# LASER SURFACE ALLOYING OF STEEL ITEMS (Review)

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Analysis of publications devoted to laser surface alloying of steel items has been performed. Processes occurring at formation of the structure of surface layers at laser alloying of steels have been studied. Examples of practical application of laser surface alloying of steels by various materials and mixtures are given. It is shown that laser alloying enables formation of surface of steel items having a high level of hardness, heat-, wear- and corrosion resistance and other physico-mechanical characteristics. It is found that the work performed in this direction was not of a systematic nature, and quite often was aimed at solving a localized task of improvement of performance of a particular material or parts made from it. Therefore, results obtained by various authors cannot be systematized, because of significant differences in the schematics and conditions of research performance. 50 Ref., 2 Figures.

***Keywords:*** *laser alloying, schematic, process, alloyed zone, steel, alloying materials, commercial application*

With increase of requirements to working layer quality [1, 2], process cost effectiveness indices [3], selection of materials, depending on surface properties and cross-section of the parts, as well as increase of volume fraction of complex-alloyed steels in manufacture of parts and tools, the tasks of application of resources-saving technologies for extension of service life of loaded steel items, for instance, by surface alloying, are becoming urgent [4].

Alloying (from Latin ligo — bind, join) means introducing additives (metals, nonmetals and their compounds) into metals, alloys and semiconductors to give them certain physical, chemical and mechanical properties [5]. Alloying of metals and alloys may lead to formation of solid solutions, mixtures of two and more phases, intermetallics, carbides, nitrides, oxides, sulphides, borides and other compounds of alloying elements with the alloy base or of these alloying elements with each other [4, 5].

Alloying results in an essential change of physico-chemical characteristics of the initial metal or alloy and, primarily, of its electronic structure [5]. Alloying elements influence the melting temperature, nature of crystalline lattice defects, formation of grains and fine crystalline structure, region of existence of allotropic modifications and kinetics of phase transformations, dislocation structure, heat- and corrosion resistance, electrical, magnetic, mechanical, diffusion and many other properties of the alloys [3–8].

Alloying is subdivided into bulk and surface [5] alloying. In bulk alloying the alloying element is on average statistically distributed in the metal bulk. As a result of surface alloying, the alloying element is concentrated on the metal surface. Alloying by several elements simultaneously, a certain of content and ratio of which yields the required set of properties, is called complex alloying and the alloys are called complex-alloyed, respectively. For instance, alloying of austenitic chrome-nickel steel by tungsten results in its heat resistance rising by 2–3 times, and at simultaneous application of tungsten, titanium and other elements — by 10 times [5].

Most of the traditional processes of surface alloying of steels (in combination with heat treatment) are based on diffusion saturation by elements from the gaseous or liquid phase and chemical deposition from the gas phase [9]. Common name of these processes is chemicothermal treatment (CTT). Such processes include aluminizing (alloying element is aluminium), carbonization (alloying element is carbon), carbonitriding (alloying elements are carbon and nitrogen), nitriding (alloying element is nitrogen), boriding (alloying element is boron), etc. [5, 9].

However, the above-mentioned CTT methods have a number of common essential drawbacks, both as to the process technology and as to alloyed layer properties. The main disadvantages, limiting the application of these processes as surface-strengthening treatment methods, include [10]:

- long duration of the operation (for instance, carbon saturation rate is about $2.8\cdot10^{-5}$ mm/s and it will take 50–70 h to obtain a nitrided layer of 0.5 mm thickness in structural steels at 773–793 K), resulting in a low efficiency of the process;
- deformation and distortion under stresses induced by conditions of heating during the tech-

nological process and subsequent cooling and, as a result, need for additional mechanical treatment operations;

- brittleness and spallation of outer part of the treated layer.

Other disadvantages of the above CTT methods are small thickness of the alloyed layer and its weak adhesion to base metal structure. At forced operation modes the alloyed layer is quickly torn off the part surface.

In view of the growing service requirements to heavy-duty parts of various components and mechanisms, the tasks of improvement of heat- and crack resistance become urgent. However, regular CTT with quenching and tempering, even though it affects the item properties, is clearly insufficient in many cases. It is the most suitable for improvement of wear- and corrosion resistance, and to a smaller degree, for increase of heat resistance as well as resistance to crack initiation and propagation [5].

Application of the above surface alloying methods is largely related to the history of development of mechanical engineering in developed countries. The evolution of these methods proper was caused by the desire to improve the performance of surface layers of loaded steel items. At the current stage of development of equipment and technology, special attention is given to new methods of surface alloying, allowing elimination of the listed disadvantages of the above methods [10]. These new methods are based on application of local heat sources. For metal surface modification preference is given to such methods, which use high energy density flows as heat sources, such as laser, ion, ultrasonic, etc.

Laser technologies provide successful solutions of the problem of development of materials with a specified set of properties by means of purpose-oriented formation of the structure [10–50]. Laser alloying enables forming such surface layers, which have a high level of hardness [10–12], heat resistance [10, 13, 14], wear resistance [10, 15–17], corrosion resistance [10, 18], and of other characteristics [10–20]. Processes of local alloying are realized using both pulsed [6, 10–13, 17] and continuous [6, 8, 10, 12–20] laser radiation. Here various treatment schematics can be applied both «with overlapping» [10, 12, 13, 15–17, 19, 20] and without it [6, 10–13, 17]. Process results also depend on the method of feeding the alloying material into the joint zone [10, 12, 13, 17], kind of alloying element(s) [6, 8, 10–20], properties of matrix material [10–13, 15, 17] and many other factors.

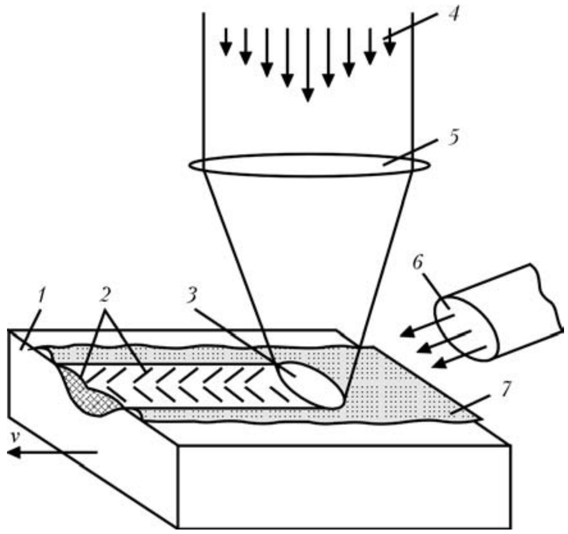

**Figure 1.** Schematic of laser alloying process [12]: *1* — sample moving at speed *v*; *2* — alloyed path; *3* — melt pool; *4* — laser beam; *5* — focusing system; *6* — shielding gas; *7* — alloying coating

Surface laser alloying consists in producing alloyed layers with forced feeding of filler materials directly into the zone of impact of focused laser radiation. Schematic of laser alloying process is shown in Figure 1 [12]. A sample with a thin layer of alloying coating is locally surface melted when moving under the laser beam, alloying components go into the volume of liquid metal pool, which then solidifies.

Investigations of the process of laser surface alloying [6, 8, 10–20] show that laser radiation, directed at the treated surface, is partially absorbed by filler and base materials, and partially reflected. As a result of absorption, an intensive heat source becomes active in the laser irradiation zone [10]. At radiation power densities of $10^5$–$10^6$ W/cm$^2$ active local heating of filler materials occurs, at which a vapour-gas phase forms on the melt pool (liquid phase) surface [12]. At laser alloying interrelated heat mass transfer processes and micrometallurgical processes take place. At laser beam movement the molten metal is driven to the pool tail part as a result of mass transfer phenomenon (integral action of vapour pressure, difference of surface tension forces in the melt pool central and tail parts, and melt turbulent flows) [10]. At the moment of liquid metal existence, mixing of molten alloying composition with metal matrix occurs due to Marangoni thermocapillary convection [21]. Here, steel surface saturation by alloying elements from the compositions, formation of chemical compounds, and partial homogenizing in the liquid metal zone take place [8, 10, 13]. At pool metal solidification an alloyed layer forms. At increase of radiation power density above $10^6$ W/cm$^2$ a transition into the keyhole penetration mode is observed, which is characterized by formation of a vapour-gas channel in the melt pool [10].

Let us consider in greater detail the processes occurring at formation of the structure of surface layers at laser alloying of steels. Depending on thermophysical characteristics of the base material, namely, on heat conductance, the metal surface is heated up to different temperatures [10, 13, 17, 22]. In the case, when the base material has a low coefficient of heat conductivity, metal in the melt pool is heated up to very high temperatures, while the melt pool depth is small. Alloying element concentration rises abruptly. At the impact of laser radiation on the surface of steels with a high coefficient of heat conductivity, the melt pool depth increases, and alloying element content in the pool decreases, respectively [10]. Here, the temperature in the surface melting zone turns out to be lower than in the first case.

In connection with the fact that laser systems with Gaussian energy distribution in the laser beam have become the most widely accepted, energy maximum is found in the beam center, and beam energy decreases towards its periphery [10, 23]. Thus, the heat source provides greater heating in the center than on the periphery. Therefore, the metal turns out to be also heated nonuniformly [12, 13, 24]. This promotes development of a circular mode of liquid movement, directed from the metal surface to the periphery and in-depth of the melt pool [10–13, 21, 23, 24]. Liquid flows as though twist symmetrically in the opposite directions, i.e. two symmetrical macrovortices are created [12, 13, 21]. They form in the case, when the physicochemical and mechanical properties of liquid metal are the same over the entire melt pool. At further movement of the heat source, several vortices form within the melt pool, as metal properties in the laser irradiation zone differ significantly [12]. On the one side, where cold, unheated by the laser beam metal is adjacent to the melt pool, heat removal is more intensive than from the side of the metal, already exposed to laser irradiation. Thus, temperature gradient turns out to be greater from one side of the melt pool than from the other side [11]. Metal movement occurs from the higher temperature regions to less heated regions [12]. Vortex mode of liquid movement leads to its intensive stirring that promotes formation of a homogeneous structure [10]. Here, the high temperatures combined with the short time, allow preserving the high concentration of alloying components [10–20].

All the experimental data show a sufficiently uniform distribution of alloying additives across liquid pool section [10–20]. This unambiguously points to the principal role of convective mass transfer compared to diffusion transfer [10]. Metal evaporation (and vapour recoil pressure, respectively) at alloying is neglected [12], as the alloying process practically always proceeds below the material boiling temperature.

Zone of treatment after laser alloying has a structure similar to that of the zone after laser quenching with surface melting. The difference lies in that alloying elements are added to molten pool metal. Element diffusion from the surface melting zone into the HAZ usually occurs to not more than 10 μm depth [10, 11]. In some cases, however, redistribution of alloying elements in the solid phase under the surface melting zone at the depth of 200–300 μm was found experimentally [10, 12, 13, 17]. This can be due to formation of thin liquid phase channels along the grain boundaries and blocks in the solid metal and mass transfer along these channels [12, 13, 17]. Processes of mass transfer in the solid phase can be also due to dislocation displacement of atoms as a result of fast local deformation [10, 12].

Difference in the structure of laser alloyed zones from that of diffusion coatings, consists in absence of lamination [10]. Convective mixing of the melt with greater distance from the surface, transition from phases with greater concentration of alloying element to those with its lower concentration does not take place [10, 12, 13, 17]. All the phases in the alloyed zone are approximately uniformly mixed by depth [10].

There exist the following methods of alloying element feeding into the laser irradiation zone [10, 12, 13]:

- application of alloying composition in powder form on the treated surface;
- surface coating with special alloying composition;
- alloying in liquid (liquid alloying medium);
- rolling of alloying material foil over the surface being treated;
- alloying in gaseous alloying medium;
- containing ferromagnetic alloying elements on the matrix surface by the magnetic flux;
- deposition of alloying composition by thermal methods (for instance, gas-flame, plasma, detonation spraying, etc.);
- electrolytic deposition of alloying coating;
- alloying composition feeding into the treatment zone in synchronism with laser radiation.

Each of these processes has its advantages and disadvantages [10–13], which determine the rationality of its application in a specific case, and the results obtained at slight changes in technological modes and method of material feeding, can make considerable corrections in the derived result. So, in [25, 26] the influence of surfactant concentration on melt convection and laser alloying results was studied experimentally. It is shown [25] that addition of selenium or sulphur as surfactants to alloying coating allowed controlling the surface profile and shape of alloyed path cross-section.

Proceeding from the objectives of laser alloying (improvement of wear resistance, corrosion resistance, back-to-back endurance and other service properties) [10], it is necessary to take into account the known results of work on CTT [1, 4, 5, 9]. On the other hand, it is not possible to perform direct comparison of the processes of formation of alloyed surface layer at laser surface melting [10–25] with CTT processes, at which alloying proceeds as solid-phase diffusion. At laser alloying, as a result of «stringent» thermal cycle with high heating and cooling rates, formation of oversaturated meta-stable highly dispersed structures is characteristic that cannot be achieved at regular CTT [10].

Dimensions of alloyed zone depend, mainly on radiation energy parameters [12], and thickness of coating from alloying material. As a rule, alloying by pulsed radiation provides smaller dimensions of alloyed zone than at treatment by continuous radiation [10–17]. In particular, if at pulsed treatment zone depth is equal to 0.3–0.7 mm, then application of continuous radiation of powerful $CO_2$-lasers and Nd:YAG lasers allows zone depth to be increased down to 3 mm [10].

A large number of scientific publications devoted to application of the method of laser alloying of a broad range of metals and alloys have appeared recently, owing to the efforts of many research teams. Three groups of materials are traditionally applied as alloying additives: nonmetals, metals and their compounds (for instance, carbides) [10–22].

Alloying by nonmetallic components (for instance, carbon, nitrogen, boron, silicon) is an alternative to traditional methods of carbonization, nitriding, boriding, and siliconizing [10, 12, 13, 17].

Low-carbon steel alloying by carbon naturally leads to formation of a fine-grained structure of martensite and residual austenite, with microhardness reaching 9000 MPa [10, 14, 17].

Steel structure after laser nitriding is nitrous martensite, residual austenite and iron nitrides [6, 10, 12, 27].

Structure of laser borided zones at a small boron content contains α-Fe and boride eutectic [10, 12, 13, 28]. Here, microhardness is equal to $(6–12)\cdot10^8$ MPa [10, 12, 13]. At increase of boron concentration, a small amount of borides (FeB, $Fe_2B$, $Fe_3B$) appear in the structure, residual austenite is absent, and microhardness abruptly rises up to $(14–21)\cdot10^8$ MPa [10, 13, 28]. Alloyed surface with increased content of FeB phase performs well at abrasive wear, whereas at shock impact it is recommended to obtain $Fe_2B$ and $Fe_3B$ borides in the structure [12, 28].

At increase of silicon concentration at laser siliconizing, $Fe_3Si$, $Fe_2Si_3$, FeSi, $FeSi_3$ silicides form in the structure of laser irradiation zone in addition to α-Fe, and steel microhardness rises from $8\cdot10^3$ up to $(14–15)\cdot10^3$ MPa, heat-, wear- and corrosion resistance are also significantly increased [10, 12, 13, 19, 20].

Alloying by pure metals (aluminium [6, 10, 12, 13, 29], cobalt [10, 12, 13, 30], chromium [6, 10–13, 30, 31], nickel [6, 10–13, 30, 32] etc.), as well as alloys on their base, leads to formation of oversaturated solid solutions and intermetallics. This promotes a significant growth of microhardness and wear resistance of alloyed layers, improves corrosion resistance and other physico-mechanical characteristics of the items. So, for instance, laser treatment promotes 1.5 to 3 times increase of wear resistance at surface hardening with further nitriding; the greatest microhardness and wear resistance of low-carbon steels are achieved by nitriding of aluminium-alloyed surface [33]. However, presence of an increased intermetallic content lowers the ductility and embrittles the alloyed layer that may lead to its premature fracture [6, 10, 17].

Presence of carbides, borides, silicides, nitrides and their combinations in the material structure allows an essential increase of its hardness and wear-, heat- and corrosion resistance [6, 10–21, 34–36]. In particular, improvement of wear resistance of friction surfaces of mill-and-boring machine parts with programmed numerical control is provided by laser alloying with coating (%: 15 Fe + 30 Ni + 20 B + 10 Si + 25 of liquid glass) in nitrogen atmosphere in the following mode: $q = 0.31\cdot10^5$ W/cm$^2$, $v$ = = 33 mm/s [36]. Here rod and bushing wear are reduced 3.44 and 3.21 times, respectively.

Given below are examples of practical application of laser alloying of steel items by various materials and mixtures. Laser alloying technology has been mastered at CJSC «SiburKhimProm» (Perm, Russia) for strengthening of surfaces of parts operating at various kinds of wear

[11]. In [11, 22, 37] it is shown that at laser alloying by ($B_4C$ + Cr) composition, layers of down to 0.15–0.25 mm depth form on the surfaces of plungers of pump-compressor equipment made from steels 10, 20, 15Kh, 12KhN3A and 12Kh2G2NMFT. X-ray microprobe analysis showed [37] that laser treatment results in intensive saturation of surface layers by alloying elements, for instance, chromium content in the layers rises 9 to 13 times. Phase composition of the layers contains highly oversaturated solid solutions based on alpha and gamma modifications of iron, as well as borides and carbides of chromium and iron. It is established that corrosion rate of alloyed layers decreases by 3 to 8 times (for 573 and 1173 K, respectively), compared to corrosion rate of untreated layers [11]. Wear testing under sliding friction demonstrated that wear resistance of alloyed layers increased 1.5 to 7 times, compared to surface untreated by laser radiation [11, 22]. Thus, it was established that application of laser alloying allows extension of service life of equipment parts 2 to 4 times due to improvement of their performance [11, 22, 37].

The authors of [38] conducted investigations on laser alloying of steel surface by molybdenum to lower the extent of wear of diverse tool equipment. During investigations molybdenum was first applied on steel surfaces by plasma spraying, and then surface-melted by continuous radiation of Nd:YAG laser. A video camera, equipment for sound analysis and a pyrometer group were used to monitor the process. Process monitoring system used the respective environment for determination of beam/material interaction. For instance, sound analysis of spikes allowed qualitative assessment of intensity drops at alloying. Measurement of melt surface temperature using a pyrometer allowed introducing a correlation by molybdenum content into the alloyed zones that has an important role and is associated with the achieved crack resistance and wear intensity [38].

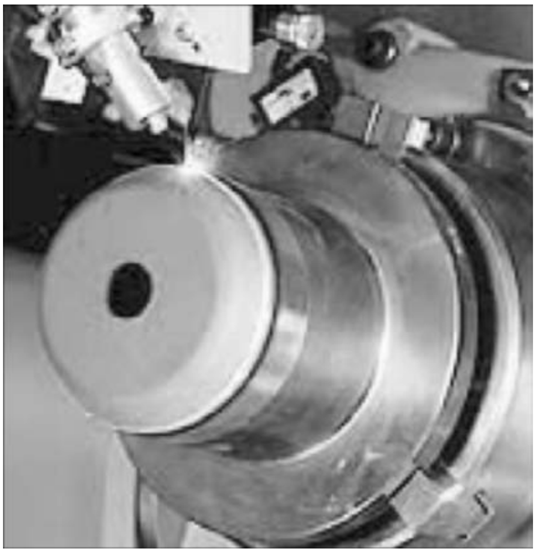

**Figure 2.** Laser alloying of die tooling elements for hot stamping made from 1.2365 steel (X32CrMoV3-3) [42]

Among the diversity of tools, shearing dies feature special operating conditions, where the matrices and punches are subjected to shock loads, high contact pressures reaching 1500 MPa at high-speed deformation of 0.1–5.0 m/s. Investigations were performed [39, 40] of the regularities of impact wear of working surfaces of matrices and punches of shearing dies, made from U8 and X12M steels, which were alloyed by mixtures based on boron, silicon and carbon compounds. Introduction of developed recommendations on laser boro-carbo-siliconizing in production at «Elektrodetal» plant and Bryansk Works of Process Equipment (Russia) was implemented that resulted in 1.5 to 3 times improvement of tool wear resistance [39].

Laser alloying of hot stamping die tooling parts (Figure 2) was performed [41–44] at Fraunhofer Institut fur Produktions technologies IPT, Aachen. The authors of [41] found that adding molybdenum and vanadium carbide as alloying element at laser alloying significantly increases the hardness of die tooling and improves heat resistance, but does not significantly affect the wear resistance. It is shown [41] that additional alloying by manganese allows improvement of wear resistance of surface layers of parts, which are exposed to high loads. Laser alloying [42–44] of 1.2365 steel (X32CrMoV3-3) was performed by titanium carbide, tungsten carbide and cobalt. Conducted full-scale testing showed that wear resistance of die tooling, which has passed laser alloying, increased by 67 % compared to untreated tooling [42–44]. In addition, important is the fact that the tooling operating time after laser alloying was also increased, that also allowed reducing the cost and increasing production volumes [42–44].

In Russian enterprises «Gidrotermal» Ltd. and OJSC «Inzhenerny Tsentr» (Nizhny Novgorod), laser alloying by mixtures of powders of chromium, molybdenum, aluminium and $(NH_2)_2CO$, as well as aluminium and $(NH_2)_2CO$, is used in manufacture and treatment of elements of power system structure of the type of nozzle, flange, bushing, rotary valve and others made from 38Kh2MYuA steel [45, 46]. It is established [45] that alloyed zones have a thin layer of dendritic structure. This layer is enriched in aluminium and, probably, aluminium nitride. During testing it was found that not the upper layers, but those located at a certain depth, have the highest wear resistance. The authors of [45, 46] assume that this is related to nitrogen diffusion into the inner layers of the treated zone and formation of aluminium nitrides. Wear resistance of 38Kh2MYuA steel after laser alloying by a powder mixture increases, Cr–Mo–Al–$(NH_2)_2CO$ mixture ensuring an increase of surface wear resistance by 6.5 to 9.5 times, and Al–$(NH_2)_2CO$ mixture increasing subsurface layer wear resistance by 2.86 to 3.58 times [45, 46].

Deep drawing presses which are used to form a standard metal sheet in the automotive industry should stand extreme loads, and even after a large number of operations they should preserve their accuracy and dimensions. Cost of repair and product losses make these items more expensive, so that industrial users are interested in extension of tool service life. Depending on strengthening purpose, during laser alloying of forging tool surface by tungsten carbide, metal tool protection from wear is provided in individual local zones due to high accuracy of laser alloying technology [47]. At Fraunhofer Institute in close cooperation with HB Seissenchmidt AG Company, such technologies allowed achieving up to 500 % extension of tool service life, compared to traditional treatment methods [47].

Investigation of the structure and properties of a wide range of parts from steels 45, U8A and 6KhS at laser alloying by nickel, molybdenum, chromium, boron and tungsten boride at continuous laser impact was performed [48–50]. Influence of the composition and thickness of alloying coating on alloyed zone depth formation was found [48]. Optimum parameters were established [48–50], technology of laser alloying has been developed and introduced in various Russian enterprises of the industry (OJSCs «Zavod «Krasnoe Sormovo», «Pavlovsky Avtobus» «Gorkovsky Metallurgichesky Zavod», «Vyksunsky Metallurgichesky Zavod», «Nizhegorodsky Aviastroitelny Zavod «Sokol»). Application of laser alloying technology provided 1.5 to 2 times increase of wear resistance of surface layer of items (cutters, plungers, axles, bushings, etc.) at simultaneous reduction of used material cost [48].

## Conclusions

1. Good prospects for application of the results of laser surface alloying in various industries are noted by many authors. However, despite the indubitable scientific and practical interest laser technologies of surface treatment have not become adequately developed and introduced at present. This is due to insufficient knowledge of general regularities of variation of treated steel properties, depending on phase and structural state at alloying by various materials under the conditions of superhigh heating and deposition rates that restrains development of specific working technologies and recommendations of applied nature.

2. Work performed in the field of laser alloying of steel items, was often aimed at solution of a localized task of improvement of service properties of a particular material or parts from it. Therefore, the results obtained by various authors cannot be systematized, because of significant differences in the schematics and conditions of research performance. This is largely due to absence of principles of controlling structure formation when producing in the steel surface layer a structure ensuring a high level of structural strength characteristics, which form the basis of development of such technologies.

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