The effect of graphite coating on the composition, structure and microhardness of the surface of structural chromium-nickel steel during laser pulse processing

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Abstract. In this work, the effect of laser pulsed radiation on the surface of 12Cr18Ni10T stainless steel with a layer of graphite coating previously applied to it was experimentally investigated. It was established that as a result of laser pulsed irradiation, a significant increase in the microhardness of the surface layer of the experimental samples occurs to H=9.56±0.1 GPa. The results of studying the elemental composition of the surface structure showed an increase in the concentration of diffused carbon in the surface layer of steel.

1. Introduction

Along with the traditional methods of chemical-thermal treatment and other various methods of saturating the surface of one metal with others, the most preferred method today is pulsed laser doping. This is explained by a number of advantages of this method: locality, the ability to process hard-to-reach areas, environmental safety, the ability to impart various properties of the treated surface [1, 2].

As a result of laser surface alloying, the chemical composition of the material, its qualitative and physico-mechanical characteristics change due to the supply of alloying elements to the molten bath. This method of surface modification is usually divided into two categories. The first includes processes where alloying elements are supplied to the surface to be treated in the form of gas, powder or wire. The second category includes processes that require the use of preliminary technological operations for the formation of surface structures, for example, galvanic ones [3-5]. Despite its effectiveness, the above methods of laser pulsed alloying have a certain drawback - the use of expensive equipment and auxiliary consumables.

Currently, methods where the alloying material is applied to the surface to be treated in the form of a previously prepared suspension (coating) are becoming most relevant. Such methods allow, for example, to achieve high hardness of the modified surface layer, to increase corrosion resistance and wear resistance. The essence of the laser doping process with pastes is to melt the applied coating layer and the surface of the base material with laser radiation, where a small amount of material is quickly heated and melted, and then it crystallizes quickly. The result is a crystalline microstructure and surface saturation with alloying elements. Often, finely dispersed or nanosized powder materials and a viscous-flowing binder are used as modifying components of the coating. However, despite a large number of experimental works, questions related to the uniform distribution of alloying elements in the modified surface layer remain incompletely studied [6–9].

In this regard, it is urgent to develop rational technological regimes of laser pulse hardening of structural chromium-nickel steel and identify patterns of formation of a uniform modified structure.
2. Methodology

The studies were carried out on stainless steel 12Cr18Ni10T. The experimental samples were plates with dimensions of 10×10 mm and a thickness of 3 mm. The samples were preliminarily air-abrasively treated with electrocorundum powder with a fineness of 200–250 µm at an air pressure of 0.5–0.6 MPa. Then, the samples were cleaned of technological impurities using a Crystal-2.5 ultrasonic bath in an aqueous solution of ethyl alcohol for 20 minutes.

Graphite paste (GOST 8295-73) was selected as the alloying material, which was applied to the steel surface with a thin layer of 150±50 μm.

The surface layer was doped in an automated setup for thermophysical coherent surface modification of LRS-50A at a pulse voltage of U=250, 300, 350, 400, and 450 V and a duration of 0.5 ms. The beam was focused into a spot with a diameter of 0.5 and 1 mm on the coating surface. Processing was carried out at a pulse repetition rate of 20 Hz and an overlap coefficient of 0.2.

The energy of a single pulse at various voltage values was determined experimentally using an instrument for determining the power and energy of laser radiation "Laserstar" from "OPHIR", Laser Measurement Group. The results of the average values of the dependence of the pulse energy on the voltage and duration of the pulse exposure are shown in (Table 1).

Table 1. The dependence of the pulse energy on the voltage and duration of the pulse exposure.

| Sample № | τ, ms | U, V | E, J  |
|----------|------|-----|-------|
| 1        | 250  | 0.08|
| 2        | 300  | 0.31|
| 3        | 350  | 0.58|
| 4        | 400  | 0.92|
| 5        | 450  | 1.35|

The morphology and structure of the modified surface layer was studied by optical microscopy using a MBS-10M microscope. The elemental composition of the modified surface was determined using scanning electron microscopy (SEM) using a MIRA II LMU electron microscope with an INCA PentaFETx3 detector.

Microhardness was measured using a PMT-3M hardness tester with a Vickers indenter at a load of 1.961 N (ISO 6507-1: 2005). The surface structure was investigated using an optical microhardness meter system. Statistical processing of the measurement results was carried out using the DataFit 9 program.

3. Results

Studies of the morphology of the modified surface showed that at a voltage of 250 V the structure has a fine-grained character and a weakly expressed microrelief (Figure 1 a). When the pulse voltage exceeds 300 V, the modified surface becomes uniformly distributed, having a scaly structure (Figure 1 b). However, when the voltage is increased to 450 V, a strong fusion of the surface with the appearance of large particles and pores is visualized (Figure 1 c).
Figure 1. Morphology of steel 12Cr18Ni10T after laser alloying of the surface with graphite coating: a - at a voltage of 250 V; b - at a voltage of 300 V; c - at a voltage of 450 V.

An analysis of the elemental composition of the modified surface showed the presence in the studied region of C, O, Al, Si, Ti, Cr, Mn, Fe, Ni, which are unevenly distributed over the alloy depth (Figure 2, Table 2). The presence of trace amounts of aluminum impurities up to 0.84 in the surface layer is associated with preliminary air-abrasive processing of samples. The formation of oxygen was established within 3-4% on the surface and in the diffusion saturation layer. Metallographic studies of the structure showed that in addition to the formation of the modified surface layer, a diffusion layer is formed, the microhardness of which is higher than the microhardness of the alloy base. This hardening effect is associated with the saturation of the treated surface with carbon (up to 1.46%), which is contained in large quantities in graphite coating. Figure 2 shows the spectra used to perform elemental analysis and the boundaries of the layers formed as a result of laser doping.

Table 2. The elemental composition of the steel surface after laser alloying, (at.%).

| Spectrum | C  | O   | Al   | Si  | Ti  | Cr  | Mn  | Fe  | Ni  |
|----------|----|-----|------|-----|-----|-----|-----|-----|-----|
| 1        | 0.41 | 6.58  | 17.61 | 1.46  | 67.46  | 6.48 |
| 2        | 0.73  | 14.08 | 2.81  | 17.61 | 10.26  | 10.54 | 1.42  | 60.16 |
| 3        | 1.46  | 4.24  | 0.84  | 1.08  | 0.26  | 14.60 | 0.52  | 71.33  | 5.67 |
| 4        | 1.25  | 3.30  | 0.47  | 17.76 | 0.96  | 67.21 | 9.05  |
| 5        | 1.19  | 3.25  | 0.67  | 17.08 | 0.74  | 71.48 | 8.06  |
Additionally, measurements of the microhardness of the surface showed its significant increase with increasing pulse energy. The maximum value of microhardness \( H = 9.56 \pm 0.1 \) GPa was obtained by treatment with a pulse voltage of \( U = 400 \) V and a radiation spot diameter of 0.5 mm. It should be noted that the microhardness of the untreated surface of 12Cr18Ni10T steel is in the range 1.4±0.2 GPa.

Based on the results obtained, an empirical model of the dependence of the microhardness of the modified surface on the laser treatment regimes was constructed (Figure 3).

The constructed empirical model is described by the regression equation:

\[
H = (-1062275.25) + (-0.37) \times x_1 + 739181.76 \times \ln(x_2) + (-192753.42) \times \ln(x_2)^2 + 22324.39 \times \ln(x_2)^3 + (-968.94) \times \ln(x_2)^4
\]

where: \( x_1 \) – is the pulse voltage (U, V); \( x_2 \) – is the diameter of the laser pulse focused in the spot (d, mm).

This graphical model shows that the change in the microhardness of the alloyed surface is influenced to a greater extent by the pulse energy, rather than the diameter of the laser beam. So, its microhardness reaches its maximum value at a voltage in the range of 380-420 V and 260-280 V. The minimum microhardness is observed at a voltage of 300 V to 350 V.

4. Conclusions

It was established that as a result of laser alloying of 12Cr18Ni10T steel, a layered surface structure with increased microhardness is formed. According to the analysis of elemental composition, the modified surface layer with a thickness of up to 5 \( \mu m \) consists of iron oxides and carbides. The carbon content on the surface of steel samples of the order of 1.4±0.1 at.% Leads to a significant increase in microhardness to 9.56±0.1 GPa and allows you to compare it with carbon tool steel. According to the
results obtained, it can be assumed that the surface of stainless chromium-nickel steel alloyed with graphite coating will be more resistant to abrasion and the effect of abrasive particles on it during operation.

Thus, based on the results obtained, it was found that laser alloying of stainless steel 12Kh18N10T in a graphite coating layer with a pulse energy from 0.31 J to 0.58 J focused into a spot with a diameter of 1 mm leads to the formation of a uniformly distributed surface layer characterized by increased microhardness (of the order 4±0.3 GPa) and carbon content up to 1.4±0.1 at.%

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