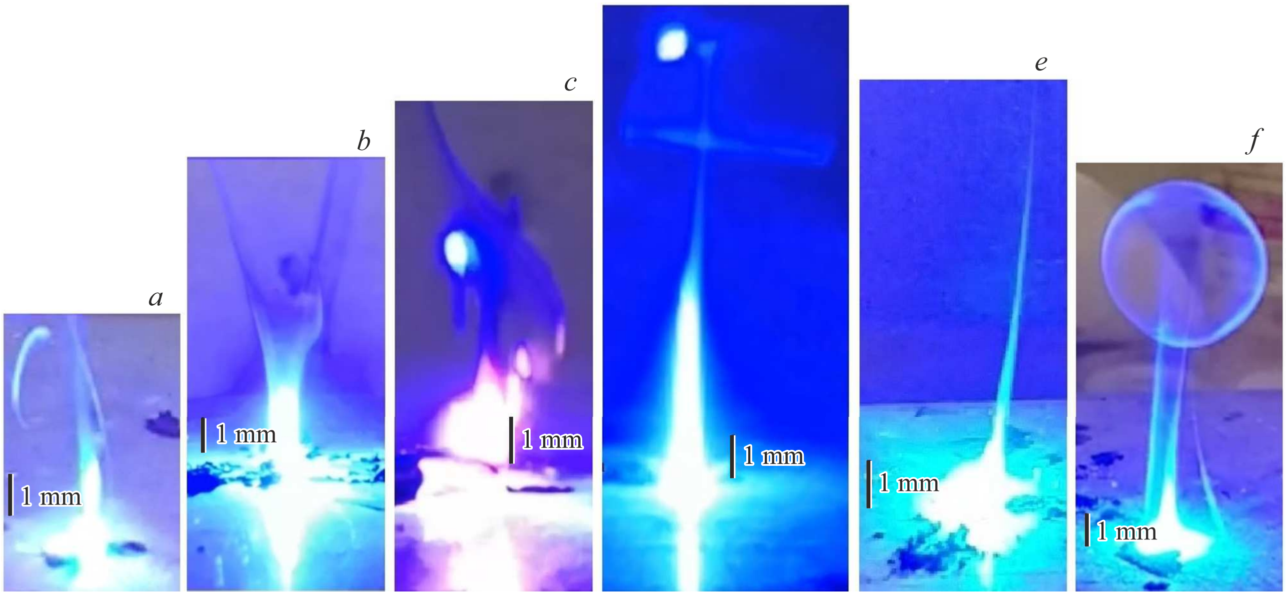

Figure 3. Maximum flame intensity of the films: *a* — 0%, Gr; *b* — 1.25% Gr; *c* — 2.5% Gr; *d* — 5% Gr; *e* — 10% Gr; *f* — 15% Gr.

Figure 4. The burning intensity of the films without a laser beam: *a* — 5% Gr; *b* — 2.5% Gr.

cathode flare (CF), which is generated from the gas pedal cathode following the electron beam [13].

2.1. Laser initiation

The initiation by the laser diode of the energy-composite films in the entire range of graphene and SCF-32 content led to the excitation of the combustion process, accompanied in some cases by smoke formation. However, the intensity of combustion and the amount and color of smoke depended on the film composition. Fig. 3 shows the maximum geometric types of the burning flames of the films, from which it can be seen that the highest combustion intensity has por-Si/Gr/ESC-32 — 50/5/47.5 (mass%).

In addition, it should be noted that only two ESC films with Gr 5 and 2.5% continued to burn without exposure to the laser beam (Fig. 4), in the remaining cases the burning process without exposure to the laser beam stopped. This is all the more strange because it is known from the literature that under the influence of elevated temperature destruction of rubber SKF-32 is accompanied by release, including gaseous fluorine [15], which is the most active oxidizer of porous silicon:

$$Si + 2F_2 \rightarrow SiF_4,$$

This reaction is accompanied by the release of large amounts of heat. The release of large amounts of heat should have intensified the combustion process, especially in ESCs, which lacked graphene and could prevent the formation of fluorine. However, this did not happen, and the composition without graphene burns with the lowest intensity, from which it follows that the process of fluorine release during SCF-32 degradation is significantly slower than the burning process of the whole ESC.

It should be noted that in the experiments in Fig. 3, *b, c* combustion of energy-saturated composites is accompanied by the formation of a secondary flame in the gas phase, which is separated from the primary flame by a dark zone. The appearance of the secondary flame zone is probably due to the fact that with increasing pressure in the dark zone, the interaction rate of the gaseous products in this zone increases, which, in fact, leads to the appearance of the secondary flame zone. That is, it implies a rapid ejection of combustible particles of the energy-saturated composite from the film surface by an upward thermal flow into the gas phase and igniting them with air oxygen. It is assumed, that in this zone, about half of the total energy contained in the energy composite is released, and the maximum combustion temperature [16,17] is reached. The formation of a secondary flame during combustion of the pyrotechnic composition in Fig. 3, *c* is also confirmed in Fig. 4, *b*.

In other cases, combustion of pyrotechnic compositions occurs with less energy release, and no secondary flame is formed, which is confirmed by the combustion termination without exposure to the laser beam.

During the experiments, it was noticed that the combustion of porous silicon (Si) + SCF-32 composition is accompanied by the emission of white smoke (Fig. 3, *a*). Previously, laser initiation of por-Si-based ESC with perchlorate oxidizer did not observe smoke [14] . What is the cause of the white smoke in this case?

Combustion of such a composition in an oxygen-free atmosphere should obviously result in the following solid products in the smoke: soot (C), silicon carbide (SiC) and some particles of porous silicon carried away from the surface of the sample by the heat flow. The quantitative composition of the smoke seemed to depend on the por-Si/SCF-32 ratio in the film. But since in practice, our experiments were always conducted in air (i.e., in the presence of oxygen), the smoke composition must have become different. It is likely that the main solid particle in the smoke was silicon oxide, formed by the reaction of silicon oxidation by air oxygen [18]:

$$\mathrm{Si_{Hard}} + \mathrm{O_2} \rightarrow \mathrm{SiO_{2Hard}}$$

or water formed by hydrogen oxidation of SCF-32 rubber:

$$\mathrm{Si_{Hard}} + \mathrm{H_2O} \rightarrow \mathrm{SiO_{2Hard}} + 2\mathrm{H_2}.$$

Silicon oxide is also easily formed by oxidizing silicon carbide with air oxygen:

$$\mathrm{SiC_{Hard}} + 2\mathrm{O_2} \rightarrow \mathrm{SiO_{2Hard}} + \mathrm{CO_2}.$$

The introduction of the third component — sheets of multilayer graphene — did not lead soot increase in the smoke. The smoke still remained white for most of the ESC (except for the composites containing 1.25%Gr and 2.5%Gr — for this composite, the smoke also turned white after some time) (Fig. 3, *c, d*). One explanation for this result — the intense oxidation of $\mathrm{Gr}_n\mathrm{Si}$ to gaseous products by air oxygen at temperatures above 400–600°C [19].

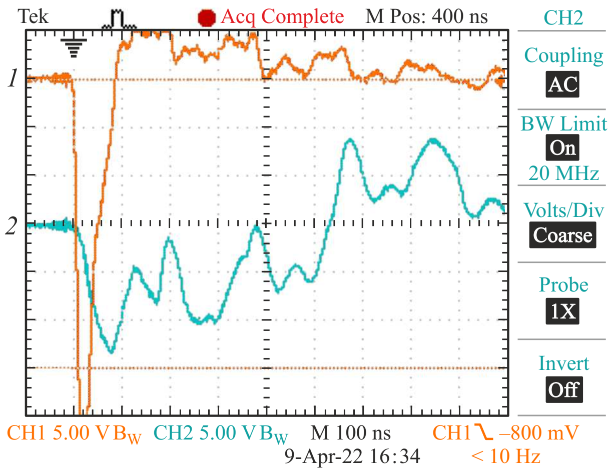

Figure 5. Voltage (*1*) and current (*2*) oscillograms.

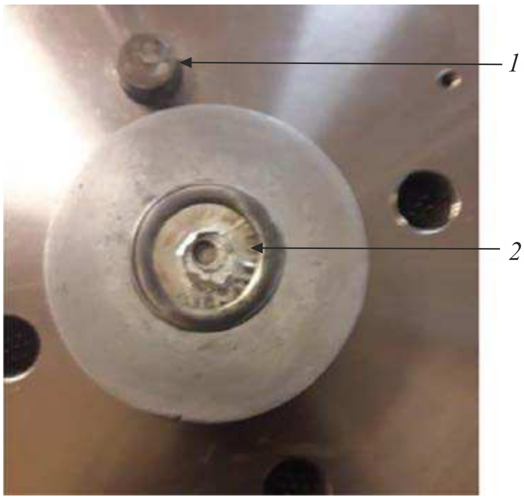

Figure 6. ESC cap (*1*) and the anode ring (*2*).

2.2. Electron beam initiation

The initiation of the investigated energy-saturated composites using a high-current electron beam (HCEB) did not result in the initiation of the combustion process and explosive transformations in general. Samples of current and voltage oscillograms are shown in Fig. 5, *c, d*. Fig. 6 shows the views of the cap with pressed ESC and the steel ring-anode after the experiment. The action of the HCEB resulted only in the fact that the shock wave generated by it, reflected from the substrate, knocked the cap with ESC from the seat of the ring anode, as a result of which it ended up in the vacuum chamber GKVI-300.

2.3. Discussion of results

The results indicate that the ignition of the investigated ESC by optical or electron-beam methods depends not on the power flux density P [20], but on the energy flux density. Thus, we estimate the power flux density during electron-beam initiation to be $9 \cdot 10^8 \leq P \leq 2.5 \cdot 10^9\,\mathrm{W/cm^2}$, while during laser initiation $P \approx 15\,\mathrm{W/cm^2}$. If we compare the energy flux densities, the result is as follows: $H = 15{-}20\,\mathrm{J/cm^2}$ for electron-beam initiation and $H > 30\,\mathrm{J/cm^2}$ for laser initiation. It can be noted that the irradiation with energy flux density $H = 15\,\mathrm{J/cm^2}$ when initiated by a high-current electron beam of TEN monocrystals (high explosive) causes their detonation [21].

In addition to the high energy flux density, the flammability of the investigated ESC during laser initiation could be affected by light-absorbing additives, which are additives of multilayer graphene. It should be noted that during the electron-beam initiation the particles of graphene (which is a conductor) were not realized as local centers of attraction of electrons, which was discussed in work [22]. As a result of the formation of such local centers, the so-called hot spot mechanism could be realized, which could lead to the excitation of the combustion process [23,24]. The lack of formation of local centers of attraction is obviously due to the low density of graphene sheets ($\sim 2.2\,\mathrm{g/cm^3}$ [25]) compared to the density of additives (copper oxide particles), which were considered in work [22] ($\rho = 6.4\,\mathrm{g/cm^3}$).

Conclusion

The following conclusions can be made according to the research results. 1. Energy-saturated composites based on porous silicon with different content of fluorine-containing polymer and multilayer graphene are ignited by laser semiconductor diode and are not ignited by high-current electron beam.

2. It was found that the highest intensity of the combustion process of ESC films is achieved at the content of 5% (mass) of graphene in the composite.

3. The process of film combustion is accompanied in some cases by the appearance of a zone of secondary flame and the emission of white smoke and fades without exposure to the laser beam, which is probably due to the self-extinction of the used fluorocarbon rubber SKF-32.

4. Laser and electron-beam methods of ESC initiation based on porous silicon have obvious prospects, so their development requires further research.

Conflict of interest

The authors declare that they have no conflict of interest.

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