Surface reinforcement of metals by carbon nanomaterials followed by high intense energy irradiation

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Abstract

The metal surface modification by carbon nanostructures followed by high intense treatment has been realized. As carbon nanostructures were used: carbon soot formed in an arc discharge with graphite electrodes remained after extraction of fullerenes; fullerene C_{60}; partially reduced graphene oxide. An intense pulsed laser and electron beam accelerator were used as high intense energy sources. Measurements performed indicate that the above described processing of the steel surface results in a considerable enhancement of the microhardness (up to 800%) and a notable decrease (up to 50%) in the friction coefficient. The degree of reinforcement depends on both the type of nanocarbon and the source of energy. The maximum effect of reinforcement is reached for fullerene C_{60} coverage and laser irradiation. The dependence of the microhardness of the treated surface on the irradiation energy has a non-monotone character reaching the maximum value of about 200 J/cm^2 at the laser irradiation and 400 J/cm^2 at the e-beam irradiation. Copyright © 2018 VBRI Press.

Keywords: Metal surface reinforcement, carbon nanostructures, fullerenes.

Introduction

Elaboration of metallic materials with improved mechanical properties allows a considerable reduction of the specific quantity of metal and to ensure the resource saving. In recent years, much attention has been paid to the development of surface reinforcement technologies, since the surface condition namely determines the level of the strength and operational properties of machine parts and tools. Enhancement of physico-mechanical and operational properties of products can be achieved through the purposeful creation of modified layers on the steel surface by the alloying with the various elements or their compositions using laser or electron beam heating [1]. This offers a possibility of contactless, fast, and strictly metered transfer energy to the treated surface of metal. The hardness and wear resistance of steels, especially containing the carbide, nitride, or boride phases are significantly improved after high intense energy treatment. Such an approach does not cause the deformation of the products, which shortens the technological process, since it is not necessary to finish the metal products.

At present, this method of the surface reinforcement of steels is used mainly for parts operating under the conditions of the wear and contact loads. Laser and e-beam technologies of surface reinforcement have the limited application during the cyclic loading of parts. This can be explained by the features of treating metals with highly concentrated energy sources when a significant temperature gradient arises at the boundary of the base metal and melted zone, which is accompanied by the appearance of tensile stresses and, as consequence, this tendency leads to cracking [2]. This drawback is eliminated by heating, but meanwhile, the level of metal strengthening achieved during the high energy treatment is significantly reduced. In this regard, the search for the new approaches to the surface strengthening of steels using the laser energy is topical.

The possibility of creating a new class of the strengthening coatings appeared in connection with the discovery of nanocarbon materials (NCMs) like fullerene, graphene, carbon nanotubes, and so on [3–6]. The present research has been stimulated by the results of metallographic studies of Damascus steel using a high-resolution electronic microscope [7]. Multilayer carbon nanotubes with a diameter of 5 nm filled with cementite of high hardness were found in the structure of this steel. The authors [7] explained the effect of the surface strengthening of steel by the formation of iron carbide with a specific modification at the interfaces between the various structural components.

It is naturally to believe that the effect of reinforcement of Damascus steel can be reproduced combining NCM coverage with thermal processing of a steel surface by the use of high intense energy treatment. This was demonstrated in recent works[8, 9] where the dependences of the microhardness of nanocardon-coated steel surface on the laser and e-beam irradiation energy were measured. In the present article these dependences compared with those obtained for fullerene C_{60} and partially reduced graphene oxide coverage. Besides of that the results of tribology tests of steel surface covered with nanocarbon and treated by laser and e-beam irradiation are compared and discussed.

Experimental

Samples to be treated. Samples fabricated made of technically pure low-carbon steel with a size of 3 × 15 × 50 mm^3 were used to study the surface reinforcement effect. The initial microhardness of non-treated steel samples accounts about 150 HV. The elemental analysis of the initial steel samples indicates the presence of C(0.017 wt. %), Si (0.087%), Mn (0.39 %), Ni (0.011 %), Cr (0.025 %) and Cu (0.035 %).

Nanocarbon coating. Nanostructured carbon soot was produced in an arc discharge with graphite electrodes in a He atmosphere. The powder remained after extraction of fullerenes by standard procedure had the specific surface area of 233 ± 4 m^2/g, according the measurement by the BET method. This corresponds to an average size of flakes of about 5 nm. The soot was carefully refined in a mortar using a pestle, then mixed with benzene to a state of homogeneous suspension in a ratio of 100:1 (by weight). The samples to be treated were immersed into the suspension and dried in air at 50°C for a day; then, in order to improve the adhesion, the samples were annealed in a furnace in a weak stream of argon (up to 100 cm^3/min) at 600°C for 20 min. The mass of the formed coating was about 16 mg and its thickness was 20 μm, which corresponds to a coating density of about 1 g/cm^3.

Fullerene coating. Fullerene C_{60} of 99.8% in purity was purchased at the Company STS Ltd (S-Petersburg). The solution of fullerene in o-xylene (≈ 14 g/l) was applied onto a steel pad layer by layer. The samples were dried and weighted after each layer application procedure. Application of a layer results in a change of the sample mass about 0.4 mg. There have been prepared four samples differed by the mass of fullerene coverage and the degree of overlapping laser trenches Two laser trenches with 40% and 50% overlapping were made on the sample No. 1 that had one layer coating. The samples No. 2 and 3 were coated with 3 and 4 fullerene C_{60} layers correspondingly. The sample No. 4 had areas with different numbers of fullerene layers (from 1 to 7).

Reduced graphene oxide coating. Graphene oxide utilized as an initial material has been produced by the standard Hummers method [10]. Paper-like sheets of graphene oxide of 40 – 60 μm thick were about 1.2 g/cm^3 in density which is about twice lower than that of crystalline graphite (2.25 g/cm^3). The sheets were cut onto rectangular fragments of 10 – 15 mm in width and 15 – 25 mm in length and were treated in a high temperature furnace PlanarGROW-2S (PlanarTech Company) at a slow Ar flow (50 cm^3/min sccm) at a pressure of 1 Torr. The procedure of thermal treatment of graphene oxide samples has been described in detail in Ref. [11]. Heating the samples at a rate higher than 1 ºC/s promotes an explosion-like destruction of the material. For this reason the furnace was heated from the room temperature up to 200 ºC at a rate of 1ºC/min while the rate of the subsequent heating up to the treatment temperature was about 20 ºC/min. The duration of the thermal treatment was 10 min. for all the temperatures. The sample of graphene oxide annealed at a temperature of 800 ºC was used to cover the steel surface. The conductivity of this material reached 3500 S/m, its density accounted 0.5 g/cm^3 and the content of oxygen did not exceed 5%. The reduced graphene oxide film was applied to the steel surface after which the sample was experienced to laser irradiation.

Laser irradiation. A pulsed laser setup ALFA-200C-(Laserform Company) on the basis of Nd-glass of pulse action with neodymium glass with wave length of 1064 nm, pulse energy up to 30 J and pulse duration (1 – 8) ms was used as a source of laser radiation. The laser beam was focused to the metal pad creating a spot of 3.5 mm in diameter or a groove of the same width.

Electron beam irradiation. The electron gun of an AELTK-12 setup manufactured by NITI Progress Ltd having a chamber volume of 12 m^3 and an accelerating voltage of 60 kV was employed as an electron-beam source. The beam diameter was ~0.5 mm. The treated surface was transversely scanned with an electron beam at a frequency of 1000 Hz. The electron beam was longitudinally moved at a speed of 5 cm/s. Thus, due to e-beam treatment, a groove 2.5 mm wide and 15 mm long appeared on the sample surface. At a fixed beam-scanning rate, the electron beam current can be varied in the range of 3–15 mA which corresponds to the variation of the irradiation intensity surface irradiation intensity in the range of 140–700 J/cm^2.

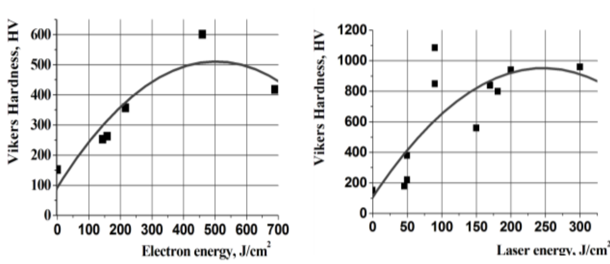
Mechanical tests. After the samples were irradiated by laser or electron beams of different intensities, their microhardness was determined via the Vickers method with the help of an Emco-Test DuraScan 20 or an automated Instron Tukon 2500 hardness tester at a load of 5 g. Besides of that, the treated samples were tribologically tested to determine changes in the friction coefficient. The tests were performed without lubrication at a temperature of 22 ± 2°C by a standard method (ball–plane method under the condition of linear reciprocal transportation of the sample with respect to an immovable body at a specified amplitude) by the use of TRB S CE 0000 (CSM Instruments SA) tribometer. The ball of 6 mm in diameter made of hard alloy based on the WC (tungsten carbides) was used as counterbody. The sample was moved relative to the fixed counterbody at a speed of

10 cm/s, at a load of 2 N, at a stroke length of 8 mm and the length of the run 300 m. Wear groove images were obtained using a Tescan MIRA 3 LMU high-resolution scanning electron microscope (SEM) with a thermal-field Schottky cathode in the reflected-electron recording mode. The wear of the sample (the coefficient of wear) was determined in the $mm^3/(H\ m)$ units using the average value of sectional area of wear track, which was evaluated by five measurements of the cross profiles of wear track *using* Dectak 150 (Veeco Instruments Inc.).

Microimages of the treated surface were obtained using a DigMicro Mobile digital microscope with a magnification of 500. The metallographic studies were performed at the cross section of the samples using optical Zeiss Observer Z1m microscope with a magnification of 1000.

Results and discussion

***Microhardness*. Fig. 1** compares the dependences of the microhardness of the nanocarbon-coated steel surface on e-beam (a) and laser (b) irradiation energy. As is seen, both the dependences have a non-monotone character reaching the maximum value at the e-beam irradiation energy of 400 J/cm^2 and laser irradiation energy of about 200 J/cm^2. Note that the maximum value of microhardness in the case of laser irradiation (950 HV) exceeds about twice that for e-beam irradiation. However the thickness of the *reinforced* layer in the case of e-beam irradiation exceeds several times that for laser irradiation.



(a) (b)

Fig. 1. Dependence of the microhardness of the steel surface with nanocarbon coating on e-beam (a) and laser (b) irradiation energy.

Fig. 2 presents the dependence of the microhardness of the steel surface with fullerene C_{60} coverage on the laser irradiation energy (a) and the number of fullerene layers (b). As is seen the dependence of the microhardness on the laser energy has again a non-monotone character with maximum at about 150 J/cm^2. The microhardness increases linearly with the number of fullerene layers. Comparison of these data with those shown on fig.1 indicates that the maximum degree of reinforcement is reached in the case of usage of fullerene coverage combined with laser irradiation. The maximum value of the microhardness of the laser-treated surface with fullerene coverage accounts about 1200 HV which exceeds the initial value by about 8 times.

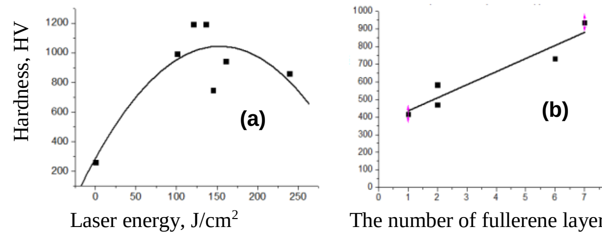
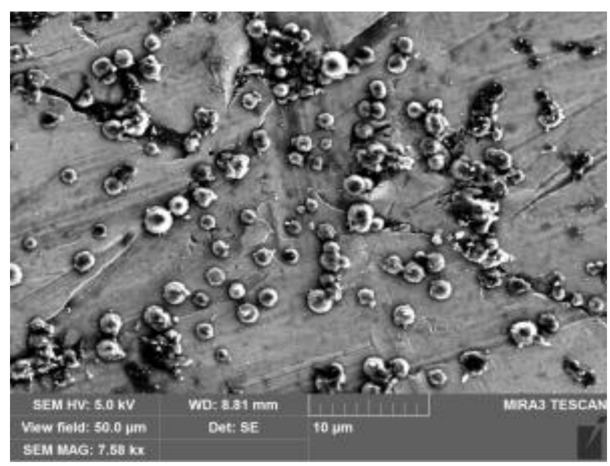
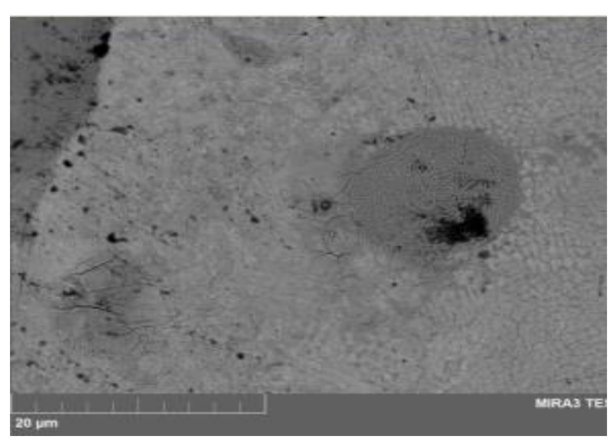


Fig. 2. (a) Dependence of the microhardness of the steel surface - coated with 7 fullerene layers on the laser energy; (b) Dependence of the microhardness of the steel surface on the number of fullerene C_{60} layers measured at a laser irradiation energy of 163 J/cm^2.

The mechanism of fullerene+laser reinforcement can be clarified on the basis of comparison of mircoimages of the surface with fullerene coverage before and after laser irradiation. These SEM microimages are presented on **Fig. 3.** As is seen, evaporation of the solvent results in formation of fullerene microcrystals of several μm in size. These microcrystals are spread randomly over the metal surface spacing up to 10 μm from each other. Laser irradiation of the surface promotes the fracture of these microcrystals and the formation of quite homogeneous film containing fragments of fullerene molecules incorporated into the steel matrix.



(a)



(b)

Fig. 3. Micromages of fullerene C_{60} coated steel surface before and after laser irradiation.

Table 1. Distribution of the microhardness of laser-treated surface over the depth of the sample with fullerene C_{60} and reduced graphene oxide coating.

Distance from the sample surface (by depth)	Microhardness, HV	
	Fullerene C_{60} coating	Reduced graphene oxide coating
5	798	379
10	485	309
20	200	236
40	207	207
60		193
80	175	171
100		155
120		147
140		146
160		139
180		123
200	187	127
400		127
1000		130

The distribution of the microhardness of laser-treated surface with a nanocarbon coverage over the depth of the sample was measured on the metallografic section that has been prepared on the samples with fullerene C_{60} and reduced graphene oxide coating. The results of measurements are given in **Table 1**. As is seen, in both cases the thickness of the reinforced film accounts about 20 µm however the degree of reinforcement for fullerene coverage exceeds by about four times that for the reduced graphene oxide coverage.

Friction and wear resistance. **Fig. 4** reports the results of tribology tests of surfaces with nanocarbon and fullerene C_{60} coverage experienced to e-beam and laser treatment. **Table 2** summarizes the measured data. As is seen both laser and e-beam treatment of both nanocarbon and fullerene-coated steel surface result in a notable (tens percent) decrease in the friction coefficient of the treated surface.

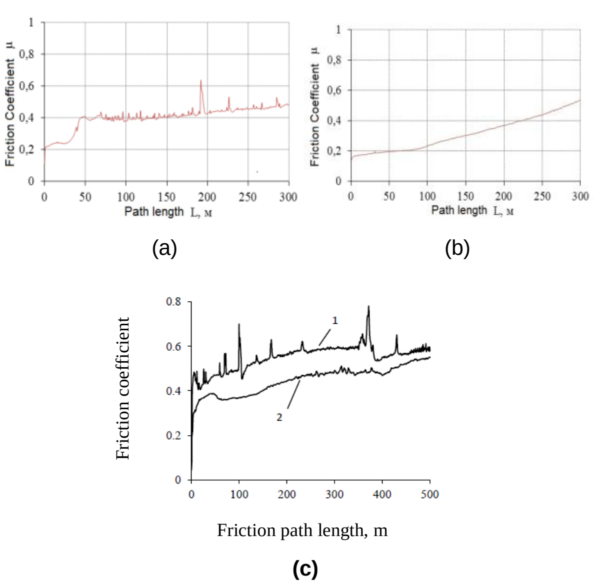


Fig. 4. Results of tribology tests of steel samples: (a)Nanocarbon coverage without laser treatment; (b) Nanocarbon coverage with laser treatment; (c)fullerene C_{60} (3 layers) coverage with (1) and without (2) laser treatment.

Table 2. Average results of tribology tests of the nanocarbon-coated steel surface.

	Friction coefficient		
	Initial	Intermediate	Final
E-beam treatment	0.14	0.195	0.25
Laser treatment	0.14	0.3	0.54
No treated	0.20	0.40	0.66

Conclusion

The measurements performed indicate a considerable enhancement (up to 8 fold) of the microhardness of a steel surface covered with a nanocarbon material followed by intense e-beam or laser beam irradiation. The degree of reinforcement depends on the electron (laser) beam energy in a non-monotone manner assuming the possibility of optimization of the treatment. The degree of reinforcement with laser fixation exceeds that with e-beam fixation about twice while the depth of the action for laser treatment is several times less than that for e-beam treatment. The nanocarbon coverage followed by a high-intense irradiation results in a lowering the friction coefficient of the treated surface by several tens percent.

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