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Mechanism of Surface Reinforcement of Steels by Nanocarbon Materials Using Laser Heating

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Abstract—The mechanism of the surface reinforcement and wear resistance of steel products are studied as a result of creating the strengthening layers with the nanocarbon using the laser heating. Laser surface treatment using soot remaining after fullerene extraction leads to a more than fivefold increase in the microhardness (up to 1086 *HV*) and a decrease in the friction coefficient by 20–30%. The conclusion that the reinforcement mechanism involves the formation of eutectic, cementite, martensite, the cellular substructure, and grain refinement is carried out based on metallographic studies of the strengthened layers of technically pure iron with a thickness of 20–70 μm.

Keywords: laser treatment, nanocarbon materials, technically pure iron, microhardness, microstructure, wear resistance, friction coefficient

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INTRODUCTION

The task of elaboration of the metallic materials with the high and ultra-high properties which allow us to considerably reduce the specific quantity of metal and to ensure the resource saving is topical at the present stage of technical development. 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.

The new (in principal) physicomechanical 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 heating [1]. The advantage of the laser method is the 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 laser treatment. Additionally laser heating 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. The laser technologies of surface reinforcement has 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 laser 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, nanocarbon tubes, and so on [3–6]. The results of metallographic studies of Damascus steel using a high-resolution electronic microscope are given in [7]. Multilayer carbon nanotubes with a diameter of 5 nm filled with cementite of high hardness was detected in the structure of this steel. The effect of the surface strengthening of steel by virtue of NCM, the authors associated with the formation of iron carbide with a specific modification at the interfaces between the various structural components. Naturally to assume that the effect of Damascus steel can be implemented by dint of mechanical penetration of NCM into the iron matrix by means of any impact, e.g., by surface plastic deformation or laser treatment, which combines a shock wave and thermal effect.

Despite the considerable number of articles devoted to the problem of strengthening structural materials using the nanocarbon coating with subsequent treatment with highly concentrated energy sources, at present, systematic studies of influence of the nanocarbon materials on the structural formation of the strengthened layer after its penetration into the steel surface using the laser beam are nearly absent. In this regard, it is topical to study the influence of the technological parameters of laser treatment, such as power and duration of impact, and also the type and thickness of the pre-deposited nanostructured carbon on the structure and wear resistance of the steel surface. The dependence of microhardness of the steel surface with nanocarbon coating on the density of laser irradiation was obtained in this article. The study of the structure of the treated material allows us to draw conclusions about the mechanism of surface strengthening.

EXPERIMENTAL

Samples made of technically pure iron ($C < 0.02$ wt %) with a size of $3 \times 15 \times 50$ mm^3 were used to study of the surface strengthening effect. The suspension of nanostructured carbon formed by the extraction of fullerenes from soot was deposited on the surface of the samples. Fullerene-coating soot is formed from HF plasma of four-electrode arc discharge with graphite electrodes in an atmosphere of helium at a gas flow of 3–6 L/min, at 66 kHz, and an arc current of 220 A. The electrodes are oriented along the edges of the pyramid at an angle of 57°. The extraction of fullerenes was produced using a SOXHLET-type installation. The specific surface area of soot remaining after the extraction of fullerenes and measured by BET using a SORBI-M installation turned out to be 233 ± 4 m^2/g. It follows that the distinctive size of the flakes is about 5 nm. The was soot 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 before strengthening 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.

An ALFA-200C-type installation of Laserform Company of pulse action with neodymium glass with wave length of 1064 nm and energy of 50 J was used in the capacity of laser radiation. The laser beam was focused to a spot of 3.5 mm in diameter. The power of laser radiation varied in the range of 2–20 J, and the pulse duration was from 1 to 9 ms. The surface of the samples was photographed 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.

The surface hardness was measured by Vickers testing using an Emco-Test DURASCAN 20 attachment at a load of 100 g. For comparison, we measured the hardness of the samples not subjected to treatment and the irradiated samples that did not contain the nanocarbon coating. The microhardness measurements of the individual structural components were performed in accordance with GOST 9450-76 using an automated Instron Tukon 2500 hardness tester at a load of 5 g.

The tribological tests of the strengthened surface were performed under dry friction by the sphere—plane method by the linear reciprocating movement of the sample relative to the fixed conterbody 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 using 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 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.).

RESULTS AND DISCUSSION

Studies have shown that the treatment of samples with a relative not high laser radiation power density (less than 50 kW/cm^2) does not lead to surface melting and is accompanied by a significant increase in hardness. Incidentally, the surface hardness is varied at a single spot in a wide range of 200–1086 *HV*. This variations in the hardness can be explained by the heterogeneous distribution of energy within the laser beam and the different distance from the measurement point to the boundary of the laser action zone with the base metal. Note that, as a rule, the hardness is maximum at the center of impact zone and decreases toward the edges. The nonhomogeneous distribution of hardness has a positive effect on the wear resistance of the surface, since the structure of metallic alloys formed according to Sharpy, a soft base and the hard inclusions, improves the tribological nature of metals and alloys; in particular, it reduces the coefficient of friction and, as a consequence, increases the wear resistance of the surface.

Samples treated with higher laser radiation power density, which leads to surface melting, have elevated hardness (550–800 *HV*), but more or less evenly distributed over the both surface and the thickness of the laser action zone. The results of the microhardness of the samples that contain the nanocarbon coating and subjected to the laser irradiation with the different pulse power and duration are given in the table. The influence of the hardness of technically pure iron modified with nanostructured carbon on the laser radiation power density is presented in Fig. 1. It should be noted that the nonmonotonic behavior of this dependence with the maximum is reached at $q = 95$ kW/cm^2.

The results of a metallographic analysis of the reinforced layer obtained on transverse sections at a magnification of 1000 times are shown in Fig. 2. It can be seen that the surface melting does not occur up to 50 kW/cm^2; however, the formation and intergranular penetration of the light-melting eutectic (IGP) deeper than 20 μm take place. The eutectic has a drop shape and is distributed nonuniformly over both the surface of the sample and the thickness of the strengthened layer (Fig. 2a). A similar phenomenon [8] was explained next, i.e., “these islands of ledeburite are formed during laser treatment near the particles of cementite, which is present in the initial structure of technically pure iron, incidentally at a considerable distance from the melting zone, which is associated with contact melting on the boundary ferrite-cementite at temperatures close to eutectic (1147°C), which is significantly lower then the melting point of technically pure iron.” However, visible inclusions of tertiary cementite (Fig. 2a) did not become the centers of eutectic formation in the body of the ferrite grains. Therefore, the most likely mechanism is IGP, which is often implemented when welding dissimilar metals.

The microhardness of the drop-shaped inclusions is 1800 ^{5}HV. The coefficient taking into account the scale factor in the measurement of the microhardness with the load of 1–5 g equals to 1.5–1.7 [9, 10]. When switching to a load 100 g, the microhardness of the drop-shaped inclusions is 110–1200 ^{100}HV, which is higher than that of martensite and, consequently, with respect to morphology, indicates the formation of a eutectic, i.e., ledeburite.

The treatment of technically pure iron with a carbon coating upon the laser radiation power density of 60–95 kW/cm^2 leads to the melting of the sample surface; incidentally, the thickness of the strengthened layer increases from 20 to 70 μm (Figs. 2b–2d). The melting zone is saturated with carbon to a concentration of white hypoeutectic cast iron and depending on the parameters of the laser treatment and cooling rate, the $\gamma \rightarrow \alpha$ transformation may end with the formation of various structural components, such as ledeburite, martensite, retained austenite, cementite, and perlite structures with different degrees of the plate dispersion. Additionally, under conditions of high rates of heating and cooling during laser treatment, the diffusion processes of dissolution and the alignment of the carbon concentration are not completed, which is the reason for the formation of inhomogeneous austenite and, therefore, of inhomogeneous martensite in the carbon content.

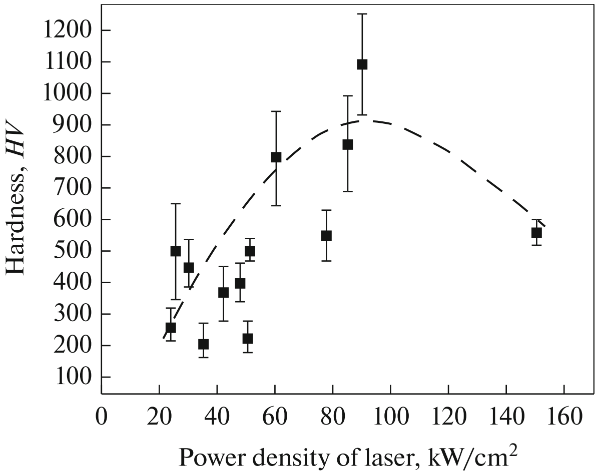

Fig. 1. Influence of power density of laser irradiation on surface hardness of technical iron modified with nanostructured carbon.

In general, a significant increase in the microhardness inside the melting zone up to 1080 *HV* (compared to the microhardness of technically pure iron in the initial state, 180 *HV*) is explained by the following possibilities:

(1) quenching from the liquid phase, which produces martensite;

(2) phase $\alpha \leftrightarrow \gamma$ recrystallization and phase reinforcement, which leads to the refinement of grain size and microstresses in the crystal lattice;

(3) plastic deformation under shock-wave and thermal influence, as a result of which the dislocation

Table 1. The microhardness of the Armco-iron samples with the nanocarbon coating subjected to the laser irradiation pulses of the different power and duration

Sample	q, kW/cm^2	τ, ms	Commentary	Microhardness, *HV*
1	31	3	No signs of melting	450 ± 90
2	49	3	The first signs of overheating at three points	400 ± 60
3	63	3	The traces of melting	800 ± 140
4	95	1	No traces of melting	1086 ± 160
5	80	3	The traces of melting	550 ± 80

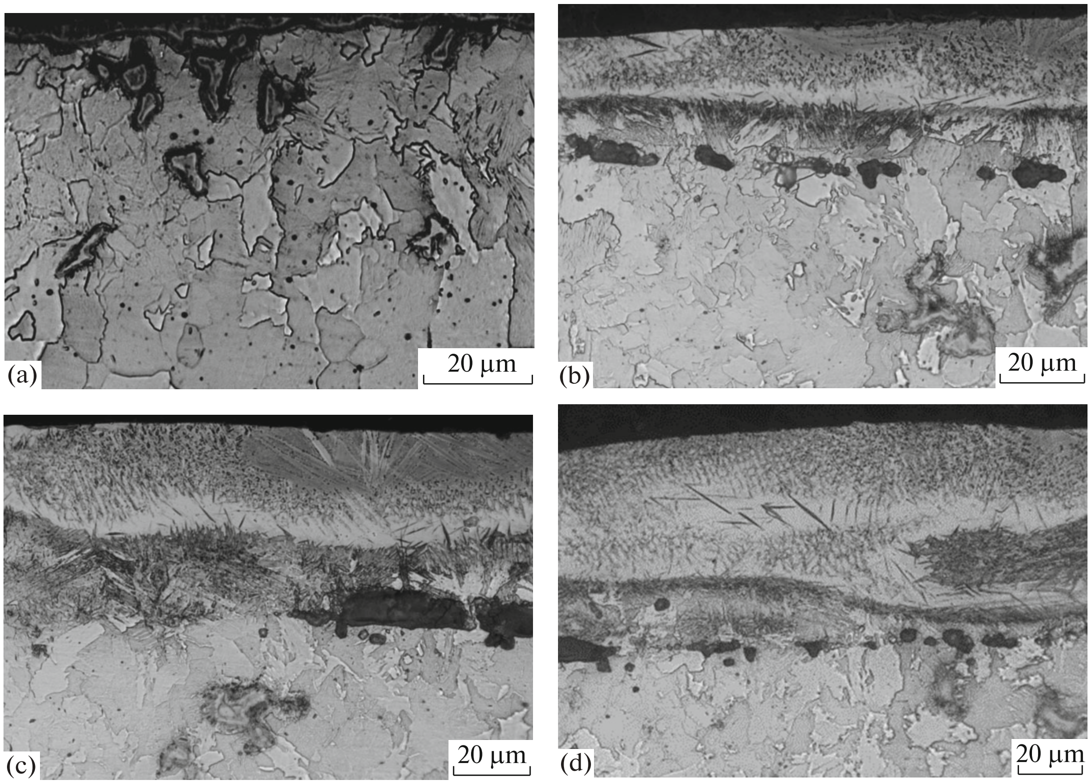

Fig. 2. Microstructure of technical iron after laser treatment at (a) $q = 31$ kW/cm^2, (b) $q = 49$ kW/cm^2, (c) $q = 63$ kW/cm^2, (d) $q = 95$ kW/cm^2, ($\tau = 3$ ms).

density and microdistortions of the crystal lattice are increased and the cell substructure is formed.

The structure of the heat-affected zone (HAZ) located below the melting zone is the fine-needle martensite with a hardness of up to 700 *HV*, which indirectly indicates the high content of carbon (0.5–0.6%). The martensite formation is associated with the appearance of ledeburite in the HAZ, which is formed due to either the intergranular penetration of the low-melting eutectic or as a result of contact melting at the ferrite–cementite boundary at the temperatures close to the eutectic. Ledeburite is an additional source of carbon, the dissolution of which in γ-Fe upon the subsequent polymorphic transformation leads to forming martensite with a high hardness.

The dark regions that represent themselves the cavities are observed below HAZ in Figs. 2b–2d. The high-speed heating up to the temperature of burnout causes the significant tensile stresses and as a consequence leads to the discontinuity of metal. The presence of these cavities in the zone of laser action was also observed by the authors of [11] when treating gray cast iron, which contains carbon in the form of graphite. However, they explain this significant porosity by the release of gases adsorbed by the graphite inclusions during the primary crystallization of cast iron. The spheroid shape and smooth inner surface indicate to the gas nature of the cavities according to the authors.

The tribological tests of technically pure iron reinforced by nanocarbon materials using the laser influence showed that the friction coefficient of the strengthened surface is 20–30% lower than of the surface in the initial state under the conditions of dry friction.

CONCLUSIONS

(1) The study of the influence of technological parameters of laser treatment on the properties of technically pure iron pre-coated with nanostructured carbon on the surface showed that, after treatment without melting, the hardness at the center of the laser influence zone is increased to 950 *HV* and more, due to the formation of the high-carbon phases, such as eutectic and cementite on the surface.

(2) The hardness of the surface is 550–800 *HV* in the outside zone and 1100 *HV* in the inside melting zone when the treatment of technically pure iron by the melting schedule due to the formation of eutectic, cementite, and martensite, as well as the cellar substructure and grain refinement.

(3) The tribological tests showed that the friction coefficient of the strengthened sample surface made of technically pure iron and modified with nanocarbon materials is 20–30% lower compared to initial samples under conditions of dry friction.

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