Graphite Surface Microhardening with Femtosecond Laser Pulses

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Abstract—The effects of direct femtosecond laser processing of a polycrystalline graphite surface are experimentally investigated. The functional graphite surfaces are fabricated at laser intensity of ~10^17 W/cm^2 in vacuum and then thoroughly analyzed by means of Raman spectroscopy and nanoindentation test. The measured Raman spectra at 257 nm show presence of an amorphous carbon phase containing sp^3 hybridized carbon atoms and a discontinuous nanocrystalline diamond film, while the results of microhardness measurements demonstrate a sixteen-fold increase in microhardness as compared to the unirradiated graphite surface. The modulus of elasticity is found to increase nearly by 3.4 times.

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INTRODUCTION

Surface engineering underpins major industry sectors including aerospace, automotive, construction, power generation, and it is crucial to many biomedical applications. Various engineering problems, concerned with protection against wear damage, corrosion or high temperatures, can be solved by depositing of appropriate coatings and hardening of near-surface layers [1, 2]. Laser peening with nanosecond pulses has been used to improve the mechanical performance of metals (mostly Al and Ti alloys [3–6]) including the resistance of aircraft gas turbine engine compressor blades to foreign object damage, cycle fatigue life of automotive rings and pinion gears [6]. The plastic deformation caused by the propagating shock wave results in a significant increase in dislocation density and in a reduction of grain size that contribute to hardening of metal surfaces and generation of compressive residual stresses. A great number of similar studies is carried out with femtosecond pulses as they have the potential to generate a stronger shock wave in a target material due to high laser intensities [3]. A femtosecond laser-induced ultrashort shock pulse has been found to generate a highly dense dislocation structure in iron [6] and silicon [7] resulting in a six-fold increase in microhardness. Nowadays, more interest is paid to synthesis of diamond-like phases from graphite [9, 10] and investigation of the physical processes obtained [11].

Diamond-like carbon (DLC) films (an amorphous carbon a-C and a tetrahedral amorphous carbon ta-C with a significant fraction of sp^3 bonds) due to its high mechanical hardness, chemical inertness, and optical transparency have wide applications as protective coatings for optical windows, magnetic storage disks, car parts, and biomedical devices [12, 13]. Coating the implants and prostheses (hip and knee joints) with protective biocompatible DLC films may significantly reduce the problems concerned with the wear, corrosion, and biological reactions with the tissue and thus extend the lifetime of the implants [14]. Recently, a strong effort has been made to intentionally grow nanocrystalline diamond or nanodiamond, because smaller grains impart to the films valuable tribological, mechanical, and electrochemical properties [15, 16]. Various synthesis techniques have been developed including detonation synthesis, chemical vapor deposition, and laser-assisted methods.

The synthesis of diamond-like phases under irradiation of graphite with femtosecond laser pulses of various intensity and in different environments was reported in many works [17–27]. Micro- and nanostructures (0.3–5 μm) of DLC and diamond have been produced by pulsed ablation with 0.1–1 KHz repetition rate of graphite target in water [20]. Amorphous-to-crystalline phase transition in a-C has been found under intense femtosecond x-ray laser pulses. At low fluence, the initial sp^2 bonded atoms start to form in-plane graphite nanocrystals, which become larger with increasing fluence [22]. By exposing a polycrystalline graphite to laser irradiation at intensity of ~10^14 W/cm^2 in air, the translucent micrometer-sized structures carrying diamond-like and onion-like carbon phases have been found in [27]. However, the most of studies are related to laser excitation of highly oriented pyrolytic graphite (HOPG). A novel structure of sp^3 bonded carbon nanodomains that differs from thermodynamically formed conventional diamond has been observed at intensity of ~10^11 W/cm^2 in [26]. Hexagonal diamond (a metastable high-pressure...
phase of carbon) has been directly synthesized from HOPG under irradiation of basal plane in air at intensity of $\sim 10^{15} \text{ W/cm}^2$. The femtosecond laser-driven shock wave of 100–300 GPa has been proposed to induce the graphite-hexagonal diamond transformation [21]. The $sp$ bonded carbon chains (carbine) and nanodiamonds [25], nanoscale cubic diamond crystals [24] and structural transformation of HOPG into nanocrystalline graphite [27] have been also observed.

However, the data on microhardness of synthesized diamond phase are almost entirely lacking. In this study, the effects of graphite-to-diamond phase transition under the action of intense femtosecond laser pulses on the microhardness and chemical composition of a polycrystalline graphite surface were experimentally investigated by means of nanoindentation tests and Raman spectroscopy.

**EXPERIMENTS**

For the experiments, a polycrystalline graphite sample of $5 \times 8 \text{ mm}^2$ with a thickness of 2 mm was cut with a diamond saw. The functional graphite surfaces were fabricated via the direct femtosecond laser surface processing in vacuum at $2.8 \times 10^{-4} \text{ mbar}$ (Fig. 1). The laser was an amplified Ti:sapphire laser system (Coherent, USA), which generates laser pulses of 40-fs duration at a central wave length of 800 nm with a maximum pulse energy of 1.5 mJ and at maximum repetition rate of 1 kHz. The laser pulse energy was controlled through a combination of a half-wave plate and a Glan prism and was measured by means of a calibrated photodiode. The Gaussian laser beam was focused by an off-axis parabola onto a sample at an angle of 45° ($p$ polarized) with respect to the surface normal to a spot of 5.5 μm diameter at a level of 1/e.

The estimation of the incident laser intensity (on the assumption that the focal spot contains $\sim 70\%$ of laser pulse energy) was $\sim 10^{17} \text{ W/cm}^2$. The sample was mounted on a three-axis computer-controlled translation stage and translated through the laser beam in a raster scanning mode. The sample surface was monitored with an imaging system coupled to a CCD. The effective number of laser pulses incident on the sample was 10. It was controlled by varying a repetition rate via a pulse picker device (Avesta, Russia) and by changing a translation speed of the sample. At higher numbers of laser pulses due to effective ablation a deep microgroove is formed that prevents the nanoindentation test to be properly carried out. A Mylar film of 20-μm thickness shielded the parabolic mirror from the debris produced by the interaction of intense laser pulses with the sample. The laser pulse contrast ratio over a nanosecond temporal range (controlled by an electro-optical shutter) was $\sim 10^{-8}$ and over a picosecond temporal range was $10^{-5}$.

The surface morphology of modified graphite surfaces was studied via optical microscopy (OM) and scanning electron microscopy (SEM). The microhardness and the modulus of elasticity were measured by nanoindentation according to ISO 14577. Chemical composition was characterized by Raman spectroscopy at excitation wave length of 257 nm.

**RESULTS AND DISCUSSION**

The SEM and OM images of a polycrystalline graphite surface (edge plane) irradiated in a raster scanning mode with femtosecond laser pulses at intensity of $\sim 10^{17} \text{ W/cm}^2$ in vacuum are presented in Fig. 2. According to the OM image (Fig. 2d), the reflectance of modified zone in the visible wave lengths is qualitatively much bigger than for the original graphite surface that appears pitch black. The SEM images demonstrate a relatively smooth surface textured with laser-induced periodic surface structures of about 300–500 nm in period (Fig. 2c), covered with nanoparticles of 30–60 nm in diameter (Fig. 2f). These observations could indicate the melting of graphite after laser excitation with the subsequent re-solidification and the formation of the textured surface [18].

The Raman spectra of the original and laser-processed graphite surfaces are shown in Fig. 3. Before laser irradiation the graphite surface has the G-peak at 1580 cm$^{-1}$ with a width of 27 cm$^{-1}$ (at FWHM) and is due to $sp^2$ (graphite-like) bonds. After laser processing the average G-peak position shifts to 1589 cm$^{-1}$ that corresponds to the increase in concentration of $sp^3$ bonds [28]. On the other hand, the G-peak full width at half maximum is a measure of disorder and as it increases to 58 cm$^{-1}$, it can be associated with surface amorphization [29]. The observed peak at 1314 cm$^{-1}$ could be attributed to shift of a peak at 1332 cm$^{-1}$[30] and could indicate the presence of nanocrystalline...