THERMALLY AND CHEMICALLY ACTIVATED CARBON

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Introduction

The thermally and chemically activated graphite foil (GF) samples were obtained from thermally expanded graphite (TEG) preliminary treated by an oxidative agent. Due to the presence of nonequilibrium defects, the GF structure is metastable; therefore, the heats of laser-induced phase transitions in GF can differ from similar characteristics for crystalline or even polycrystalline graphite samples. Total energies of nonequilibrium defects of crystalline structure were determined by laser ablation of these samples.

Experimental

The GF samples with densities of 0.5 g/cm^3 (nos.1-3) and 0.7 g/cm^3 (nos.4-5) obtained by rolling (without binders) of TEG that was prepared by thermal treatment of hydrolysed intercalated graphite compounds with sulfuric acid at 1200-1300 K were examined. The GF samples with different concentrations of nonequilibrium defects were obtained by variations in the conditions of the synthesis of graphite bisulfate and the temperature of the thermal treatment. The previously studied sample of polycrystalline graphite (PCG, 1.7 g/cm^3) was chosen as reference sample no.6.

GF samples were vaporised in air by focused radiation of the second harmonic of an Nd:YAG laser [wavelength 532 nm, pulse energy 5 mJ, pulse width (FWHM) 25 ns and pulse repetition rate 12.5 Hz] at the laser power density range Io=0.01-3 GW/cm^2. The specific depth of a crater $X_R = X*R/Io$ [$\mu m*cm^2/GW$] per laser pulse (Fig.1, left), which takes into account the difference in the densities of various graphite samples (R is the ratio of the sample density to the density of crystalline graphite 2.2 g/cm^3), was considered as the efficiency of the degradation at different Io values. Using time-of-flight mass spectroscopy, we obtained other characteristics of the degradation of graphite materials, viz., temperatures of the substance in the region of the hot core and in the expansion zone of the laser plasma (Fig.2). These values were determined by Saha equation from the ratio of intensities of multiply charged atomic carbon ions (up to triply charged) and from the expression for the half-width of the Maxwell distribution of velocities for the laser plasma particles, respectively.

Results and Discussion

The experimental dependencies of X_R on Io (Fig.1, left) show that there are two characteristic ranges of Io in which the behavior of the graphite materials is fundamentally different. At Io>1 GW/cm^2, the degradation proceeds similarly for all of the graphite materials: the efficiency of degradation X_R decreases gradually. Judging from the increase in the maximum plume temperature in the hot core and expansion zone (Fig.2), this is due to substantial absorption of radiation by the degradation products and screening of the target. By contrast, in the region of moderate values Io<1 GW/cm^2, differences in the properties of the test materials appear (Fig.1,2). Therefore, at the Io range 0.1-1 GW/cm^2 differences in the efficiency of degradation likely appear during the formation of the final (before degradation) state of carbon rather than at the stage of removal (due to plasma formation and screening of the target surface).

All test graphite samples can be subdivided into two groups by the efficiency of degradation X_R. The group with higher efficiency of degradation contains the GF sample nos. 4,5 (0.7 g/cm^3) and 3 (0.5 g/cm^3) with high defect concentrations. The second group with low efficiency consists of the low-defect GF sample nos. 1 and 2 with a bulk density of 0.5 g/cm^3 as well as PCG sample. The comparison of the GF sample nos. 1-3 with the same density and different defect concentrations shows that it is the latter factor that plays the determining role in the laser-induced degradation of these materials.

Since the mechanism of substance removal under the action of pulsed laser radiation on GF samples was not known beforehand, we considered the overall process as sample degradation taking into account the entire set of related processes (heating, melting, evaporation, vapor absorption, *etc.*). For the PCG sample the degradation energy Ed is as high as $6*10^5$ J/mole in the Io range 0.1-0.3 GW/cm^2 due to heating, melting and evaporation of liquid carbon surface layer ($\Delta H(liq.,P,T) \approx (2.0-2.5)*10^5$ J/mole [1], $\Delta_{ev}H(liq.,P,T) \approx 3.6*10^5$ J/mole [2]) under temperatures $T \geq 4*10^3$ K (Fig.2). This value decreases to $\Delta H(liq.,P,T)$ at Io$\geq$0.3 GW/cm^2 when the hydrodynamic removal of a vapor-liquid mixture occurs in the surface vaporization of the PCG sample due to the spinodal decomposition of the labile liquid carbon phase [3].

Then assuming the steady-state laser vaporization process (i.e. crater depth per pulse for the GF samples is much larger than that one for the PCG) we can evaluate the degradation energies for the GF samples (Fig.1, right) using the equation

$$Ed = 6*10^5 (J/mole) * \frac{X_R(PCG, 0.1-0.3GW/cm^2)}{X_R(Io)},$$

where $6*10^5$ J/mole and $X_R(PCG, 0.1-0.3 \text{ GW/cm}^2)$ are the degradation energy and the corresponding degradation efficiency for the PCG sample.

It has been shown that the degradation of the low-density high-defect GF sample no. 5 proceeds via hydrodynamic removal of the substance (carbon in the labile or supercritical state) from the laser-heated surface layer of the target [4] as well as in the case of the PCG sample. This is the case even for the low-defect low-density GF sample no.1 (Fig.2) because the internal laser evaporation into pores is the peculiar property of low-density materials. Therefore the calculated Ed values of the GF samples correspond to the difference between the minimal Ed value for the PCG sample at the Io 0.4-0.5 GW/cm^2 ($2.0\pm0.3*10^5$ J/mole) and the total energy of nonequilibrium defects of these samples supposing the negligible total energy of structural nonequilibrium defects for the PCG. Characteristic values of the total energy of nonequilibrium defects for the GF samples nos.1 and 2 (overoxidative treatment for 3 and 6 hours) are close to that one of the PCG (Fig.1, right). On opposite the total energies of nonequilibrium defects for the GF samples nos.3, 4 and 5 (overoxidative treatment for 12 and 24 hours) are equal to $1.7\pm0.3*10^5$ J/mole.

Thus we have prepared the thermally and chemically activated carbon samples and evaluated their total energies of nonequilibrium defects using the developed laser vaporization technique.

References

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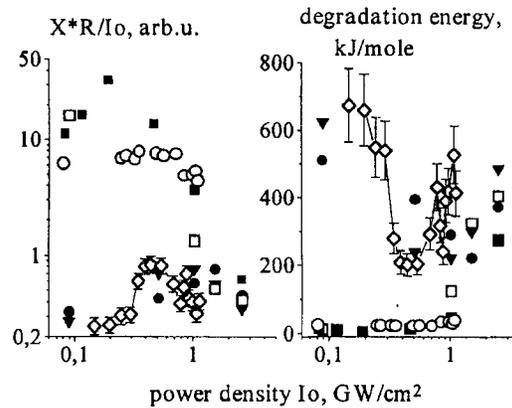
Fig.1. Dependence of the specific depth of a crater (degradation efficiency) X*R/Io (left) and degradation energy Ed (right) on the laser power density Io for graphite samples nos.1 (dark down triangles), 2 (dark circles), 3 (open squares), 4 (dark squares), 5 (open circles) and 6 (open diamonds).
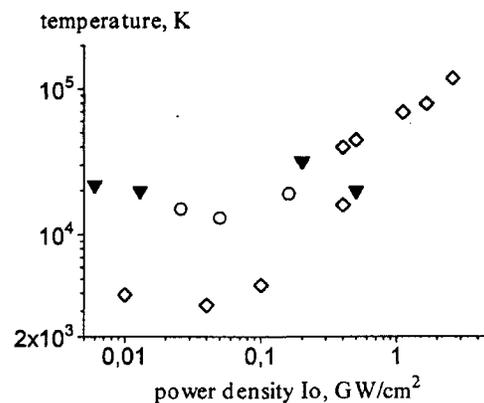

Fig.2. Maximal temperature of laser plasma particles versus the laser power density Io for the GF samples nos.1 (dark down triangles) and 5 (open circles) and a PCG sample (open diamonds).

673