Development and research of functional coatings with laser modification

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Abstract. The paper presents the study results of functional coatings of steel 45 formed by Ni, Cr, Mo, W alloying. The mechanical properties and relative resistance of steel 45 after alloying with these elements are presented. It is shown that the alloying coating thickness influence on the thickness of the functional coating. The analysis of the microstructure in the alloying area shows that the mass transfer of alloying components is realized mainly due to the convective motion of the melt. The surface tension of the melt depends on the temperature and the heterogeneity of the free surface heating of the alloying area. It was also found that the degree of hardening, the thickness and the microstructure of laser alloying depends on both the type of alloying component and the properties of the matrix material. The thickness of the alloying area depends not only on the thermophysical characteristics of the system but also on the energy parameters of the laser radiation.

At present there is a tendency to intensify the widely used traditional types of chemical and thermal treatment with the use of new high-performance technologies. For example, electrospark and laser alloying, ion nitriding, electron beam treatment of diffusion layers, etc. are successfully used in engineering to increase the products resistance [1].

When laser alloying it is necessary to provide a predetermined thickness where the alloying elements will penetrate to. The authors [2] suppose that one of the features of laser alloying is that the thickness of the alloyed layer is both a parameter and a result of processing. At the same time the dependence of the alloyed layer thickness on the main processing parameters was determined experimentally to describe the results of laser alloying; the concentration of the alloying element is considered as an amount inversely proportional to the penetration thickness.

It is suggested in the paper [3] that the alloying area thickness can be deeper than the penetration thickness of the material, as the diffusion process can be both in the molten area and solid material.

The choice of technological parameters of laser alloying begins with the selection of the radiation power, the diameter of the radiation focused into the spot and the speed of its movement to ensure the mode of possible melting of the surface.

The layer thickness of the alloying coating often is not stated in the papers on laser alloying. Some papers state the applied thickness of the coating, but the its effect on the properties of the alloyed material is not studied [4].
In general the study of the structure and properties of steel as a result of laser alloying at different power densities were performed without taking into account the thickness of the layer of pre-used alloying coating.

With the laser alloying the alloying elements penetrate into the inner layers from the metal surface. The authors [4] suppose that the question of the mixing mechanism when laser alloying is one of the most basic and controversial. Two possible mixing mechanisms are discussed: convective motion and diffusion. The convective flows in a liquid bath are described by a model of thermocapillary convection that estimates the speed of the melt, the degree of its mixing and the degree of distortion of the surface profile of the alloyed area [5].

One of the distinctive features of the process of the microstructure formation with laser alloying is the possibility of creating a greater saturation of the solid solution; the solution concentration is much higher than the solubility in equilibrium conditions.

The structure and properties of functional coatings were studied at steel samples 45 with Ni, Cr, Mo, W laser alloying, which was performed at power density of continuous laser radiation of CO₂-laser "LATUS-31" W=18,0-24,0 kW/cm²; the speed of the laser beam is V=4,0-8,0 mm/s. It was found that the microhardness of the alloyed area significantly increases compared with the initial metal while laser alloying steels with carbide-forming and refractory components; Ni alloying decreases the microhardness of this area. In all cases the hardening area is located deeper than the alloying area, having approximately the same level of microhardness regardless of the type of the used alloying component [6].

If before laser alloying the steels was subjected to volumetric hardening heat treatment (hardening + low tempering) the area with a reduced level of microhardness is located deeper than the area of laser thermal hardening, due to the heating of the metal at this thickness corresponded to tempering temperatures [7].

The most hardened alloying area is observed at saturation of Mo or W samples (up to 8000-9500 MPa). The distribution of microhardness deep into the samples is shown in Figure 1.

![Figure 1. Microhardness in the laser alloying area of steel 45](image-url)

If the laser treatment melts the surface of the product, the microstructure is formed at the solidification of the liquid metal while cooling. The lower layer is the basic material where the martensitic transformation occurs. The laser heating has supercritical temperatures, therefore there was a rapid removal of heat into the inner layers of the metal.

The melting temperature of the used alloying components differs from the melting temperature of the basic layer, therefore the effect of the thickness of the coating containing the alloying components on the thickness of the alloying area formation was studied.
The study found that allowing with more refractory alloying components forms a smaller thickness of the alloyed layer, as all the thermal energy of the laser radiation can be localized only in the coating with a sufficiently thick alloying layer. At the same time the surface layer of the material will be melted, i.e. the laser surface coating will take place instead of laser alloying. For example, when W alloying of 45 steel (Figure 2) the maximum coating layer is 0.40-0.45 mm when processing at a laser power density $W=18$ kW/cm$^2$ or 0.70-0.75 mm when processing at a power density $W=24$ kW/cm$^2$.

![Figure 2](image)

**Figure 2.** The dependence of the thickness of the laser alloying area of steel 45 on the thickness of the laser surface coating: a) $W=18.0$ kW/cm$^2$, speed $V=6$ mm/s; b) $W=24.0$ kW/cm$^2$, speed $V=6$ mm/s

The study of the steel microstructure while laser alloying shows that the effect of high cooling rates is shown primarily in the grinding of grains and the dendritic crystals are not always formed while solidification. It is connected with the main parameters of crystallization: the rate of crystal growth and the number of formed crystallization centers have a complex dependence on the temperature difference between the equilibrium liquidus and the actual crystallization temperature [8].

During x-ray structural study of the area of 45 steel with Mo alloying, $\alpha$-phase is revealed on the surface. This phase is a solid solution of substitution with the deformation due to the difference in the atomic radii of Fe and Mo, BCC-lattice, and deeper together with the $\alpha$-phase there is $\varepsilon$-phase (Fe$_3$Mo$_2$) and MoC; the absence of $\gamma$-phase shows the absence of residual austenite in the alloying area.

The study of samples with W alloying found that W, the compound Fe$_2$W and $\alpha$-phase are on the surface of the alloying area; $\alpha$-phase, $\varepsilon$-phase (Fe$_3$W$_2$) WC, WC$_2$ are in the alloying bath. The Cr alloying of surface showed that $\alpha$-phase, Cr$_2$O$_3$ (oxidation of Cr in the air) are formed on the surface and in addition to $\alpha$-phase, the Cr carbides (Cr$_3$C$_2$, Cr$_7$C$_3$) and Cr$_2$O$_3$ are found in the alloying area.

The microstructure formed with Cr is an alloying martensite ($\alpha$-phase). Grains have different shapes and sizes (from small polyhedral to large elongated). The degree of etchability in the alloying area is different, that also indicates the heterogeneity of the formed structure in the alloying area.

Mainly the melting of Ni and the small melting of the basic layer and a clear formation of the transition area occurs when Ni alloying. Therefore the thickness of the Ni alloying area weakly depends on the thickness of the coating; it has the smallest dimensions of penetration deep into the material with all the studied processing parameters.

The study of the structure in the alloying area showed that the mass transfer of the alloying components is performed mainly due to the convective motion of the melt. At the same time the surface tension of the melt depends on the temperature and the heterogeneity of the free surface heating of the alloying area [9]. As a result at the initial stages of mass transfer the impurity is redistributed in the surface layer, forming a drop-shaped alloying area. The formation of this form depends on the distribution of energy and temperature at the initial moment of the processing that has a maximum on the surface in the focal spot center of focused laser radiation. Superheated metal in the center of the bath is moved to the edges of the alloying area by surface tension. The viscous friction forces between the melt layers prevent the movement of the melt. In the center of the focal spot with the maximum heating
due to the fading of the molten metal, a less heated layer appears. It results in a vortex ring area with an increased temperature. The metal continues to move from this place to the edge of the area under the action of thermocapillary forces; from this area it begins to move back to the center of the alloying area. Then due to the vortex motion of the melt the alloying area takes a spiral form, where the areas enriched or depleted by alloying components alternate. Under the influence of thermodiffusion concentration fields can be transformed but a more uniform redistribution of impurities in the melt bath can be achieved by increasing the time of laser radiation, contributing to the intensification of mixing [11].

The influence of laser alloying with the various components on the relative resistance was studied during the abrasion resistance test of the alloyed samples of steel 45 of the softer counterbody. Laser alloying of cylindrical samples was carried out by applying ring tracks. The test showed that the resistance coefficient of the laser-alloyed surface increases with increasing its microhardness (Figure 3).

The obtained test results are consistent with the results of the paper [11]. The study of relative resistance of pure metals depends on their hardness. It is shown that the relative resistance of Fe is lower than the resistance of Cr, the resistance of Cr is lower than the resistance of Mo, and the resistance of Mo is lower than the resistance of W.

Based on the obtained results it is possible to conclude that the elements consisting the alloying coating increase resistance exactly in the same sequence in which they are resistant relative to each other.

The thickness of the formed alloying area has a complex dependence on the size of the pre-used layer of the alloying element (coating). Up to a certain thickness of the used alloying coating (for example up to 0.2 mm when using W or 0.35 mm when using Cr) the thickness of the alloyed layer monotonically decreases. Based on this we can assume that the share of laser energy used for the melting of the alloying coating is proportional to the thickness of the coating layer. Therefore the thickness of the melt area should decrease monotonously with an increase of the coating thickness. The study results show that the thickness of the alloying area decreases more intensively with an increase of the coating thickness of refractory elements of Mo and W above 0.2-0.3 mm. Apparently in this case the shielding effect appears when a certain part of the laser energy is either reflected or fixed in the alloying coating. But despite the increase of the alloying coating thickness there is a slowdown in the intensity of reducing the depth of the alloying area. Apparently, it depends not only on the absorption of the molten metal surface coating layer but also on developing of the chemical processes with the release of heat in the alloying area.

As it was shown the basis structure of the alloyed area in all cases when using carbide-forming elements is the α-phase. Also intermetallics (Fe₂Mo₃; Fe₂W₃), carbides (WC, MOC; Cr₃C₂, Cr₇C₃) oxide (Cr₂O₃) can be present in the alloying area depending on the alloying component. It indicates that not only phase transformations but also chemical processes occur in the surface layer during laser
alloying [12]. The formation of carbides and oxides of most metals takes place with a large release of heat. Therefore when the alloying element interacts with the base metal (Fe), carbon or oxygen, the heat and thermal energy release as the result of the absorption of laser radiation, which appears as a result of the formation of chemical compounds such as carbides, oxides. Also it is possible that an additional part of the carbon can be added to the alloying area from the combustion products of the binder.

Unlike the thermal energy produced in the surface layer of the metal while the absorption of laser radiation, the energy of chemical processes is released within the melt area more evenly throughout the volume, as the alloying process is connected with convective mass transfer. It contributes to an additional increase of the alloying area.

Thus, the shielding effect of the alloying coating layer is compensated in the considered systems due to the release of additional heat, contributing to an increase of the thickness of the alloying area.

Thus when laser alloying with Mo, W, Cr and Ni the similar results are obtained: solid solutions are formed, microhardness is increased in the alloying area, the structure and properties of the laser impact area depend on the properties of the basic material and the used coating. However, there are some differences: the presence of newly formed phases, different thickness of the forming alloying area and different hardening area, located deeper than the alloying area.

The study also found that the degree of hardening, the thickness and microstructure of laser alloying depend on both the type of alloying component and the properties of the matrix material. The thickness of the alloying area depends not only on the thermophysical characteristics of the system but also on the energy parameters of the laser radiation. Sufficiently uniform distribution of the alloying elements in the thickness of the alloying area is provided by the convective mass transfer.

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