Study of processes of decomposition of modified low-molecular polymer stirosil in the field of intense continuous laser radiation

A E Zaponov¹, M V Sakharov¹ and Z S Tsibikov²
¹ Military Academy of Strategic Rocket Troops after Peter the Great, Kitaygorodskiy 9, Moscow 109074, Russia
² Federal State Unitary Enterprise “Russian Federal Nuclear Center—All-Russian Research Institute of Experimental Physics”, Mira Avenue 37, Sarov, Nizhniy Novgorod Region 607188, Russia
E-mail: nopaz@mail.ru

Abstract. This article covers the theoretical and experimental studies of the processes of modified low-molecular polymer (MLP) stirosil decomposition in the field of intense continuous laser radiation. The mass loss rate of the MLP per unit surface area as a function of average laser radiation power density in the exposure area was obtained, as well as the polymer decomposition depth as a function of laser radiation power density under fixed duration of the laser exposure. To describe the decomposition processes, the calculation model of continuous laser radiation effect on the MLP stirosil was developed and verified with the use of obtained experimental data.

1. Introduction
At present, technologies of laser processing for various materials [1–4] are widespread. The laser operation regime intended for the laser cutting can differ depending on the processed material. Currently the fiber lasers of 1.07 μm operating wavelength and the output up to several tens of kW are usually used for the laser cutting. The fireproof material layer over the pressure shell makes laser cutting of the constructional materials difficult. The MLP stirosil is often utilized as a binder in the given coatings. Thus, the important problem is to determine the reasonable regimes for the laser cutting of the constructional materials covered with the MLP stirosil. The goals of the work were to determine the reasonable regimes for laser cutting of the constructional materials, covered with the MLP stirosil, by continuous laser radiation with 1.07 μm wavelength resulting in various damages of MLP stirosil, and to develop and verify the calculation model of the continuous laser radiation effect on the MLP stirosil. In order to achieve the above goals, the following theoretical and experimental studies were carried out:

(i) the experimental studies of continuous laser radiation effect on the MLP stirosil;
(ii) the development of the calculation model for continuous laser radiation effect on the MLP stirosil;
(iii) the verification of the calculation model for continuous laser radiation effect on the MLP stirosil.
2. The experimental facility

The experiments were carried out with the use of fiber ytterbium laser LK-1000-OM with the power to 1 kW and wavelength $\lambda = 1.07 \, \mu m$. The optical arrangement is shown in figure 1. The scheme adjustment was realized by the radiation of a pilot laser built in the fiber laser. The laser radiation power was measured before the starts in the plane of a specimen. For this purpose the input power of laser beam in the specimen was measured using the Ophir FL 400-A-BB-50 transformer connected to the power meter Ophir-Pulsar-2. The fluctuation of the output power values during the adjusting starts was not more than 1%. The optical line length was less than 5 m and the laser radiation power loss was negligible.

The average laser radiation power density on the specimen was determined at the level of 0.9:

$$ q_{av} = \frac{P}{S}, $$

where $P$ is laser radiation power on the sample at the level of 0.9; $S$ is the laser radiation spot area corresponding to the power level of 0.9.

To determine $S$ before the starts, the Spiricon SP620U analyzer of the beam profile was set in the attaching point of the irradiated sample. The beam profile was registered at the laser radiation power of $P = 250 \, W$ in the specimen plane. The spatial profiles of the beam are shown in figure 2. The laser radiation energy in the spot was distributed in accordance with the Gaussian law and was approximated by the formula

$$ q(r) = -P \frac{\exp[\ln(0.1) r^2 / r_n^2]}{\pi r_n^2 / \ln(0.1)}, $$

where $r_n$ is radius of the laser radiation spot in the specimen plane; $r$ is distance from the center of the laser radiation spot to the current point.

The CaF$_2$ lens with focal distances of 500 mm was utilized to form the laser beam spot with $S = 1-8 \, cm^2$ on the specimen. The cylindrical MLP stirosil specimens 5 mm thick and with a radius of 5–15 mm were used as test objects.

The specimen mass in the process of exposure to laser radiation was measured in the experiments. To do this, the specimens were weighed with the analytical balance connected to the computer. The balance values with the frequency from 1 to 10 Hz depending on the
Figure 2. Spatial profile of the laser beam at $q_{av} = 250$ W/cm$^2$: (a) laser radiation energy distribution in the specimen plane; (b) the plot of the laser radiation power density distribution in the exposure area.

specimen mass loss rate were sent to the computer. The obtained data were further used to graph the specimen mass loss as a function of laser radiation exposure duration.

3. The analysis of experimental data of continuous laser radiation effect on the MLP stirosil

The experimental data on the MLP stirosil exposure to continuous laser radiation are presented in table 1.

The following symbols are used in table 1: $S$ is the spot area at 0.9 level of laser radiation; $q_{av}$ is the average power density of laser radiation in the spot; $t$ is exposure time.

In order to determine the threshold power density of laser radiation which results in characteristic damage of MLP stirosil, the samples were cut crosswise along the exposure axis and were recorded by a digital microscope. Then the images were processed by the image file analysis program in order to determine the damage area size. After this the laser radiation power density distribution plot from (3) was put over the damage area image. Figure 3 shows the image of a crater formed in the MLP stirosil specimen after exposure to laser radiation with $q_{av} = 700$ W/cm$^2$ at the exposure time $t = 5$ s, and the plot of the power density distribution in the exposure zone put over the image.

The analysis of the images provided the estimated values for the laser-radiation-threshold power density in the exposure area: the start of physical and chemical transformations of the specimen (binder pyrolysis with carbon formation) was observed at $q_{pcf} \approx 500$ W/cm$^2$; at $q_{crl} \approx 1100$ W/cm$^2$ the carbon residue loss started. The obtained experimental data were used to plot the MLP stirosil mass loss rate per unit area as a function of power density of laser radiation the specimens were exposed to (figure 4).

In experiment 22 with longer exposure of the specimen to less intensive laser beam the carbon residue for the MLP stirosil $k$ was determined. The initial mass of the specimen was $m_0 = 2.286$ g, and it was $m_1 = 1.246$ g at the total decomposition of the material. The carbon residue for this material was:

$$k = m_1/m_0.$$  

Hence, in the experiments the dependences of the MLP stirosil mass loss rate on the power density of the laser beam irradiating the specimens were obtained. The experimental results on decomposition depth and mass loss in the test specimens were then used for a determination
Table 1. The experimental data on MLP stirosil exposure to continuous laser radiation.

| Experiment | Specimen | $S$, cm$^2$ | $q_{av}$, W/cm$^2$ | $t$, s |
|------------|----------|-------------|-------------------|--------|
| 1          | 1        | 0.9         | 1000              | 5      |
| 2          | 2        | 0.9         | 1000              | 5      |
| 3          | 3        | 0.9         | 900               | 5      |
| 4          | 3        | 0.9         | 900               | 5      |
| 5          | 4        | 0.9         | 900               | 5      |
| 6          | 5        | 0.9         | 800               | 5      |
| 7          | 6        | 0.9         | 800               | 5      |
| 8          | 7        | 4.9         | 200               | 5      |
| 9          | 8        | 4.9         | 200               | 5      |
| 10         | 9        | 6.6         | 150               | 5      |
| 11         | 10       | 6.6         | 100               | 5      |
| 12         | 11       | 3.1         | 300               | 5      |
| 13         | 12       | 3.1         | 300               | 5      |
| 14         | 13       | 1.3         | 700               | 5      |
| 15         | 14       | 1.3         | 700               | 5      |
| 16         | 15       | 1.3         | 600               | 5      |
| 17         | 16       | 1.3         | 600               | 5      |
| 18         | 17       | 2.0         | 500               | 5      |
| 19         | 18       | 2.0         | 500               | 5      |
| 20         | 19       | 2.0         | 400               | 5      |
| 21         | 20       | 2.0         | 400               | 5      |
| 22         | 21       | 8.0         | 50                | 200    |

Figure 3. The image of a crater formed in the MLP stirosil specimen after exposure to laser radiation with $q_{av} = 700$ W/cm$^2$ at the exposure time $t = 5$ s overlaid with the plot of power density distribution in the exposure area.
of the chemical reactions constants depending on the heating rate and for making a calculation model of continuous laser radiation on the MLP stirosil.

4. The calculation model of continuous laser radiation effect on the MLP stirosil

The calculation model of continuous laser radiation effect on the MLP stirosil is used for a description of laser radiation thermal effect on the MLP stirosil. This model is based on the known equations of conservation in multicomponent media [5]. The following processes are taken into account in the model: the volume absorption of the composite; the binder pyrolysis; the convective cooling with gaseous products of pyrolysis of the material surface layers; the chemical reaction between the glass filler and the carbon residue; the radiative heat conductivity; the laser radiation absorption in material thermodestruction products; the thermal characteristics of the material as a function of temperature and heating rate.

The composite heating by the laser radiation, including all the processes mentioned, is described with the nonstationary thermal conductivity equation:

\[
\rho(T, n_i)c(T, n_i) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda(T, n_i) \frac{\partial T}{\partial x} - c_g G(T) T \right) + W_{\text{chem}}(T) + W_{\text{LR}}(T),
\]

(4)

where \(\rho(T, n_i)\), \(c(t, n_i)\), \(\lambda(T, n_i)\) are density, heat capacity and thermal conductivity of the material respectively; \(n_i\) is mass fraction of carbon, filler and binder; index \(i\) corresponds to name of material (carbon, filler or binder); \(c_g\) is gas heat capacity; \(G(T)\) is consumption of the gaseous products of thermal decomposition; \(W_{\text{chem}}(T)\) is the energy consumed for the chemical reactions; \(W_{\text{LR}}(T)\) is the absorbed laser radiation energy determined by the Bouguer law considering the radiation reflection and absorption in the products of thermal destruction of the material:

\[
W_{\text{LR}}(T) = q_0[1 - R(T)][1 - \Theta(T)] \exp \left( -\frac{x}{\delta} \right),
\]

(5)

where \(q_0\) is power density of incident laser radiation; \(R(T)\) is the coefficient of laser radiation reflection from the material surface; \(\Theta(T)\) is the coefficient taking into account the attenuation of laser radiation in the products of thermal destruction of the composite and depending on the mass loss rate of the material; \(\delta\) is the depth of laser radiation penetration.

The thermal conductivity factor \(\lambda(T, n_i)\) in (4) is a function of temperature and of material composition changing during the chemical reactions. At high temperatures it is necessary to consider not only the variation of the rigid structure thermal conductivity with temperature but also the heat transport by the radiation [6]. Here, the effective heat conductivity factor \(\lambda(T, n_i)\) is the sum of the heat conductivity factor \(\lambda_H(T, n_i)\) and of the radiative heat conductivity factor \(\lambda_R(T, n_i)\) [5]:

\[
\lambda(T, n_i) = [1 - \Pi(T)] \lambda_H(T, n_i) + \Pi(T) \lambda_R(T, n_i),
\]

(6)
Figure 5. Stirosil mass loss rate per unit area as a function of the average laser radiation power density in the exposure spot.

Figure 6. Stirosil decomposition depth as a function of the laser radiation power density at the irradiation duration of 5 s.

where \( \Pi(T) \) is the material porosity; \( \lambda_R = 2\varepsilon^2\sigma T^3h \); \( \varepsilon \) is emissivity factor; \( \sigma \) is Stefan-Boltzmann constant; \( h \) typical pore size [7, 8].

Gaseous products consumption \( G(T) \) is determined from the continuity equation in accordance with the generally accepted assumptions: [9]

\[
\frac{\partial}{\partial t} (\Pi(T) \rho_g \nu_k) + \frac{\partial}{\partial x} (\Pi(T) \rho_g \nu_k) = -\frac{\partial}{\partial x} (\Pi(T) j_g(T)) + \omega_g(T),
\]

where \( j_g(T) \) is diffusion gas flux; \( \omega_g(T) \) is mass rate of the chemical components formation as a result of reactions per unit volume of the porous medium.

The first assumption in the model is that flow resistance of the porous structure and the possibility of gas accumulation inside the pores are neglected:

\[
\frac{\partial}{\partial t} (\Pi(T) \rho_g) = 0.
\]

The second assumption is that the diffusion process is not taken into account because the diffusion flux rate is significantly smaller than the gas rate in direction towards the external surface.

Taking into account the accepted assumptions and the expression \( \omega_g(T) = \frac{\partial \rho_g}{\partial t} \), and by integrating (7) we get:

\[
G(T) = \Pi(T) \rho_g \nu_k = -\int_L^x \frac{\partial \rho_g}{\partial x} dx.
\]

The change in the density of decomposing substance with regard for pyrolysis and chemical reactions, used in the calculation model, is described by the equation:

\[
\frac{\partial \rho}{\partial t} = (\rho_k - \rho) B \exp \left( \frac{E_a}{RT} \right).
\]

5. The results of calculations and verification of the calculation model of continuous laser radiation effect on the MLP stirosil

For calculations to be automated with the use of the developed calculation model of continuous laser radiation effect on the MLP stirosil, the model software support with the high-level programming language C++ was carried out. As a result of the calculations the dependences of the MLP stirosil mass loss and of the material decomposition depth on the laser radiation power density were obtained. Figure 5 shows the plot of the MLP stirosil mass loss rate per unit area as a function of the average laser radiation power density in the exposure spot.

From figure 5 it follows that the MLP stirosil mass loss rate per unit area under continuous laser radiation effect increases with the rise of the laser radiation power density. However, it was also discovered that the increase of the rate of sample mass loss velocity decreased at further growth of the laser radiation power density.
In figure 6 one can see the plot of the MLP stirosil decomposition depth as a function of laser radiation power density at the irradiation duration of 5 s, and the overlaid experimental data obtained earlier.

From figure 6 it follows that the most reasonable laser cutting regime for the constructional materials covered with the MLP stirosil without the carbon residue loss is the regime of effect by the laser radiation with \( q = 800 \text{ W/cm}^2 \); this regime provides the maximum depth of MLP stirosil decomposition.

The analysis of adequacy of the developed calculation model for continuous laser radiation effect on the MLP stirosil was conducted. The satisfactory agreement between the experimental and the theoretical results was obtained. The maximum relative error of the MLP stirosil mass loss rate per unit area as a function of average radiation power density in the spot and of the decomposition depth as a function of radiation power density at the exposure duration of 5 s does not exceed 10\%. Thus, the developed calculation model of the continuous laser radiation effect on the MLP stirosil makes it possible to predict adequately the MLP stirosil decomposition during its heating by the laser radiation at the power densities that prevent the carbon residue loss.

6. Conclusion
The paper defines and solves the scientific problem of the theoretical and experimental studies of the MLP stirosil decomposition in the continuous laser radiation field. The dependences of the MLP stirosil mass loss rate on the laser radiation power densities affecting the specimens were obtained. The obtained experimental data on the decomposition depth and on the test specimen mass loss were then used for the determination of the chemical reactions constants depending on the heating rate and for making the calculation model of continuous laser radiation effect on the MLP stirosil. The calculation model of continuous laser radiation effect on the MLP stirosil was developed and verified. The experimental and the theoretical results agreed adequately. It was determined that the most reasonable regime of laser cutting of the constructional materials covered with the MLP stirosil without the carbon residue loss was the regime of the laser radiation effect with \( \lambda = 1.07 \mu\text{m} \) and \( q = 800 \text{ W/cm}^2 \).

Further research will be aimed at an improvement of the calculation model for continuous laser radiation effect on the MLP stirosil. It will allow predicting adequately the MLP stirosil decomposition at the power densities preventing the carbon residue loss.

References
[1] Krasyuk I K, Pashinin P P, Semenov A Yu, Khishchenko K V and Fortov V E 2016 Laser Phys. 26 094001
[2] Abrosimov S A, Bazhulin A P, Voronov V V, Geras'kin A A, Krasyuk I K, Pashinin P P, Semenov A Yu, Stuchebryukhov I A, Khishchenko K V and Fortov V E 2013 Quantum Electron. 43 246–51
[3] Abrosimov S A, Bazhulin A P, Voronov V V, Krasyuk I K, Pashinin P P, Semenov A Yu, Stuchebryukhov I A and Khishchenko K V 2012 Dokl. Phys. 57 64–6
[4] Geras'kin A A, Khishchenko K V, Krasyuk I K, Pashinin P P, Semenov A Yu, Stuchebryukhov I A and Khishchenko K V 2012 Contrib. Plasma Phys. 49 451–4
[5] Zakharov N S, Urlin V D and Shentsev N I 2004 Thermal, Hydrodynamic and Plasma Effects at Laser Radiation Interaction with Substance (Sarov: FSUE RFNC-VNIIEF)
[6] Schornhorst J R and Viskanta R 1968 AIAA J. 6 1450–5
[7] Polezhaev Y V and Yurevich F B 1976 Heat Protection (Moscow: Energy)
[8] Paderin L Ya, Prosuntsov P V, Reznik S V and Fisher V P P 2005 J. Eng. Phys. Thermophys. 78 60–7
[9] Pankratov B M, Polezhaev Y V and Rudko A K 1975 The Material and Gas Flow Interaction (Moscow: Engineering)