Surface Modification Features of Tool Steels by Laser Radiation

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Abstract—In this paper, we present the study results of the surface layers of carbon steels U8 and U10 performed by X-ray photoelectron spectroscopy after laser exposure. The thicknesses of oxidized surface layers were determined to be 43 nm and 108 nm for U8 and U10 steels, respectively. Both the total thickness of the formed oxide film and its phase composition (FeO, Fe_2O_3, Fe_3O_4) with depth were found to change depending on the concentration of iron, oxygen, and carbon atoms in the considered steels. The "layer" structure effect of the oxides of the layer modified by laser irradiation on the frictional characteristics of steels is shown. In particular, the presence of FeO oxide on the U8 steel surface increases the wear characteristics, while the presence of Fe_2O_3 and Fe_3O_4 oxides provides a higher wear resistance of steel U10 compared to an unirradiated steel surface.

INTRODUCTION

Depending on the processing parameters, the composition of the gas medium, the elemental composition, and methods of heat treatment of steels, laser action has a multifactorial effect on the state of their surface and near-surface layers, which is the subject of numerous studies [1–3]. One of the essential results of laser action in an air environment is the formation of a thin oxide film on the steel surface [3–6]. As established in this study, one of the determining factors is the formation of thin oxide films that are functionally dependent on the ratio of the components involved in their formation on the steel surface after laser modification in air. Oxide films with a thickness of 100–200 nm reduce the value of the friction coefficient [1–4], contributing to a decrease in the intensity of the stress field, temperature and force loading on the operating surfaces of the tool, and an increase in the tool durability. However, in the scientific literature, there are practically no experimental study results devoted to the following: the method of X-ray photoelectron spectroscopy on the chemical state of elements over the steel depth in the laser action zone and the effect of oxide phases formed during this treatment on tribological properties.

This paper is aimed at studying the distribution of the elemental and phase compositions of oxide films and evaluating the effect of the formed layers after laser modification on their tribological characteristics.

MATERIALS AND RESEARCH METHODS

Laser treatment of U8 and U10 steel samples with dimensions of $10 \times 10 \times 2$ mm³ was performed using an LK-150/1500-QCW-AC fiber-optic laser source with a wavelength of 1.07 μm. The laser power was 130 W, and the processing speed was 3 mm/s. The pulse frequency was 25 kHz at a single pulse duration of 20 μs.

The qualitative and quantitative composition of the oxide layer formed due to laser treatment in air for U8 and U10 tool steels was studied by X-ray photoelectron spectroscopy using a SPECS surface analysis system. Studied samples had a size of $10 \times 10 \times 2$ mm³ [2, 3]. Al$K\alpha$-monochromatic radiation with an energy of 1486.6 eV was used as a source of exciting radiation. The energy resolution of the analyzer is no worse than 0.6 eV. The Fermi level and the C $1s$ carbon line, the energy of which was taken to be 285 eV, were used as the standard for determining the binding energies. When film shooting, the vacuum was maintained at a level of 6×10^{-10} mbar. Ar^+ ions were used for ionic profiling. Ionic profiling of steel samples was performed in the preparation chamber of the SPECS surface analysis system at an argon pressure of no more than 4.2×10^{-5} mbar.

Tribological studies were carried out using an Anton Paar GmbH TRB tribometer in the linear motion mode. The amplitude of the reciprocating
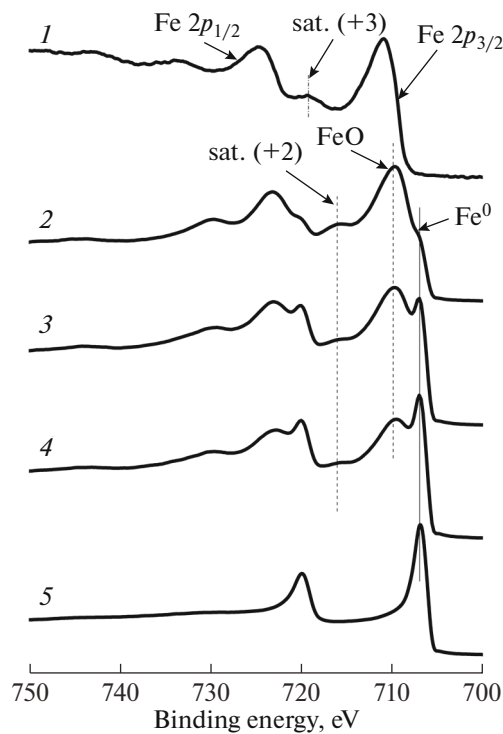
Fig. 1. Fe 2*p*-electron spectra obtained in depth of U8 steel after ion etching times: (*1*) initial surface, (*2*) 4, (*3*) 7, (*4*) 8, and (*5*) 12 h.
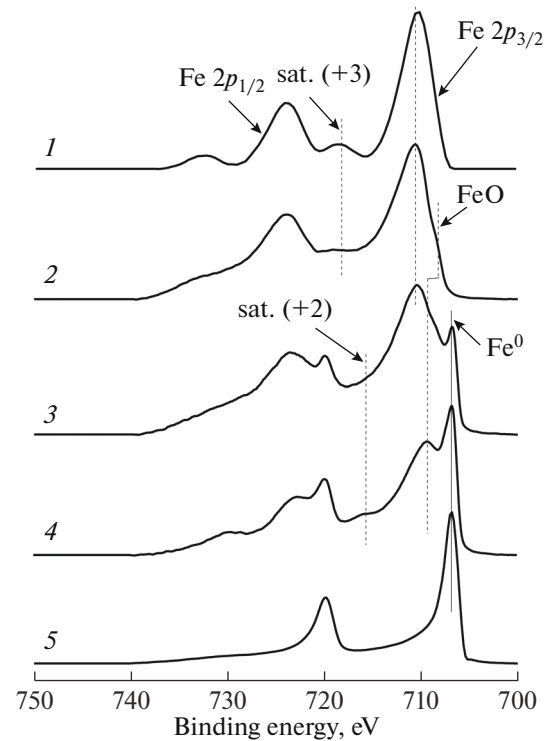

Fig. 2. Fe 2*p*-electron spectra obtained in depth of U10 steel after ion etching times: (*1*) initial surface, (*2*) 3, (*3*) 7, (*4*) 8, and (*5*) 10 h.

motion was 1 mm, the oscillation frequency was 10 Hz, and a vertical load was 5 N. The indenter was an aluminum oxide(III) ball with a diameter of 6 nm.

The surface morphology of the sample wear hole was determined using a Zygo NewView 600s interference microscope. Scanning was performed using a lens with a magnification of 10× and a field of view of $0.52 \times 0.70 \text{ mm}^2$ with subsequent stitching.

RESULTS AND DISCUSSION

Figures 1 and 2 show the spectra of the 2*p* line of iron atoms obtained for various times of ion profiling along the depth of the U8 and U10 steels after laser treatment. For each steel, ion etching was performed every 5 min for the first hour, and then every 10 min thereafter. Thus, the total time of ion profiling was 13 h for U8 steel and 10 h for U10 steel.

The presented spectra clearly demonstrate the processes of oxidation and reduction of the base metal of the considered steels, i.e., iron. According to the data of [2, 3, 6–9], the lines of Fe $2p_{3/2}$-level of iron with a binding energy in the range of 706.7–707.8 eV correspond to unoxidized iron, in the range of 710.3–710.7 eV correspond to oxide Fe_3O_4, in the range 711.0–711.5 eV correspond to Fe_2O_3, and with a binding energy of 709.5 eV correspond to FeO. The presence of Fe_3O_4 oxide in the studied steel samples is

indicated by two facts: the absence of a sat. (+3) charge transfer satellite with an energy of 718.5 eV and the presence of a feature in the fine structure of the spectrum located at a distance of 1.8 eV towards the decrease of binding energy from the main iron peak. An electronic spectra analysis of Fe 2*p* shows differences in the oxidation state of iron over the oxidized layer thickness from the modified surface into the sample's interior.

Figures 3a and 3b show the diagrams of the distribution of carbon, oxygen, and iron atoms over the modified layer's thickness. The obtained results presented in the figures illustrate the differences in the formed oxide layers on the surface of both steels already at the stage of studying the concentration dependences on the etching time. Such dependences can be recalculated depending on the etching depth in nanometers if the ion etching rate is known. Such estimates in individual cases will be made below. As can be seen in Figs. 3a and 3b, the initial surface, i.e., before ionic profiling of U8 and U10 steels, contains a large number of oxygen and carbon atoms that can be attributed to surface contamination of steels under environmental conditions [2, 3, 6, 7]. A certain contribution to the number of carbon atoms on the surface can be made by carbon, which is contained in the steels themselves due to their surface enrichment from laser action. Furthermore, the elemental surface com-
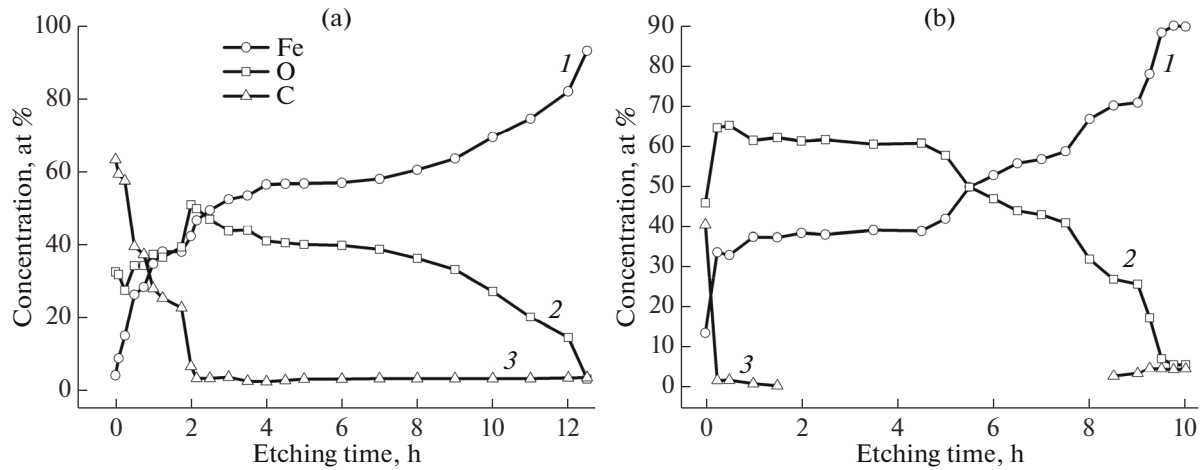
Fig. 3. The percentage of (*1*) Fe, (*2*) O, and (*3*) C elements over the depth of steels U8 (a) and U10 (b) after laser treatment, depending on the time of ion etching with an Ar$^+$ beam.
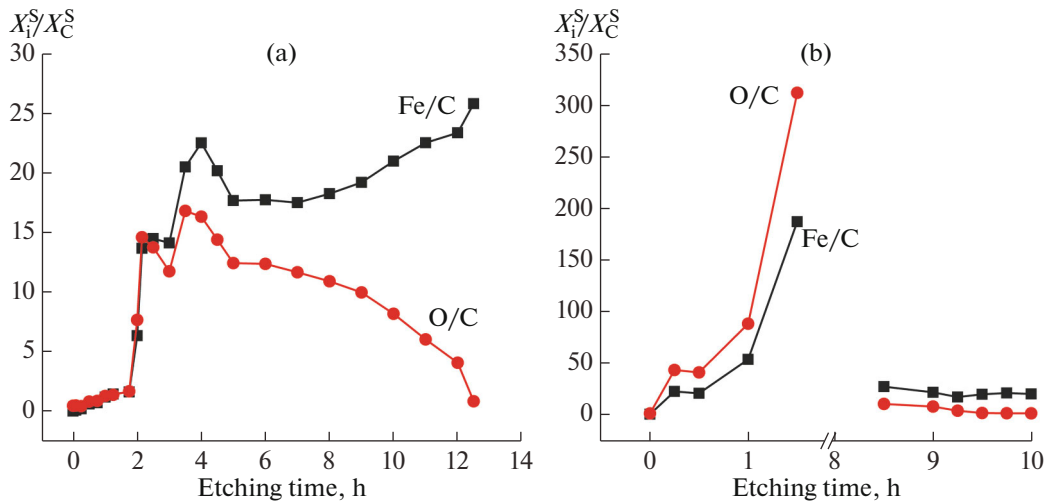

Fig. 4. Ratio of atomic concentrations (*i* = Fe, O) to carbon content along the depth of steels (a) U8 and (b) U10 after laser treatment depending on the ion etching time.

position also depends on the type of oxide formed under conditions of high-speed laser heating. In the near-surface layer, the concentrations of carbon, oxygen, and iron for steels U8 and U10 are equal to 62, 35, and 3 at % (Fig. 3a) and 40, 45, and 15 at % (Fig. 3b), respectively. The carbon and oxygen content decreases with increasing etching time along the steel depth in both steels. However, in U8 steel, the carbon content becomes close to the bulk one (3.5 at %) only for an etching time equal to 2 h while, for U10 steel, it sharply decreases and becomes equal to the bulk one already for an etching time of 0.3 h.

In the initial U8 and U10 steels, the content of chemical elements is the same, with the only difference that the carbon content in U10 steel is 0.2% higher than that in U8 steel. To estimate the concentration distribution over the modified layer depth, we

performed comparative characterizations with respect to carbon atoms. Figures 4a and 4b show data illustrating the concentration ratio of the of iron and oxygen atoms to the carbon concentration on the surface from the time of ion profiling.

Starting from 1 h and up to 2 h by ion etching, the oxygen content in U8 steel after removal of surface carbon and oxygen contaminants coincides with the iron content (Fig. 3 and Fig. 4a), which may indicate the formation of a compound of iron oxide FeO in this layer. After 2 h of etching, the oxygen content in the test layer gradually decreases, remaining less than the iron concentration, which indicates a change in the oxidation state of iron along the oxidized layer depth. In steel U10, the behavior of the concentration dependences of iron and oxygen atoms differs in comparison with those in steel U8. After removing surface
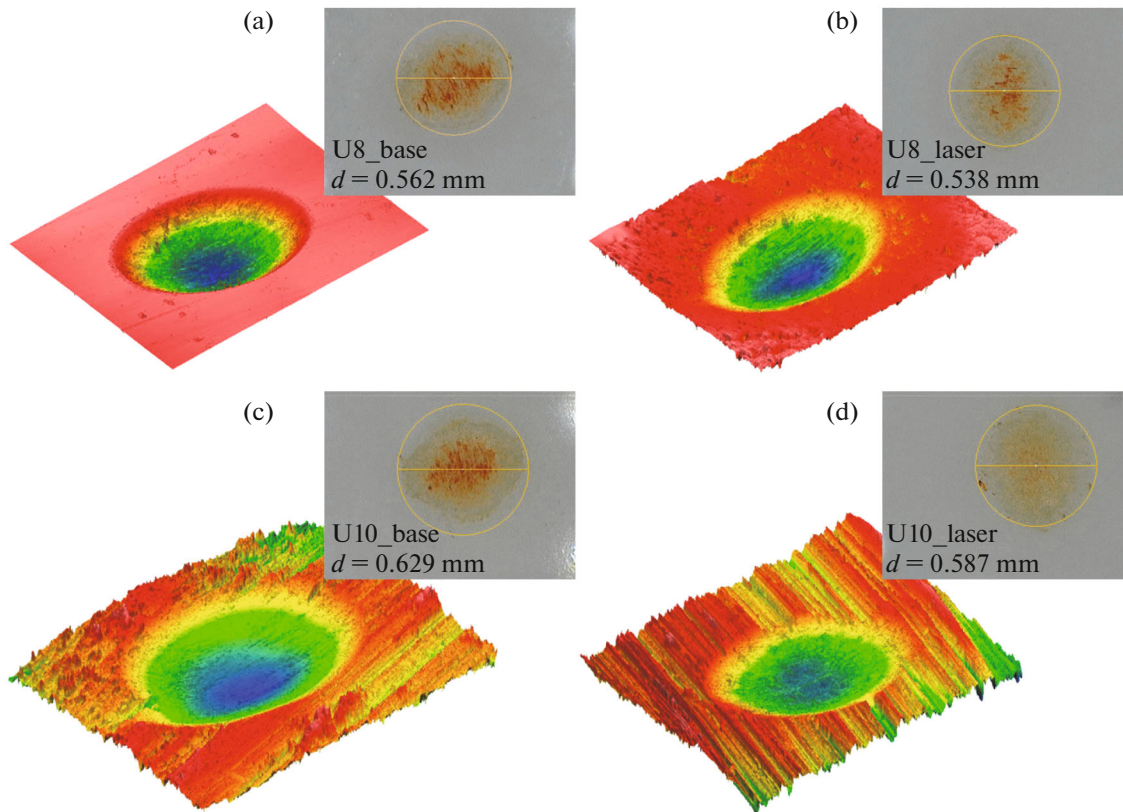
Fig. 5. Three-dimensional image of the surface of the sample wear hole and an image of the indenter wear after tribological tests: (a) U8, initial; (b) U8, after processing; (c) U10, initial; and (d) U10, after processing.

contaminants to the etching point of 5.5 h, the oxygen content exceeds the iron content by 1.5 times. As seen in Fig. 4b, in the time interval of 1.5−8.5 h, the concentration ratio graph of oxygen and iron atoms to the carbon content undergoes a gap. Thus, this is due to the fact that a thick layer consisting of a mixture of iron oxides(II) and (III), as well as unoxidized iron, is formed in this time interval. According to Figs. 1 and 2, iron atoms on the surface of both steels are in two oxidized states Fe^{2+} and Fe^{3+}, indicating the presence of two oxides of iron(II) and (III). For U8 steel, the layer containing iron(II) and (III) oxides is very thin. The surface layer of steel U10 containing oxides of iron(II) and (III) extends into the depth of up to 2 h of ion etching.

For U8 steel, the oxide layer after 15 min of etching and up to 2 h inclusive consists of iron in the oxidation state (+2), which is consistent with the data shown in Figs. 3a and 4a. The surface state corresponding to the etching time interval between 2 and 2.5 h is represented by a thin layer of Fe_3O_4 oxide. After 2.5 h of etching, iron at the studied depth appears for the first time in the zero oxidation state and iron in the Fe^{2+} oxidation state.

Steel U10 also has a thin layer of iron oxide Fe_3O_4 located above the layer where the XPS method detects iron in the zero oxidation state. Under the layer of iron oxide Fe_3O_4, there is a layer already consisting of a mixture of iron(II) oxide and iron in the zero oxidation state, i.e., iron in the zero oxidation state Fe^0, in which the content of iron(II) oxide gradually decreases and the iron concentration in the zero oxidation state increases until it becomes equal to the iron concentration in the bulk of the steel.

According to estimates [2, 3], the ionic profiling rate of steels using the used ion gun was ~0.3 nm/min. This allows determining the thicknesses of the oxidized surface layers formed under high-temperature laser heating, which are 43 nm for U8 steel, and 108 nm for U10 steel. Thus, the thickness of the oxide film on U10 steel is two and a half times greater than the value obtained for the thickness of the oxide film on U8 steel.

To estimate the phase composition effect of oxides on the surface of U8 and U10 steels on their tribological characteristics, wear tests were carried out, with results shown in Fig. 5. The measurements were performed both for the oxidized surface after laser modification and for the steel surfaces without treatment. The table 1 shows the tribological characteristics of friction processes, which together with the data in Fig. 4 allow evaluating the effect of oxidized layers on

Table 1. Tribological characteristics of the friction process

Steel grade, processing condition	Friction coefficient μ	Sample wear rate, 10^{-6} mm^3/N/m	Indenter wear rate, 10^{-6} mm^3/N/m
U8, initial	0.90	7.84	2.75
U8, after processing	0.92	5.84	3.27
U10, initial	0.90	5.72	5.14
U10, after processing	0.86	4.68	3.90

the friction process. Thus, the wear resistance is, respectively, by 26% and 18% higher for the modified samples of U8 and U10 steel than that for the samples before their modification, while the treatment of U10 steel leads to a 25% decrease in the wear rate of the counterbody.

To determine the nature and type of wear, we performed surface morphology studies of both the initial steel and steel after surface modification. The morphology of the sample wear holes is characterized by signs of fatigue failure [10]. In all the given samples despite their differences in surface preparation, the nature of wear does not have significant differences. These data show that laser modification has a significant effect on the wear resistance of tool steel.

CONCLUSIONS

(1) The changes in the layer depth modified by laser radiation of low-alloy tool steels U8 and U10 of both the concentrations of chemical elements and the phase composition of oxide films were experimentally established. The oxide film thickness on the surface of U10 steel was found to be two and a half times greater than the thickness on the U8 steel surface.

(2) According to X-ray photoelectron spectroscopy data, the oxide films formed on the surfaces of U8 and U10 steels have a "layered" structure and differ significantly from each other both in total thickness and in the thicknesses of oxide films of various phase compositions within them.

(3) Tribological tests showed that both the thicknesses of thin oxide layers on the surface of modified steels and their phase composition affect the frictional characteristics of steels: the surface film presence of iron oxide(II) on U8 steel surface determines its low wear characteristics, while a thick layer containing oxides Fe_2O_3 and Fe_3O_4 provides high wear resistance of U10 steel after laser modification.

(4) The presence of oxides FeO, Fe_2O_3, and Fe_3O_4 on the surfaces of tool steels U8 and U10 increases the wear characteristics and, according to [2−4], helps to reduce the stress field intensity, temperature and force loading on the contact surfaces of the tool, which in turn leads to increasing tool durability.

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